I. A STUDY OF PYROLYTIC AND PHOTOLYTIC DECOMPOSITION OF TRITYL PROPIONATE AND TRITYL β-NAPHTHOATE

II. REACTIONS OF ORGANOMETALLIC REAGENTS WITH ORTHOESTERS AND ACETALS

By

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INTRODUCTION

Investigations in two different fields of organic chemistry are presented in the two parts of this thesis. Each part has its corresponding chapter on historical, discussion and experimental sections and bibliography, and is complete by itself.

The first part of the thesis concerns the studies on the pyrolytic and photolytic decomposition of trityl esters. Cleavage of such esters was predicted to occur via homolytic carbon-oxygen bond severance at elevated temperatures. The investigations provided an opportunity to study the relative stability of trityl and acyloxy or aroyloxy radicals as well as the decay routes of most radicals produced.

The second part of the thesis describes investigations on the use of the orthoesters and acetals as the precursors for dialkoxy and alkoxycarbenes. Dialkoxycarbenes, although proposed as intermediates in the formation of orthoesters, have been the most elusive type of carbenes to trap and consequently not studied extensively. Attempts to generate such carbenes and study the competitive reaction between compounds having electron-rich centers appeared worthwhile. It was surprising to note that although reactions of orthoesters and acetals with Grignard reagents have been studied, parallel reactions with lithium reagents are unreported.

PART I

A STUDY OF PYROLYTIC AND PHOTOLYTIC DECOMPOSITION OF TRITYL PROPIONATE AND TRITYL β-NAPHTHOATE

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CHAPTER I

HISTORICAL

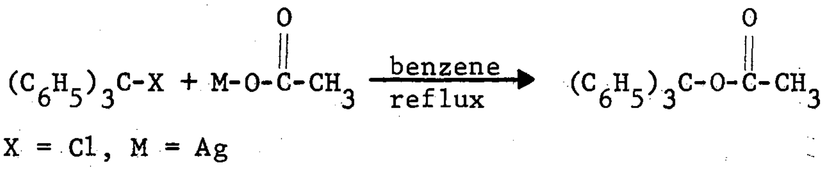
Esters of Tertiary Alcohols

Syntheses of esters of tertiary alcohols present different and, on a number of occasions, difficult problems. The conventional esterification reaction with a tertiary alcohol and a carboxylic acid in the presence of an acid catalyst often leads to dehydration of the alcohol to give an olefin and/or rearrangement of the carbon skeleton. Steric considerations alone are a formidable obstacle in the process. Acetylation of a highly hindered tertiary hydroxyl group can be achieved by reaction with ketene which is generated by pyrolysis of acetone. t-Butyl acetate can be prepared from t-butyl alcohol with acetic anhydride and zinc chloride (6) or with acetyl chloride in presence of N,N-dimethylaniline (30). Perhaps a more convenient laboratory method of synthesis of such esters employs the reaction of the corresponding tertiary halide with the silver salt of the acid (53). Esters of certain aliphatic tertiary alcohols can be made from the olefin and the corresponding acid as exemplified by the preparation of tertiary butyl acetate from isobutylene and glacial acetic acid in presence of zinc chloride (37) or

$$CH_3CO_2H + H_2C{=}C(CH_3)_2 \xrightarrow{ZnCl_2} CH_3CO_2{-}C(CH_3)_3$$

sulfuric acid (40). Such an approach is not feasible for synthesis of esters of triarylmethanols.

Triphenylmethanol has been known for a long time, but relatively few of its esters are recorded. Gomberg and Davis (25) were the first to report the synthesis of trityl acetate obtained from trityl chloride and excess silver acetate in boiling benzene.

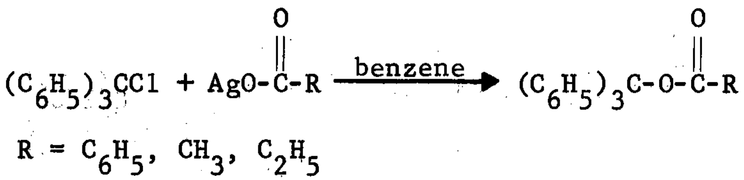


$$(C_6H_5)_3C\text{-}X + M\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3 \xrightarrow[\text{reflux}]{\text{benzene}} (C_6H_5)_3C\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3$$

X = Cl, M = Ag

This general reaction has been studied and expanded by a number of investigators. Ammonium, sodium and potassium salts (2, 10, 15, 50) have been used in addition to silver salts with varying degree of success. Trityl bromide, although not readily available, is more reactive and less hygroscopic than trityl chloride (10, 50).

Preparation of trityl formate from triphenylmethanol and anhydrous formic acid by Bowden and Watkins (16) is the only reported direct synthesis of a trityl ester from the acid and the alcohol. The ester was not isolated as it was unstable above 49°. Although the mechanism of the esterification was not substantiated, it was probably ionic in nature involving the formation and reaction of trityl carbonium ion. Trityl acetate has been obtained (95%) by shaking a solution of trityl bromide with ammonium acetate in benzene by Schoepfle (50). Trityl propionate was also prepared via the reaction of a large excess of silver propionate with trityl chloride in boiling benzene (2). Silver benzoate and trityl chloride condensed in benzene at 60° to give trityl benzoate (15) in unspecified yield.

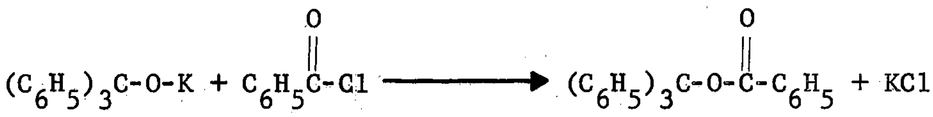


$$(C_6H_5)_3CCl + AgO-\overset{\overset{O}{\|}}{C}-R \xrightarrow{\text{benzene}} (C_6H_5)_3C-O-\overset{\overset{O}{\|}}{C}-R$$

$R = C_6H_5,\ CH_3,\ C_2H_5$

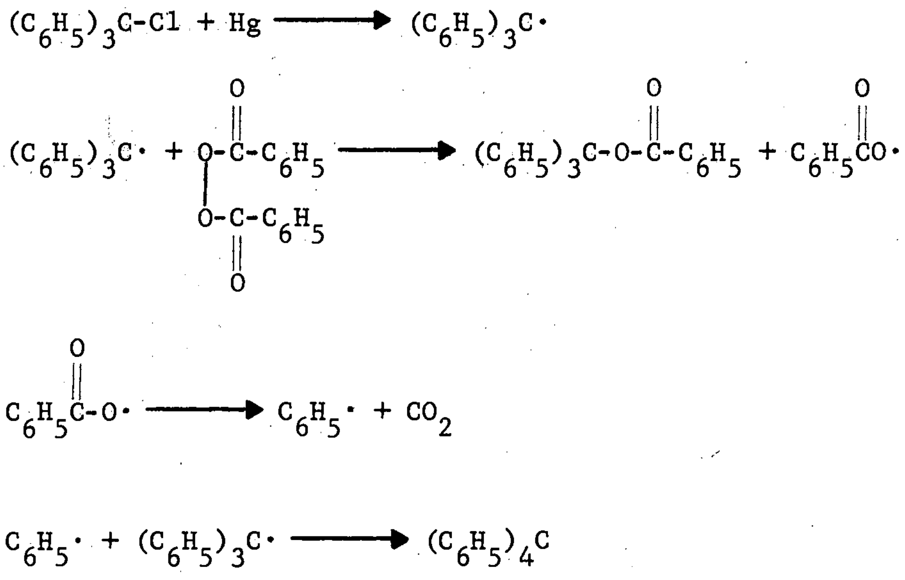
Andrews and Keefer (2) have prepared trityl acetate and trityl propionate from trityl chloride and the corresponding acid in the presence of β-bromoallyl-n-hexylamine as the hydrogen chloride trap. Two mechanisms have been discussed. In one case the acid is presumed to act as an electrophile in establishing the equilibrium in ionization of trityl chloride. This is followed by reaction of the carbonium ion with the carboxylate anion. It is also possible to consider a concerted mechanism involving attack of the carboxylate anion on carbon and electrophilic solvation of chloride ion. Up to 39 per cent conversion of trityl chloride to the esters was reported. The studies, however, were more from the kinetic rather than synthetic point of view.

A change in the general procedure has been reported by Blicke (15) who prepared trityl benzoate from potassium triphenylmethoxide and benzoyl chloride. He noted the reaction was exothermic in benzene solution and obtained trityl benzoate although the yield was not given.



$$(C_6H_5)_3C-O-K + C_6H_5\overset{\overset{O}{\|}}{C}-Cl \longrightarrow (C_6H_5)_3C-O-\overset{\overset{O}{\|}}{C}-C_6H_5 + KCl$$

Another approach, somewhat specific for preparation of trityl esters, is the reaction of peroxides of carboxylic acids with trityl radicals or triphenylmethane. Wieland and co-workers (56, 57) have prepared trityl benzoate, trityl p-toluate and trityl p-anisate by this procedure. Trityl radicals were generated by the reaction of pure trityl chloride with mercury in benzene solution. Trityl radicals initiate a chain reaction, as shown below.



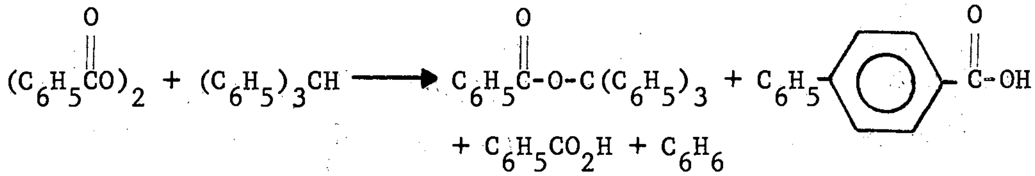
$$(C_6H_5)_3C\text{-}Cl + Hg \longrightarrow (C_6H_5)_3C\cdot$$

$$(C_6H_5)_3C\cdot + \begin{matrix} O\text{-}\overset{O}{\overset{\|}{C}}\text{-}C_6H_5 \\ | \\ O\text{-}\underset{O}{\underset{\|}{C}}\text{-}C_6H_5 \end{matrix} \longrightarrow (C_6H_5)_3C\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}C_6H_5 + C_6H_5\overset{O}{\overset{\|}{C}}O\cdot$$

$$C_6H_5\overset{O}{\overset{\|}{C}}\text{-}O\cdot \longrightarrow C_6H_5\cdot + CO_2$$

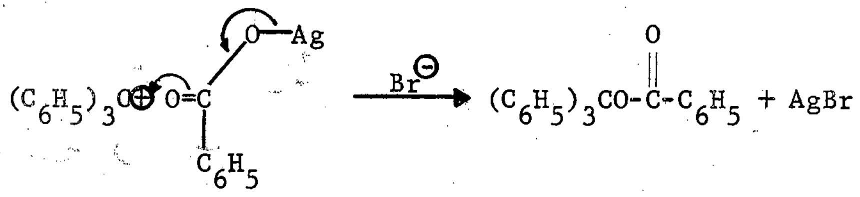
$$C_6H_5\cdot + (C_6H_5)_3C\cdot \longrightarrow (C_6H_5)_4C$$

The benzoyloxy radical may either react with another trityl radical or it may lose carbon dioxide to give phenyl radical. Phenyl radical in turn could react with trityl radical to yield tetraphenylmethane. Wieland has also investigated the thermal decomposition of various mixtures of benzoyl peroxide with triphenylmethane, and he has reported the formation of trityl benzoate, benzoic acid, p-phenylbenzoic acid, carbon dioxide and benzene (57).



Hammond, Rudesill, and Modic (28) have also studied the decomposition of benzoyl peroxide in the presence of trityl radicals in benzene solution. Yields of 20-30 per cent for tetraphenylmethane were recorded.

Although several trityl esters have been studied by a number of workers, satisfactory synthetic procedures were not available. In a number of cases the reaction mixture was quite complex, requiring tedious recrystallization procedures to get products. Recently Berlin and coworkers (10) have reported the syntheses of several trityl esters using sodium, potassium and silver salts of aliphatic and aromatic acids with trityl bromide. Trityl esters of acetic, propionic, hydrocinnamic, pivalic, benzoic, _o_-toluic, _p_-anisic and cinnamic acids were realized in excellent yields (60-94 per cent). The process consisted of heating at reflux a mixture of trityl bromide with a slight excess of the corresponding metal salt of the carboxylic acid in carbon tetrachloride or a hydrocarbon solvent. In addition to new esters, the yields of many previously reported esters were markedly improved and should stimulate research with these materials. Two possible mechanisms have been suggested. The classical carbonium ion process is predictable in which ionization of trityl bromide occurs in benzene (19). Attack of the trityl carbonium ion on the oxygen atom of the carboxylate salt or the anion seems reasonable although whether C-O formation is synchronous with O-Ag cleavage is problematical.



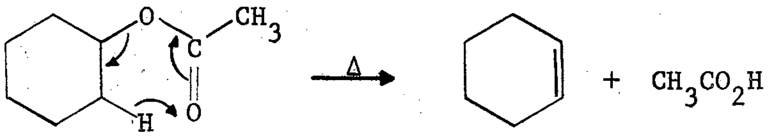
$$(C_6H_5)_3C^{\oplus}\;O{=}\underset{C_6H_5}{\underset{|}{C}}{-}O{-}Ag \xrightarrow{Br^{\ominus}} (C_6H_5)_3CO{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5 + AgBr$$

This mechanism parallels that suggested to explain esterification of the silver salt of 2,4,6-trimethylbenzoic acid with methyl iodide. Since the carbonyl oxygen atom is sterically less hindered compared to the carbonyl carbon atom, the reaction is less affected by structural alterations.

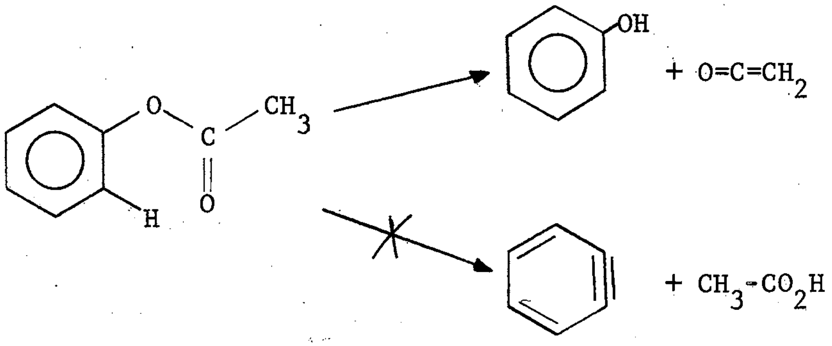
Different procedures available for the synthesis of trityl esters have been discussed above. In view of the steric strain involved in the trityl esters and stability of trityl radicals, it was of interest to study the mode of decomposition in trityl-substituted compounds.

Pyrolysis of Trityl Esters and Related Compounds

Thermal decomposition of esters has been investigated by different workers from a synthetic as well as from a mechanistic point of view. Even a few trityl esters have been pyrolyzed, but in most of the cases the investigations have been limited to identification of a few compounds. High-boiling or nondistillable residues have generally been referred to as tars and conveniently discarded. Pyrolyses of acetates and xanthates have been widely used in the preparation of olefins (20). A concerted mechanism involving a quasi six-membered ring transition state is believed to be operative in the cis eliminations of acetates and xanthates as shown below.

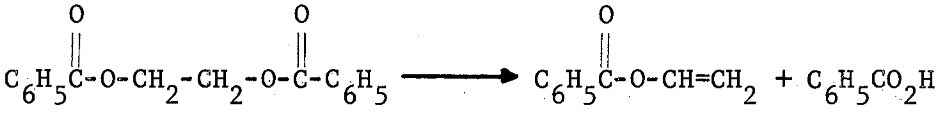


In contrast to the above reaction is the work by Hurd (32) in which he examined the pyrolysis of phenyl acetate to give ketene and phenol. Formation of benzyne and acetic acid would not have been unreasonable in view of the results from pyrolysis of cyclohexyl acetate.

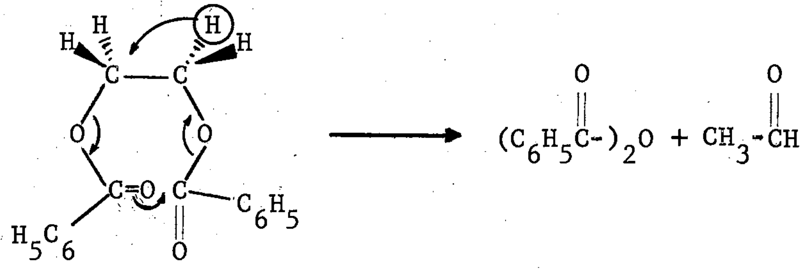


Hurd tried to extend (33) the above pyrolysis to the practical synthesis of methylketene. He obtained methylketene from phenyl propionate at 650° in small amounts along with a number of products including phenol, styrene, carbon monoxide, ethylene, ethane, methane and hydrogen.

Besides acetates, benzoates have been pyrolyzed extensively. Szwarc (52) has reported pyrolysis of several benzoates. For example, benzyl benzoate at 900-1000° K, using the toluene carrier gas technique, leads to 1,2-diphenylethane. Vapor phase pyrolysis of ethylene glycol dibenzoate gives benzoic acid and vinyl benzoate, whereas the same ester on pyrolysis at 400-500° gives benzoic anhydride and acetaldehyde. Pyrolysis of vinyl benzoate (52) led to benzoic acid and acetylene, styrene and carbon dioxide and even acetophenone depending on the conditions. Similar results have also been obtained by Rashbrook and Taylor (46).



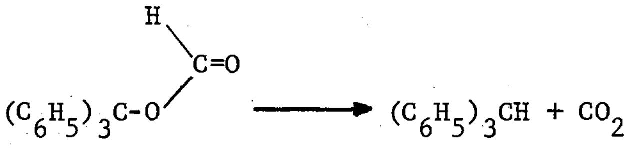
$$C_6H_5\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \longrightarrow C_6H_5\overset{O}{\overset{\|}{C}}-O-CH=CH_2 + C_6H_5CO_2H$$



Similar pyrolyses in the series of polycyclic aromatic acids are virtually unknown. Decarboxylation of β-naphthoic acid by heating with soda-lime has been reported to give naphthalene and carbon dioxide (41). No thermal studies of unsubstituted β-naphthoic acid or any of its esters were found in the literature. Wystrach and Tarbell (59) have reported that pyrolysis of 4-allyl-3-(allyloxy)-2-naphthoic acid resulted in the formation of only 26 per cent carbon dioxide and an intractable tar.

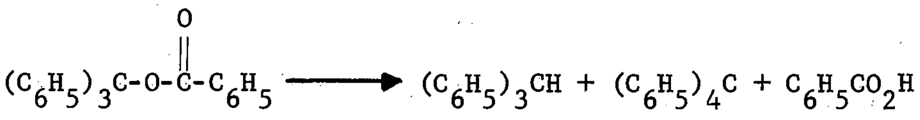
Pyrolysis of esters of many tertiary aliphatic alcohols proceeds smoothly to the olefins. For example, 1,1-dimethylpropyl acetate was smoothly decomposed at 400° (5) to give a mixture of 2-methyl-1-butene (76%) and 2-methyl-2-butene (24%). Pyrolysis of 1,1,2-trimethylpropyl acetate (5) at 400° proceeded in a similar manner yielding 2,3-dimethyl-1-butene (88%) and 2,3-dimethyl-2-butene (12%).

Pyrolyses of trityl triphenylacetate and di-trityl fumarate appear to be the first recorded cases of trityl esters (3). Anschutz reported triphenylmethane and carbon dioxide as the only identifiable products in both examples. Gomberg noted pyrolysis of trityl carbonate (23) gave di-trityl ether in the presence of finely divided copper upon heating at reflux in xylene. Triphenylmethane and carbon dioxide were the only products reported from the decomposition of trityl formate (16). Trityl formate is stable at room temperature but decomposes at 49° as follows.



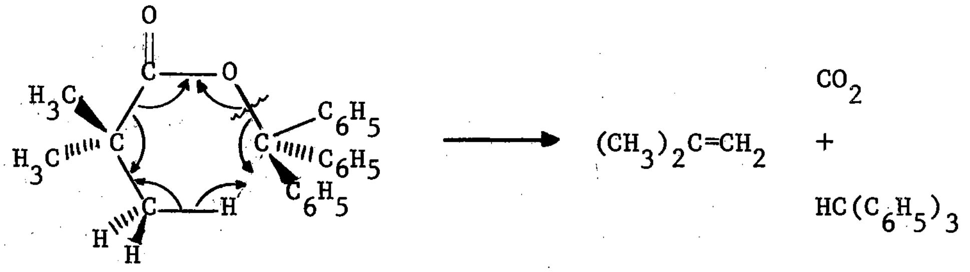
$$(C_6H_5)_3C{-}O{-}\overset{H}{C}{=}O \longrightarrow (C_6H_5)_3CH + CO_2$$

Decomposition of trityl trifluoroacetate (51) has also been published but no analytical details were given. Pyrolysis of trityl benzoate was studied at 225° and 500° (34). Essentially identical pyrolysates were obtained at both temperatures. At 500° the main products were benzoic acid, triphenylmethane, tetraphenylmethane, and carbon dioxide. Small quantities of benzene, carbon monoxide and benzoic anhydride were also detected. At 225° benzoic acid and triphenylmethane were the only products identified. An unidentified compound was isolated but not characterized. The high-boiling residue appeared to be tar and no attempts were made to determine its nature.



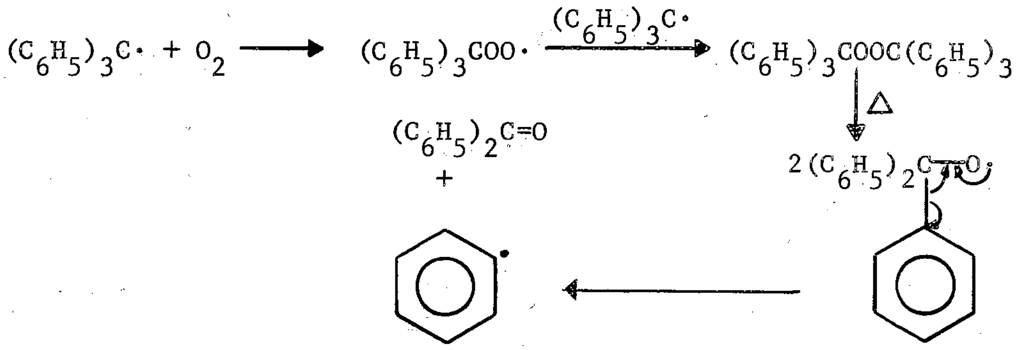
$$(C_6H_5)_3C\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}C_6H_5 \longrightarrow (C_6H_5)_3CH + (C_6H_5)_4C + C_6H_5CO_2H$$

Recently, data from this laboratory (11) have been concerned with the pyrolysis of trityl hydrocinnamate, trityl propionate and trityl pivalate at temperatures varying from 250 to 450° in static as well as rapid-flow systems. Thermolysis of trityl pivalate occurred smoothly at 430° in a rapid-flow system to yield isobutylene, carbon dioxide and triphenylmethane in high yields. A small amount of triphenylmethanol and traces of benzophenone and biphenyl were also detected. The ester was remarkably stable in a static system as little decomposition occurred at 300° after three hours. Radical pairs may be formed.



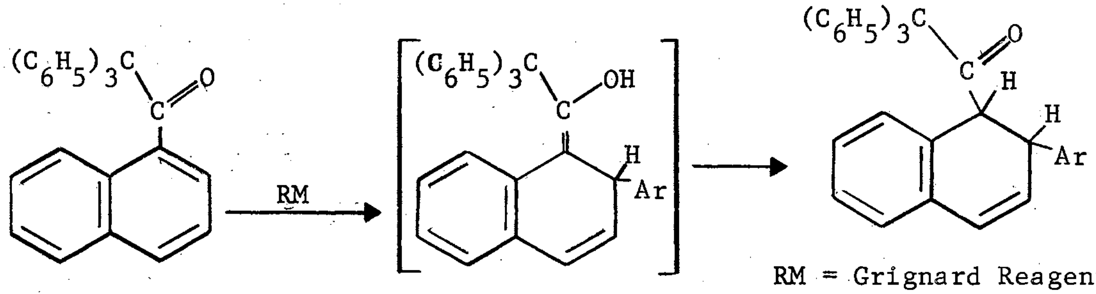
Pyrolysis of trityl hydrocinnamate was much more complex and fifteen products were identified. The major products were triphenylmethane, hydrocinnamic acid (and its anhydride), carbon dioxide, styrene, benzophenone and <u>trans</u>-stilbene. Minor products included benzene, toluene, ethyl benzene, 1,2-diphenylethane, diphenylmethane, water, triphenylmethanol, carbon monoxide and traces of an unknown product. An elaborate mechanism involving decay of trityl and hydrocinnamoyloxy radicals, the major products of the initial homolytic cleavage, has been proposed. Formation of hydrocinnamic acid anhydride by pyrolysis of the corresponding acid had been noted earlier (17).

Berlin and Sturm (13) have also studied the pyrolysis of trityl <u>p</u>-toluate in rapid-flow and static systems and have obtained results parallel to those cited with the other esters. Support for the postulated radical mechanism was obtained from experiments in which pyrolysis of the esters was conducted in an oxygen atmosphere, thereby oxidizing trityl radicals to triphenylmethoxy radicals (23). Decomposition of trityl peroxide to benzophenone and phenyl radicals at higher temperatures has been previously reported (23, 26).

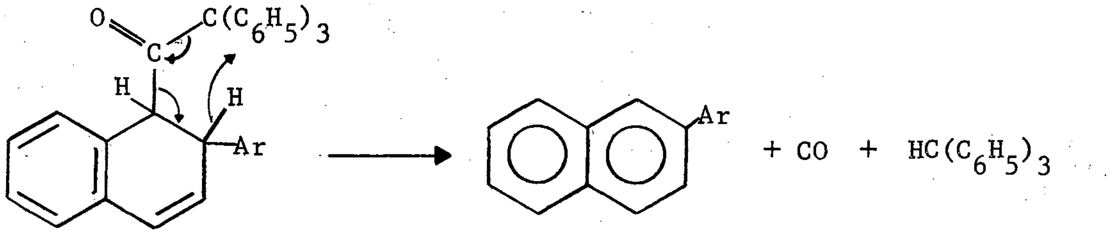


An increased yield of benzophenone was observed in all the cases when the pyrolysis was conducted in oxygen.

Other pertinent trityl compounds whose behavior at elevated temperatures has been examined include trityl ketones and trityl ethers. Fuson and Berlin (22) studied the conjugate addition of Grignard reagents with 1-naphthyl trityl ketone. This condensation, as exemplified by the following reaction, leads to formation of 1-(1,2-dihydro-2-aryl)naphthyl trityl ketones. Attempts to aromatize the dihydro ketones by the use of palladium at high temperature led to a novel cleavage of the ketones to give 2-arylnaphthalenes, triphenylmethane and carbon dioxide.



RM = Grignard Reagent



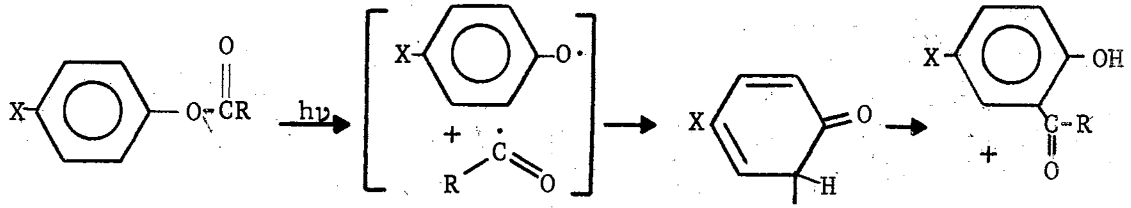
Decarbonylation of triphenylacetaldehyde to triphenylmethane and carbon monoxide appeared remarkably simple as noted by Orekhoff and Tiffeneau (44). Triphenylmethane was the main product from the pyrolysis of β-benzopinacolone (18) although the pyrolysate is complex.

Trityl alkyl ethers are readily obtained by alcoholysis of trityl esters (10). Trityl methyl ether has been prepared in nearly quantitative yields from triphenylmethanol and absolute methanol (14). Norris and Young (43) have prepared trityl alkyl ethers by the condensation of trityl chloride with an equimolar amount of sodium alkoxide using excess of the alcohol as solvent. They have further studied decomposition of these ethers at 250-300°. Trityl ethyl ether, for example, decomposes to triphenylmethane and acetaldehyde. Their results showed that the structure of the alkyl group had a marked effect on the stability of the bond between the trityl group and the oxygen atom, thereby influencing the temperature of decomposition. The reactions may be radical in nature.

Trityl aryl ethers have been the subject of recent reports by Zimmerman and Somasekhara (60) who photolyzed the compounds. Such ethers can be prepared by the reaction of sodium phenoxide with trityl chloride in boiling benzene solution. The photolysis of ethers in dioxane-water system gave the corresponding phenol and triphenylmethanol. An ionic mechanism was suggested, although formation of 9-phenylfluorene was noted in some photolyses. A radical mechanism is more reasonable in view of the ioslated fluorene derivative and the possibility is mentioned in a footnote by the authors (60). Isolation of trityl peroxide by them in one of the photolyses is an even stronger argument in favor of a radical process.

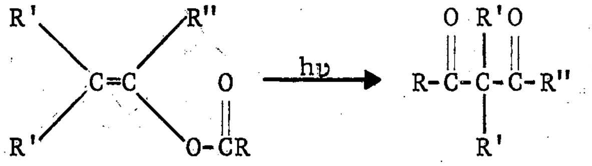
Aryloxy radicals and their analogs, vinyloxy radicals, have recently been studied in an interesting reaction, namely the photolysis of vinyl and phenyl esters of substituted benzoic acids (21, 36). Rearrangement of the phenyl esters to ortho and para hydroxy phenyl ketones (reminiscent of the classic Fries rearrangement) occurred under photodissociation conditions. The aluminum chloride catalyzed Fries rearrangement with p-t-butyl benzoates invariably results in complex reaction mixtures involving loss of the t-butyl group. Kobsa (36) was able to achieve a photo-Fries rearrangement involving similar esters and obtained substituted benzophenones in which no loss of the t-butyl group was evident.

Yields of the substituted phenols was remarkable (up to 55 per cent). Rearrangement to the para isomer was observed when there was no substituent on that position.



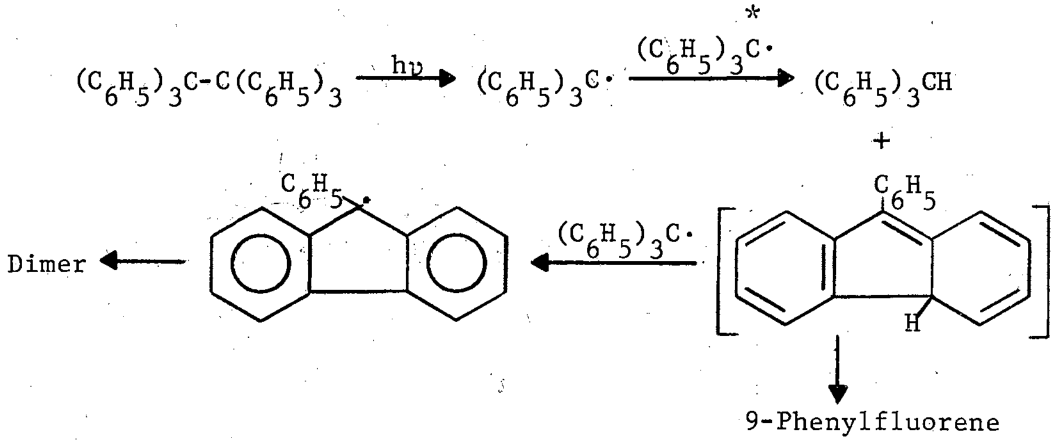
p-isomer
where X=H

Finnegan (21) has also studied the photolysis of certain vinyl



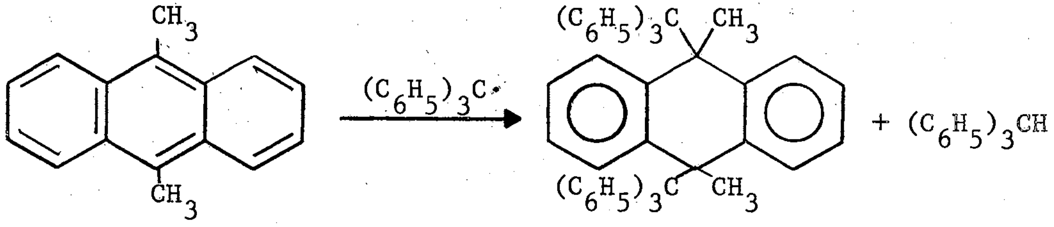
esters, which resulted in the formation of β-diketones. Results of the mixed photolyses indicate an intramolecular rearrangement through an initial photodissociation of the ester to radical pairs which subsequently react in a solvent cage.

Photolysis of trityl p-toluate has been reported by Berlin and Sturm (13) to give results parallel to those obtained by pyrolysis which thereby support a radical mechanism proposed for the pyrolytic decompositions. Photolysis of trityl radicals formed as a result of dissociation of hexaphenylethane has been found to yield 9-phenylfluorene, triphenylmethane and di(9-phenylfluorenyl) by Letsinger, Collat and Magnusson (38).

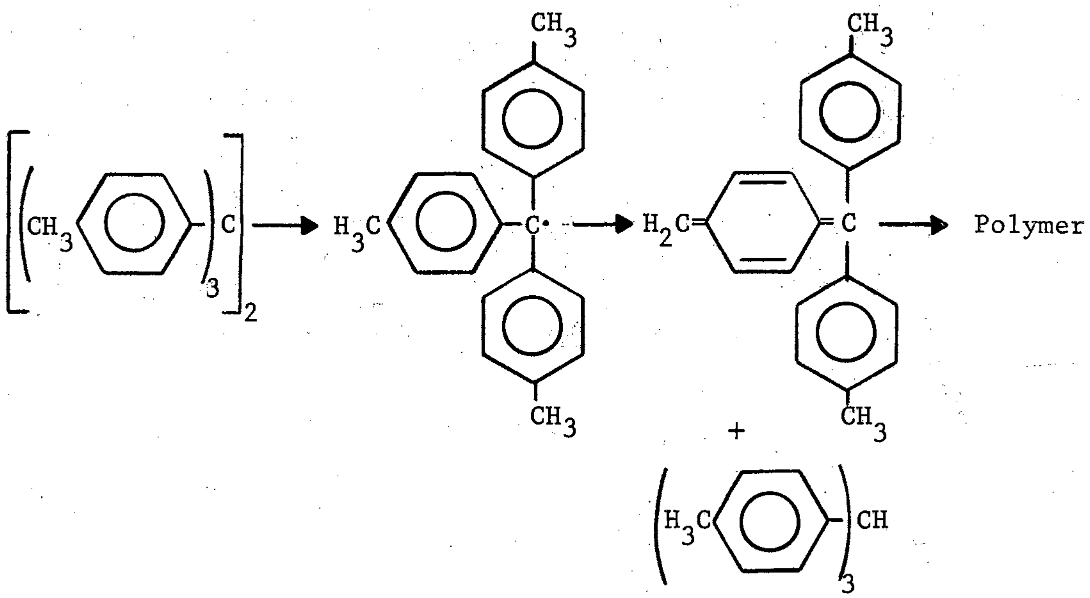


Benkeser and Schroeder (8) have observed aromatic substitution by trityl radical to be very selective and susceptible to influence of substituent groups. The product distribution of the various isomers was nearly statistical in general, but nitrobenzene was essentially unreactive.

An interesting addition of trityl radicals to 9,10-dimethylanthracene was recorded by Mikhailov (36) although the yield was low.



Marvel and co-workers (39) have further investigated the observation of Gomberg (24) that hexa-p-tolylethane does not dissociate reversibly. They have proposed an initial disproportionation to tri-p-tolylmethane and a biradical which can be stabilized by assuming a quinonoid structure. The quinonoid compound obtained could further polymerize to the polymeric material obtained by them. Support for the disproportionation mechanism is obtained by the results of Schlenk and Meyer (49) who have isolated a polymer from diphenyl-p-tolylmethyl chloride in



pyridine. Marvel and co-workers also found a polymer from the reaction of tri-p-tolylmethyl chloride with pyridine which seemed to be identical to the polymer they obtained under free radical conditions.

Formation of 9-phenylfluorene has also been observed in an ionic medium by Benkeser (9) [who obtained essentially the same products as Letsinger (38)] by reaction of triphenylmethanol with acetic acid and sulfuric acid. The reaction products obtained by him were complex and were not investigated in detail, however.

CHAPTER II

DISCUSSION OF THE RESULTS AND CONCLUSIONS

Trityl propionate (I) has been prepared in improved yields (96.5%) by the reaction of trityl bromide and silver propionate in carbon tetrachloride. Similarly, trityl β-naphthoate (II) was obtained in 86.7 per cent yield from the condensation of trityl bromide with sodium β-naphthoate in boiling benzene.

The reaction series is thought to be ionic proceeding through the initial ionization of the trityl bromide followed by attack of the trityl carbonium ion on the oxygen atom of the carboxylate ion.

$$R\text{-}CO_2M + BrC(C_6H_5)_3 \xrightarrow{\text{benzene}} RCO_2C(C_6H_5)_3$$

(1) $R = C_2H_5$, $M = Ag$

(2) $R = 2\text{-}C_{10}H_7$, $M = Na$

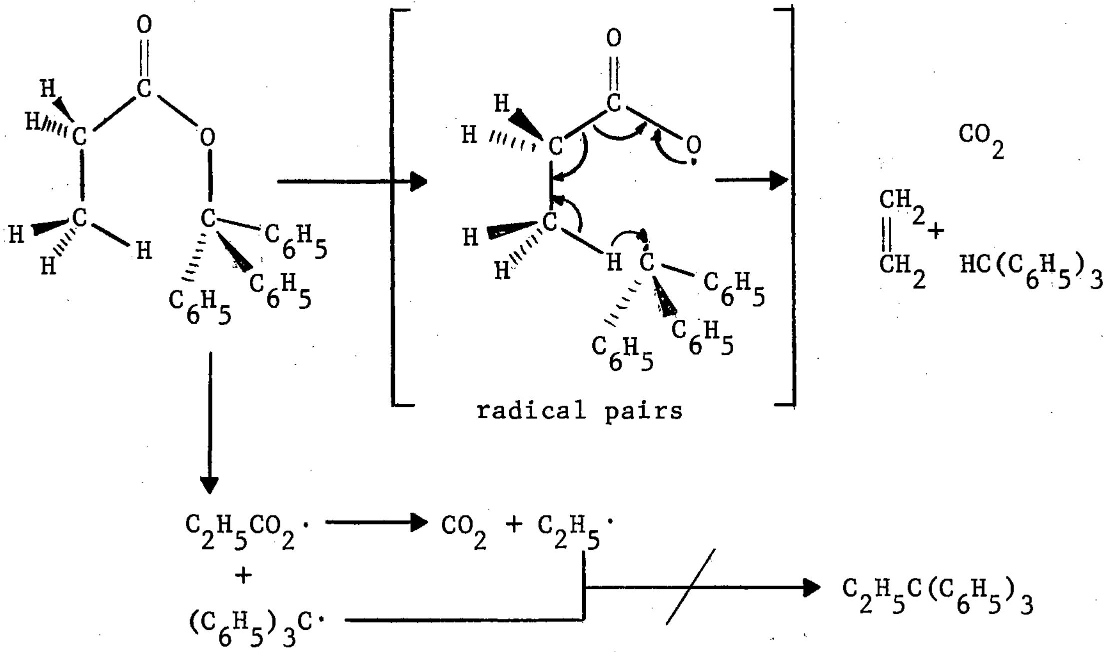
An investigation has been made on the pyrolytic and photolytic decomposition of the esters I and II. Pyrolysates in both cases were complex and were analyzed by gas chromatography, infrared analyses and nuclear magnetic resonance (NMR) spectroscopy.

The results indicate that the pyrolysis reaction of I probably proceeds through radical pairs, that is via formation of trityl and propionyloxy radicals by an initial homolytic cleavage at the alkyl-oxygen bond. In addition, in the pyrolysis of II rapid formation of biradical is offered to explain the mechanism operative after carbon-oxygen bond cleavage to β-naphthoyloxy and trityl radicals. Oxidation of the melts of I and/or II at high temperature resulted in an increased yield of benzophenone which supports a radical mechanism for the pyrolyses.

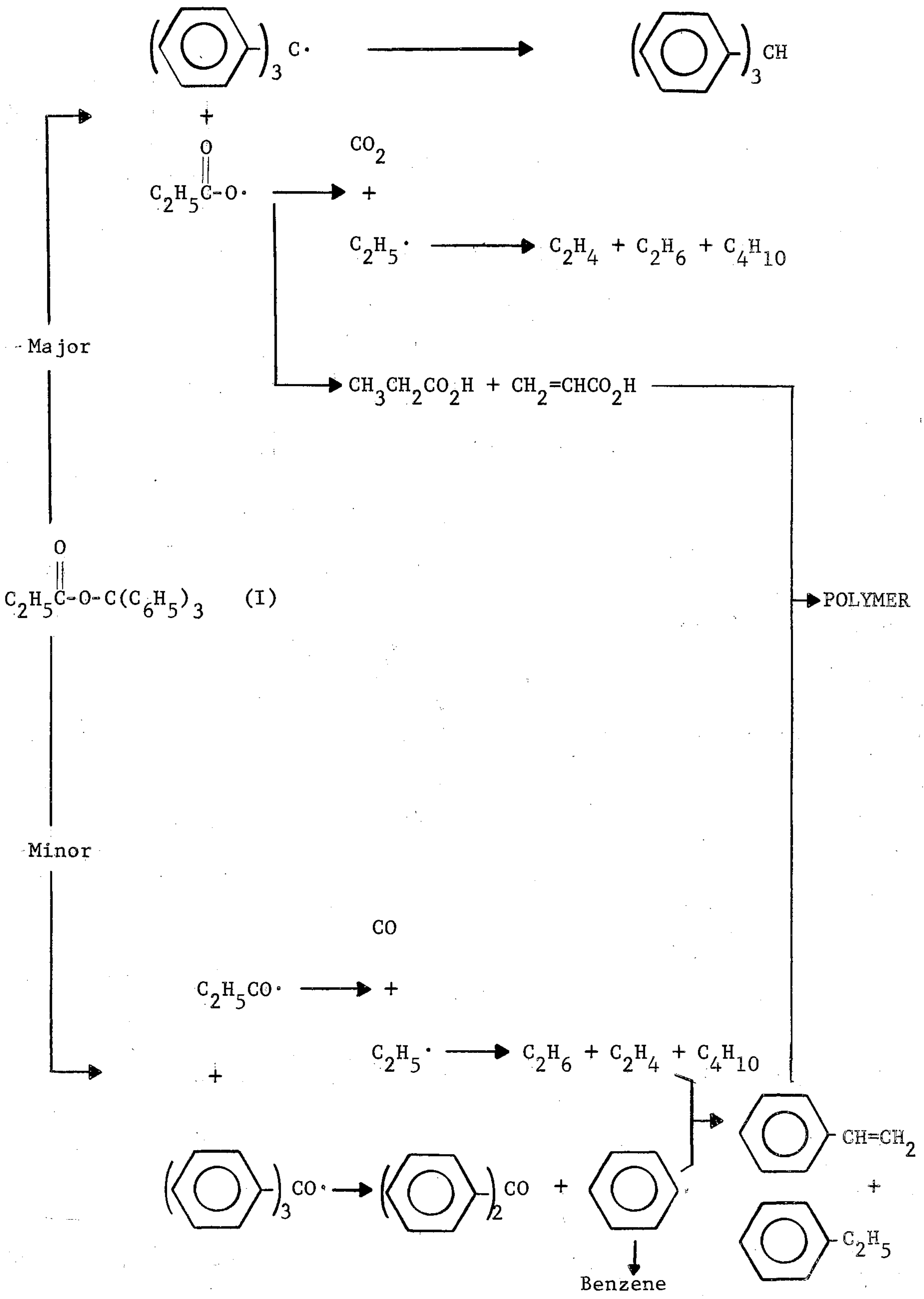
Initial cleavage of the two esters into acyloxy (or aroyloxy) and trityl radicals through alkyl-oxygen bond severance was anticipated for the following reasons: (a) a considerable steric strain is relieved with the formation of a very stable trityl radical; (b) a probable low O-C bond dissociation energy (31); and (c) an acyl-oxygen bond cleavage would result in the formation of triphenylmethoxy radicals which are very unstable at high temperature. The acyloxy radicals, known to be unstable (48) at above 200°, were expected to decarboxylate and the resulting alkyl radical could couple with a trityl radical to give 1,1,1-triphenylpropane or 2-tritylnaphthalene from I and II, respectively. Another interesting possibility was the abstraction of hydrogen by the trityl radical from the beta carbon atom of the initially formed acyloxy-radical to give a biradical which could easily collapse with the loss of carbon dioxide to produce ethylene from I or 1,2-naphthyne from II. The same products would be expected if the trityl radical abstracted a hydrogen from the decarboxylated radicals.

Pyrolysis of trityl propionate resulted in cleavage, both at the acyl-oxygen and alkyl-oxygen bonds as evidence by the major products found, which were triphenylmethane, propionic acid, benzophenone, triphenylmethanol and carbon dioxide. A number of other products were obtained in smaller yields along with a polymeric acid which was identified to be a copolymer of acrylic acid and styrene. Volatile components like benzene, ethylbenzene and styrene were found in the traps and the uncondensed gases, n-butane and carbon monoxide, were detected in the carrier gas which was collected over a salt solution. Extraction of the pyrolysate with sodium hydroxide solution separated the acidic materials from the nonacidic residue which was mainly triphenylmethane, benzophenone and triphenylmethanol. Identification of the gases was completed by the use of infrared spectroscopy. The nonacidic components were analyzed by gas chromatography and identified by comparing their retention times with those of known compounds. The products are listed in Table IV and a radical mechanism is proposed for their formation in scheme 1.

As mentioned above and in view of the results of pyrolysis of trityl pivalate (11), it was postulated that decomposition of trityl propionate might occur through a concerted mechanism or perhaps a process involving radical pairs. Rembaum and Szwarc (48) have reported



Scheme 1

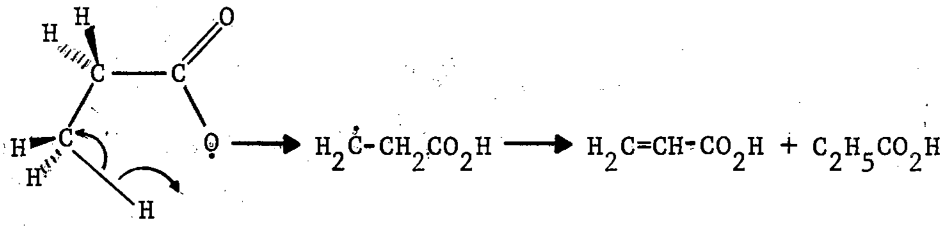

C·
CH
3
CO2
C2H5C-O·
C2H5·
C2H4 + C2H6 + C4H10
CH3CH2CO2H + CH2=CHCO2H
Major
C2H5C-O-C(C6H5)3
(I)
POLYMER
Minor
CO
C2H5CO·
C2H5·
C2H6 + C2H4 + C4H10
CO·
CO
2
CH=CH2
C2H5
Benzene

thermal decomposition of propionyl peroxide in the vapor phase at 245° and recorded the formation of ethylene, ethane and n-butane which was suggested to result from coupling and disproportionation of ethyl radicals. n-Butane was tentatively identified and traces of other hydrocarbons (one appears to be ethane) were also present in the pyrolysate of I. These facts support the formation and then decomposition of propionyloxy radical. The appearance of styrene was not too surprising in view of the result of Hurd and co-workers (33) on the pyrolysis of phenyl propionate. In an effort to obtain methylketene from the pyrolysis of phenyl propionate one of the products identified by them was styrene.

Formation of styrene most likely takes place through the disproportionation of two phenethyl radicals arising from the addition of phenyl radicals to ethylene. This could also account for the formation of ethylbenzene to a certain extent. Ethylbenzene can also arise from a coupling of phenyl and ethyl radicals.

Formation of the polymeric acid which showed the presence of a monosubstituted phenyl group in the infrared spectrum (Plate II) was surprising as was the high yield of propionic acid. The polymer was first thought to contain a trityl ester but attempted methanolysis of the polymer with methanol and saponification with potassium hydroxide failed to yield trityl methyl ether or a carboxylic acid salt. Detection of styrene as one of the products was suggestive that the polymer could contain styrene as one of the polymerizing units. The appearance of the polymer and its infrared spectrum implied a possible copolymer structure consisting of acrylic acid and styrene. Esterification of the polymer was achieved by heating it at reflux with absolute ethanol and concentrated hydrochloric acid (3 ml. of each) for twenty-four hours. The infrared spectrum of the polyester thus obtained was nearly superimposable on that of a copolymer of ethyl methacrylate and styrene.

Recently Pritzkow and Dietzsch (45) have recorded an intramolecular hydrogen transfer by the acyloxy radical as shown below through a



five membered cyclic transition state. The radical thus formed could disproportionate to propionic and acrylic acids. Transfer reactions in radical processes have been discussed by Wallace and Gritter (55). Intramolecular hydrogen abstraction followed by the disproportionation as depicted above would also explain the high yield of propionic acid.

A minor route of decomposition occurs through acyl-oxygen bond cleavage resulting in the formation of propionyl and triphenylmethoxy radicals. Decomposition of triphenylmethoxy radicals into benzophenone and phenyl radicals has been investigated previously (23, 26). Propionyl radical could easily decompose into ethyl radical and carbon monoxide in a manner analogus to propionyloxy radicals (48). Formation of triphenylmethanol by the abstraction of hydrogen atom by a triphenylmethoxy radical from one of the alkyl radicals is reasonable. The realtively low yield of triphenylmethanol as compared to benzophenone suggests that decomposition of the triphenylmethoxy radicals is preferred over hydrogen abstraction.

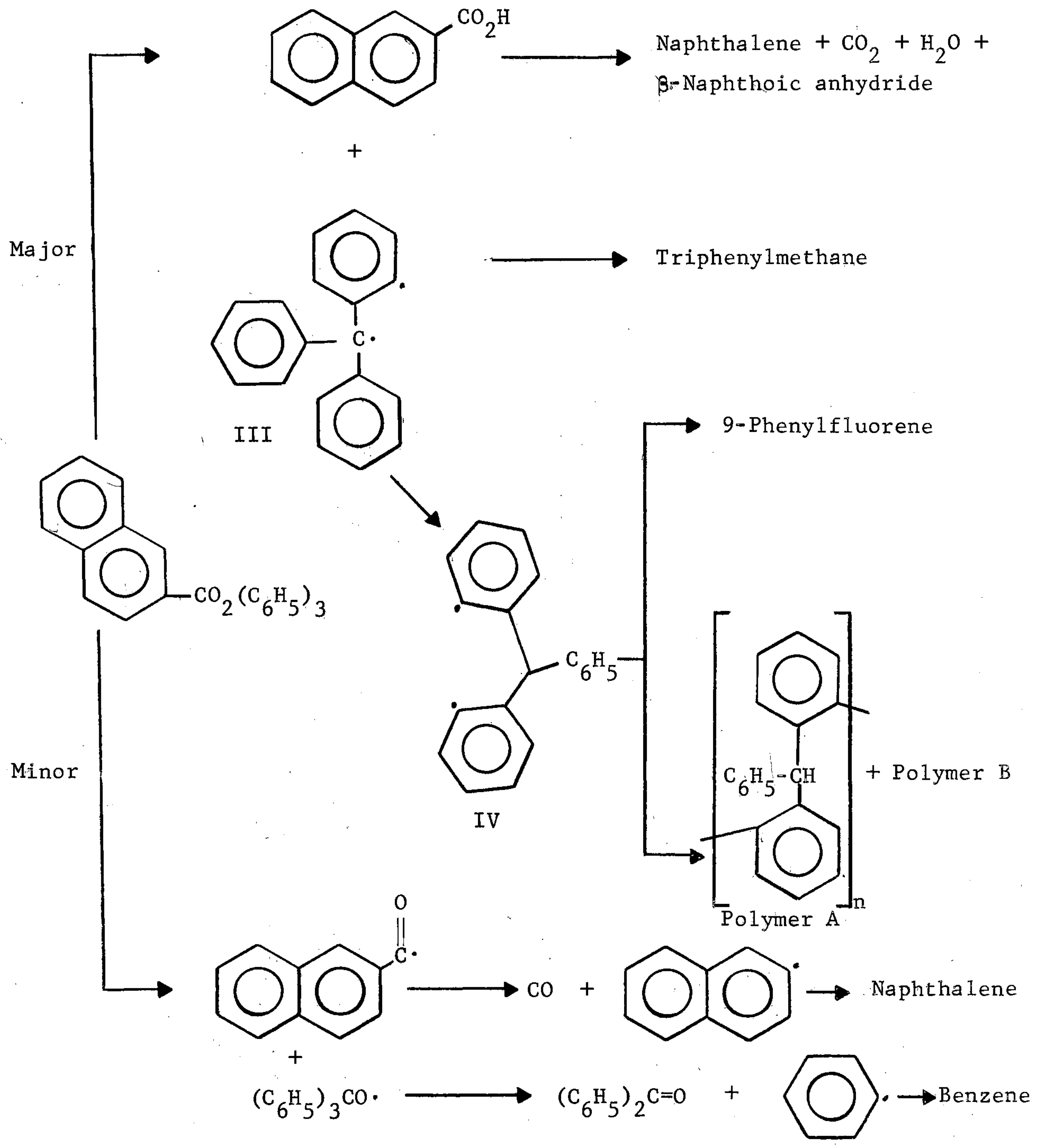
Further support for the postulated radical mechanism was gained through study of the pyrolysate (of I) obtained when oxygen was bubbled into its melt at 350° for one hour. An increased yield of benzophenone was observed as expected which probably resulted from the oxidation of trityl radicals to triphenylmethoxy radicals.

Pyrolysis of trityl β-naphthoate (II) proceeded in a manner (12) somewhat different than that observed in trityl propionate. A much higher yield of the acid and a relatively low yield of triphenylmethane were obtained. Two polymers were isolated along with traces of several other components as listed in Table VII. The identity of the known compounds such as β-naphthoic acid, naphthalene, triphenylmethane, 9-phenylfluorene, benzophenone, carbon dioxide, and carbon monoxide was established by isolation and characterization by gas chromatography, infrared and NMR spectroscopy. Structures for the polymers have been proposed on the basis of physical and chemical data. These polymers were exceedingly resistant to chemical degradations and it was not possible to degrade the polymers to identifiable organic fragments.

Scheme 2 is proposed to explain the formation of various products through an initial cleavage of the ester II via a biradical mechanism. Pyrolyses of β-naphthoic acid and β-naphthoyl peroxide were done in order to obtain further support for the proposed mechanism.

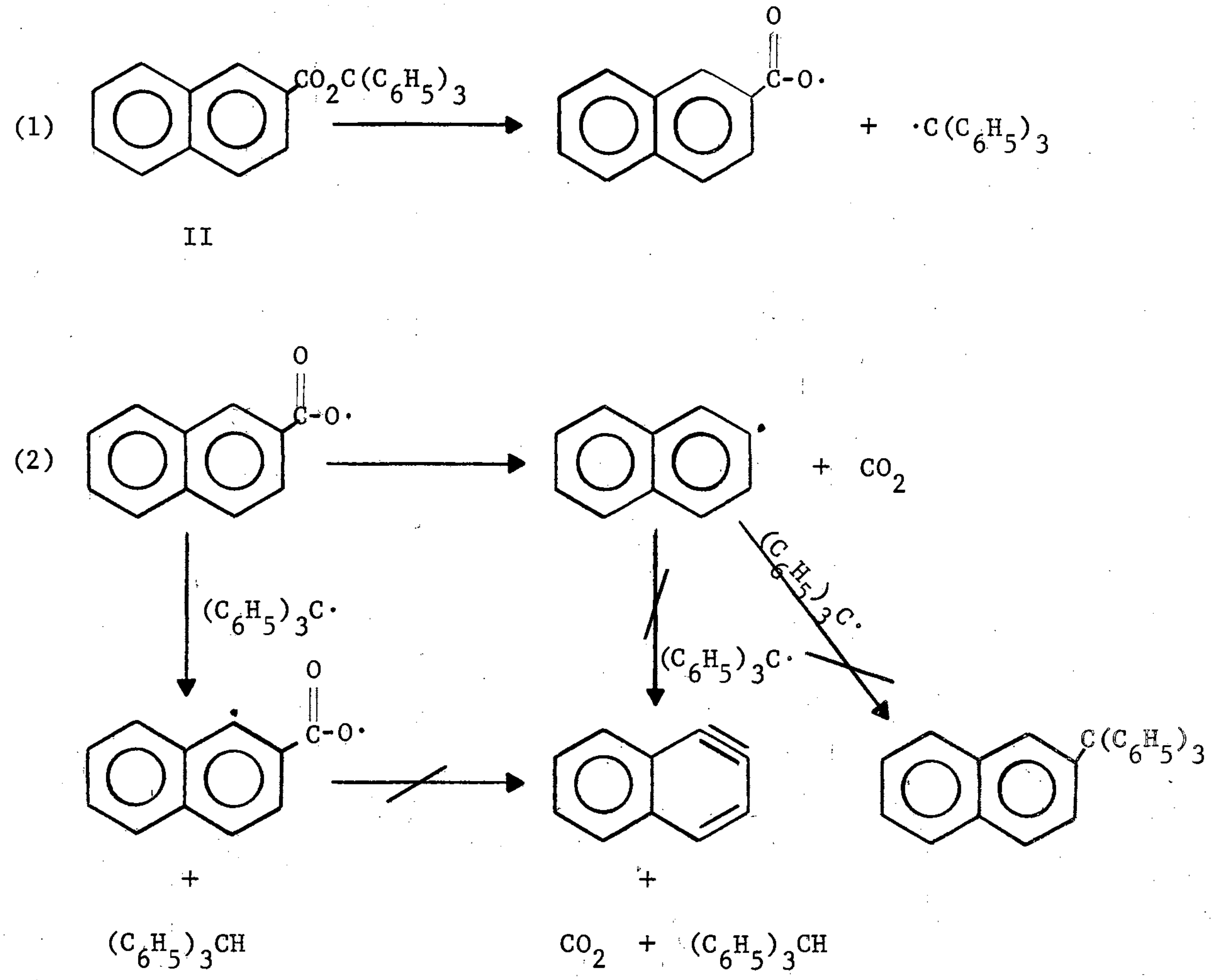
In view of the work of Kharasch and Dannley (35) who have found that β-naphthoyl peroxide decomposes at the boiling point of carbon tetrachloride, it was anticipated that β-naphthoyloxy radicals generated at the pyrolytic conditions would also be unstable. Since abstraction of hydrogen by trityl radicals was well documented (11, 13), the decomposition of the ester II was expected to proceed by the route shown in

Scheme 2


CO2H
Naphthalene + CO2 + H2O +
β-Naphthoic anhydride
+
Major
Triphenylmethane
C·
III
9-Phenylfluorene
CO2(C6H5)3
C6H5
IV
C6H5-CH
+ Polymer B
n
Polymer A
Minor
O
C·
CO
+
Naphthalene
+
(C6H5)3CO·
(C6H5)2C=O
+
Benzene

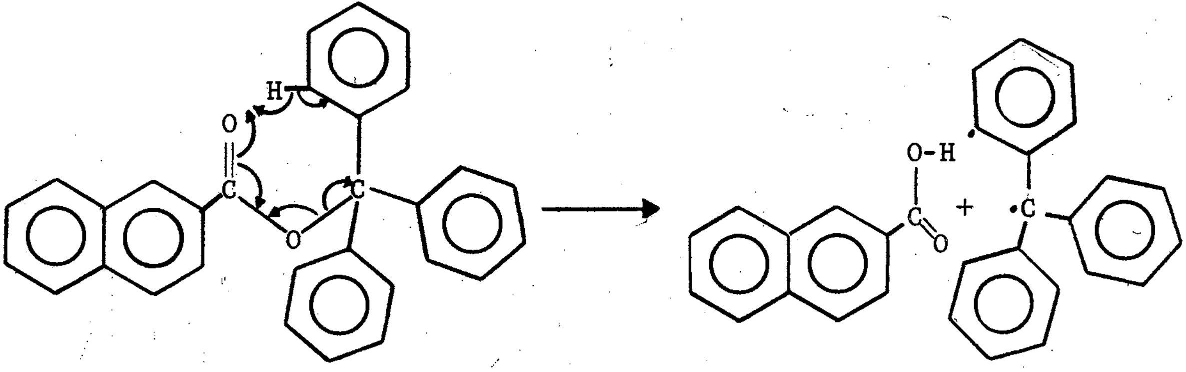
scheme 3. A naphthyne intermediate was also a reasonable possibility as a benzyne type intermediate has been suggested by Reininger in pyrolysis of phenyl cyclohex-1-enecarboxylate at 600° (47).

Scheme 3



High yields of the acid and the small extent of decarboxylation was the first indication that there was a deviation from the expected pathway of the pyrolysis. The quantity of triphenylmethane found was also much lower than anticipated. A study of molecular models indicated the ester to be highly hindered and demonstrated a close proximity of the carbonyl oxygen atom of the naphthoate residue to an ortho hydrogen on the phenyl groups. A concerted mechanism as shown is conceivable. It may be argued that initial cleavage of the ester takes place at the alkyl-oxygen bond resulting in formation of trityl and β-naphthoyloxy radicals (radical pairs). Rapid attack on the trityl radical by the naphthoyloxy radical follows. The two radicals formed initially may exist as radical pairs for a very short time during which the hydrogen transfer may take place.

Scheme 4



To investigate this point, β-naphthoyl peroxide was pyrolyzed. As shown in Table VIII considerable decarboxylation occurred but also a 44.6 per cent return of β-naphthoic acid was realized probably as a result of intermolecular hydrogen abstraction by the β-naphthoyloxy radicals as discussed. The pyrolysate was pale yellow when pyrolysis was terminated but during the work-up, the nonacidic residue acquired a deep red color. The infrared spectrum of the nonacidic solid (fraction H) showed absorption at 1724 and 1695 cm.^{-1} suggesting the presence of ester and keto groups in the compound. Attempts to purify the solid by sublimation gave an orange sublimate which turned red on exposure to air.

The infrared spectrum of the purified material showed no differences from the infrared spectrum of the parent solid. Recrystallization of the fraction H from Skelly F also was ineffectual. Though no definite structure can be assigned to this product it appears to contain a carbonyl function, as ester or keto groups, and is very susceptible to autoxidation. The infrared spectrum of this compound was definitely different from that of any of the polymers. This experiment also indicated the thermal unstability of the β-naphthoyloxy radicals and their tendency to attack like species. Studies could not be done at the pyrolysis temperatures used for the ester II because the peroxide decomposed with a mild report at 109°.

Pyrolysis of the peroxide in presence of triphenylmethane was then studied. If the acid formed in the pyrolysis of ester II was created as a result of attack of the naphthoyloxy radicals on the trityl radicals or triphenylmethane, the amount of decarboxylation in this experiment should be much less than that observed in the pyrolysis of the peroxide itself. If the tertiary benzylic hydrogen was attacked and β-naphthoic acid was formed in yields comparable to those obtained in pyrolysis of II, it would suggest that triphenylmethane was a probable source of hydrogen atoms for β-naphthoic acid. Furthermore, if polymers A and/or B were obtained it would indicate that β-naphthoyloxy radicals are capable of abstracting an aromatic hydrogen from phenyl nucleus.

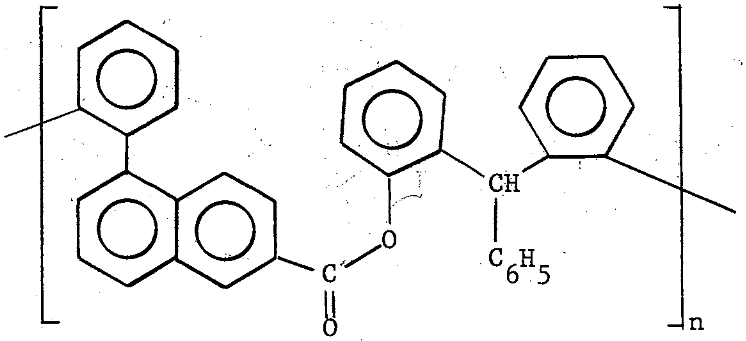
As shown in Table IX triphenylmethane was recovered in nearly 90 per cent yield. The extent of decarboxylation and the amount of β-naphthoic acid formed were comparable to the results of the pyrolysis of β-naphthoyl peroxide itself. A small amount of triphenylmethanol and traces of benzophenone were detected indicating attack on the tertiary benzylic hydrogen atom of triphenylmethane. β-Naphthyl β-naphthoate was also formed apparently as a result of coupling of β-naphthoyloxy radicals with β-naphthyl radicals. About 0.050 g. of a residue obtained displayed an infrared spectrum nearly superimposable on the infrared spectrum of the residue isolated in the pyrolysis of β-naphthoyl peroxide. There was no indication of any product that could have been formed as a result of attack on the ortho hydrogens on the phenyl rings of triphenylmethane. Due to the explosive nature of β-naphthoyl peroxide these pyrolyses were conducted at temperatures nearly 200° lower than the conditions used for the ester II. Similar results would be expected at elevated temperatures. The individual reactivity as well as the rate of decarboxylation of β-naphthoyloxy radicals would be enhanced at higher temperatures. These data show that attack on β-naphthyl or β-naphthoyloxy radicals and decarboxylation is the preferred mode of reaction of β-naphthoyloxy radicals as opposed to abstraction of aromatic hydrogens or the tertiary hydrogen of triphenylmethane.

Based on these considerations a mechanism involving the cleavage of the ester II into β-naphthoic acid and a biradical has been proposed as shown in scheme 2. The biradical III may undergo an intramolecular rearrangement to another biradical IV which could couple in a ring closure step to give 9-phenylfluorene or polymerize to give polymer A. 9-Phenylfluorene was isolated and identified. A biradical mechanism for the formation of 9-phenylfluorene from photolysis of hexaphenylethane has been proposed earlier (38). The biradical proposed by Letsinger is postulated to form as a result of attack of a photo-activated trityl radical on another trityl radical, triphenylmethane being the other product. He has not proposed a definite structure for the biradical.

The proposed structure for the polymer A fits the analytical data. The infrared spectrum (Plate IV) shows strong peaks at 744 (ortho-substituted phenyl) and 700 $cm.^{-1}$ (monosubstituted phenyl groups). The NMR spectrum (Plate VIII) shows a peak for tertiary hydrogen at δ 5.46, a field position nearly identical to that of the tertiary benzylic hydrogen of triphenylmethane. The elemental analysis corresponds to the empirical formula $C_{19}H_{14}$. Fractions melting at 80-142° were obtained by fractional reprecipitation of the polymer from an ethanolic solution with water. These different fractions had identical infrared spectra.

A comparison of the ultraviolet spectrum of polymer A with two model compounds, 2,2'-dimethylbiphenyl and 9-phenylfluorene, is shown in Plate IX. Though some differences in the ultraviolet spectrum would be expected because of the molecular crowding in the polymer, there were remarkable similarities to the spectra of the simple hydrocarbons. The polymer showed maxima at 280, 269, and 240 mμ. As compared to the model compounds, these bands are shifted to higher wave lengths (bathochromic shift) indicating an extended conjugation in the polymer. Molecular weight determinations gave values of 598 and 600 for a fraction melting at 132-144°. Average molecular weight for fractions containing equal amounts of polymer with $n = 2$ and $n = 3$ would be 607.

Polymer B shows all characteristic absorptions of polymer A in the infrared spectrum (Plate V) and shows additional peaks at 1739 and 1279 $cm.^{-1}$ which are characteristic of carbonyl and [C-O-C] groups and suggest the presence of naphthoate functions in the polymer. The absorption is somewhat weak indicating that the amount of ester functions is not in the ratio of one group to each repeating unit. The polymer was exceedingly resistant to chemical reactions or degradations and could be recovered in yields of approximately 90 per cent from attempted hydrolyses with aqueous sodium hydroxide (10%) even after heating at reflux for twenty-four hours. Oxidation with basic potassium permanganate in an attempt to degrade the polymer to simpler organic molecules was also unsuccessful. Fractions with melting ranges varying from 150° to above 300° were obtained. Analyses showed variation in oxygen content in fractions with different melting ranges. The polymer also did not react with Girard T reagent indicative of a hindered or nonreactive carbonyl group as in an ester. Though it is not possible to suggest a definite structure for the polymer, it is possible that it contains a naphthoate moiety in its backbone. The polymerizing radical proposed in the formation of polymer A would be expected to be very reactive and may arylate the naphthalene ring. Perhaps through such reactions a naphthoate moiety may be incorporated in the polymer which would be very resistant to chemical degradations mainly due to steric interactions. Some possible modes of linkage are shown below. Another argument in the favor of such moieties being in the backbone is the fact that a terminal naphthoate would be hydrolyzed under these conditions. For example trityl β-naphthoate can be easily hydrolyzed by heating at reflux a solution of II with aqueous sodium hydroxide (10%) for an hour. Triphenylmethanol and sodium β-naphthoate are formed in nearly quantitative yields.

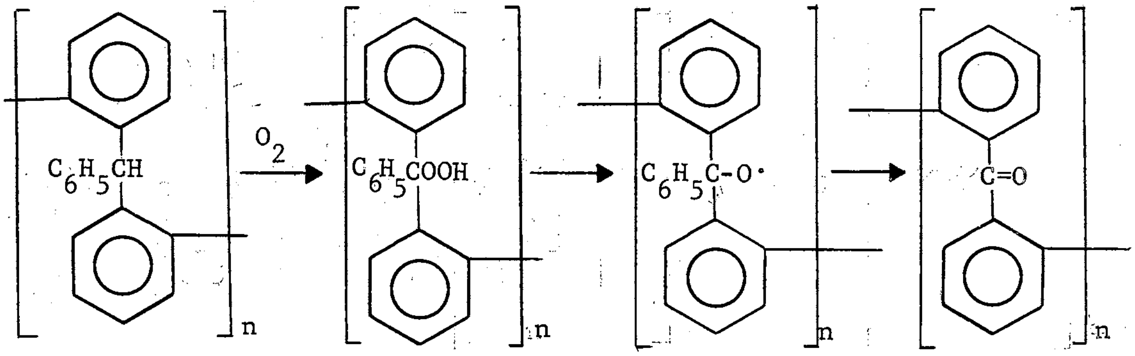


Formation of β-naphthoic anhydride, naphthalene, carbon dioxide and water is proposed to result from a secondary pyrolysis of β-naphthoic acid. Pyrolysis of this acid was done to verify this point, and as shown in Table X, the same products were obtained in nearly comparable yields.

A minor route for the decomposition of trityl β-naphthoate is through the acyl-oxygen bond cleavage, resulting in the production of triphenylmethoxy and β-naphthoyl radicals. Triphenylmethoxy radicals decompose through the route already discussed earlier to benzophenone and phenyl radicals. Phenyl radicals could abstract a hydrogen to give benzene or react with some polymerizing species and terminate the polymerization. Benzene was however not detected. β-Naphthoyl radicals would decarbonylate to form β-naphthyl radicals, and the latter could have a fate similar to that proposed for phenyl radicals.

Further support for a radical mechanism was obtained through pyrolysis of II in an oxygen atmosphere. An increase in the yield of benzophone was expected as a result of oxidation of the radical intermediates and was observed (Table XI). The yield of β-naphthoic acid should be independent of the nature of the carrier gas as was found to be true. Since oxidation of trityl radicals is facile, the increased yield of benzophenone (from decay of triphenylmethoxy radicals) reinforces the argument for a radical mechanism. A polymeric residue was also obtained which showed remarkable similarities with polymers A and B, but was different from these two polymers. The infrared spectrum (Plate VI) of this material (polymer C) not only showed all the characteristic peaks of polymers A and B but showed an extra peak at 1666 $cm.^{-1}$ The position of this peak is identical to carbonyl absorption frequency of benzophenone, suggesting an aromatic keto group in the molecule. Polymer

C was suspected to be an oxidation product of polymers A and B. Oxidation of both the polymers (A and B) was effected by bubbling oxygen into a melt at 350° and gave polymers which showed absorption at 1666 cm.$^{-1}$ The infrared spectrum of oxidation product from polymer B was nearly superimposable on the spectrum of polymer C. This oxidation might be visualized as follows for the origin of polymer C.



Final support for a radical mechanism was obtained from photolysis studies of the ester II. Irradiation of a benzene solution of the ester II (5.0 g. in 70 ml. of benzene) with ultraviolet irradiation for seventy-two hours in a constant stream of oxygen resulted in a definite cleavage, though to only a small extent. The excess ester was hydrolyzed by heating with an aqueous sodium hydroxide solution. The non-acid residue showed the presence of a small quantity of benzophenone.

In summary, an improved synthesis of trityl propionate (I) and synthesis of a new trityl ester, trityl β-naphthoate (II) are described. Pyrolytic decomposition of the two esters was studied and both gave rather complex mixtures. Major pathway for the decomposition of trityl propionate occurred through the alkyl-oxygen bond fission with the formation of trityl and propionyloxy radicals. Formation of propionic acid and acrylic acid is probably through an intramolecular rearrangement of propionyloxy radicals to β-carboxyethyl radicals followed by disproportionation of the latter. Propionic acid may also be formed by an intermolecular hydrogen transfer. Some acyl-oxygen bond severance was also observed as evidenced by the minor products like triphenylmethanol and benzophenone. A radical mechanism (conceivably involving radical pairs) is proposed to explain the formation of various products. Pyrolysis of II followed a somewhat different mechanism resulting in very high yield of β-naphthoic acid and relatively low yield of triphenylmethane. Formation of the two polymers and the corresponding carboxylic acid was rationalized in accord with a biradical mechanism. Investigations on the stability of β-naphthoyloxy radicals were also made through pyrolysis of β-naphthoyl peroxide. The results are parallel to those obtained from the pyrolysis of II which is accepted as evidence for the generation of β-naphthoyloxy radicals from II.

Additional support for the radical mechanisms was afforded through a study of the oxidation process (with molecular oxygen) during pyrolyses of both the esters. Photolysis of II resulted in limited decomposition but benzophenone was detected, which is definitive support for a radical mechanism.

CHAPTER III

EXPERIMENTAL[1,2,3,4,5,6]

Preparation of Sodium β-Naphthoate. A solution of sodium hydroxide (10% in water) was added to a slurry of 40 g. (0.23 moles) of naphthoic acid in 200 ml. of absolute ethanol until pH 7.6 was attained. The precipitate was filtered and a second crop of the salt was isolated by concentrating the filtrate. A yield of 44.4 g. (99.8%) was obtained, m.p. above 300° (54).

Preparation of Trityl Bromide. A one liter, three-necked flask equipped with an addition funnel, stirrer, condenser, nitrogen inlet tube, and a calcium chloride drying tube was charged with 121.7 g (0.45 moles) of triphenylmethanol and 70 ml. of anhydrous benzene. The slurry was

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[1] All melting points are corrected.

[2] The infrared spectra were recorded on Beckman IR-5 and IR-7 spectrophotometers with sodium chloride crystals and potassium bromide pellets.

[3] The nuclear magnetic resonance (NMR) spectra were recorded using a Varian Model A-60 high-resolution spectrometer fitted with a field sensing stabilizer ("Super Stabilizer"). Tetramethylsilane was used as an internal standard.

[4] Gas chromatographic analyses were performed using an Aerograph Hy-Fi Model A-550 unit with a hydrogen flame ionization detector and an Aerograph model A-350B unit with thermal detector cell from Wilkens Instrument and Research, Inc.

[5] The microanalyses were performed by Midwest Microlab Inc., Indianapolis, Indiana.

[6] Skelly F and Skelly B are petroleum ether fractions boiling at 35-45° and 60-70°, respectively.

heated to near reflux and 66.5 g. (0.54 mole) of acetyl bromide was added dropwise over a period of one-half hour. Precipitation of a solid occurred when nearly one-half of the bromide had been added. The contents were heated at reflux for one-half hour and then cooled. The precipitate was filtered and dissolved in 400 ml. of hot benzene. Activated charcoal (ca . 5 g.) was added to the hot solution which was heated for ten minutes, filtered, and diluted with 200 ml. of Skelly F and cooled. The solid which crystallized from solution was filtered. Additional trityl bromide was obtained by concentrating the filtrate and diluting with 200 ml. of Skelly F; yield, 129.5 g. (87.0%) m.p. 152-4° C. (4).

Preparation of Trityl Propionate (I). A three-necked, 250-ml. flask covered with aluminum foil, equipped with a stirrer, and a thermometer was charged with 22.05 g. (0.07 mole) of trityl bromide, and 100 ml. of dry benzene. After the bromide had dissolved, 13.95 g. (0.077 mole) of silver propionate was added with constant stirring over a period of fifteen minutes. The addition initiated an exothermic reaction, and the temperature rose to 50°. A brownish-colored precipitate formed initially and turned yellow. The contents were stirred for an additional one-half hour and were then diluted with 25 ml. of isopropyl ether. Silver bromide, a yellow-colored precipitate, was filtered and washed with 25 ml. of isopropyl ether, and the filtrate was concentrated to an oil. Additional (10 ml.) isopropyl ether was added, and the contents were evaporated on a rotary evaporator. Fifteen milliliters of isopropyl ether and 60 ml. of Skelly F solvent were added to the yellow oil. After standing for about twenty minutes, a pale-yellow, crystalline solid separated from the yellow solution. The solid was filtered on a Buchner funnel under suction and dried in vacuum dessicator; yield 19.678 g.

(84.2%), m.p. 81-3°. This compound was reported while our work was in progress (2). When the preparation of I was carried out using 21.72 g. (0.0675 mole) of trityl bromide, 16.2 g. (0.0834 mole) of silver propionate in 60 ml. of carbon tetrachloride, a yield of 20.48 g. (96.5%) of the ester I was obtained. The infrared spectrum (Plate I) showed strong absorption at 1742 (carbonyl in ester group) and 700 cm.$^{-1}$ (monosubstituted phenyl group). The NMR spectrum (Plate VII) displayed a singlet at δ 7.18 (aromatic protons), a quartet centered at δ 2.36 (methylene protons) and a triplet δ 1.11 (methyl protons).

Preparation of β-Naphthoyl Chloride. A 50 ml., round-bottom flask was charged with 9.8 g. (0.06 mole) of β-naphthoic acid and 34 g. (0.3 mole) of thionyl chloride and the contents were heated at reflux for three hours. Evolution of hydrogen chloride and sulfur dioxide was observed for the initial two and one-half hours. Excess thionyl chloride was distilled under reduced pressure. Residual traces of thionyl chloride were removed by azeotropic distillation with three 15-ml. portions of benzene. The liquid obtained solidified to pale yellow needles on standing, yield 10.97 g. (quantitative). The acid chloride was used directly without further purification (58).

Preparation of Trityl β-Naphthoate (II). To trityl bromide (10.1 g.,) 0.05 mole) dissolved in 70 ml. benzene, was added 10.9 g. (0.056 mole) of sodium β-naphthoate, and the mixture was boiled for thirty-nine hours under nitrogen. The reaction mixture was filtered while hot and the filtrate was concentrated to an oil. About 15 ml. of isopropyl ether was added and the contents were concentrated a second time. The pale yellow solid obtained was washed with about 25 ml. of isopropyl ether containing 2 ml. of triethyl amine, yield 17.7 g. (86.7%), m.p. 146-149°. Recrystallization from isopropyl ether raised the m.p. to 149-150°. The infrared spectrum (Plate III) showed peaks at 3030 (aromatic C-H stretch), 1724 (carbonyl in ester), 1282, 781, 763, 743, and 714-689 $cm.^{-1}$ (monosubstituted phenyl groups).

<u>Anal</u>. Calcd. for $C_{30}H_{22}O_2$:

C, 86.95; H, 5.31.

Found: C, 86.59; H, 5.39.

<u>Preparation of β-Naphthoyl Peroxide</u>. A 100-ml., three-necked flask equipped with an addition funnel, condenser, and stirrer was charged with 3.55 g. (0.045 mole) of sodium peroxide and 30 ml. of anhydrous acetone. The contents were cooled in an ice-bath and a solution of 16.112 g. (0.085 mole) of β-naphthoyl chloride in 30 ml. of anhydrous acetone was added dropwise through the addition funnel. Water (1 ml.) was added, the ice-bath was removed, and the resulting mixture was stirred at room temperature for twenty hours. The mixture was then poured into 100 ml. of water with stirring which was continued until the oil, which separated initially, solidified. The pale yellow solid was washed successively with a Skelly F-water mixture (150 ml. of each), 20 ml. of 10% sodium bicarbonate solution, and again with 200 ml. of the Skelly F-water mixture. The solid was then filtered with suction and dried in a vacuum dessicator; yield of the peroxide 7.732 g. (50.6%), m.p. 130-133°. Further purification of the peroxide was achieved by washing the solid with 15 ml. each of carbon disulfide, ethylene dichloride, and a Skelly B-dioxane mixture (1:3). A white, amorphous solid was thus isolated which decomposed sharply and vigorously at 138° [lit. 138° (35)].

Pyrolysis of Trityl Propionate (I). The system consisted of a 50-ml. two-necked flask equipped with a helium inlet tube and a reflux condenser. The top of the condenser was connected to the trap system. The trap system consisted of two preweighed traps (cooled with Dry Ice and acetone) followed by a preweighed Ascarite tube and a glass system designed to collect gases by displacement of an aqueous salt solution. The heating bath was composed of a mixture of potassium nitrate and sodium nitrate in 80:65 ratio which melted at about 250°.

The pyrolysis flask was charged with 18.96 g. (0.06 moles) of trityl propionate. After flushing the system with helium, the pyrolysis flask was immersed in the salt bath (preheated to 295°) and heated at 295-305° for six hours and at 315° for the final fifteen minutes. During the heating period, evolution of carbon dioxide was detected by a change in color of the Ascarite. After heating was discontinued, the contents of the flask were allowed to cool slowly to room temperature. The system was disassembled and the traps were weighed.

The first trap contained 0.1815 g. of liquid which, on warming to room temperature, separated into two layers. The lower layer (0.021 ml.) was removed with a hypodermic syringe and was identified as water. Analysis of the remaining liquid showed it to be a mixture of benzene, ethylbenzene and styrene. These were identified by gas chromatography. The retention times and the conditions are listed below and are identical to the retention times obtained by injection of authentic samples under identical conditions.

TABLE I

QUALITATIVE GAS CHROMATOGRAPHIC ANALYSIS OF THE LIQUIDS IN THE FIRST TRAP IN THE PYROLYSIS OF I

Column: Apiezon L, 10% on Chromosorb W, 80-100 mesh, 4 ft. x 0.125 in.

Conditions: N_2 flow=28 ml./min.; H_2 flow=22 ml./min., Temp. 95°; A-550 Unit.

Compound	Retention Time
Benzene	0 min. 30 sec.
Ethylbenzene	2 min. 50 sec.
Styrene	3 min. 50 sec.

The separation obtained above was satisfactory for qualitative determinations. Quantitative determinations were made from gas chromatography of the mixture on a di-*n*-butyl phthalate column. The conditions, retentions times, and the relative areas are shown below in Table II.

TABLE II

QUANTITATIVE GAS CHROMATOGRAPHIC ANALYSIS OF THE LIQUIDS IN THE FIRST TRAP IN THE PYROLYSIS OF I

Column: Di *n*-butyl phthalate, 10% on Fluoropak 90, 40/60 mesh, 6 ft. x 0.125 in.

Conditions: N_2 flow = 22 ml./min.; H_2 flow = 22 ml./min., Temp. 100°; A-550 Unit.

Compound	Retention time	Relative area
Benzene	13 min. 0 sec.	4.76
Ethylbenzene	39 min. 10 sec.	10.4
Styrene	64 min. 0 sec.	1.0

Weights of individual hydrocarbons were calculated according to the following equation. Independent observations have shown that this expression holds true for compounds similar in structure. These values should be correct to within 5 per cent in several experiments.

$$\text{Wt. of the Compound} = \frac{\text{Total weight} \times \text{area of the peak}}{\text{Total area of all peaks}}$$

$$\text{Thus Wt. of benzene} = \frac{.1601 \times 7906}{26966} = 0.047 \text{ g.}$$

$$\text{Wt. of ethylbenzene} = \frac{.1601 \times 17380}{26966} = 0.103 \text{ g.}$$

$$\text{Wt. of styrene} = \frac{.1601 \times 1680}{26966} = \underline{0.010 \text{ g}}.$$

$$\text{Total Wt.} \quad 0.160 \text{ g.}$$

Infrared analysis of the gases collected over the brine solution indicated it to be a mixture of carbon monoxide and n-butane. Only trace quantities of other gases were found.

The residue was dissolved in a minimum quantity of ether (ca 75 ml.) and extracted with 75 ml. (0.4848 N) of potassium hydroxide solution. A clear brown solution was obtained and was titrated against a standard solution of hydrochloric acid to determine the amount of propionic acid. The titrations were followed using a Beckmann pH meter (Model 72). Addition of hydrochloric acid to the basic solution resulted in the formation of a turbid mixture from which precipitation occurred. The mixture was made acidic (ca pH 1-2) after titration, and a brown solid was filtered with suction and dried in a vacuum dessicator. Evaporation of an ether solution of the solid left a glassy residue which appeared to be polymeric in nature. The solid weighed 1.938 g. and melted at 70-75°. An infrared spectrum of the acid (Plate II) showed a broad band at 3600-2500 (hydroxyl of the carboxyl group), strong absorption at 1710 (carbonyl), and 710 cm.^{-1} (monosubstituted phenyl).

The polymeric acid was esterified by heating 0.180 g. of the solid under reflux with 3 ml. of concentrated hydrochloric acid and 3 ml. of absolute ethanol for twelve hours. The contents were evaporated to dryness and a mixture of ether-water (15 ml. of each) was added. The ether layer was separated and dried over calcium chloride. Evaporation of the ether left a heavy oil which was chromatographed over acid-washed alumina. Elution with a mixture of ether and benzene (25:75) gave a pale yellow, oily liquid which hardened to a glassy solid. This solid possessed an infrared spectrum which was nearly superimposable on a spectrum of a copolymer of styrene and ethyl methacrylate.

An aliquot (2.5 ml.) of the non-acidic, ether extract of the pyrolysate was reserved for gas chromatographic analysis. Identification of the volatile components was done by comparison of the retention times with those of authentic samples by means of gas chromatography. Analysis revealed the presence of two compounds which are listed along with the conditions in Table III.

TABLE III

QUALITATIVE GAS CHROMATOGRAPHIC ANALYSIS OF THE NONACIDIC RESIDUE FROM PYROLYSATE OF I

Column: SE 30, 10% on Chromosorb W, 80/100 mesh, 5 ft. x 0.25 in.

Conditions: He Flow=82.4 ml./min., Temp. 200°; A-350B Unit.

Compound	Retention time
Benzophenone	3 min. 50 sec.
Triphenylmethane	12 min. 20 sec.

The remaining solution (44.5 ml.) was chromatographed over acid-washed alumina. Appearance of each compound in the eluate was followed by analysis of each fraction by gas chromatography. The eluant was changed when no additional compound was obtained in the eluate. Fractions containing the same material were mixed and evaporated to determine the weight of the particular compound.

Elution of the column (30 in. x 1.25 in.) with Skelly F gave 10.668 g. of residue (Fraction A) which was essentially triphenylmethane with traces of benzophenone and a colored impurity. Thirty fractions of about 35-40 ml. each were collected using Skelly F as eluant. Skelly B was used to elute 10 fractions of 35-40 ml. each. These fractions were composed of solvent only. Further elution of the column was done with a benzene-acetone mixture (1:1) [9 fractions] and gave 1.341 g. of a dark brown, viscous, oily residue (Fraction B). Further development of the column with acetone [11 fractions of 35-40 ml. each] gave 1.182 g. of a dark brown residue (Fraction C) which partially crystallized. Fraction A was chromatographed on a separate column and 10.37 g. of triphenylmethane was obtained. The colored material (0.300 g.) was not identified.

An infrared spectrum of fraction B showed the presence of both aromatic and carbonyl groups. This material was purified by chromatography on acid-washed alumina from which a pale brown oily liquid was obtained. This was distilled in a short path distillation apparatus under reduced pressure to give a colorless liquid. Analysis by gas chromatography showed it to be benzophenone. A small amount of the liquid was further purified by gas chromatography on the Aerograph A-350B unit. The product collected did not solidify on cooling to near zero degrees. The infrared spectrum of the compound was nearly superimposable on the spectrum of alpha benzophenone. A sample of alpha benzophenone was injected onto the Aerograph A-350B gas chromatograph under the same conditions [SE-30 (10%) column on Chromosorb W, 80/100 mesh, 5 ft. x 0.25 in., column temperature 225°]. This sample also did not solidify on cooling and had an infrared spectrum which was identical to the one obtained above. This evidence confirmed the identity of fraction B and indicated that the compound isolated was actually beta or delta benzophenone, an isomorphoric modification of alpha benzophenone.

Fraction C was dissolved in minimum amount of benzene and chromatographed on alumina. A pale yellow eluate was obtained when benzene was used as the eluant. The eluate was concentrated to near dryness to yield 0.284 g. of a pale yellow, crystalline solid. This was identified as triphenylmethanol by its infrared spectrum and melting point. Elution of the column with a carbon tetrachloride-acetone mixture (4:1) gave a yellowish-brown, glassy solid. The infrared spectrum of this solid was remarkably similar to that of the polymeric acid obtained earlier except for the following differences. It showed stronger absorption at 1754 $cm.^{-1}$ and only a shoulder at 1710 $cm.^{-1}$. Absorption at 2500-3300 $cm.^{-1}$ was also much weaker. The data indicate this fraction to be also a acrylic acid-styrene copolymer in which a considerable number of carboxyl groups are esterified. All of the information is summarized in the Table IV. The data reported are the results of this pyrolysis and are comparable with results obtained in other pyrolyses of the ester I.

TABLE IV

PYROLYSIS OF TRITYL PROPIONATE (I)
(UNDER NITROGEN)

Temperature 300-310°; time 6 hr.

Products	Wt., g.	Mole % of ester
Carbon dioxide	0.3343	12.62
Carbon monoxide	0.2053	
n-Butane		
Benzene	0.047	1.03
Water	0.021	0.25
Ethylbenzene	0.103	1.62
Styrene	0.010	0.16
Propionic acid	2.12	47.74
Triphenylmethane	10.952	74.83
Benzophenone	1.408	12.99
Triphenylmethanol	0.299	1.82
Copolymer	2.8864	27.26
Trace materials (mixture)	0.316	
	18.7020	
Wt. of ester I	18.96	

Pyrolysis of Trityl Propionate (I) in an Oxygen Atmosphere. Pyrolysis of 3.2 g. (0.01 mole) of the ester was conducted in an apparatus similar to the one described previously but the trap system was not used. An oxygen inlet tube was extended into the reaction flask so that it dipped below the surface of the melted ester. The ester was pyrolyzed at 300° for a period of two and one-half hours in a continuous stream of oxygen. After cooling to room temperature, the pyrolysate was analyzed by infrared spectrometry and gas chromatography which indicated the presence of propionic acid, triphenylmethane and benzophenone as the major products. The amount of benzophenone in the oxygenated pyrolysate was considerably increased as compared to that observed in the pyrolysate obtained from the decomposition conducted in a nitrogen atmosphere.

Pyrolysis of Trityl-β-Naphthoate (II). The system was composed of a 50-ml., two-necked flask equipped with a nitrogen inlet tube and a reflux condenser the top of which was connected to a series of three traps. The first trap was cooled with Dry Ice and acetone, the second contained a solution of lime water and the last trap contained a dilute, aqueous solution of palladium dichloride. Pyrolysis of 5.9 g. (0.014 mole.) of trityl β-naphthoate was examined on a qualitative basis in order to determine the conditions required and the nature of decomposition products. The pyrolysis was conducted in a continuous stream of dry nitrogen at 230-250° for a period of four and one-half hours. Since carbon dioxide was not detected during this period, the temperature was raised to 315°, at which slow evolution of carbon dioxide was observed after one-half hour. Heating was continued at 315-330° for an additional eight hours after which the evolution of carbon dioxide ceased. Formation of carbon monoxide was indicated by deposition of a black palladium mirror in the palladium dichloride trap (1). A small amount of crystalline sublimate was also observed in the condenser. The infrared spectrum of the solid showed it to be naphthalene. The pyrolysate was dissolved in a minimum amount of benzene (ca. 100 ml.), and the solution was extracted with three portions of 10% sodium bicarbonate (25 ml.). Acidification of the basic extract gave 1.2 g. (48.9%) of β-naphthoic acid.

Qualitative gas chromatographic analysis of the nonacidic extract showed the presence of 4 volatile components, three of which could be identified by comparison of the retention times with those obtained from authentic samples. Results of the analyses along with the conditions are tabulated in Table V.

TABLE V

QUALITATIVE GAS CHROMATOGRAPHIC ANALYSIS OF THE NONACIDIC EXTRACT FROM THE PYROLYSATE OF II

Column: SE 30, 10% on Chromosorb W, 80/100 mesh, 5 ft. x 0.25 in.

Conditions: He flow=90 ml./min., Temp. 200^{o}; A-350 B Unit.

Compound	Retention time
Naphthalene	1 min. 0 sec.
Unknown product (traces)	2 min. 30 sec.
Benzophenone	3 min. 20 sec.
Triphenylmethane	11 min. 10 sec.

The nonacidic benzene extract was dried over anhydrous potassium carbonate and filtered through a bed of about 100 g. of acid-washed alumina in a Buchner funnel. Washing of the alumina with 100 ml. of n-hexane gave filtrates which were combined and concentrated to an oily residue (Fraction D). Washing of the alumina bed with ether gave a highly colored filtrate which on evaporation gave a dark-brown residue (Fraction E).

Fraction D was then chromatographed on an acid-washed alumina column (30 in. x 1.25 in.). Fractions of approximately 25 ml. each were collected and analyzed by gas chromatography. Pure n-hexane was used as eluant for the first 44 fractions. Fractions 1-5 were blank, but the next 15 fractions contained triphenylmethane and naphthalene. The following 24 fractions contained only triphenylmethane. The eluant was then changed to pure ether. Benzophenone, traces of triphenylmethane and an unknown were found in the first fraction. Fractions 2-3 contained benzophenone and traces of the same unknown as in fraction 1. The last three fractions, on evaporation of solvent under aspirator pressure, gave only a very small amount of glassy residue, which was absorbed on the gas chromatography column, indicating that the solid had a high molecular weight. Consequently, it was not possible to separate the mixture into pure compounds, thereby facilitating the identification of the unidentified products and calculation of the yields of the products directly. Quantitative determinations were done by gas chromatography in the next pyrolysis.

Fraction E, which was considerably less soluble than fraction D, was dissolved in benzene (ca. 100 ml.) and chromatographed over acid-washed alumina (column, ca. 24 in. x 1 in.). Elution of the column was started with n-hexane, and fractions of about 25 ml. each were collected. The first 11 fractions were eluted with n-hexane, followed by a 1:1 mixture of n-hexane-cyclohexane (4 fractions). Pure cyclohexane was added and 15 fractions were taken. Analysis by gas chromatography of all solutions obtained showed them to be only solvents. A cyclohexane-benzene mixture (1:1) was next used as eluant and 9 fractions were collected. Further development of the chromatography column was continued using benzene-cyclohexane mixture (3:1; 3 fractions), benzene (25 fractions), ether (20 fractions) and methanol (10 fractions) successively as eluants. Fractions 4-6 obtained with cyclohexane-benzene mixture (1:1) on evaporation, gave a shiny, yellow solid which softened at 173-183° and became beadlike in appearance but did not have a sharp melting point up to 200°. The infrared spectrum indicated the material to be a hydrocarbon and showed strong absorption at 754 (ortho-substituted phenyl) and 700 $cm.^{-1}$ (monosubstituted phenyl groups). It also showed three peaks in the region 1000-1040 $cm.^{-1}$. The solid was placed in a glass frit thimble in a Soxhlet extractor and extracted with warm Skelly F until the overflowing filtrate was colorless. The pale yellow solid thus obtained softened to a yellow bead at 230-240° and did not have a sharp melting point up to 260°. Its infrared spectrum was identical to the infrared spectrum of the parent solid. The filtrate was chromatographed over alumina, and the column, on elution with benzene gave a small amount of a pale yellow glassy solid, melting at 130-140°, whose infrared spectrum was also nearly superimposable on the infrared spectrum of the parent solid. The above data indicated the material was probably polymeric in nature, and we obtained fractions of varying molecular weight.

Evaporation of solvents from fractions obtained with benzene gave small amounts of glassy solids ranging in color from yellow to orange to red. Analysis of several fractions by infrared spectrometry showed absorption at 1738 (carbonyl group in an ester), 1655 (carbonyl group in conjugated ketone), 754 (ortho-substituted phenyl), and 700 $cm.^{-1}$ (monosubstituted phenyl group). It also showed the characteristic absorption in the 1040-1000 $cm.^{-1}$ region. Attempts to separate the mixture into pure components by extraction with Skelly F in a Soxhlet apparatus led to fractions with melting ranges from 120 to 240° and which had essentially superimposable infrared spectra. These data suggest that the material is a polymer (Polymer C). Further investigations were not performed at this stage because of the small amounts of the materials. The above data also indicated that the work-up procedure needed to be modified so as to effect an easier separation of the known and soluble compounds from considerably less soluble polymeric material.

Second Pyrolysis of Trityl β-Naphthoate (II). Pyrolysis of 20.7135 g. (0.05 mole) of the ester II was conducted in a system essentially identical to that described earlier except for the following changes. Helium was used as the carrier gas rather than nitrogen and the lime water trap was replaced by an Ascarite U tube. A heating bath (80:65 mixture of potassium nitrate and sodium nitrate) preheated to 322° was applied to the pyrolysis flask which was secured in place so that the level of molten ester was below the bath level. The bath temperature fell to 300° but was quickly raised to 350°. Within ten minutes at this temperature the color of the ester started to change from white to yellow, to a yellowish brown, to brown and finally to dark brown. After another five minutes, effervescence was detected and was observed to continue for about thirty minutes. Heating was continued for a total of one and one-half hours at 344-350° during which period a small amount of carbon monoxide was detected by the formation of black mirror in the palladium dichloride trap. Formation of carbon dioxide (0.0799 g., 3.63%) was substantiated by weighing the Ascarite tube. A small amount of sublimate noted in the condenser, was shown to be naphthalene by infrared spectrometry and gas chromatography.

The first trap (cooled with Dry Ice and acetone) was found to contain a few drops (c.a. 50-100 μl.) of a colorless liquid which evaporated on warming to room temperature. The infrared spectrum of a gas sample showed strong absorption at 2980 (aliphalic C-H), 1375, 1340, 1175, 1128, 1025 and 795 cm^{-1}. This gas was not identified. It is not methane, ethane, propane, n-butane, isobutane, acetylene or ethylene as evidenced by comparison with the infrared spectra of authentic samples. A very small amount of water was also detected in the same trap.

In order to remove the pyrolysate, which had set to a hard, solid mass, it was dissolved in about 400-500 ml. of hot carbon tetrachloride and the solution was diluted with 250-300 ml. of Skelly F. The resulting solution was evaporated to dryness. The yellow mass thus obtained was extracted with 300 ml. of warm Skelly F. The extract, on evaporation to dryness, gave 6.16 g. of a yellow solid (Fraction F). Extraction of the Skelly F insoluble residue with 300 ml. of 10% sodium bicarbonate removed β-naphthoic acid leaving 7.33 g. of residue (Fraction G). Acidification of the bicarbonate extract with concentrated hydrochloric acid to pH 1-2 gave 5.8795 g. (68.4%) of β-naphthoic acid.

Fraction F on gas chromatographic analysis showed the presence of triphenylmethane, benzophenone and a component (first thought to be triphenylmethanol because of identical retention times) which was later identified as 9-phenylfluorene. The residue was chromatographed on acid-washed alumina (ca . 24 in. x 1 in.) and fractions of about 25 ml. were collected. Elution with Skelly F (24 fractions) gave 4.342 g. of triphenylmethane. The last fraction obtained with Skelly F was found to be pure 9-phenylfluorene[7] by infrared spectrometry. Pure n-hexane (16 fractions) and n-hexane-benzene mixture (3:1, 24 fractions) were used next as eluants but did not remove any materials from the column. Further elution of the column with a 1:1 mixture of n-hexane

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[7] An authentic sample was kindly supplied by Mr. James Rea, Department of Chemistry, University of Missouri, Columbia, Missouri.

and benzene gave a pale yellow eluate, which on evaporation to dryness gave 0.906 g. of oily liquid which hardened to a glassy solid on standing. This residue, which had an infrared spectrum (Plate IV) nearly superimposable on that of the polymeric hydrocarbon obtained earlier from the first pyrolysis of II, was designated as Polymer A. No other product was obtained from the column with methanol. The ratios of triphenylmethane, 9-phenylfluorene and benzophenone were determined by quantitative gas chromatography as shown in Table VI.

TABLE VI

QUANTITATIVE GAS CHROMATOGRAPHIC ANALYSIS
OF FRACTION F

Column: Silicone Rubber, 10% on Chromosorb W, 80/100 mesh, 8 ft. x 0.125 in.

Conditions: N_2 flow = 34 ml./min., H_2 flow = 46 ml./min., Temp. 220°; A-550 Unit.

Compound	Retention time	Relative area
Benzophenone	1 min. 10 sec.	1
Triphenylmethane	2 min. 40 sec.	572
9-Phenylfluorene	4 min. 0 sec.	23.6

Fraction G, the infrared spectrum of which showed a close similarity with a spectrum of Polymer A, was designated Polymer B. Further fractionation of this residue was done by extraction with warm Skelly B in a Soxhlet extractor. The Skelly B insoluble residue (3.539 g.) softened at 260° and turned brown near 270-280° with no sharp melting point up to 300°. Extraction of the Skelly B insoluble residue with methanol gave only a tar that was absorbed by charcoal. The material thus obtained was polymer B, the infrared spectrum of which (Plate V) showed all the characteristic peaks of polymer A and additional absorption at 1739 cm.$^{-1}$ suggesting the presence of an ester group in the molecule. Concentration of the filtrate gave 0.986 g. of polymer B melting at 180-200°. The filtrate was then evaporated to dryness to give 2.36 g. of a glassy solid which on extraction with methanol gave additional fractions of polymer B which melted from 150 to 170°. The methanol extract was treated with Girard T reagent to remove traces of benzophenone, and the insoluble residue was then heated to reflux with a solution of 2.2 g. of sodium hydroxide in 25 ml. of water for twenty-four hours. Acidification of the basic extract gave 0.758 g. of β-naphthoic acid. The base insoluble residue was found to be a mixture of triphenylmethane, 9-phenylfluorene and Polymer A. Column chromatography (similar to one used for fraction F) gave 0.438 g. of mixture of triphenylmethane and 9-phenylfluorene. The results are summarized in Table VII.

TABLE VII

PYROLYSIS OF TRITYL-β-NAPHTHOATE (II) (UNDER NITROGEN)

Temperature 345-350°; time 1.5 hr.

Products	Wt., g.	Mole % of ester
Carbon dioxide	0.0799	3.63
Carbon monoxide	0.1723	
Naphthalene		
Water		
Unknown gas		
β-Naphthoic acid	5.8795	68.4
β-Naphthoic anhydride	0.865	10.6
Triphenylmethane	4.6672	38.2
9-Phenylfluorene	0.1938	1.6
Benzophenone	0.0073	0.008
Polymer A	2.137	17.4
Polymer B	4.80	
Tar	0.683	
	19.485	
Wt. of Ester	20.700	

Polymer A: This material was soluble in ethanol, benzene, acetone, and carbon tetrachloride and could be separated into fractions with melting ranges from 80 to 144° by fractional precipitation from an ethanolic solution with water. The polymer softens to a glassy bead which can be tapped off from the melting point capillary tube. The infrared spectrum (Plate IV) showed absorption at 3030 (aromatic C-H), 1600, 1492, 1449, 1034, 744 (ortho-substituted phenyl), 700 cm.$^{-1}$ (monosubstituted phenyl). NMR analysis (Plate VIII) showed a multiplet for aromatic hydrogens (δ 7.18) and a multiplet for a tertiary benzylic hydrogen (δ 5.46).

Molecular weight determinations[8] on a fraction melting at 132-144° gave values of 598 and 600.

<u>Anal</u>. Calcd. for $C_{19}H_{14}$:

C, 94.21; H, 5.78

Found: C, 93.66; H, 5.78.

Polymer A (15-20 mg.) was heated in a small test tube to 340-350°, and a stream of oxygen was bubbled into the melt for four to five minutes. A brown glassy residue was obtained which melted at 150-160° and showed weak absorption in the infrared spectrum at 1666 cm^{-1}. The peak at 1666 $cm.^{-1}$ is characteristic of aromatic ketones like benzophenone (7) and suggests the formation of a keto group during oxidation.

Polymer B: This material was fairly soluble in carbon tetrachloride and benzene but considerably less soluble than polymer A in ethanol. Fractions with melting ranges from 150 to above 300° were obtained during the work-up. The infrared spectrum (Plate V) showed absorption at 3030, (aromatic C-H), 1739 (carbonyl group), 1600, 1492, 1449, 1279, (C-O-C in esters) 1187, 1034, 744 (ortho-substituted phenyl), and 700 $cm.^{-1}$ (monosubstituted phenyl).

<u>Anal</u>.

Found: C, 88.96; H, 5.18 (fraction melting 233-242°)

C, 91.75; H, 51.25 (fraction melting above 300°)

Polymer B (15-20 mg.) was oxidized in the manner described with polymer A and the product showed a weak absorption at 1666 cm^{-1}. Polymer B was recovered in 94% yield from a reaction with Girard T reagent. It

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[8] We acknowledge our thanks to Dr. Paul O. McCoy, Department of Chemistry, University of Oklahoma, Norman, Oklahoma, for the molecular weight determination.

could be recovered (92%) unreacted from an attempted oxidation with boiling solution of alkaline potassium permanganate (1.16%) after forty hours.

Peaks at 1739 and 1279 cm.$^{-1}$ are characteristic of esters and suggest the presence of a naphthoate moiety in the polymer. This group is not terminal because the polymer could be recovered (90%) from an attempted hydrolysis with 10% sodium hydroxide after boiling for twenty-four hours. Trityl β-naphthoate, though very hindered, can be hydrolyzed by heating at reflux with a solution of sodium hydroxide (10%) within one hour to sodium β-naphthoate and triphenylmethanol in quantitative yields. A definite structure cannot be assigned because fractions varying in oxygen content were always isolated.

Pyrolysis of β-Naphthoyl Peroxide. Pyrolysis of 1.710 g. (0.005 mole) of crude[9] β-naphthoyl peroxide melting at 120-125° was conducted in the system as described for the pyrolysis of ester II. The contents were carefully heated to 107° in an oil-bath. Slight softening of the solid was observed at this stage, and after ten minutes of heating at 107-109°, the contents decomposed vigorously with a mild report. Heating was stopped and after checking for damages, the system was flushed with helium for an additional one hour. A considerable amount of white residue identified by infrared spectrometry to be β-naphthoic acid, was found in the condenser and the traps. All residue from the flask and traps was dissolved in ether (ca . 100 ml.) and the ether solution was stirred with 35-40 ml. of 10% sodium bicarbonate solution for six hours. Separation of the aqueous layer and acidification with

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[9] Pure β-naphthoyl peroxide decomposes explosively at 138° (35).

concentrated hydrochloric acid to pH 1-2, gave 0.768 g. (44.6%) of β-naphthoic acid. The neutral ether extract was evaporated to dryness and the residue obtained was dissolved in 30 ml. of benzene to which a solution of 1.2 g. of sodium hydroxide in 20 ml. of water was added. The contents were heated to reflux with stirring on a steam bath for two hours. After cooling, the contents were poured into a separatory funnel and 50 ml. each of benzene and water were added successively. The benzene layer, after drying over anhydrous calcium chloride and evaporation to dryness, gave 0.183 g. of a deep red-colored residue (Fraction H). Acidification of the aqueous layer gave 0.313 g. of a dull red, tarry residue, which was not characterized further.

Fraction H on gas chromatographic analysis showed the presence of naphthalene in small amounts and traces of two unknown products. The infrared spectrum showed absorption at 1724 (carbonyl in ester) and 1695 cm.$^{-1}$ (carbonyl in conjugated ester). Sublimation of a small sample gave a yellowish orange sublimate which on exposure to air turned red and an infrared spectrum of which was identical to the infrared spectrum of the parent solid. The compound is probably a polynuclear compound and contains a small amount of ester functions. It is also very susceptible to autoxidation. Purification by recrystallization from Skelly F was also unsuccessful. The results are shown in the Table VIII.

TABLE VIII

PYROLYSIS OF β-NAPHTHOYL PEROXIDE

Temperature 107-109°; Time 10 Min.

Products	Wt., g.	Mole % of Peroxide
Carbon dioxide	0.1225	27.8
β-Naphthoic acid	0.768	44.6
Naphthalene	Traces	
Residue	0.510	
	1.4005	
Wt. of Peroxide	1.710	

<u>Pyrolysis of β-Naphthoyl Peroxide with Triphenylmethane</u>. Pyrolysis of 1.71 g. (0.005 mole) of pure β-naphthoyl peroxide and 2.44 g. (0.01 mole) of triphenylmethane was conducted in the system described. The pyrolysis flask was slowly heated to 140° over a period of one hour during which time the contents melted and effervescence was detected. Heating was continued at 142-145° for one hour. A small amount of naphthalene was observed as sublimate in the condenser. Formation of 0.136 g. (30.9%) of carbon dioxide was determined by weighing the Ascarite tube. The residue was dissolved in about 130 ml. of Skelly B, and the resulting solution was stirred with a saturated solution (100 ml.) of sodium bicarbonate for six hours. A solution of benzene and ether (100 ml. of each) was added to the mixture. The aqueous layer which separated was acidified with concentrated hydrochloric acid to pH 1-2 and gave 0.525 g. (30.9%) of β-naphthoic acid.

The organic layer was evaporated to dryness to give 3.39 g. of residue. A sample (0.11 g.) of the residue was saved for gas chromatographic analysis, which indicated the presence of naphthalene, triphenylmethane, triphenylmethanol, traces of benzophenone and a high molecular weight compound.

Infrared analysis of the residue showed absorption for carbonyl groups at 1724 and 1695 cm.$^{-1}$ which were identical to those observed in the spectrum of the residue obtained from the pyrolysis of β-naphthoyl peroxide only. The residue was chromatographed over acid-washed alumina (column ca 12 in. x 0.75 in.) and fractions of about 25 ml. each were collected. Elution of the column with Skelly F (20 fractions) gave 2.038 g. of solid identified as triphenylmethane containing traces of naphthalene. A Skelly F-benzene mixture (3:1) was used as the next eluant (5 fractions) which gave traces of trityl peroxide. Further elution of the column with 4 fractions each of Skelly F-benzene mixtures (1:1 and 1:4) gave only traces of unidentified materials. Further elution with benzene (3 fractions) gave 0.05 g. of triphenylmethanol. Pure ether (3 fractions) gave 0.05 g. of an ester contaminated with traces of triphenylmethanol. The ester corresponded to the high molecular weight component and had an infrared spectrum nearly superimposable on that of β-naphthyl β-naphthoate. In addition gas chromatographic analysis showed the ester to have a retention time nearly identical to that for pure β-naphthyl β-naphthoate. Further elution of the chromatogram with chloroform and methanol did not give any additional compounds. The data are summarized in the Table IX.

TABLE IX

PYROLYSIS OF β-NAPHTHOYL PEROXIDE WITH TRIPHENYLMETHANE

Temperature 142-145°; Time 60 Min.

Products	Wt., g.	Mole % of Peroxide
Carbon dioxide	0.136	30.9
β-Naphthoic acid	0.525	30.5
Triphenylmethanol	0.05	
Trityl peroxide	Traces	
β-Naphthyl β-naphthoate	0.05	
Benzophenone	Trace	
Naphthalene	Trace	
Triphenylmethane	2.14	87.7 (recovered)
Residue	0.05	
Wt. of Peroxide	1.71	
Wt. of Triphenylmethane	2.44	

<u>Pyrolysis of β-Naphthoic Acid</u>. Pyrolysis of 4.502 g. (0.25 mole) of β-naphthoic acid was conducted at 345-355° for one and one-half hours in the same system as used previously. Slight effervescence was observed during pyrolysis and a small amount of sublimate was deposited in the condenser. The sublimate was identified as naphthalene. Traces of naphthalene and water were also detected in the first trap. The pyrolysate was scraped from the flask and extracted with 100 ml. of saturated sodium bicarbonate solution. Acidification of the sodium bicarbonate extract gave 3.106 g. of β-naphthoic acid. The sodium bicarbonate insoluble residue (1.040 g.), on recrystallization from Skelly B, melted at 136-137° and was identified to be β-naphthoic anhydride [lit. (29) m.p. 133-134°] by infrared spectrometry and by

hydrolysis to β-naphthoic acid with a boiling solution of 10% sodium hydroxide. The results are summarized in Table X.

TABLE X

PYROLYSIS OF β-NAPHTHOIC ACID

Temperature $345-355^{\circ}$; Time 1.5 hr.

Products	Wt., g.	Mole % of Acid
Naphthalene	0.146	
Carbon dioxide		
Water		
β-Naphthoic anhydride	1.040	24.4
β-Naphthoic acid	3.106	69.0
	4.292	
Wt. of Acid	4.502	

Pyrolysis of Trityl β-Naphthoate (II) in Oxygen. Pyrolysis of 9.5795 g. (0.023 moles) of the ester was conducted in the system used previously with the exception that oxygen was used as the carrier gas rather than helium. The gas inlet tube extended below the surface of the melted ester which was heated for a period of one and one-half hours at $340-350^{\circ}$. Evolution of carbon dioxide and traces of carbon monoxide were observed, and traces of naphthalene were deposited in the condenser as a sublimate. Moreover, traces of water were found in the first trap. The infrared spectrum of the pyrolysate showed strong absorption (1690 cm.$^{-1}$) reminiscent of β-naphthoic acid and relatively weak absorption for β-naphthoic anhydride, and benzophenone. The pyrolysate was dissolved in 125 ml. of benzene and the solution was stirred with 100 ml. of aqueous 10% sodium bicarbonate solution for ten hours. Acidification of the aqueous layer gave 2.601 g. (65.3%) of β-naphthoic acid. The anhydride was hydrolyzed to the acid and the latter was removed by boiling the benzene layer with a solution of 5.0 g. of sodium hydroxide in 50 ml. of water for four hours. Acidification of the aqueous layer gave an additional 0.4026 g. of β-naphthoic acid. Gas chromatographic analysis showed benzophenone and triphenylmethane as the only components present in the ratio of 1:3.64. Benzophenone was removed from the mixture by reaction with Girard T reagent. The residue thus obtained was a mixture of triphenylmethane and a polymer which had an infrared spectrum (Plate VI) similar to the spectrum of a polymer from the fraction E in the pyrolysis of II (under nitrogen). The infrared spectrum suggests the presence of aromatic ketone as well as an ester function in the polymer. These groups must be in the backbone and highly hindered since the polymer is exceedingly resistant to hydrolysis with a solution of sodium hydroxide (10%) or reaction with Girard T reagent. Chromatography of the residue on alumina with 600 ml. of Skelly F gave 1.62 g. of triphenylmethane. The final residue was essentially Polymer C. The yield of benzophenone was 0.445 g. (calculated from the weight of triphenylmethane). The details are tabulated in Table XI.

TABLE XI

PYROLYSIS OF TRITYL β-NAPHTHOATE (II) (IN OXYGEN)

Temperature 345-355°; Time 1.5 hr.

Products	Wt., g.	Mole % of Ester
Carbon dioxide	0.075	7.35
Naphthalene	0.065	
Water		
β-Naphthoic acid	2.601	65.3
β-Naphthoic anhydride	0.380	10.0
Triphenylmethane	1.620	28.9
Benzophenone	0.445	10.55
Polymer C	2.601	
Insoluble residues	0.310	
	8.097	
Wt. of Ester	9.5795	

Photolysis of Trityl β-Naphthoate (II). A solution of 5.0 g. (0.012 mole) of the ester in 70 ml. of benzene in a 100 ml. quartz flask was subjected to ultraviolet radiation for seventy-two hours, with oxygen bubbling through the solution. A 140 watt, 3.9 amp. Hanovia ultraviolet lamp was used for the photolysis. An aliquot (25 ml.) of the photolysate was taken and analyzed by infrared spectrometry, but the infrared spectrum indicated only the starting material. Analysis by gas chromatography was not informative because the pure ester pyrolyzed under the same conditions to give peaks for three components which corresponded to benzophenone, triphenylmethane and triphenylmethanol or 9-phenylfluorene. The remaining solution was evaporated to dryness and the residue obtained was boiled with a solution of 5.0 g. of sodium hydroxide in 50 ml. of water for one hour. After filtering, the nonacidic residue was washed with 50 ml. of water and analyzed by gas chromatography. The residue was found to be mainly triphenylmethanol containing traces of benzophenone. Since triphenylmethanol is not pyrolyzed on the column under these conditions (silicone rubber 10% on Chromosorb W 80/100 mesh, 8 ft. x 0.125 in. at 253°), formation of benzophenone definitely indicates cleavage of the ester, though only to a small extent.

PLATE I

Trityl Propionate (I), Mull With Nujol

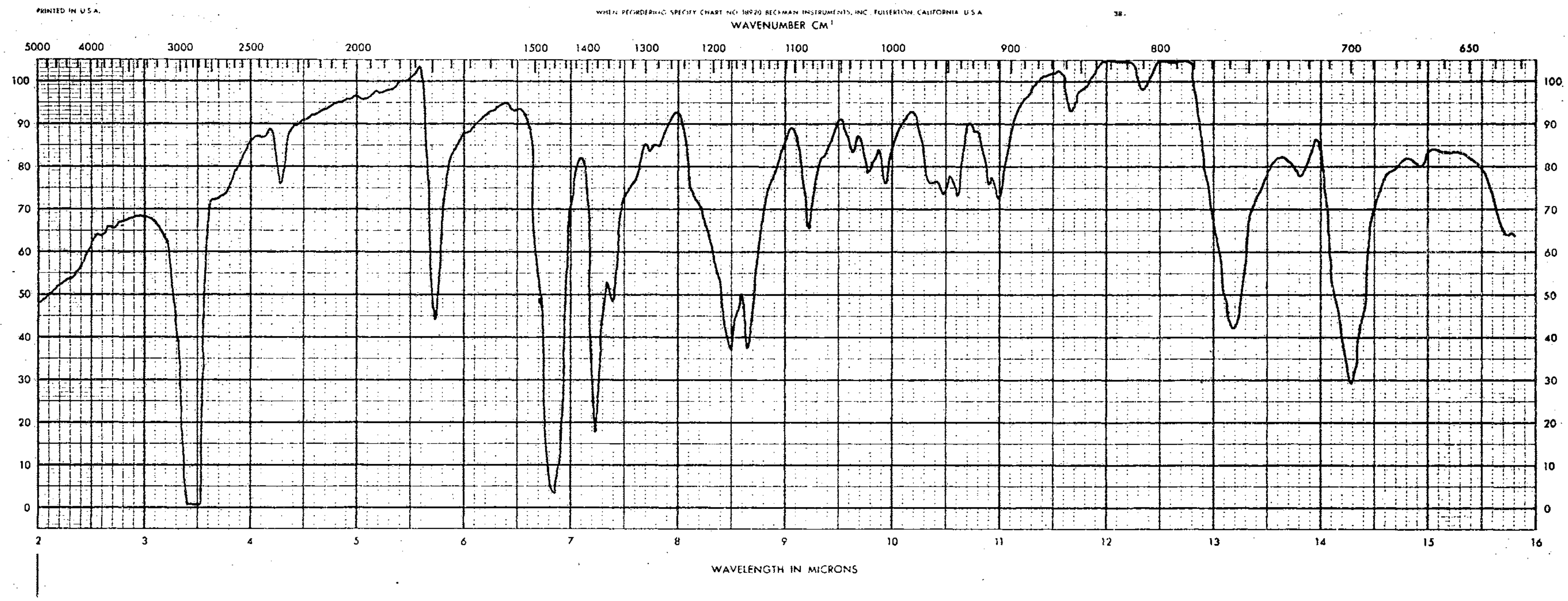


PLATE II

Copolymer of Styrene and Acrylic Acid From Pyrolysis of I, KBr Pellet

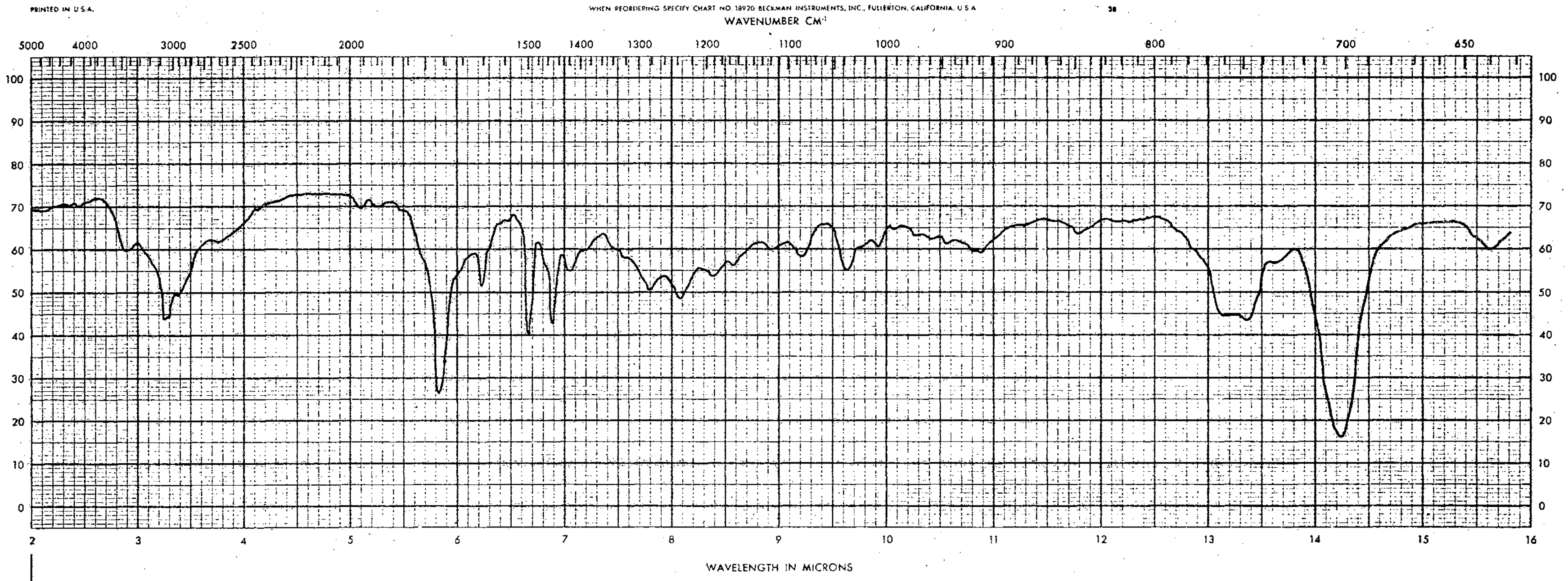


PLATE III

Trityl β-Naphthoate (II), KBr Pellet

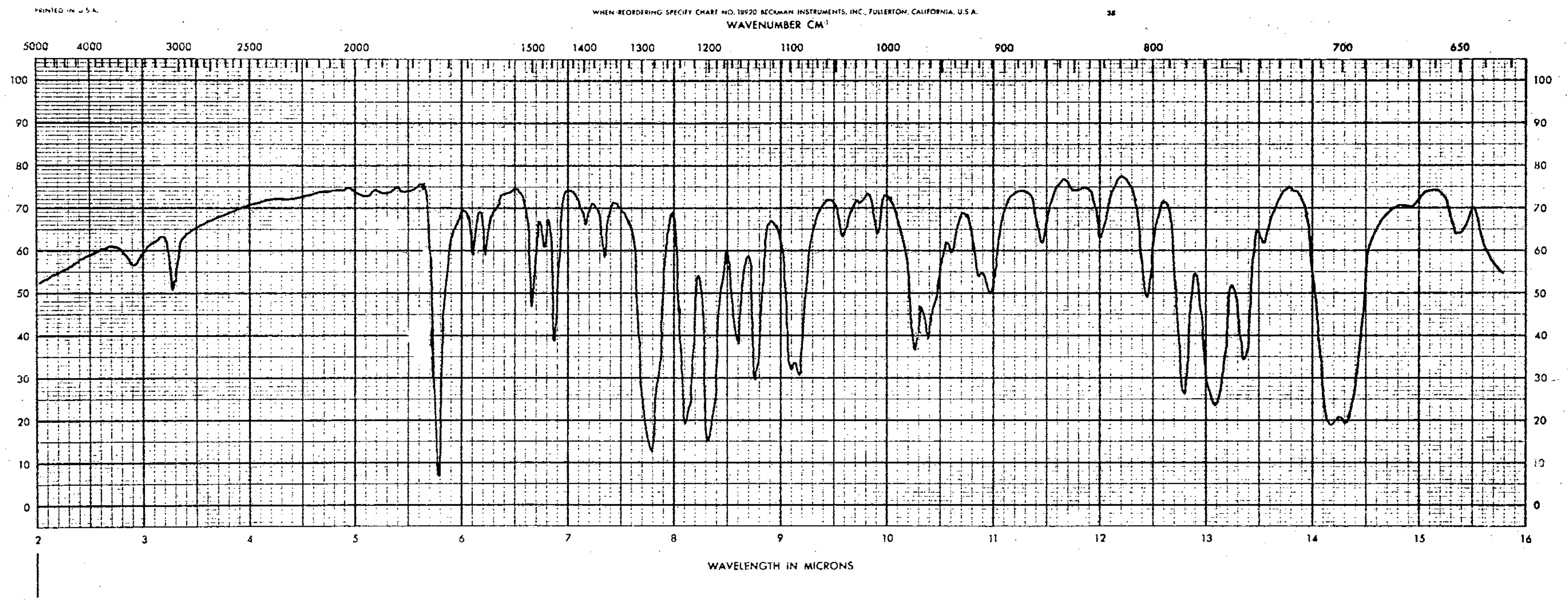


PLATE IV

Polymer A, KBr Pellet

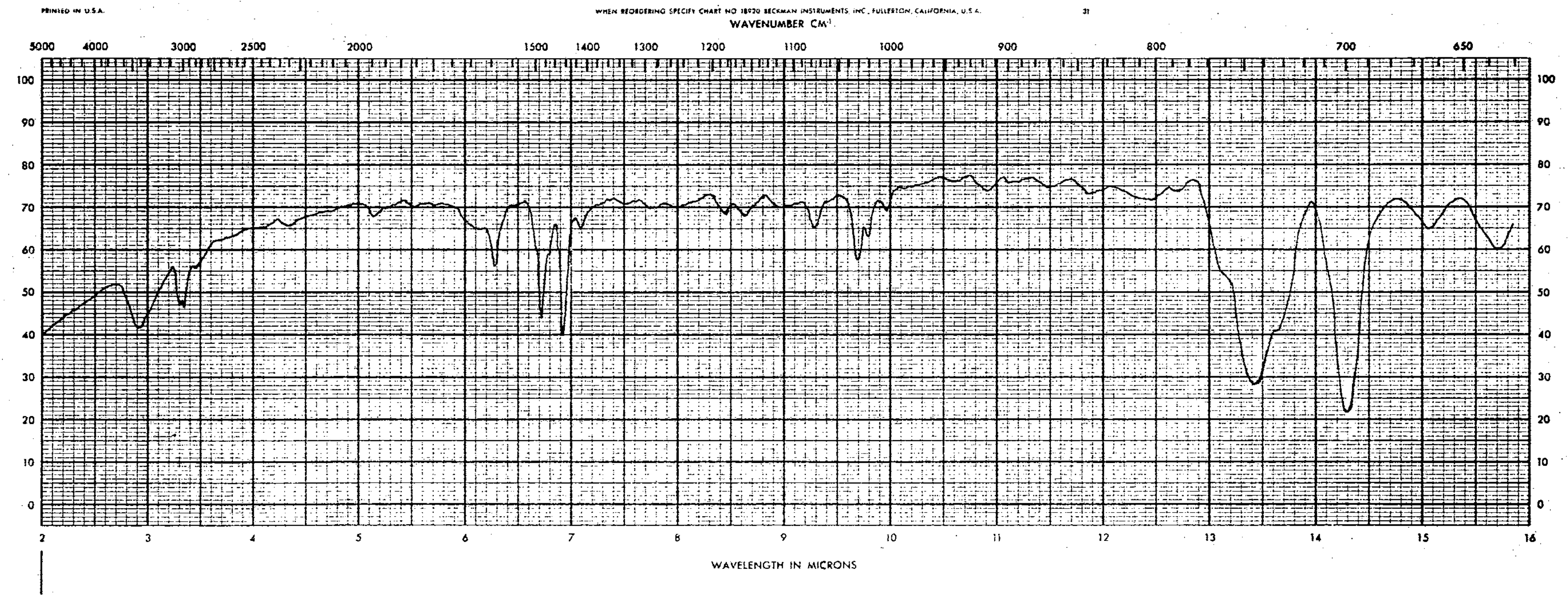


PLATE V

Polymer B, KBr Pellet

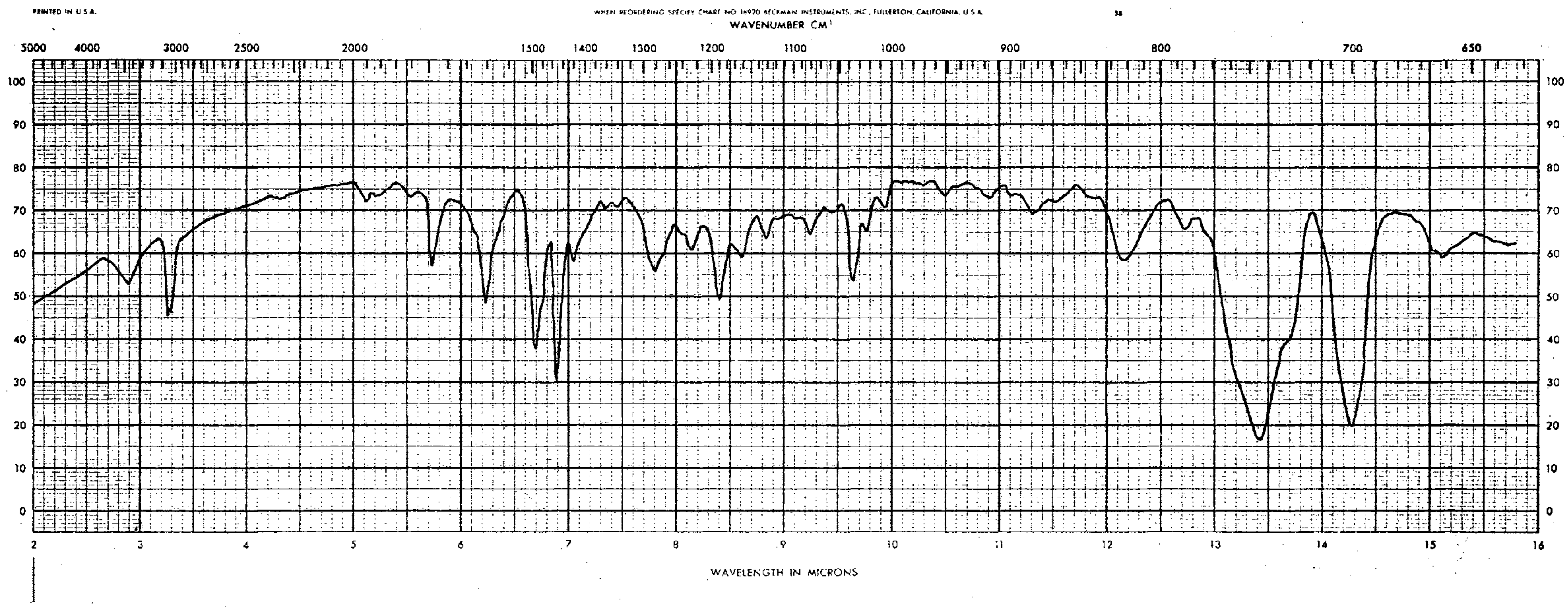


PLATE VI

Polymer C, KBr Pellet

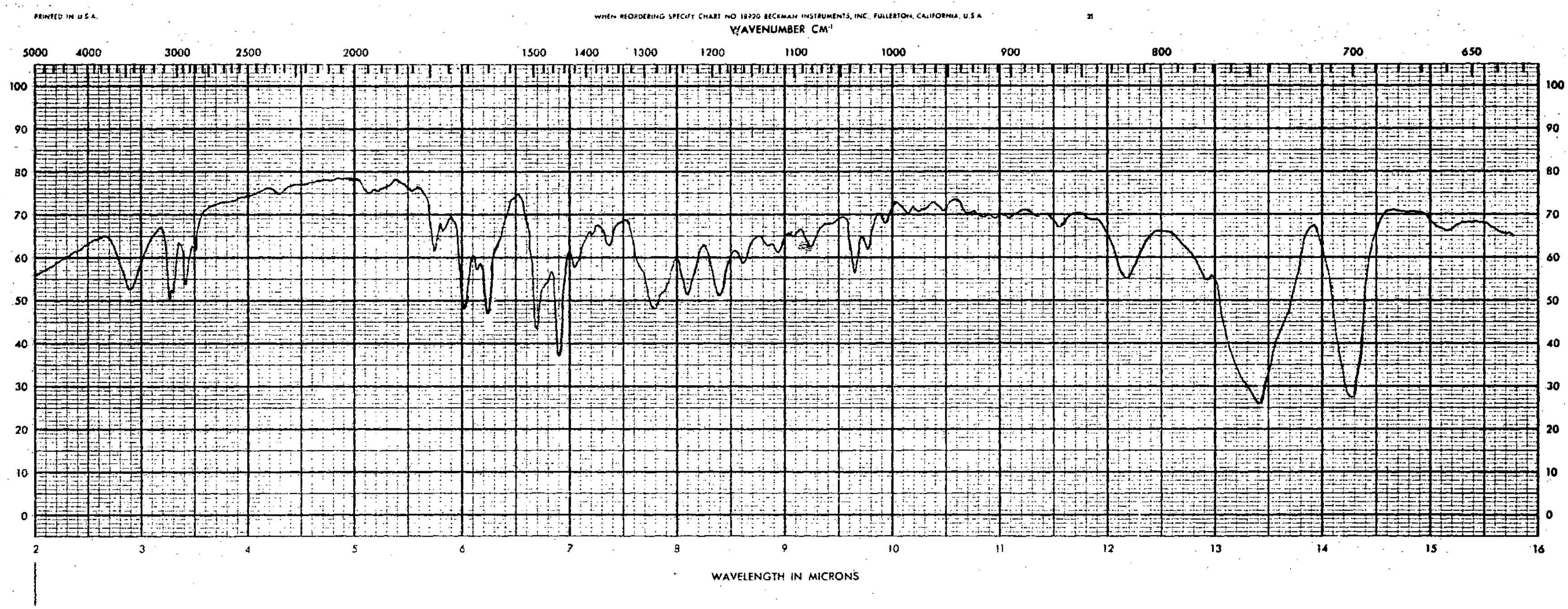
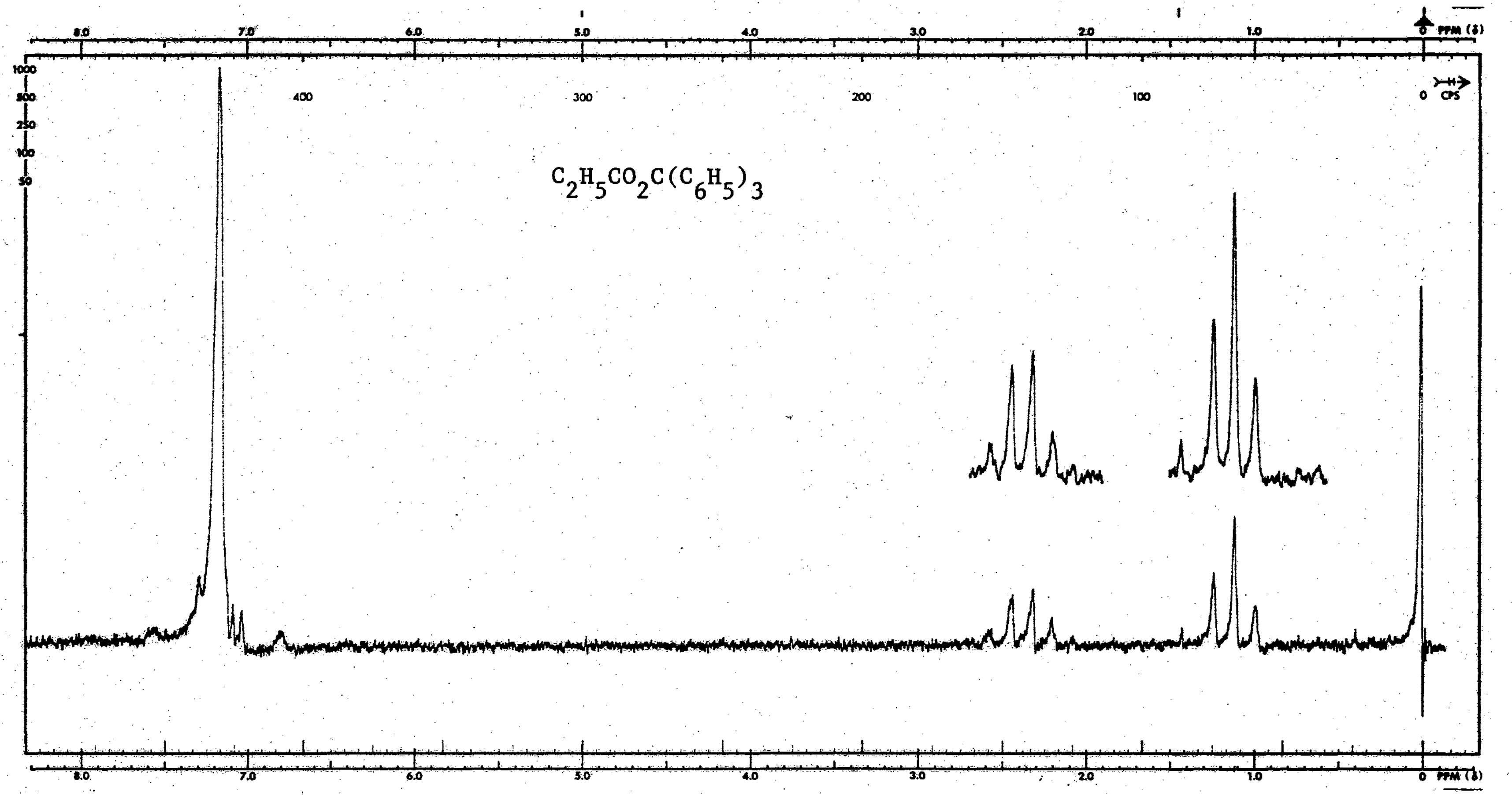


PLATE VII

Trityl Propionate (I)



Solvent: CCl_4

F.B.: 2 cps

R.F. Field: 0.2 mG

S.T.: 500 sec

S.W.: 500 cps

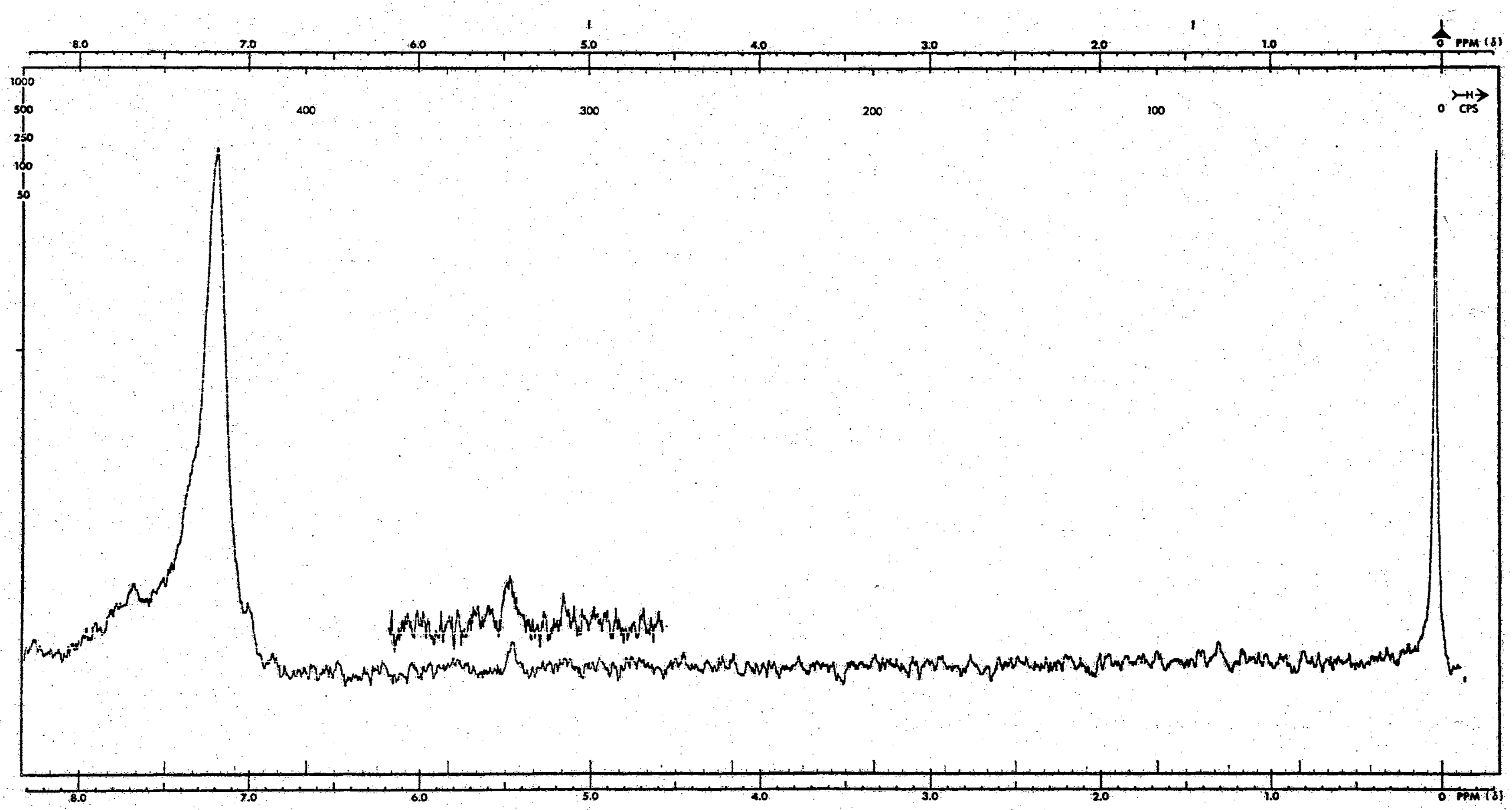
S.O.: 0 cps

S.A.: 16

I.A.: Off

PLATE VIII

Polymer A



Solvent: CCl_4

F.B.: 0.2 cps

R.F. Field: 0.2 mG

S.T.: 500 sec

S.W.: 500 cps

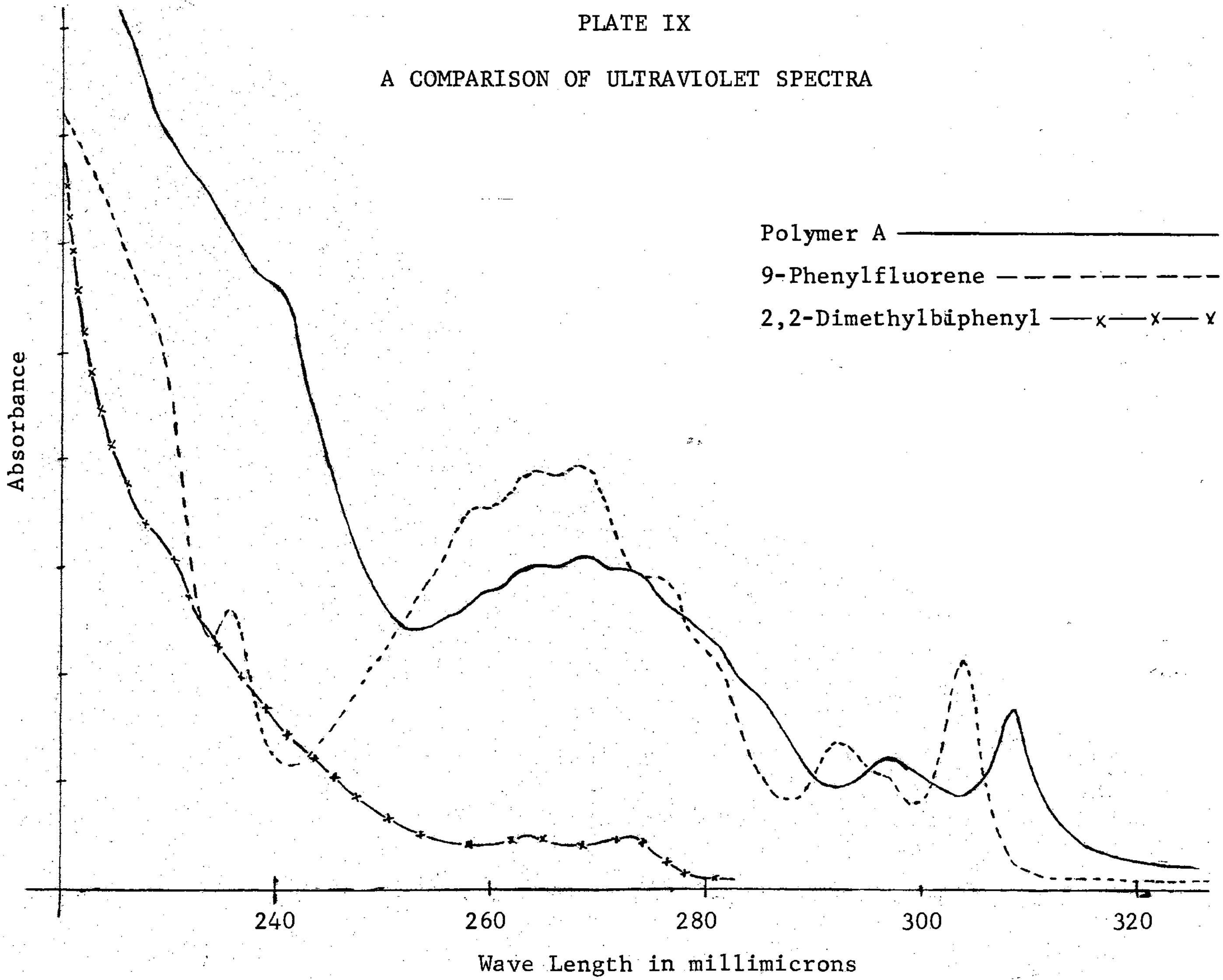
S.O.: 0 cps

S.A.: 32

I.A.: Off

PLATE IX

A COMPARISON OF ULTRAVIOLET SPECTRA



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PART II

REACTIONS OF ORGANOMETALLIC REAGENTS WITH ORTHOESTERS AND ACETALS

TABLE OF CONTENTS

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Plate

Infrared Spectra

Nuclear Magnetic Resonance Spectra

CHAPTER I

HISTORICAL

Carbenes as Reactive Intermediates

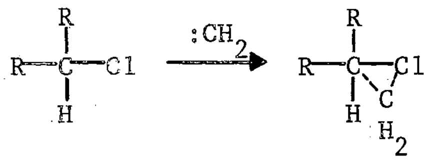
Carbenes ($:CR_2$), derivatives of bivalent carbon, have been the subject of much current interest and investigations. Literally hundreds of papers have been published on the generation and reaction of carbenes. The R substituent may be H, alkyl, aryl, halogen, COOR, COR, CN, or a combination thereof. Such derivatives are short-lived intermediates and are invariably generated in situ. Though electrically neutral, they are highly electrophilic and attack the electron rich centers such as multiple bonds, anions or other atoms in a molecule with an unshared pair of electrons as in phosphorus, for example. Several reviews (14, 18,22,40,41) have been written.

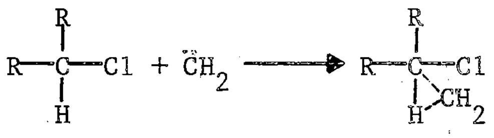
The photolysis of diazomethane is known to give methylene (the simplest possible carbene) in a singlet state with high energy content, which reverts to a triplet state; apparently the preferred ground state (34). Methylenes undergo several types of reactions with unsaturated compounds, such as addition to olefins to give cyclopropane derivatives (26) and insertion at covalent bonds (11). Formation of olefins from methylenes takes place through either coupling of two species (36) or isomerization (31).

Insertion reactions of methylene with alkyl halides and competitive addition between C-H and C-Cl bonds have been studied by Bradley and

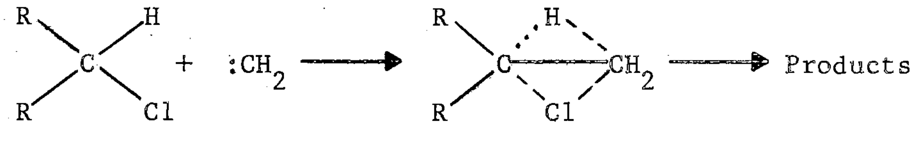
Ledwith (11). The number and quantity of different products were determined by gas chromatography by measuring the area under each peak. Since the conversions were small, only relative areas could be determined with any accuracy.

Since methylene adds to a double bond to give a cyclopropane derivative, it is possible that a three-membered ring intermediate is formed during the insertion reactions also. However the mechanism is probably

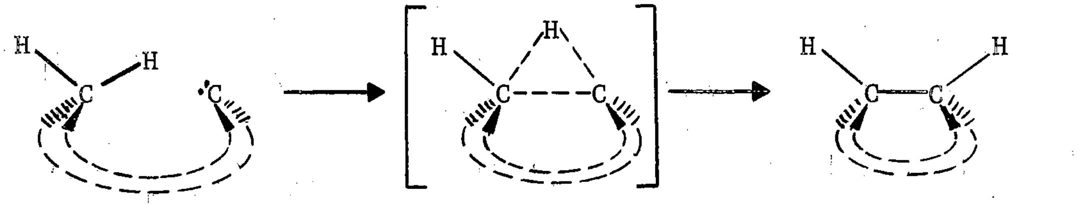




not as simple as this because it does not explain a number of characteristics of this reaction, such as (a) the preferential attack at the alpha position, and (b) the reactivity in a series of isomers is primary > secondary > tertiary. Furthermore, the extent of C-H attack is independent of the reactivity of the C-Cl bond. A more satisfactory mechanism, especially for the halides which have an α-hydrogen, may involve a bicyclic intermediate of the following type. Such an intermediate can break down in two ways to form a stable compound.

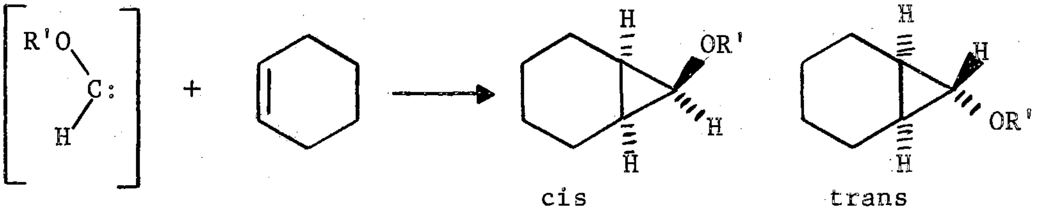


An interesting series of decompositions of diazocycloalkanes has been studied by Friedman and Schechter (31). The reaction products are to a large extent dependent on the size of the ring. For example, decomposition of diazocyclopentane and diazocyclohexane gives only cyclopentene and cyclohexene, respectively. On the other hand, _cis_ and _trans_ cyclodecenes are formed only to the extent of twenty per cent from diazocyclodecane. The major product in the decomposition is formed through stereospecific transannular insertion. The formation of only _cis_ bicyclo compounds, that is _cis_-decalin and _cis_-bicyclo[5,3,0]-decane, is consistent with the principle that carbenic insertions occur with retention of configuration (25).



Among the substituted carbenes, monoalkoxy and monoaryloxycarbenes have been the subject of recent investigations by Schollkopf and co-workers (57,58,59,60). They have generated such carbenes by the reaction of α-halomethyl ethers and alkyllithium reagents. The reaction can be generalized according to the following mechanism which involves metallation on the alpha carbon followed by the loss of lithium chloride and

$$R'\text{-}O\text{-}\overset{\displaystyle Cl}{\underset{\displaystyle R''}{C}}\text{-}H \xrightarrow{RLi} \left[R'\text{-}O\text{-}\overset{H}{C}:\right]$$



cis _trans_

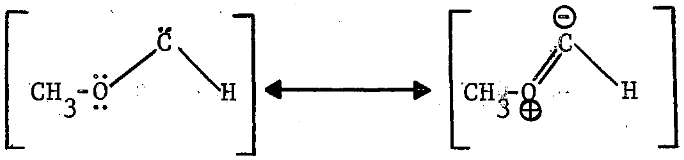
R' = CH_3, isoC_3H_7, $\underline{n}$-C_4H_9, $\underline{n}$-C_6H_{13}, C_6H_5

R'' = H, Cl

R = CH_3, $\underline{n}$-C_4H_9

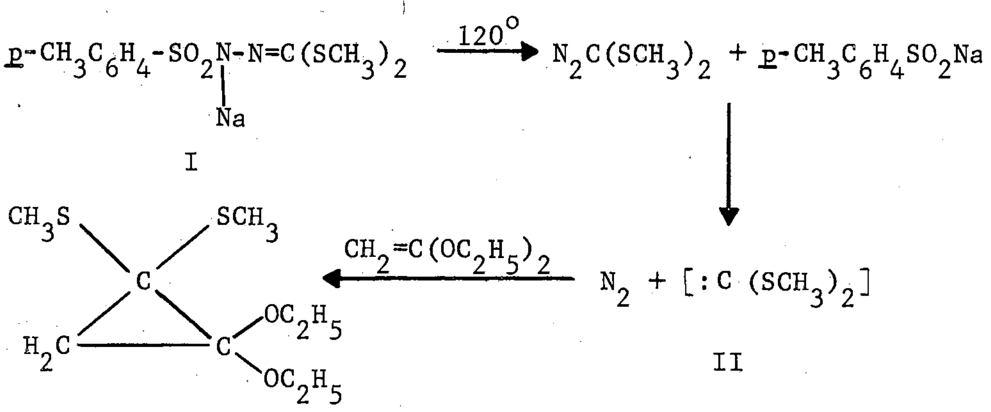
formation of the alkoxy or aryloxycarbene. Carbenes generated in this manner have been trapped by use of a number of olefins including isobutylene, cyclohexene, cis- and trans-2-butenes, butadiene, and cyclopentadiene. A variety of cyclopropane derivatives has been obtained by this method. Addition to cyclohexene gives rise to norcarane derivatives. In these additions where steric requirements of the carbenes are influential, the ratio of the cis and trans addition products has been studied to determine the selectivity of the carbenes. By comparison of these ratios, the order of the selectivity in alkoxycarbenes was found to be isopropoxy > n-butoxy > methoxy. This order is in agreement with the steric requirements. Comparison of methoxy and phenoxycarbene indicated that the latter is more reactive and hence less selective. The explanation that has been offered is that in phenoxycarbene delocalization of the free electron pair on oxygen through the phenyl ring stabilizes the carbene. Such a stabilization is not possible in methoxycarbene, hence it is less reactive and consequently more selective.

It seems reasonable that in methoxycarbene where delocalization of the electron pairs of oxygen is not possible, a resonance form like that shown below may contribute also. In such a form, the electrophilic nature of the divalent carbon would be greatly reduced, and consequently



reduce the reactivity of the carbene.

Schöllkopf (61) found di(methylthio)carbene (II) to be selective toward the type of olefin. When II was generated by thermal decomposition of I in diglyme in the presence of cyclohexene, it failed to add to

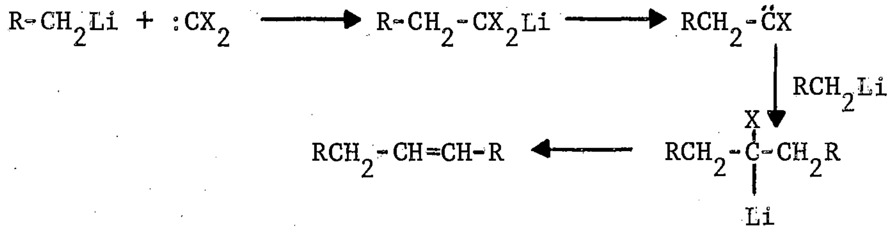


the latter and yield a cyclopropane derivative. However, II did add to ketene diethyl acetal and 1-morpholino-1-phenylethylene. The electrophilic nature of this carbene is reduced apparently by the unshared electron pairs on the sulfur atoms.

Dihalomethylenes seem to be the most thoroughly investigated among the substituted methylenes. This is probably due to the extreme ease of generation and their tremendous ability to add to olefins and other electron-rich centers in the molecules. An attractive feature in the investigations with dihalomethylenes has been the addition to olefinic compounds and a great number of such cases has been studied (8,23,26,43). However, an equally interesting series of reactions involve the reactions in which the carbenes have been generated in the absence of olefins. The carbenes, as expected, reacted with the anions of the organometallic reagent used. The sequence followed after the initial addition varied according to the structure of the anion.

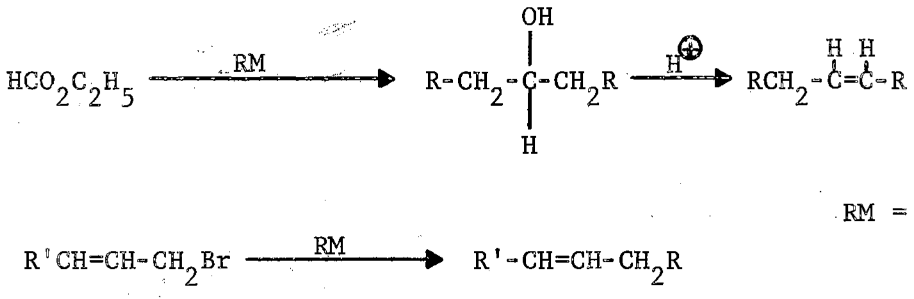
An interesting synthesis through dihalocarbenes has been recently reported by Franzen and Fikentscher (30). Reaction of a large number of organometallic reagents with trifluorobromomethane and difluorodibromomethane has been found to give olefins in 40 to 70 per cent yield.

Primary alkyllithium or Grignard reagents gave internal olefins, whereas secondary lithium reagents gave substituted vinyl halides.



$$R\text{-}CH_2Li + :CX_2 \longrightarrow R\text{-}CH_2\text{-}CX_2Li \longrightarrow RCH_2\text{-}\ddot{C}X \xrightarrow{RCH_2Li} RCH_2\text{-}\underset{Li}{\overset{X}{C}}\text{-}CH_2R \longrightarrow RCH_2\text{-}CH{=}CH\text{-}R$$

Although the final step in the formation of olefin as well as the stereochemistry of the olefin have not been discussed, an elegant mechanism has been proposed. This method consists of the synthesis of olefins under mild conditions. These olefins have been prepared previously and are reported in literature. The earlier procedures for synthesis of such olefins have been through dehydration of the corresponding alcohols (67). Acid catalysts used for dehydration may also cause double-bond migration. The alcohols are obtained by the Grignard synthesis. Another procedure for obtaining the olefins is by the condensation of an allylic bromide with a Grignard reagent (47). These syntheses are shown below.



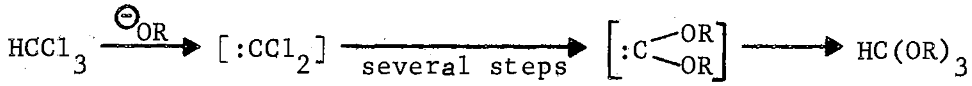
$$HCO_2C_2H_5 \xrightarrow{RM} R\text{-}CH_2\text{-}\underset{H}{\overset{OH}{C}}\text{-}CH_2R \xrightarrow{H^{\oplus}} RCH_2\text{-}\overset{H}{C}{=}\overset{H}{C}\text{-}R$$

$$R'CH{=}CH\text{-}CH_2Br \xrightarrow{RM} R'\text{-}CH{=}CH\text{-}CH_2R$$

RM = Grignard Reagent

Conversion of the alcohol to an olefin can also be done by pyrolysis of the acetate (7,21). The high temperatures may cause rearrangement and/or yield mixtures of <u>cis</u> and <u>trans</u> isomers.

Among other reactions of dihalocarbenes in the absence of olefins is reaction with alkoxides to give orthoformates (24,50). In the sequence the last intermediate is a dialkoxycarbene.. Such carbenes



$$HCCl_3 \xrightarrow{\ominus OR} [:CCl_2] \xrightarrow[\text{several steps}]{} \left[:C\begin{matrix}OR\\OR\end{matrix}\right] \longrightarrow HC(OR)_3$$

though suggested as intermediates in the above reaction, have been the most elusive type of carbenes and have not yet been trapped with olefins to yield cyclopropanone acetals.

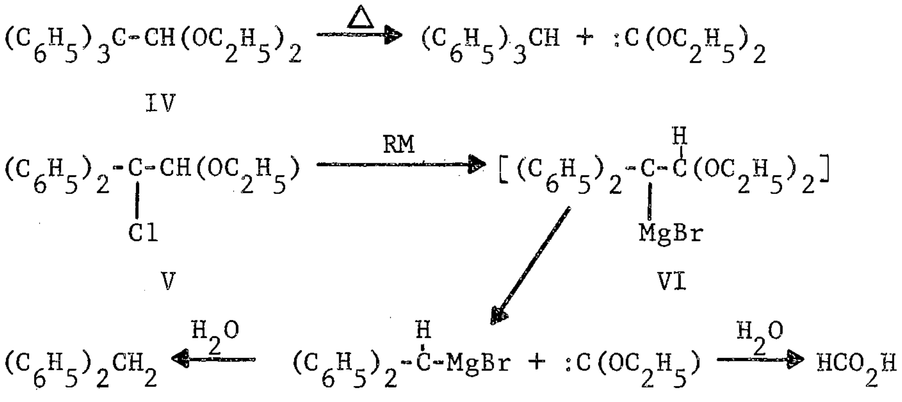
Such carbenes were the subject of studies by Scheibler and co-workers in a series of controversial papers (51-55). In his first paper (51) he described the preparation of carbon monoxide diethyl acetal (diethoxymethylene) from the reaction of ethyl diethoxyacetate with sodium ethoxide. Formation of diethoxymethylene (III) is proposed to result from the cleavage of the intermediate tetraethoxyethylene. The yield of III is low because ethyl diethoxyacetate

$$(C_2H_5O)_2CHCO_2C_2H_5 \xrightarrow{C_2H_5O^{\ominus}} (C_2H_5O)_2C{=}C(OC_2H_5)_2 \longrightarrow \underset{\text{III}}{(C_2H_5O)_2C:}$$

$$HCO_2C_2H_5 \xrightarrow{NaOC_2H_5} NaO\text{-}\ddot{C}\text{-}OC_2H_5 \xrightarrow{H_2O} NaOH + CO + C_2H_5OH$$

enolizes only to a small extent with sodium ethoxide. Synthesis of III and other similar bivalent carbon compounds is also described from ethyl formate. (Sodiumoxy)ethoxymethylene formed as a reaction product from ethyl formate and sodium ethoxide is reported as stable in the dry state but decomposes in moist air to carbon monoxide, ethanol and sodium hydroxide. The validity of Scheibler's observations has been questioned by Arbuzov (3) and Adickes (1).

Another approach to such carbenes was conceived by Scheibler (55) through a possible cleavage of triphenylacetaldehyde diethyl acetal (IV). He expected (IV) to cleave on heating to give triphenylmethane and



$$(C_6H_5)_3C\text{-}CH(OC_2H_5)_2 \xrightarrow{\Delta} (C_6H_5)_3CH + :C(OC_2H_5)_2$$

IV

$$(C_6H_5)_2\text{-}\underset{Cl}{C}\text{-}CH(OC_2H_5) \xrightarrow{RM} [(C_6H_5)_2\text{-}\underset{MgBr}{C}\text{-}\overset{H}{C}(OC_2H_5)_2]$$

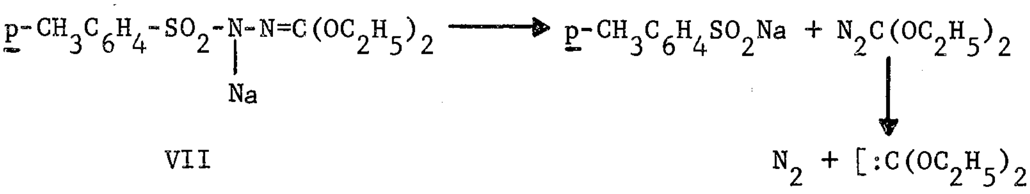
V VI

$$(C_6H_5)_2CH_2 \xleftarrow{H_2O} (C_6H_5)_2\text{-}\overset{H}{C}\text{-}MgBr + :C(OC_2H_5) \xrightarrow{H_2O} HCO_2H$$

RM = Grignard Reagent

diethoxymethylene. In an attempt to obtain (IV) from the reaction of diphenylchloroacetaldehyde diethyl acetal (V) and phenyl Grignard reagent, he obtained VI. The latter decomposed at high temperature to give diethoxymethylene (detected by hydrolysis to formic acid) and diphenylmethyl Grignard reagent (which gave diphenylmethane with water).

Recently Crawford and Raap (20) have presented evidence for diethoxymethylene as an intermediate in the photolytic cleavage of VII. The specie VII is the oxygen analog of Schollkopf's precursor for di(methylthio)methylene. Diethoxydiazomethane and sodium p-toluenesulfinate are the products of initial cleavage. The former loses nitrogen and yields diethoxymethylene. A radical mechanism is proposed to explain the formation of various products obtained from the decomposition of diethoxymethylene under anhydrous conditions.



$$\underline{p}\text{-}CH_3C_6H_4\text{-}SO_2\text{-}\underset{\substack{|\\ Na}}{N}\text{-}N{=}C(OC_2H_5)_2 \longrightarrow \underline{p}\text{-}CH_3C_6H_4SO_2Na + N_2C(OC_2H_5)_2 \xrightarrow{} N_2 + [:C(OC_2H_5)_2]$$

VII

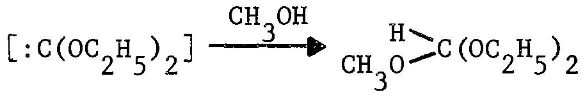
$$[:C(OC_2H_5)_2] \longrightarrow C_2H_5O\cdot + CO + C_2H_5\cdot$$

$$C_2H_5O\cdot + \text{Solvent H} \longrightarrow C_2H_5OH + \text{Solvent}\cdot$$

$$C_2H_5\cdot \longrightarrow C_2H_4 + C_2H_6$$

$$C_2H_5\cdot + C_2H_5O\cdot \longrightarrow (C_2H_5)_2O$$

$$C_2H_5\cdot + \text{Solvent H} \longrightarrow C_2H_6 + \text{Solvent}\cdot$$



$$[:C(OC_2H_5)_2] \xrightarrow{CH_3OH} \begin{matrix} H \\ CH_3O \end{matrix}\!\!>\!C(OC_2H_5)_2$$

Decomposition of VII in methanol led to diethyl methyl orthoformate which is explained to result from reaction of diethoxymethylene with methanol. Attempts to capture diethoxymethylene with cyclohexene were also made but were unsuccessful.

Orthoesters obtained through a sequence of carbene reactions (24,50) find equally interesting uses in organic syntheses. In presence of acids triethyl orthoformate is hydrolyzed to ethanol and ethyl formate. This type of cleavage is used in preparation of acetals of sensitive aldehydes. For example, acrolein diethyl acetal can be prepared in good yield from acrolein and triethyl orthoformate in presence of ammonium nitrate (68).

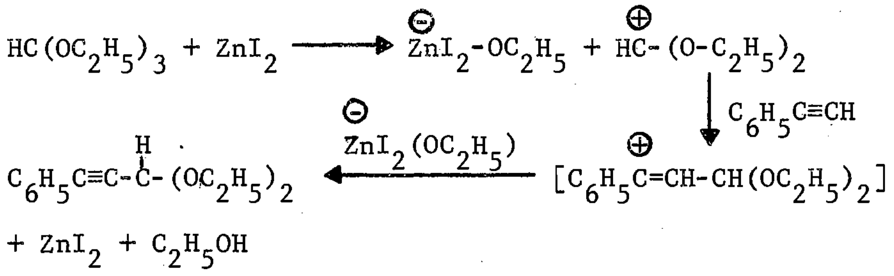
Synthesis of aldehydes is another useful synthesis involving orthoformates. Chichibabin (16,17) appears to be the first one to utilize the reaction of triethyl orthoformate with aryl or alkyl Grignard reagents for the preparation of diethyl acetals. The latter can be conveniently hydrolyzed with dilute acids to the corresponding aldehydes.

$$HC(OC_2H_5)_3 \xrightarrow{RM} C_6H_5CH(OC_2H_5)_2 \xrightarrow{H^{\oplus}} C_6H_5CHO$$

RM = Grignard Reagent

The first ethoxy group is replaced without the use of ether and with the evolution of heat. The second ethoxy group is removed with some difficulty while the third group is replaced only to a very small extent in boiling ether, even in the presence of a large excess of the Grignard reagent. However, triphenylmethane can be obtained at higher temperatures from the above reaction. This reaction is now one of the standard procedures for the preparation of aldehydes (4).

Synthesis of acetylenic aldehydes from acetylene or 1-alkynes described by Howk and Sauer (38) is shown where phenylacetylene, triethyl orthoformate and zinc iodide react to give phenylpropiolaldehyde diethyl acetal. The initial step in the reaction is the formation of a



$$HC(OC_2H_5)_3 + ZnI_2 \longrightarrow \overset{\ominus}{Z}nI_2\text{-}OC_2H_5 + \overset{\oplus}{H}C\text{-}(O\text{-}C_2H_5)_2 \xrightarrow{C_6H_5C{\equiv}CH} [C_6H_5\overset{\oplus}{C}{=}CH\text{-}CH(OC_2H_5)_2] \xrightarrow{\overset{\ominus}{Z}nI_2(OC_2H_5)} C_6H_5C{\equiv}C\text{-}\overset{H}{C}\text{-}(OC_2H_5)_2 + ZnI_2 + C_2H_5OH$$

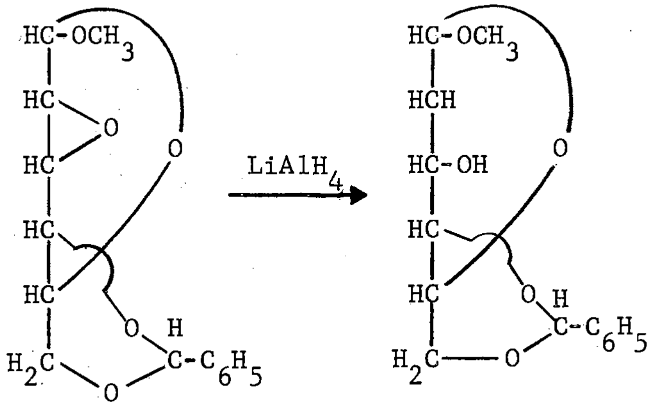
carbonium ion which adds to the triple bond. The triple bond is regenerated by the loss of a proton.

A study of the reaction of trialkyl orthothioformates with a strong base such as potassium amide has been made but similar studies with the orthoformates are unknown. Tris(methylthio)methyl anions are unstable and lose alkylthio anions. Hine (36) was able to isolate tetrakis-(alkylthio) ethylenes from the reaction of methyl and ethyl orthothioformates with potassium amide in liquid ammonia. Bis-(alkylthio)-methylenes are postulated as intermediates which couple to give tetra-substituted ethylenes in yields up to 40 per cent.

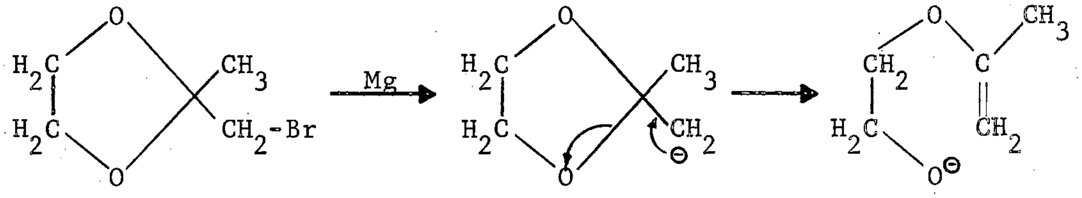
$$HC(SCH_3)_3 \xrightarrow{KNH_2} \overset{\ominus}{C}(SCH_3)_3 \longrightarrow [:C(SCH_3)_2] \longrightarrow (CH_3S)_2C{=}C(SCH_3)_2$$

As mentioned earlier the reaction of Grignard reagents with acetals is slow but it can be utilized under proper conditions for the synthesis of ethers. Kranzfelder and Vogt (42) have prepared a series of acetylenic ethers (yields, 80%) by reaction of various acetals with alkynyl Grignard reagents. The latter were obtained by the reaction of 1-alkynes with an equimolar amount of ethyl Grignard reagent in ether. The resulting solution was then treated with an acetal at 80-90°.

Such reactions, although studied to a limited extent with the ordinary acetals, are virtually unknown with cyclic acetals. 1,3-Dioxolanes (often called ethylene glycol acetals), and 1,3-dioxanes are conveniently prepared by heating the parent carbonyl compound with the diol in the presence of trace quantities of _p_-toluenesulfonic acid in benzene. Water formed in the reaction is removed by azeotropic distillation (49,65). Conversion of aldehydes or ketones with ethylene glycol to 1,3-dioxolanes is a general procedure for protection of the carbonyl function through a series of reactions. The carbonyl group is regenerated smoothly by acid hydrolysis of the dioxolane (13). As can be seen from the following reduction of methyl-2,3-anhydro-4:6-benzylidene-α-D-allopyranoside, such derivatives are stable toward a powerful reducing agent as well as a strong base like lithium aluminum hydride (48).

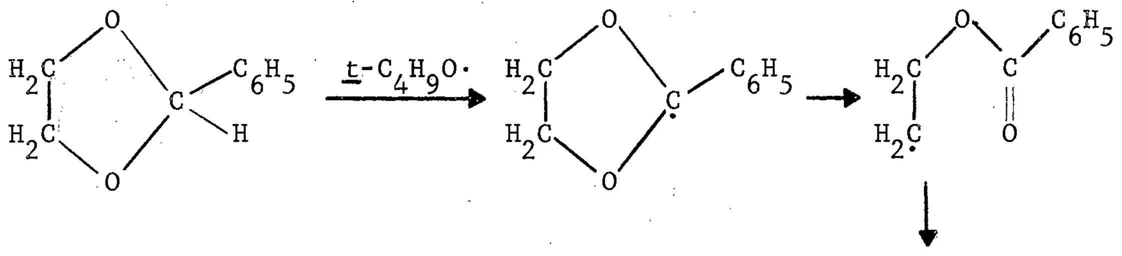


An interesting cleavage of a 1,3-dioxolane is reported recently through an intramolecular Grignard reaction by Feugeas (29). 2-Methyl-2-bromomethyl-1,3-dioxolane on reaction with magnesium in tetrahydrofuran undergoes a ring cleavage. The reaction can be visualized as



shown. Reaction of the halide with magnesium must yield an anion which causes a displacement that results in a ring opening. The driving force in this reaction is probably the formation of a stable alkoxide anion.

Free radical cleavage of 2-phenyl-1,3-dioxolane into benzoates is the only reported case of a cleavage of dioxolane to an ester (39). The mechanism involves abstraction of the tertiary benzylic hydrogen by the t-butoxy radical followed by bond fission between oxygen and carbon of the glycol. The termination of the radical chain reaction is by



coupling of this radical with any of the other radical intermediates formed in the reaction. Analysis of the reaction mixtures by gas chromatography has shown the presence of t-butyl alcohol. Formation of traces of benzaldehyde as one of the by-products was also noted. When 4-methyl-2-phenyl-1,3-dioxolane was studied under similar reaction conditions, bond cleavage between either of the oxygen atoms and the carbon atoms was observed indicating a non-selectivity in the bond cleavage step.

CHAPTER II

DISCUSSION OF THE RESULTS AND CONCLUSIONS

A study has been made of the reactions of alkyl and aryllithium reagents with orthoesters and acetals. n-Butyllithium reacted in a stereospecific manner with trimethyl orthoformate in ether and cyclohexane to yield trans-4-nonene. A carbene mechanism involving dimethoxymethylene has been proposed for the reaction. The reaction of n-butyllithium with 4-ethyl-2,6,7-trioxabicyclo[2.2.2]octane also yielded trans-4-nonene as the main product (76%), and its formation is proposed to proceed through the reaction of a cyclic dialkoxymethylene derivative. This process, though accompanied by formation of some by-products, in small amounts, constitutes a stereospecific synthesis of trans-monoalkenes containing an odd number of carbon atoms. The conditions are mild and work-up procedures simple which minimizes the opportunity for migration of the internal double bond. The general applicability of this reaction has been studied. trans-6-Tridecene and trans-7-pentadecene were obtained from n-hexyl- and n-heptyllithium, respectively, in fair yields (32-37%).

Extension of the reaction was relatively unprofitable with lithium reagents containing an aromatic nucleus. Phenyllithium condensed with trimethyl orthoformate to form unstable reaction products which were decomposed by the addition of water. Only small amounts of benzophenone could be detected in the reaction mixture. Benzyllithium could not be obtained in high concentration by procedures similar to those used above, and consequently the investigations using benzyllithium were inconclusive. A somewhat anomalous behavior of β-phenethyllithium with the orthoester was noted as only 3-β-phenethyl-1,5-diphenylpentane was obtained as the major product while the expected olefin was not found.

Reaction of n-butyllithium with 2-phenyl-1,3-dioxolane resulted in a novel ring-opening by cleavage between oxygen and C-4 with the formation of n-valerophenone as the final product (87%). A carbanion mechanism has been proposed as shown in scheme 3. The mechanism is supported by identification of ethanol as the other expected reaction product. In a similar fashion n-butyllithium condensed with p-methoxyphenyl-1,3-dioxolane and n-hexyllithium reacted with 2-phenyl-1,3-dioxolane under nearly identical conditions. p-Methoxy-n-valerophenone and n-heptanophenone were obtained from these reactions, respectively, in good yields (78 and 66%). The over-all process can be viewed as a method of alkylation of an aldehyde by replacement of the hydrogen attached to the carbonyl function.

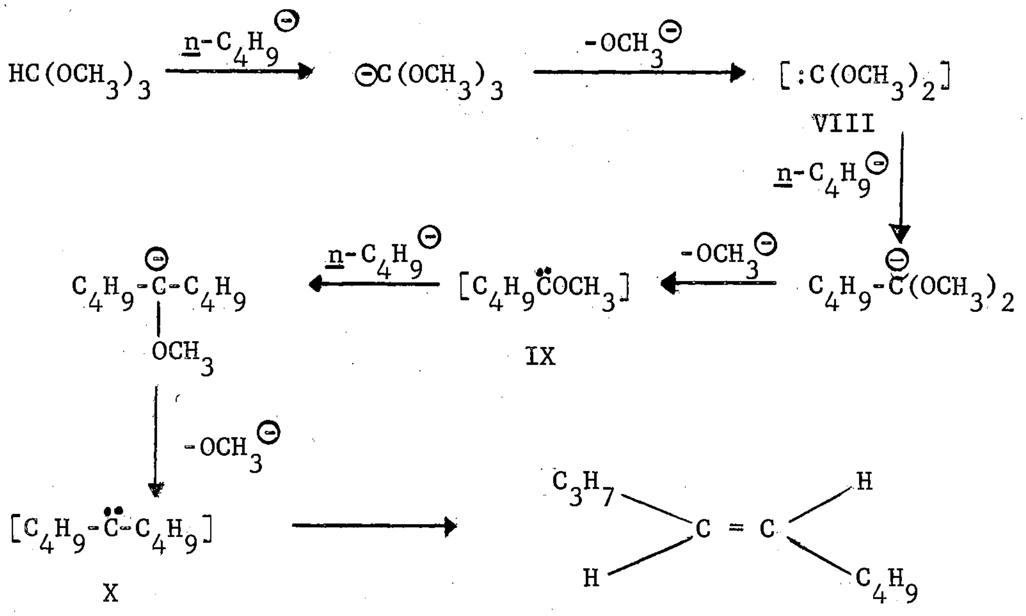
A general procedure for quantitative gas chromatographic determinations is described. The conventional methods employ measurement of peak areas (a tedious procedure) which involves opportunities for considerable error when peaks are narrow. The method described here involves the use of an internal standard and calculations are made using only the peak height ratios thereby ensuring a greater degree of precision and accuracy.

The object of this research was to investigate the possibility of generating a dialkoxymethylene from orthoesters and trapping these reactive species with an olefin. Success in the latter step would have constituted a new synthesis of cyclopropanone dialkyl acetals. Attempts were then to be made to convert such compounds to cyclopropanone derivatives.

The lithium reagents were prepared according to the standard procedures (69) or slight modifications thereof. Trimethyl orthoformate and 4-ethyl-2,6,7-trioxabicyclo[2.2.2]octane are commercial materials. n-Valeraldehyde dimethyl acetal, 2-phenyl-1,3-dioxolane and 2-p-methoxyphenyl-1,3-dioxolane were prepared from the corresponding aldehyde and the appropriate alcohol using standard procedures (33,49,65).

n-Butyllithium reacted with trimethyl orthoformate in a stereospecific manner to yield trans-4-nonene as the major product (42%). Structure of trans-4-nonene has been established by infrared and nuclear magnetic resonance (NMR) spectroscopy and by oxidative ozonolysis to n-valeric and n-butyric acids. The acids were converted into the corresponding methyl esters by treatment with diazomethane. Gas chromatographic analyses were made on the mixture of esters obtained above and comparison with known samples of the esters completed the identification of the ozonolysis products. Although 4-nonene has been reported in literature (30), no reference is made to its stereochemistry. These detailed studies were made to unequivocally establish the structure of the reaction product. The proposed mechanism for the formation of trans-4-nonene is shown in scheme 1.

Scheme 1



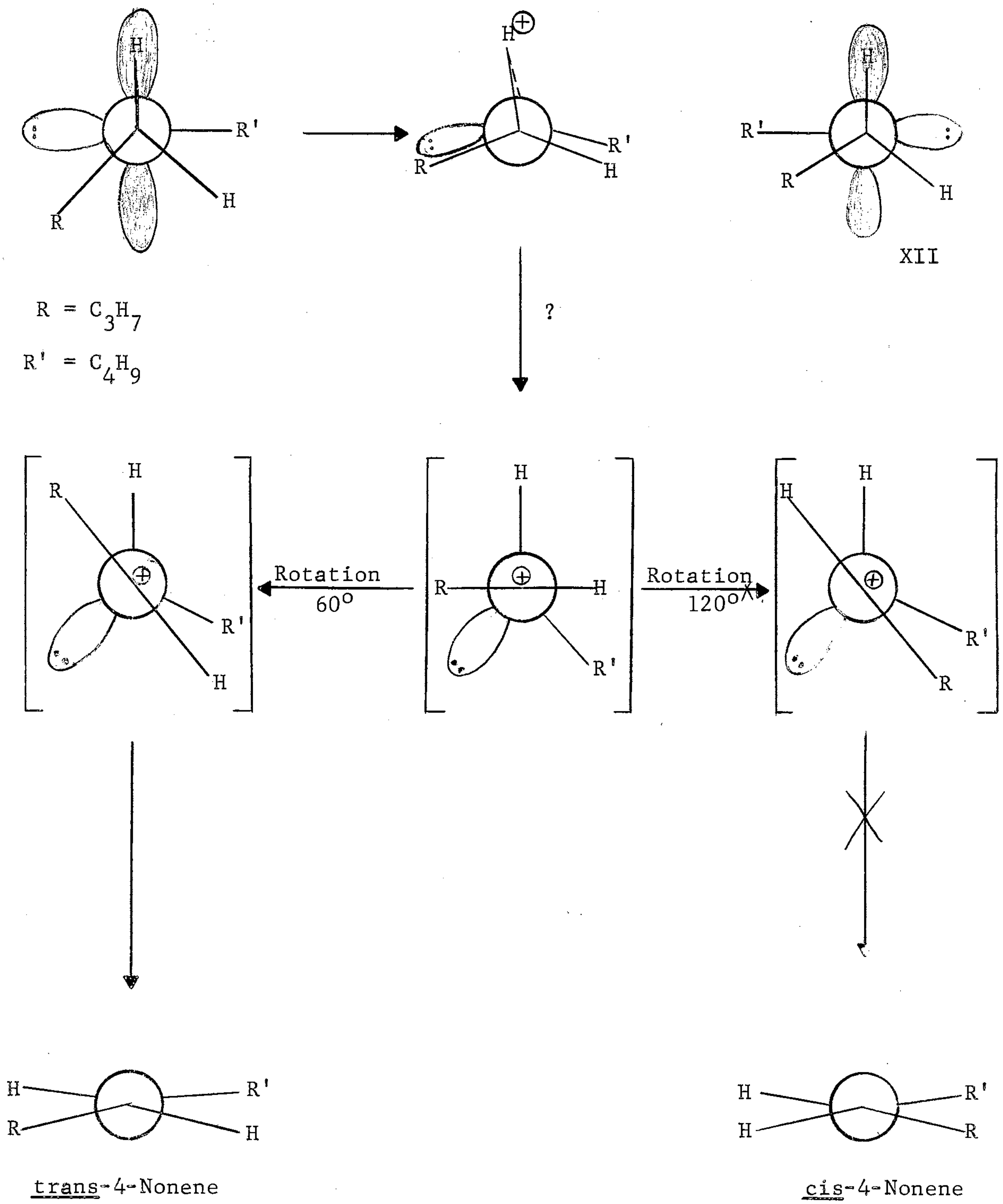
The mechanism as shown consists of abstraction of the tertiary hydrogen from the orthoester by the lithium reagent to give the trimethoxymethyl carbanion which loses a methoxide anion to yield dimethoxymethylene (VIII). Attack by a butyl anion on the species VIII can be envisioned to give a new carbanion. Loss of another methoxide anion with the formation of n-butyl(methoxy)methylene (IX) is reasonable. The next two steps are again the addition of a n-butyl anion and loss of a methoxide anion. Di-n-butylmethylene (X) may undergo an intramolecular hydride shift to give trans-4-nonene. Addition of another n-butyl anion could be expected with the formation of 5-n-butylnonyl anion. This anion would give rise to 5-n-butylnonane when water is added to the reaction mixture. Although not isolated this saturated hydrocarbon may be formed and located in the higher boiling fraction in small quantities.

A similar mechanism has been proposed by Franzen (30) for the formation of 4-nonene by the reaction of n-butyllithium and difluorodibromomethane. Formation of 5-halo-5-nonyllithium is proposed as the immediate precursor to be used in the final step in the formation of the olefin. However, neither is the stereochemistry of the olefin nor the mechanism for the final transformation discussed.

Moore and co-workers (43) in studies on the addition reaction of a dihalocarbene to bicyclo[2.2.1]-5-heptene have proposed that bonding in the transition state arises from the overlap of the vacant p-orbital of the carbene with the π orbital of the olefin. In view of the mechanism proposed by them it seems reasonable that the vacant p-orbital of the carbene may be involved here also in the hydride shift. The latter may involve a three-membered transition state. It is assumed that the substituted methylene exists in a singlet state as proposed by Skell (62). Scheme 2 shows a possible mechanism for the hydride shift.

The conformation XI may be preferred as there are less steric interactions in this molecular arrangement as compared to XII. An examination of the Newman projection formulas indicate that after the hydride shift occurs, a rotation about the carbon-carbon bond must occur before the double bond may be formed. Formation of a trans-olefin requires a rotation of only about 60 degrees. However, a rotation of nearly 120 degrees must occur in the opposite direction which involves increased interactions of the alkyl chains for the formation of a cis alkene. The energy difference in the two processes may provide an unsurmountable energy barrier toward the formation of cis olefin with the result that the trans olefin is formed exclusively. To be sure it is also feasible that loss of the last methoxide ion may occur with concomitant hydride migration to give the trans olefin

Scheme 2

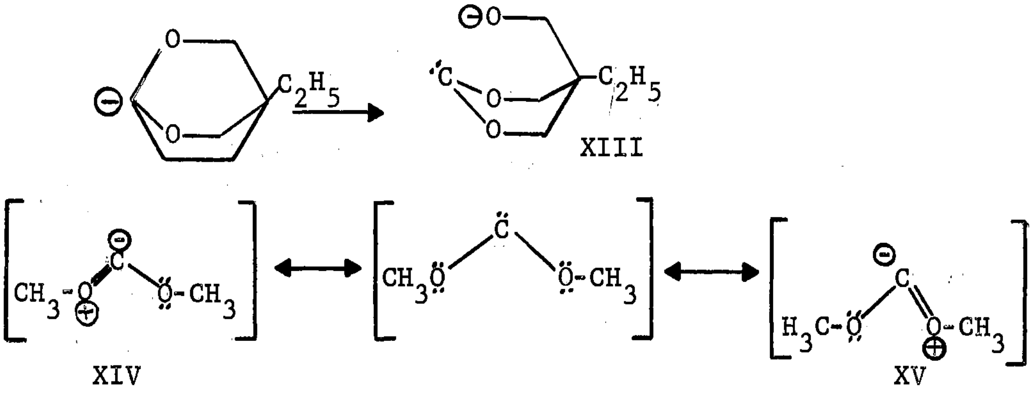


$R = C_3H_7$

$R' = C_4H_9$

without intervention of IX. Our data cannot discount this possibility. The reaction temperature appeared to be an important factor in this series of reactions. Although the condensation did not proceed to any appreciable extent at room temperature, it was rapid at 55°.

The reaction of n-butyllithium was also studied with 4-ethyl-2,6,7-trioxabicyclo[2.2.2]octane and yielded trans-4-nonene in higher yield (76%). A cyclic dialkoxy carbene (XIII), similar to dimethoxy methylene, is proposed to be the first carbene formed via ring cleavage of the anion produced by abstraction of the tertiary hydrogen from the ester. The remaining steps in the formation of trans-4-nonene are similar to those mentioned in scheme 1.



XIII

XIV

XV

Attempts were also made to trap these species (dialkoxymethylenes) by adding a large excess of cyclohexene to the reaction mixture but in no case was a product formed as a result of the addition of the dialkoxymethylene to the double bond. As mentioned earlier Crawford (20) has postulated dimethoxy methylene as an intermediate and has found that it could not be trapped with cyclohexene. This passive reaction of the carbene toward a double bond may be explained by the following reasoning. The unshared pairs of electrons on the neighboring oxygen atoms may alleviate part of the electronic deficiency on the divalent carbon permitting one to envision resonance forms (XIV and XV) where the electrophilic nature of the carbene would be greatly reduced. This would, in effect, make the carbene more selective toward the electron rich centers. n-Butyl anions being considerably richer in electrons than cyclohexene are therefore preferentially attacked.

Schollkopf (61) has found that bis(methylthio)methylene was also selective toward the type of olefin and could be trapped only with olefins containing an electron rich double bond such as in ketene dimethyl acetal or 1-phenyl-1-morpholinoethylene. Cyclohexene was not attacked.

It may be possible to capture the dialkoxycarbenes by use of olefins such as employed by Schollkopf (61). In analogy to this work (61) a suggested procedure in our system might involve addition of the alkyllithium reagent to a solution containing the olefin and the orthoester in boiling cyclohexane.

During the work-up procedures two unknown components (Unknown A and B) were also collected. Unknown A corresponds to a molecular formula of $C_7H_{16}O$. Although a complete structure has not been assigned, the infrared spectrum (Plate II) indicated it to be an ether. The NMR spectrum (Plate VI) shows that it is not a methyl ether as might have been expected if one of the intermediates in the Scheme 1 picked up a proton when water was added to the reaction. Unknown B is a monoalkene. From consideration of the NMR spectrum (Plate VII) and the postulated mechanism concerning the source of the methylene chain, the structure suggested is 5-n-butyl-5-decene. However, these unknowns are formed in yields of less than 5 per cent and may be a result of some side reaction.

The reaction was extended to n-hexyl and n-heptyllithium reagents. trans-6-Tridecene was the only major product isolated (37%) from the reaction of n-hexyllithium with trimethyl orthoformate. In the reaction of n-heptyllithium with trimethyl orthoformate a small amount of n-heptanol (formed as a result of hydrolysis of unreacted n-heptyl bromide) and an unknown (Unknown C) were also obtained. The infrared spectrum of unknown C (Plate IV) showed weak absorption at 3120-3580 cm.$^{-1}$, suggestive of the hydroxyl group, and an oxygen containing functional group was also indicated by the elemental analysis. Unknown C is probably an alcohol, but perhaps its structure could be partially elucidated by the use of deuterium oxide in a series of dilution studies with NMR.

The use of potassium t-butoxide was also attempted for the generation of dimethoxymethylene but no fruitful results were obtained. The former may not be a strong enough base to abstract the tertiary hydrogen from the orthoformate. Another contributing factor toward the reaction's failure could be its heterogeneous nature, and hence only a low concentration of the t-butoxide anions in solution would be expected.

Phenyllithium, benzyllithium and β-phenethyllithium were also examined in the condensation with trimethyl orthoformate. In the first case, since an olefin cannot be formed, triphenylmethane was the expected product. The reaction was studied in cyclohexene as well as in cyclohexane. A deep red coloration and a precipitate were noticed in both the cases. Analyses of the reaction mixture indicated that trimethyl orthoformate was destroyed and that identical reaction mixtures were obtained in both instances. Gas chromatographic analyses indicated the presence of a small amount of benzophenone but no triphenylmethane was detected. The red coloration was destroyed and the precipitate dissolved when water was added. Since no new product in any appreciable amount was detected it seems likely that the reaction products were unstable toward water. An extended reaction time or a higher reaction temperature and some modification in the work-up procedure may be helpful in the elucidation of the exact path followed in this process.

The reactions of benzyllithium were inconclusive as the lithium reagent could not be obtained in high enough concentrations. The latter reacts with benzyl bromide and 1,2-diphenylethane is formed in high yields.

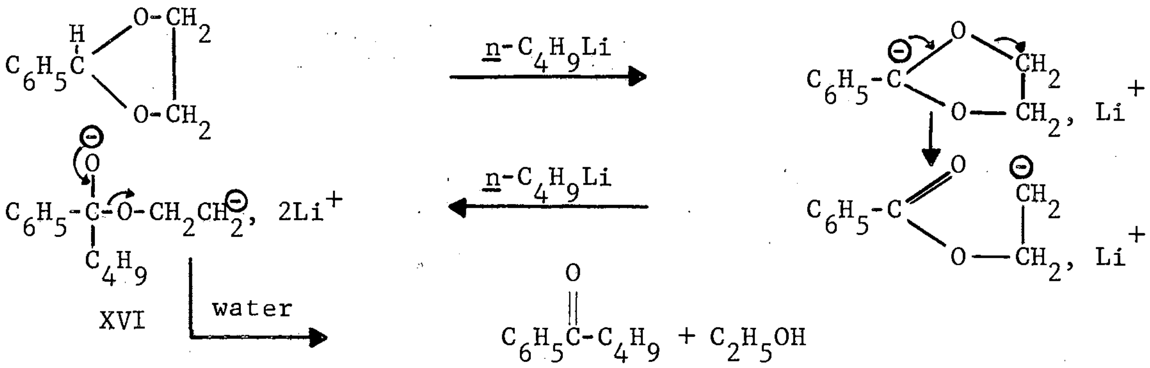
β-Phenethyllithium also reacted in a somewhat anomalous manner. The expected product 1,5-diphenyl-trans-2-pentene was not detected but a hydrocarbon which appears to be 3-β-phenethyl-1,5-diphenylpentane, was formed in about 15 per cent yield. All the instrumental data and elemental analysis support this structure. Formation of this product can be explained as a result of attack of another anion on the di-β-phenethylmethylene. This species could be created in a manner similar to the formation of di-n-butylmethylene (X in scheme 1). As mentioned earlier a similar product 5-n-butylnonane, though not isolated, may be formed in the reaction with n-butyllithium with the orthoester.

It was not possible to determine the reason for the anomalous behavior of the lithium reagents having an aromatic nucleus in the molecule. The presence of an aromatic compound in the reaction mixture may be responsible for such a behavior. It should be interesting to examine whether the presence of benzene or some other aromatic compound has any effect on the reaction of n-butyllithium with trimethyl orthoformate.

In an effort to obtain additional support for the proposed carbene mechanism for the reaction of alkyllithium reagents, the reaction of n-butyllithium with n-valeraldehyde dimethyl acetal was studied. The acetal was, however, recovered unchanged. The acidity of the tertiary hydrogen is probably insufficient for reaction due to the adjacent alkyl chain, and the hydrogen could also be sterically hindered.

The condensation of n-butyllithium with 2-phenyl-1,3-dioxolane was investigated. Since a benzylic hydrogen can be abstracted by a strong base [Stevens' rearrangement (70)], it was expected that the lithium reagent might remove a proton from the dioxolane also. The reaction of n-butyllithium with 2-phenyl-1,3-dioxolane proceeded in an unexpected manner. A ring cleavage analogous to the ring cleavage observed by Huyser (39) in a radical reaction was observed. n-Valerophenone was formed from the present reaction in 87.5 per cent yield. This process constitutes a new and novel ring cleavage of the dioxolane in basic medium (such derivatives are generally considered stable toward the base). The following mechanism is proposed to explain the formation of the ketone.

Scheme 3



The initial step is an abstraction of the benzylic hydrogen. A fission of C-O bond (between oxygen and C-4) takes place next with formation of a primary carbanion and an ester function in the same molecule. This species is then attacked by a n-butyl anion and the dianion (XVI) is produced. The precipitate that is formed in the reaction is probably this organometallic derivative. This would also explain why only a ketone is obtained from the above reaction even in the presence of excess lithium reagent. The addition of water decomposes the dianion, which is essentially a hemiketal, into n-valerophenone and ethanol. In an experiment with n-butyllithium and 2-p-methoxyphenyl-1,3-dioxolane, the reaction mixture was investigated for the presence of ethanol. The aqueous layer was neutralized with dilute hydrochloric acid to a pH of 7, and the resulting solution was distilled. The first 10 ml. of the distillate (b.p. 65-98°) were collected. Ethanol was definitely identified as one of the volatile organic components in this fraction. Traces of ethanol were also found by gas chromatography in the distillate (b.p. 25-78°). The existence of ethanol definitely supports the proposed reaction mechanism. p-Methoxy-n-valerophenone was formed in the reaction in 78 per cent yield. Extension of the condensation to n-hexyllithium and 2-phenyl-1,3-dioxolane gave similar results, n-heptanophenone being formed in nearly 70 per cent yield.

A study of various substituents on the aromatic ring and their effect on the facility of the ring cleavage would certainly be relevant. Also, it would be appropriate to determine if 2-alkyl- and 2-cycloalkyl-1,3-dioxolanes would undergo a similar ring cleavage.

In summary, a study of the condensation of alkyllithium reagents with orthoesters and cyclic acetals (1,3-dioxolanes) of substituted benzaldehydes has resulted in the discovery of two new reactions. The first reaction is the stereospecific synthesis of internal olefins (trans) by the condensation of orthoesters with n-alkyllithium reagents. This synthesis was examined using trimethyl orthoformate and three different lithium reagents (n-butyl, n-hexyl, and n-heptyllithium). trans-4-Nonene, trans-6-tridecene and trans-7-pentadecene have been prepared by this method in 32-42 per cent yield. An increased yield (76 per cent) was obtained for trans-4-nonene when 4-ethyl-2,6,7-trioxabicyclo-[2.2.2]octane was used as the orthoester. A carbene mechanism involving a dialkoxymethylene intermediate has been proposed.

The second new reaction is the synthesis of n-alkyl phenyl ketones by the condensation of 2-aryl-1,3-dioxolane with a n-alkyllithium reagent. n-Valerophenone, p-methoxy-n-valerophenone and n-hepthanophenone were prepared in excellent yields (66-87%) by this procedure from the appropriate dioxolane and alkyllithium reagents. The value of this chemical transformation is that it can be used to convert an aromatic aldehyde to an alkyl aryl ketone under mild conditions by substituting an alkyl group for the hydrogen atom attached to the carbonyl group in the aldehyde.

EXPERIMENTAL[1,2,3,4,5,6,7]

A General Method for Quantitative Gas Chromatographic Determinations Using Peak Height Ratios. This method was developed so that the yield of individual compounds in the reaction mixtures could be determined without going through the tedious procedures of measurement of areas of the peaks. Furthermore, in a number of cases where the compounds have short retention times and peaks are narrow, there may be a considerable

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[1] All melting points are corrected; all boiling points are uncorrected.

[2] The infrared spectra were recorded on a Beckman IR-5 spectrophotometer with sodium chloride crystals and potassium bromide pellets.

[3] The nuclear magnetic resonance (NMR) spectra were recorded on a Varian model A-60 high resolution spectrometer fitted with a field sensing stabilizer ("Super stabilizer"). Tetramethylsilane was used as an internal standard.

[4] Thanks are acknowledged to Dr. E. J. Eisenbraun for furnishing samples of some of the hydrocarbons used as standards in the gas chromatographic analyses.

[5] Qualitative as well as quantitative analyses of various samples were made using an Aerograph Hy-Fi Model A-550 unit with a hydrogen flame ionization detector. Preparative gas chromatography was done using Aerograph A-350B and A-700 units from Wilkens Instrument and Research, Inc.

[6] The microanalyses were performed by Midwest Microlabs, Inc., Indianapolis, Indiana, and Galbraith Laboratory, Knoxville, Tennessee.

[7] Skelly F and Skelly B are petroleum ether fractions distilling at 35-45° and 60-70°, respectively. These solvents and *n*-hexane were purified by stirring with concentrated sulfuric acid for several days, washing with water, and drying over silica gel before distilling.

error in the measurement of areas. This procedure, besides being convenient, is more accurate because a greater degree of precision can be attained in the measurement of only the peak heights.

Since the proportionality constant is dependent on the type of column and conditions, the determinations must be made using identical conditions, the same instrument and the same detector system and preferably on the same day. With the above restrictions, the method can be used without removing the solvents. The principle requirement of this procedure is that a small sample (25-50 mg.) of pure material (the yield of which is to be determined from the reaction mixture) must be obtained and a reference standard selected. The most convenient standard is a compound which differs by one carbon atom from the compound under investigation. For example, in the investigations with trans-4-nonene, the reference standard used was n-decane. Similarly, n-tetradecane and n-hexadecane were used as standards in the estimations of trans-6-tridecene and trans-7-pentadecene, respectively.

Approximately equal amounts of the unknown (P) and the standard (Q) are weighed accurately into a sealed vial. Liquids are most conveniently introduced with a micro-syringe through the seal. The amount of solvent added depends somewhat on the sensitivity of the instrument and the conditions required for the compounds being investigated. A series of injections (4 to 8) are made using the same amount of solution every time, and the peak heights are measured. The micro-syringe is rinsed with pure solvent and dried between two successive injections. An exact amount of the sample is taken from the reaction mixture and transferred to another sealed vial. The mixture is diluted, if necessary, and a small amount of the standard compound is introduced. Injection of a small sample is made to determine whether the compounds are present in approximately the same ratio as the original standard mixture. If necessary, an additional quantity of either the reference standard or the reaction mixture is added to the vial so that the two components P and Q are present in about equal amounts. A series of 4 to 8 injections is made using the same volume each time and peak heights are measured. The method of calculations and the principle of the method are exemplified by the determination of yield of _trans_-4-nonene in the mixture obtained from the reaction of trimethyl orthoformate with _n_-butyllithium in ether and _n_-hexane.

Wt. of _trans_-4-nonene	(P)	0.0355 g.
Wt. of _n_-decane	(Q)	0.0338 g.
Volume of solvent (acetone)		0.5 ml.

Injection No.	Peak Height P	Peak Height Q	Peak Height Ratio P/Q
1	74.0	48.0	1.54
2	86.0	52.0	1.65
3	91.0	61.0	1.49
4	80.0	52.0	1.54
5	33.0	22.0	1.50
6	65.0	42.5	1.53
7	63.5	41.5	1.53
8	97.5	62.5	1.56
9	37.5	23.5	1.59
10	82.5	54.0	1.53
11	70.5	46.0	1.53
	780.5	505.0	1.545

It is not necessary to calculate the peak height ratio P/Q since summations of the peak heights are used in the calculations. These calculations are shown to demonstrate the consistency of results.

$$\text{Peak height P} \propto \text{Area of the peak for P} \propto \text{Wt. of P}$$

$$\text{Peak height Q} \propto \text{Area of the peak for Q} \propto \text{Wt. of Q}$$

By comparison of the proportionalities mentioned above

$$\frac{\text{Peak height P}}{\text{Peak height Q}} = \frac{\text{Wt. of P}}{\text{Wt. of Q}} \times K \left[\begin{array}{l}\text{Where K is the proportionality} \\ \text{constant.}\end{array}\right]$$

On rearranging the above equation and substituting the values for the different terms, the value of K is calculated.

$$K = \frac{\text{Wt. of Q} \times \text{Peak height P}}{\text{Wt. of P} \times \text{Peak height Q}} = \frac{0.0355 \times 780.5}{0.0338 \times 505.0} = 1.622$$

Wt. of reaction mixture	8.104 g.
Wt. of aliquot (containing P)	0.4001 g.
Wt. of <u>n</u>-decane (Q)	0.0691 g.
Vol. of solvent (acetone)	2.0 ml.

Injection No.	Peak Height P	Peak Height Q	Peak Height Ratio P/Q
1	48.0	39.0	1.23
2	76.5	60.0	1.255
3	70.5	56.5	1.245
4	54.0	42.6	1.265
5	53.0	43.0	1.23
6	59.0	44.0	1.34
	285.1	361.0	1.267

Using the value of K obtained above and substituting the other values obtained above, the weight of P is calculated.

$$\text{Wt. of P} = \frac{\text{Wt. of Q} \times \text{Peak height P}}{K \times \text{Peak height Q}} = \frac{0.0691 \times 361.5}{1.6\ 2 \times 285.1}$$

$$= 0.0540 \text{ g.}$$

$$\text{Total wt. in the reaction mixture} = \frac{0.540 \text{ g.} \times 8.104}{0.4001}$$

$$= 1.091 \text{ g. } (0.00866 \text{ moles})$$

$$\text{Per cent yield from trimethyl orthoformate} = \frac{\text{Moles of P} \times 100}{\text{Moles of starting material}}$$

$$= \frac{0.00866 \times 100}{0.02} = 43.3 \text{ per cent}$$

These measurements were made using a silicone rubber, 10% on Chromosorb W, 80/100 mesh, 8 ft. x 0.125 in. column on the Aerograph Hy-Fi Model A-550 unit with hydrogen flame ionization detector. Temperature 122°, H_2 flow = 20 ml./min., N_2 flow = 30 m./min., sample size = 0.6 µl.

A method similar to that described above after the latter had been developed, has been published (12). The method of Brewster and Bayer (12) makes use of naphthalene as the internal standard. Naphthalene is added to the reaction mixture initially and the amount of the unknown is calculated from the relative areas of the corresponding peaks. A disadvantage of this procedure is that naphthalene may not always be inert in the chemical reaction. Furthermore, addition of the standard compound is not practicable for preparation of the desired product on a larger scale, as an additional purification step would be required.

Preparation of *n*-Butyllithium. (69) A two-liter, three-necked flask equipped with a magnetic stirrer, condenser, nitrogen inlet tube, a thermometer, an addition funnel, and a calcium chloride-Ascarite drying tube was charged with 800 ml. of anhydrous ether. The system was flushed with oxygen-free nitrogen. Freshly chipped lithium (cut to the size of small peas and weighed under *n*-hexane; 14.5 g., 2.07 mole) was added to the flask. The contents were cooled with a Dry Ice-acetone bath to -10°. Butyl bromide (137 g., 1.0 mole) and 100 ml. of anhydrous ether were added to the addition funnel, and about 10 ml.

of the resulting solution was run into the flask. The reaction mixture of became cloudy after some time and bright spots appeared on the lithium. Addition of the remaining halide-ether solution was done over a period of one-half hour while the temperature was maintained at 0 ± 5°. Stirring was continued for one hour while the temperature rose to 20°. Excess lithium was removed by filtration through glass wool under nitrogen pressure, and the filtrate made up to 1070 ml. with more ether.

Estimation of the yield of butyllithium was done by removing 3 aliquots (2.0 ml. each) of the above solution and adding each to 50.0 ml. of 0.08971 N hydrochloric acid (33). The solution was heated to boiling and the excess acid was titrated to phenolphthalein end point against 0.1067 N sodium hydroxide solution.

Vol. of NaOH required for excess acid=24.95 ml.

meq. of NaOH = 24.95 x 0.1067 = 2.662
meq. of HCl = 50.00 x 0.08971 = 4.485
meq. of BuLi = 1.823

$$\text{The yield of BuLi} = \frac{\text{meq. in the aliquot x total volume}}{\text{1000x volume of the aliquot}}$$

$$= \frac{1.823 \times 1090}{1000 \times 2} = 0.993 \text{ moles} \quad (99.3\%)$$

The remaining solution was used for further reactions. Other alkyllithium reagents were prepared using the same procedure and same type of equipment. Any variations are mentioned at the proper place.

Reaction of n-Butyllithium With Trimethyl Orthoformate and Cyclohexene. A 500-ml., three-necked flask equipped with an addition funnel, condenser, thermometer, nitrogen inlet tube, magnetic stirrer and a calcium chloride-Ascarite drying tube was charged with 56 ml. (0.56

mole) of cyclohexene and 10.6 g. (0.1 mole) of trimethyl orthoformate. A solution of n-butyllithium (120 ml. containing 0.1 mole) was placed in the addition funnel and was slowly added to the contents of the flask with stirring. The addition was accompanied by a slightly exothermic reaction as the temperature rose from 25 to 33°. However, the temperature dropped to 31° after some time while the addition was in progress. The contents were heated slowly after the addition was complete to allow ether to escape through the condenser until the temperature reached 79°. During the heating considerable precipitation took place. The contents were heated at reflux for one hour. After cooling to room temperature, the reaction mixture was treated carefully with 60 ml. of water. There was no vigorous reaction as was observed when butyllithium solution was added to water, indicating that there was no excess butyllithium. The contents, which formed two clear layers, were transferred to a separatory funnel and the organic layer was separated. Extraction of the aqueous layer was done with 25 ml. of Skelly F, and the combined organic layers were dried over anhydrous magnesium sulfate for one hour. Most of the solvents were removed by distillation. Infrared analysis of the residue (pale yellow liquid) showed a peak at 970 $cm.^{-1}$ which was not present in the starting materials or in any of the solvents. Analysis by gas chromatography also indicated the presence of at least one major component (trans-4-nonene) in the reaction mixture in addition to starting materials and solvents.

The residue was fractionated by distillation into three main fractions, (a) b.p. 20-103°, (b) b.p. 103-120° and (c) b.p. 70-103°/200-220 mm. Gas chromatographic analysis showed fractions (a) and (b) to contain the solvents, _n_-octane and traces of _trans_-4-nonene. Fraction (c) contained _trans_-4-nonene as the major component. This fraction was redistilled and the portion boiling at 78.5-79°/93 mm. was collected. Gas chromatography showed it to be essentially _trans_-4-nonene containing small amounts of a number of other components. The major constituent in the above mixture was collected by gas chromatography on the A-350B unit (silicone rubber, 10% on Chromosorb W, 80/100 mesh, 10 ft. x 0.25 in. at 95°).

The infrared spectrum of the purified liquid showed peaks at 2940 (aliphatic C-H), 1492 (C-H deformation in methylene), 1392 (C-H deformation in methyl) and 970 cm^{-1}. The peak at 970 $cm.^{-1}$ was suggestive of the presence of a _trans_ double bond in the molecule (6). Comparison of the above infrared spectrum with the spectrum of _trans_-3-heptene showed the two spectra to be nearly superimposable except for the intensities of the individual peaks. The compound decolorized a solution of bromine in carbon tetrachloride, confirming the presence of unsaturation in the molecule. Elemental analysis gave the following results which indicated the compound to be a hydrocarbon with an empirical formula CH_2.

Anal. Calcd. for C_9H_{18}:

C, 85.71; H, 14.28

Found: C, 86.00; H, 14.40

The reaction of cyclohexene, trimethyl orthoformate and _n_-butyllithium as carried out above gives an aliphatic _trans_-monoalkene as the main reaction product.

The lower-boiling fractions (b.p. 20-78°) were found to contain unreacted thrimethyl orthoformate (by infrared spectrometry). It was also found that cyclohexene and trimethyl orthoformate formed an azeotrope distilling at 78° and these two components could not be separated by distillation. Moreover, the two compounds also had identical retention times when analyzed by gas chromatography. Several columns (silicone rubber on Chromosorb W, Apiezon L on Chromosorb W and di-_n_-butyl phthalate on Fluoropak 90) were employed for gas chromatographic separation of these two compounds but none was completely successful in resolving the mixture.

The above reaction was repeated using the same conditions and same molar ratios of the reactants. The lower-boiling fractions (b.p. 20-78°) were removed by distillation and were found to contain the unreacted trimethyl orthoformate (by infrared spectrometry). The residue was transferred to a micro-distillation apparatus and the contents were distilled under reduced pressure. Four fractions were collected and are listed in the following order: number, boiling point, pressure and weight.

(1) 25-70°/97-98 mm., 0.9795 g.; (2) 70-74.5°/97-98 mm., 0.437 g.;
(3) 74.5-78°/97-98 mm., 0.408 g.; (4) 78-81°/97-98 mm., 0.630 g.

Gas chromatographic and infrared analyses showed all four fractions to be a mixture of at least seven to nine compounds, of which three were major components, while the other four were present only in trace amounts. Preparative gas chromatography was used to separate and collect the major products. Details are shown in Table I.

TABLE I

SEPARATION BY PREPARATIVE GAS CHROMATOGRAPHY OF THE REACTION MIXTURE FROM TRIMETHYL ORTHOFORMATE, n-BUTYLLITHIUM AND CYCLOHEXENE

Column: SE 30, 30% on Chromosorb P, 45/60 mesh, 20 ft. x 0.375 in., A-700 unit.

Conditions: He Flow=150 ml./min., Col. 110°, Det. 252°, Inj. 222°.

Compound	Retention Time
n-Octane	16 min. 40 sec.
Unknown A	19 min. 30 sec.
trans-4-Nonene	28 min. 0 sec.

n-Octane was identified by its NMR spectrum, infrared spectrum, and by gas chromatography.

Unknown A was present in the least amount of the three fractions. The sample obtained was sufficient only for determination of its infrared spectrum (Plate II), NMR spectrum (Plate VI) and elemental analysis which corresponded to the molecular formula $C_7H_{15}O$.

Anal. Calcd. for $C_7H_{16}O$:

C, 72.40, H, 13.70

Found: C, 72.05, H, 13.71

Although a complete structure has not been assigned to this compound, the infrared spectrum suggests the presence of an ether linkage in the molecule.

The major product was found to be identical to the one isolated earlier from the first reaction and its structure was proven to be *trans*-4-nonene.

Structure Proof of trans-4-Nonene. The evidence for the olefin to be an internal olefin (trans) has already been discussed. Reductive ozonolysis of 4-nonene to n-butyraldehyde and n-valeraldehyde has recently been reported (30) but no reference is made to the stereochemistry.

The NMR spectrum (Plate V) showed the following types of protons: 2 protons vinylic (a complex multiplet centered at δ 5.3, 4 protons in methylene groups next to a double bond (allylic, δ 1.92), 6 protons in methylene groups flanked by methylene or methyl groups (δ 1.28), and 6 protons in methyl groups at the end of a carbon chain (δ 0.89).

Oxidative ozonolysis of the olefin was done as follows to establish the position of the double bond. A solution of 0.5 g. of the olefin in 35 ml. of methylene chloride in a 100-ml. flask was cooled in Dry Ice-acetone bath. Ozone was slowly bubbled into the solution until a permanent blue color (ca twenty minutes) was visible. The color disappeared on standing for about ten minutes. Ozone was once again bubbled into the solution for an additional five minutes. A solution of hydrogen peroxide (2.0 ml. of 30% solution) was added to the solution, the cooling bath was removed, and the contents were stirred with a magnetic stirrer for two and one-half hours. Palladized charcoal (ca 15-20 mg.) was added to the solution and brisk effervescence was observed. Stirring of the solution was continued for two hours when the evolution of oxygen ceased. The contents were then extracted with 50 ml. of sodium bicarbonate (10%) solution. After acidification of the sodium bicarbonate extract with concentrated hydrochloric acid to pH 1-2, the contents were extracted with three portions of ether (25 ml. each). A small sample of the ether extract was evaporated to dryness and the residue was analyzed by infrared spectrometry. The infrared spectrum showed the residue to contain an aliphatic acid.

An ethereal solution (25 ml.) of diazomethane obtained from EXR-101 (N,N'-dinitroso-N,N'-dimethylterephthalamide) was added to the remaining ethereal solution obtained above until the yellow color of diazomethane persisted. After allowing to stand overnight, the contents were slowly warmed on a steam bath to expel the residual traces of diazomethane. The ether extract was then analyzed by gas chromatography and showed the presence of two components in nearly equal amounts. These two esters were identified to be methyl n-butyrate and methyl n-valerate by comparing their retention times with those obtained with authentic samples of the methyl esters of n-butyric, n-valeric, n-caproic, and n-heptanoic acids. It has proven valuable to use several esters of similar structures for gas chromatographic analysis to establish the size of injection and the retention times. The evidence discussed earlier and the identification of these two esters from the ozonolysis product of the olefin establishes its structure as trans-4-nonene, b.p. 143-144°/ 731 mm., n_D^{27} 1.4168 [lit. (30) n_D^{18} 1.4224, b.p. 145-146°].

The above experiments were carried out on a qualitative basis to determine the course of reaction and type of reaction products.

Reaction of n-Butyllithium With Trimethyl Orthoformate. A 500-ml., three-necked flask equipped with a condenser, addition funnel, magnetic stirrer, thermometer, nitrogen inlet tube and a calcium chloride-Ascarite drying tube was charged with 2.16 g. (0.02 mole) trimethyl orthoformate and 50 ml. of ether. n-Butyllithium solution (200 ml. of ethereal solution containing 0.1 mole of butyllithium) was placed in the addition funnel and slowly added to the contents in the flask. Addition of n-butyllithium solution was slightly exothermic in the beginning. After stirring for eighteen hours the contents were heated at reflux for two hours. n-Hexane (50 ml.) was added to the reaction mixture, and the contents were heated to allow ether to escape until the temperature inside the flask rose to 60°. Additional heating at reflux was done for two hours. After the reaction mixture had cooled to room temperature, 50 ml. of ice water was cautiously added. The organic layer was separated and the aqueous layer was extracted with 50 ml. of ether. The combined organic layers were dried over anhydrous magnesium sulfate for one hour, and the lower-boiling fractions distilling up to 80° were removed by distillation. Gas chromatographic and infrared analyses of the residue (8.104 g.) showed the presence of trans-4-nonene in the reaction mixture. This experiment proved conclusively that trans-4-nonene is formed as a result of reaction of n-butyllithium and trimethyl orthoformate. The yield of trans-4-nonene (calculated by gas chromatographic analysis) was found to be 1.067 g. (42.3%). The details are described along with the general procedure outlined for the quantitative estimations by peak height ratios.

The reaction of n-butyllithium with trimethyl orthoformate in the presence of cyclohexene was repeated for quantitative determinations using 58.3 g. (0.71 mole) of cyclohexene, 53.0 g. (0.5 mole) of trimethyl orthoformate and 530 ml. of ethereal solution containing 0.5 mole of n-butyllithium. The experiment was carried out under the same conditions as used earlier and worked up in the same manner. Considerable unreacted trimethyl orthoformate along with cyclohexene and n-hexane were found in the lower-boiling fractions distilling at 25-78°.

After distillation 12.698 g. of reaction mixture was obtained. The yield of trans-4-nonene was found to be 3.39 g. (5.38%) according to gas chromatographic determinations. The presence of unknown A and n-octane was also detected.

The reaction was repeated without cyclohexene and using 10.6 g. (0.1 mole) and 0.4 mole of n-butyllithium with the following variation in the procedure. Trimethyl orthoformate was run into the n-butyllithium solution. The contents were warmed to 50-55° after the addition was completed and heating was continued for three hours. The reaction mixture was worked up as usual. Lower-boiling fractions were distilled (25-55°) and were found to contain ether and n-hexane only. No trimethyl orthoformate was detected in these fractions. After distillation 18.091 g. of reaction mixture was obtained which contained 5.34 g. (42.4%, by gas chromatography) of trans-4-nonene.

In order to attempt structure determinations on the unknown A, it was necessary to collect more of the material. The reaction was repeated starting with 0.2 mole of trimethyl orthoformate. The reaction mixture was combined with the reaction mixtures obtained in the two experiments described immediately above. The contents were then fractionally distilled and a series of fractions were collected: (1) b.p. 25-80°/108 mm., 48.35 ml., (2) 80-83°/108 mm., 7.05 ml., (3) 50-108°/12 mm., 2.05 ml., (4) 25-105°/6 mm., 2.901 g. Residue 3.9 g.

Gas chromatographic analyses were performed to determine the purity and the contents of various fractions distilled. Fraction (1) was found to contain unknown A, n-octane, trans-4-nonene and the solvents, (2) was essentially trans-4-nonene, (3) a terrible mixture of 8-10 components, and (4) a mixture of 8-10 components containing at least one major component (Unknown B, 15-20 per cent of the mixture).

Preparative gas chromatography was attempted on 48.35 ml. of the fraction distilling at 25-80°/108 mm. Only about 0.3 g. of the fraction containing unknown A could be collected after nearly half the reaction mixture had been used. This fraction was also found to be contaminated with n-octane. No further attempts were made to collect more of unknown A as this component was formed in very small amounts only. The yield of unknown A is only about 5-10 per cent of the amount of trans-4-nonene (i.e. about 2-4 per cent from trimethyl orthoformate).

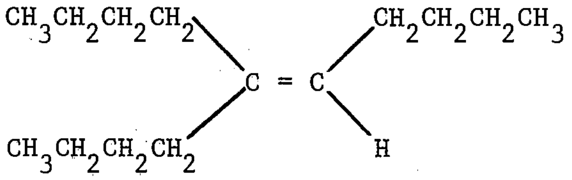
Preparative gas chromatography was then attempted on the fraction (4) which had at least one major component (unknown B). The same instrument and the same column as shown in Table I was used, but at higher temperatures, col. 240°, inj. 255°, det. 262°, retention time was 8 min., 50 sec. About 0.50 g. of unknown B containing small amounts of 3-4 impurities were collected. Chromatography of the fraction collected above gave about 0.3 g. of pure unknown B. The infrared spectrum (Plate III) and the NMR spectrum (Plate VII) indicated the compound to be only a hydrocarbon. A bromine-carbon tetrachloride solution was decolorized in the cold by unknown B indicating the presence of unsaturation in the molecule. Elemental analysis indicated the empirical formula CH_2 for unknown B.

Anal. Calcd. for CH_2:

C, 85.71; H, 14.28

Found: C, 85.70; H, 14.37

The following structure is proposed based on the NMR data and elemental analysis. No chemical evidence has been obtained and no mechanism is proposed to explain its formation. The yield of unknown B is less than one per cent from trimethyl orthoformate.



5-n-Butyl-5-decene

The NMR spectrum shows four peaks: (1) a complex multiplet for 1 olefinic proton at δ 5.07, (2) 6 allylic protons at δ 1.94, (3) 12 methylene protons at δ 1.29, and (4) 9 methyl protons at δ 0.9; $n_D^{30.5}$ 1.4342 [lit. (19), n_D^{20} 1.4412 for a mixture of 5-n-butyl-5-decene and 5-n-butyl-4-decene].

Reaction of n-Butyllithium With 4-Ethyl-2,6,7-trioxabicyclo(2.2.2)-octane. A one-liter, three-necked flask equipped with stirrer, condenser, addition funnel, nitrogen inlet tube, drying tube and thermometer was charged with 14.4 g. of the bicyclo compound and 80 ml. of cyclohexane. The mixture was warmed to 55-60° to obtain a homogeneous solution. An ethereal solution (400 ml.) of n-butyllithium (0.4 mole) was added through the addition funnel. An exothermic reaction and precipitation accompanied the addition of the lithium reagent. The addition was done over a period of one-half hour and a maximum temperature of 57° was attained in the reaction flask. Stirring was continued for an additional period of eighteen hours. Ether was carefully distilled until the reaction temperature approached 80°. The contents were heated at reflux for two hours. Ice water (100 ml.) was carefully added through an addition funnel to the reaction mixture and after stirring for about fifteen minutes, the contents were transferred to a separatory funnel. The oily layer was extracted with 100 ml. of ether and dried over anhydrous magnesium sulfate for two hours. After removal of solvents, the residual liquids weighed 16.996 g. Gas chromatographic analysis showed trans-4-nonene to be the only major constituent in the reaction besides the residual solvents. No unreacted bicyclo starting material was indicated by gas chromatography or infrared analyses. The yield of trans-4-nonene was calculated by the general procedure described above using n-decane as the internal standard and was found to be 9.57 g. (76.0%).

In another experiment, carried out using 0.1 mole of n-butyllithium and 0.1 mole of the bicyclo compound in the presence of cyclohexene, the only new product was trans-4-nonene. A considerable amount (ca 50-60%) of the bicyclo compound was also recovered.

Preparation of n-Valeraldehyde Dimethyl Acetal. The preparation was carried out following the procedure of Adkins and Nissen (2). Methanol (6.4 g., 0.2 mole) was added to 1.78 g. of anhydrous calcium chloride in a 50 ml. flask with constant swirling. The contents were cooled in ice water and 8.6 g. (0.1 mole) of freshly distilled n-valeraldehyde was added. An exothermic reaction accompanied the addition. After being shaken vigorously for five minutes, the flask was set aside for two and one-half days. The contents had separated into two clear layers, from which the upper layer was removed and washed twice with 5 ml. of water. After drying over anhydrous potassium carbonate, the liquid was distilled under reduced pressure, b.p. 80-90°/ca 50 mm. (aspirator), 131°/739 mm. (with slight decomposition) [lit. (44)].; yield 6.3 g. (48%). The infrared spectrum showed peaks at 1140 and 1060 cm.$^{-1}$ indicating the presence of an acetal (9). NMR analysis showed peaks at δ 4.28 (tertiary hydrogen), δ 3.2 (protons on methoxy group), δ 1.4 (methylene protons), and δ 0.9 (methyl protons).

Reaction of *n*-Butyllithium With *n*-Valeraldehyde Dimethyl Acetal. A 250-ml., three-necked flask equipped as usual was charged with 100 ml. of a solution containing 0.1 mole *n*-butyllithium and 2.64 g. (0.02 mole of *n*-valeraldehyde dimethyl acetal. The reaction was performed as described with trimethyl orthoformate. A brisk reaction was noticed when the contents were decomposed with water, indicating the presence of excess *n*-butyllithium. Analysis of the reaction mixture, after the work-up, by gas chromatography as well as infrared spectrometry failed to show the formation of *trans*-4-nonene, but indicated the presence of unreacted acetal.

Preparation of Potassium *t*-Butoxide. (26) A 250-ml., three-necked flask equipped with a magnetic stirrer, condenser and calcium chloride drying tube was charged with 100 ml. of (1.0 mole) of dry and distilled *t*-butyl alcohol. Potassium (4.0 g., 0.1 mole) was added and the contents were heated at reflux until all the metal dissolved (forty-five minutes). About 75 ml. of excess alcohol was removed by distillation under reduced pressure (aspirator). The slurry thus obtained was dried in a vacuum oven for two hours at 160°. A pale yellow solid was obtained which was used without further purification.

Reaction of Potassium *t*-Butoxide With Trimethyl Orthoformate and Cyclohexene. The flask containing potassium *t*-butoxide (0.1 mole) was further charged with 56.0 ml. (0.7 mole) of cyclohexene. Trimethyl orthoformate (10.6 g., 0.1 mole) was slowly added through an addition funnel. After boiling for two hours, the contents were poured into 50 ml. of distilled water. The organic layer was separated and dried over anhydrous magnesium sulfate. Distillation gave 56 ml. of distillate boiling at 47-78°, and a small amount of liquid remained. Analysis by infrared spectrometry showed the residue as well as the distillate to be a mixture of trimethyl orthoformate and cyclohexene. Extraction of the aqueous layer with 2 portions of 5 ml. of Skelly F did not yield an organic product. The aqueous layer was then acidified to pH 1-2 with concentrated hydrochloric acid and once again extracted with 25 ml. of Skelly F but nothing was obtained.

Preparation of *n*-Hexyllithium. (32) A one-liter, three-necked flask equipped with a condenser, calcium chloride, Ascarite drying tube, nitrogen inlet tube, thermometer, addition funnel and a magnetic stirrer was charged with 450 ml. of anhydrous ether. The system was flushed with oxygen-free nitrogen and 2.8 g. (0.4 mole) of freshly chipped lithium, and the reaction mixture was cooled to -10° with Dry Ice-acetone bath. A solution of 26.5 g. (0.16 mole) of *n*-hexyl bromide and 50 ml. of anhydrous ether was added from the addition funnel to the reaction flask with constant stirring while maintaining the temperature at 0 ± 5°. After the addition, stirring was continued until the contents warmed to room temperature. Excess lithium was removed by filtration through glass wool. Three aliquots of 2.0 ml. each were removed from the resulting 475 ml. of ethereal solution of *n*-hexyllithium, for estimation of the lithium reagent. The yield of the lithium reagent [by titration (33)] was 88 per cent.

Reaction of n-Hexyllithium With Trimethyl Orthoformate. A 500-ml., three-necked flask equipped as in the previous experiment was charged with 250 ml. of an ethereal solution containing 0.175 mole of n-hexyllithium. Trimethyl orthoformate (5.03 g., 0.05 mole) in 80 ml. of cyclohexane was slowly added to the reaction flask. Ether was allowed to escape through the condenser as the contents were heated until the temperature rose to 55°. Additional heating was done at this temperature for one hour. After careful decomposition of excess n-hexyllithium with 100 ml. of ice water, the contents were extracted with two 20-ml. portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate for one hour and the solvents were removed by distillation at atmospheric pressure. The residual liquid (11.352 g.), on gas chromatographic analysis, showed the presence of only two major components which were identified to be n-dodecane and trans-6-tridecene. Further distillation of the reaction mixture was done under reduced pressure (b.p. 25-110°/35-40 mm.), and the distillate was used for the isolation of pure olefin by preparative gas chromatography. The results of the preparative gas chromatography are shown in Table II.

The NMR spectrum of trans-6-tridecene (Plate VIII) showed four types of protons: 2 vinylic protons (a complex multiplet at δ 5.36), 4 allylic protons (δ 1.95), 14 methylene protons (δ 1.28) and 6 methyl protons (δ 0.89); yield 3.29 g. (37%, by gas chromatography); $n_D^{22.5}$ 1.4394, b.p. 91°/5 mm. [lit. (47) n_D^{20} 1.4342, b.p. 222-225°].

TABLE II

SEPARATION BY PREPARATIVE GAS CHROMATOGRAPHY OF THE REACTION MIXTURE FROM n-HEXYLLITHIUM AND TRIMETHYL ORTHOFORMATE

Column: SE 30, 30% on Chromosorb P, 45/60 mesh, 20 ft. x 0.375 in., A-700 unit.

Conditions: He flow=150 ml./min., Col. 225°, Det. 294°, Inj. 225°.

Compound	Retention Time
n-Dodecane	13 min. 0 sec.
trans-6-Tridecene	17 min. 10 sec.

Preparation of n-Heptyllithium. The title compound was prepared from 2.1 g. (0.3 mole) of lithium and 25.0 g. (0.14 mole) of n-heptyl bromide in 250 ml. of anhydrous ether following the procedure described for n-hexyllithium. The solution thus obtained was filtered through glass wool and used for the next reaction. n-Heptyllithium has also been prepared from lithium and n-heptyl chloride in hexane (66).

Reaction of n-Heptyllithium With Trimethyl Orthoformate. A 500-ml., three-necked flask equipped as in previous experiments was charged with 4.24 g. of trimethyl orthoformate and 60 ml. of cyclohexane. The heptyllithium solution prepared above (ca 0.14 mole in 250 ml. of ether) was run into the reaction flask with constant stirring. No immediate reaction was observed either by change in the temperature or in consistency of the reaction mixture. The contents were then heated allowing ether to escape through the condenser until a temperature of 70° was attained inside the reaction flask. Precipitation was noticed to occur at this point. The contents were heated at reflux for an additional two hours. After cooling to room temperature, the contents were worked up as in the reaction of n-butyllithium with trimethyl orthoformate. Infrared analysis of the reaction mixture (11.176 g.) showed the presence of a trans olefin. Gas chromatographic analysis showed the reaction mixture to contain three major and five minor components. It also showed the reaction mixture to be relatively free from high-boiling residues as evidenced by almost no trailing after the last peak. A sample (0.136 g.) was saved for quantitative determination of the expected product trans-7-pentadecene. The remaining solution was used as such for preparative gas chromatography. The three major components were identified as n-heptanol, n-tetradecane and trans-7-pentadecene. One of the minor components (Unknown C) could also be obtained in pure state. Table III shows the details of preparative gas chromatography.

TABLE III

SEPARATION BY PREPARATIVE GAS CHROMATOGRAPHY OF THE REACTION MIXTURE FROM n-HEPTYLLITHIUM AND TRIMETHYL ORTHOFORMATE

Column: SE 30, 30% on Chromosorb P, 45/60 mesh, 20 ft. x 0.375 in.

Conditions: He Flow=200 ml./min., Col. 262°, Det. 305°, Inj. 275°, A-700 unit.

Compound	Retention Time
n-Heptanol	4 min. 0 sec.
n-Tetradecane	10 min. 0 sec.
trans-7-Pentadecene	12 min. 30 sec.
Unknown C	21 min. 0 sec.

The NMR spectrum of trans-7-pentadecene (Plate IX) showed 4 types of protons: 2 vinylic protons (a complex multiplet at δ 5.35), 4 allylic protons (δ 1.9), 18 methylene protons (δ 1.28), and 6 methyl protons (δ 0.89); yield 3.46 g. (32.9%, by gas chromatography); n_D^{23} 1.4388, b.p. 119°/5 mm. [lit. (67) n_D^{20} 1.4370, b.p. 137°/30 mm.]

Unknown C was a white crystalline material, m.p. 51-52°. About 0.2 g. of the pure compound was isolated by preparative gas chromatography. It could be crystallized from acetone-water. The infrared spectrum (Plate IV) showed weak absorption at 3580-3120 (probably a hydroxyl group), 2920, 2860 (aliphatic C-H) and 1475 cm^{-1}. The NMR spectrum (Plate X) showed three peaks at δ 1.62, δ 1.32 (methylene protons) and δ 0.9 (methyl protons) in an approximate ratio of 1:36:9. Elemental analysis indicated the presence of some oxygen-containing functional group in the molecule. It is not possible to propose a definite structure from the available data. The yield of the unknown C is less than 5 per cent based on trimethyl orthoformate. It is proposed to substantiate the presence of the hydroxyl group through studies with deuterium oxide.

Anal.

Found: C, 78.22; H, 14.14.

Preparation of Phenyllithium. (27) A one-liter flask equipped as in the earlier reactions was charged with 500 ml. of anhydrous ether and 7.0 g. (1.0 mole) of freshly chipped lithium. Bromobenzene (70.7 g., 0.45 mole) and 50 ml. of ether were placed in the addition funnel and about 10 ml. of the halide-ether solution was added to the reaction mixture. The reaction of lithium with bromobenzene did not start below room temperature and had to be initiated by warming the reaction mixture to 33°. Dropwise addition of the remaining halide-ether solution was necessary to maintain the reaction mixture at gentle reflux. The mixture obtained was used for further reactions after filtration of excess lithium.

Reaction of Phenyllithium With Trimethyl Orthoformate. A 500-ml. flask was charged with 5.03 g. (0.05 mole) trimethyl orthoformate and 100 ml. of freshly distilled cyclohexene. An ethereal solution (300 ml.) containing about 0.225 moles of phenyllithium was added to the reaction mixture through the addition funnel. No indication of a spontaneous reaction was observed by any change in the appearance or temperature of the mixture. The contents were then heated allowing ether to escape until the reaction mixture attained a temperature of 70°. Heating was continued for one and one-half hours and was accompanied by formation of a deep reddish-brown color in the mixture as well as a precipitate. After the mixture was cooled to room temperature, 100 ml. of ice water were carefully added. An exothermic reaction was noted during the addition of water. The red color was destroyed during decomposition, and the pale yellow-colored, oily layer was removed by extraction of the reaction mixture with 2 portions of 35 ml. of ether. Distillation of the dried (over magnesium sulfate for one hour) organic layer yielded only cyclohexene, benzene, and ether. Trimethyl orthoformate was not present in the lower-boiling fraction. Gas chromatographic analysis of the residual liquids indicated the presence of three major components which were identified to be bromobenzene, benzophenone and biphenyl, of which biphenyl was present in the largest amount. The ratio of biphenyl to benzophenone was about 4:1. Trace quantities of three unknown compounds were also detected but in no case was triphenylmethane identified as a product. Further investigations to identify the unknown materials were discontinued since the yield was less than 2-3 per cent of the total mixture. The above reaction indicated that trimethyl orthoformate was decomposed by phenyllithium but the reaction products were unstable in the presence of water.

In another experiment cyclohexane was used instead of cyclohexene and the reaction was run under conditions identical to those used above. The formation of the red color and the precipitate was observed as in the above reaction. Gas chromatographic as well as infrared analyses indicate that nearly identical mixtures were obtained in the above reactions.

Preparation of Lithium Dust. The procedure is essentially the same as that of Bartlett, et al. (5). A one-liter, three-necked flask equipped with a high-speed mechanical stirrer, a condenser and a nitrogen inlet tube was charged with 200 ml. of mineral oil (Fisher paraffin oil, white and heavy) and 6.5 g. (0.93 mole) of freshly chipped lithium. The contents were heated until the lithium began to melt, and the mixture was stirred vigorously until the lithium dispersed into droplets about 1-3 mm. in diameter. Heating and stirring were discontinued and the contents were allowed to cool to room temperature. The mineral oil was forced out with nitrogen through a tube reaching to the bottom of the flask. The lithium dust was washed with four portions of ether (100 ml. each), and the ether was removed through the same tube. The lithium dust was finally suspended in 600 ml. of ether and used for the next reaction.

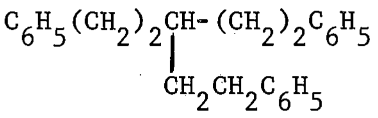
Preparation of Benzyllithium. Benzyl bromide (34.2 g., 0.2 mole) and 30 ml. of ether were placed in the addition funnel and 5 ml. of the halide ether mixture were run into the flask containing the suspension of lithium dust (0.93 mole) in ether. The contents were warmed to initiate the reaction, and after a brisk reaction had begun, the heating bath was removed. The yield of the lithium reagent was found to be only 8 per cent (by titration) which is in approximate agreement with the results of Ziegler (71). He reported that benzyllithium could not be prepared by reaction of benzyl chloride with lithium, because as soon as benzyllithium was formed it reacted with benzyl chloride to give 1,2-diphenylethane. It seems that benzyl bromide also reacts like benzyl chloride.

Reaction of Benzyllithium With Trimethyl Orthoformate. A 500-ml., three-necked flask equipped as in the previous experiments was charged with a solution of benzyllithium (prepared from 3.08 g., 0.44 mole of lithium and 33.77 g., 0.197 mole of benzyl bromide in 250 ml. ether). Trimethyl orthoformate 6.36 g. (0.06 mole) and 80 ml. of cyclohexane were added. The reaction was worked up as usual. The low-boiling fractions (b.p. 25-78°) were essentially cyclohexane and ether. It could not be determined definitely whether there was any trimethyl orthoformate in these fractions. Gas-chromatographic analysis of the residual liquids showed presence of cyclohexane, toluene and 1,2-diphenylethane (80-90% or more of the total). The reaction was inconclusive as the concentration of benzyllithium was probably too low.

Reaction of Benzyllithium With 4-Ethyl-2,6,7-trioxabicyclo[2.2.2]-octane. A 500-ml., three-necked flask equipped as usual was charged with 145 ml. of an ethereal solution containing 0.008 mole of benzyllithium, 0.384 g. (0.0026 mole) of the bicyclo compound, and 100 ml. of cyclohexane. The reaction was carried out and the reaction mixture worked up as in the previous reaction. Another reaction was carried out (under identical conditions) using the same amount (0.008 mole) of benzyllithium but only 0.23 g. (0.0016 mole) of the bicyclo compound was added. Both the reaction mixtures were analyzed by gas chromatography and found to contain 1,2-diphenylethane (major component) and the bicyclo compound. No new compound was indicated by gas chromatography.

Preparation of β-Phenethyllithium. A 500-ml., three-necked flask equipped with a condenser, nitrogen inlet tube, thermometer, magnetic stirrer, an addition funnel and a calcium chloride-Ascarite drying tube was charged with 300 ml. of anhydrous ether and 2.45 g. (0.35 mole) of freshly chipped lithium. β-Phenethyl bromide (29.6 g., 0.16 mole) and 75 ml. of ether were placed in the addition funnel. The halide-ether solution was added to the reaction flask while maintaining the reaction temperature at 20 ± 5°. Stirring was continued at room temperature for two and one-half hours and for an additional hour while heating the contents at reflux (34°). The reaction mixture was used for further reaction after removal of lithium by filtration through glass wool.

Reaction of β-Phenethyllithium With Trimethyl Orthoformate. A 500-ml., three-necked flask, equipped as usual, was charged with 5.03 g. (0.05 mole) of trimethyl orthoformate, 75 ml. of cyclohexane and the ethereal solution of β-phenethyllithium (ca 0.16 mole). The contents were slowly heated allowing ether to escape until a reaction temperature of 54° was attained. Formation of a white precipitate was noted during heating at about 48-49° which was continued for an additional period of one hour. After allowing the mixture to cool to room temperature, 50 ml. of water were carefully added. The organic layer was separated and the aqueous layer was extracted with two portions of cyclohexane (25 ml. each), and the combined organic layers dried over anhydrous magnesium sulfate for one hour. Lower-boiling fractions (b.p. 25-78°) were found to contain only ether and cyclohexane. The infrared spectrum of the residual liquid showed it to be hydrocarbon in nature but there was no characteristic absorption for a trans-olefin (970 $cm.^{-1}$). Gas chromatographic analysis showed the reaction products to be a mixture of cyclohexane, ethylbenzene, β-phenethyl bromide, 1,4-diphenylbutane and an unknown which appeared to be 3-β-phenethyl-1,5-diphenylpentane. Distillation of the residual liquids was continued and a series of fractions were collected: (1) b.p. 78-125°; (2) b.p. 25-150°/30-35 mm., (3) 150-190°/30-35 mm., (4) 125-161°/2 mm., (5) 161-194°/2 mm., (6) 194-216°/2 mm., (7) 216-223°/2 mm., (8) 223-230°/ 2 mm., and residue 2.3 g. The various fractions obtained were analyzed by gas chromatography and were found to contain the following components. Fraction (1) was cyclohexane and ethylbenzene while (2) and (3) were a mixture of ethylbenzene, β-phenethyl bromide and traces of 1,4-diphenylbutane. Fractions (4) and (5) solidified on standing and contained essentially 1,4-diphenylbutane. A small sample was recrystallized from methanol, m.p. 51-53° [lit. (63) m.p. 52°]. Fraction (6) was a mixture containing 1,4-diphenylbutane and the unknown. Fraction (7) was essentially pure (greater than 99%) 3-β-phenethyl-1,5-diphenylpentane. Fraction (8) was a mixture.



$$C_6H_5(CH_2)_2\underset{\displaystyle CH_2CH_2C_6H_5}{\underset{|}{CH}}-(CH_2)_2C_6H_5$$

The structure of 3-β-phenethyl-1,5-diphenylpentane is supported by elemental analysis, NMR spectrum (Plate XI) and other physical constants; $n_D^{24.2}$ 1.5720, b.p. 177-178°/0.2 mm. [lit. (56) n_D^{20} 1.5725, b.p. 195°/0.5 mm.], yield 3.203 g., 15.2%.

<u>Anal</u>. Calcd. for $C_{25}H_{28}$:

C, 91.46; H, 8.54

Found: C, 91.82; H, 8.16.

<u>Preparation of 2-Phenyl-1,3-dioxolane</u>. This compound was prepared from freshly distilled benzaldehyde and excess ethylene glycol by azeotropic distillation with benzene in the presence of <u>p</u>-toluenesulfonic acid, b.p. 228-231°/747 mm., according to the procedure of Sulzbacher and co-workers (65) [lit. (35), b.p. 225°].

<u>Preparation of 2-p-Methoxyphenyl-1,3-dioxolane</u>. This compound was prepared according to the method of Sulzbacher (65); $n_D^{26.5}$ 1.5328, b.p. 121-125°/2.2-2.3 mm., [lit. (65), $n_D^{19.5}$ 1.53622, b.p. 158-160°/17 mm.]

<u>Reaction of n-Butyllithium With 2-Phenyl-1,3-dioxolane</u>. A 500-ml., three-necked flask equipped with a condenser, magnetic stirrer, thermometer, nitrogen inlet tube, an addition funnel, and a calcium chloride-Ascarite tube was charged with 215 ml. of an ethereal solution containing 0.076 mole of <u>n</u>-butyllithium, and 60 ml. of cyclohexane. The dioxolane (3.45 g., 0.023 mole) was added dropwise through the addition funnel and an exothermic reaction was observed, (the reaction temperature

rose from 28 to 35°). The contents were heated until the reaction temperature of 60° was attained. Formation of a white precipitate started, and in a few minutes, the contents became pasty and semisolid. Cyclohexane (40 ml.) was added, and after stirring for fifteen minutes, 60 ml. of water was carefully added to the mixture. An exothermic reaction was observed indicating the presence of some unreacted _n_-butyllithium. After removing the organic layer the aqueous layer was extracted with 15 ml. of cyclohexane, and the combined organic layers were dried over anhydrous potassium carbonate for fifteen minutes. The infrared spectrum did not show the presence of a _trans_-olefin (970 cm.$^{-1}$) but indicated the presence of an aromatic carbonyl compound (1695 cm.$^{-1}$). From theoretical considerations this compound was suspected to be _n_-valerophenone. The reaction mixture was distilled and 3.26 g. (87.5%) of _n_-valerophenone was isolated; b.p. 237-243°/740 mm., 2,4-dinitrophenylhydrazone m.p. 166° [lit. (15) b.p. 242°, 2,4-dinitrophenylhydrazone, m.p. 166°].

Reaction of n-Butyllithium With 2-_p_-Methoxyphenyl-1,3-dioxolane. A 500-ml., three-necked flask was charged with 150 ml. of an ethereal solution of _n_-butyllithium (0.077 mole) and 125 ml. of cyclohexane. An exothermic reaction was observed when the dioxolane (4.5 g., 0.025 mole) in 5 ml. of cyclohexane was added to the reaction flask through an addition funnel. The reaction mixture was worked up exactly as in the previous experiment. Dilute hydrochloric acid was added to the aqueous layer until a pH of 7 was attained. The neutralized contents were distilled and the first 10 ml. of distillate (b.p. 25-99°) were analyzed by gas chromatography. Besides water, traces of three organic components were also detected. One of these was identified as ethanol. The solvents were removed from the dried organic layer by distillation at atmospheric pressure (b.p. 25-78°). Gas chromatographic analysis of the solvents indicated the presence of traces of ethanol. The residual liquids were distilled under reduced pressure to give 3.709 g. (78%) of p-methoxy-n-valerophenone, n_D^{24} 1.5266, b.p. 136-142°/2.3 mm., 2,4-dinitrophenylhydrazone, m.p. 156-157° [lit. (45) b.p. 150.5°/6 mm.; (46), 2,4-dinitrophenylhydrazone, m.p. 157°].

Reaction of n-Hexyllithium With 2-Phenyl-1,3-dioxolane. A 500-ml., three-necked flask, equipped with a magnetic stirrer, condenser, addition funnel, thermometer, nitrogen inlet tube, and a calcium chloride-Ascarite drying tube was charged with a solution of 234 ml. of an ethereal solution containing 0.069 mole of n-hexyllithium. A solution of 3.75 g. (0.025 mole) of the dioxolane in 10 ml. of ether was added through the addition funnel. The addition was accompanied by an exothermic reaction and the solvent began to boil. After working up the reaction mixture exactly as in the previous procedure in which n-butyllithium was used, the residual liquids were distilled under reduced pressure, and 4 fractions were collected. Fraction (1) b. 25-78°/4.3 mm., (2) 75-78°/4.3 mm., (3) 78-130°/4.3 mm., (4) 130-132°/4.3 mm. Fractions (1) and (2) were mixtures containing solvents and n-hexanol, and (3) was also a mixture containing some n-heptanophenone. Fraction (4) was essentially (more than 98%) pure n-heptanophenone; yield 3.16 g. (66.5%) n_D^{29} 1.5016, 2,4-dinitrophenylhydrazone, m.p. 126-127° [lit. (64) b.p. 138-139°/14 mm.,; 2,4-dinitrophenylhydrazone, m.p. 131°(28) and 135° (10)].

PLATE I

trans-4-Nonene, Film on NaCl Crystals

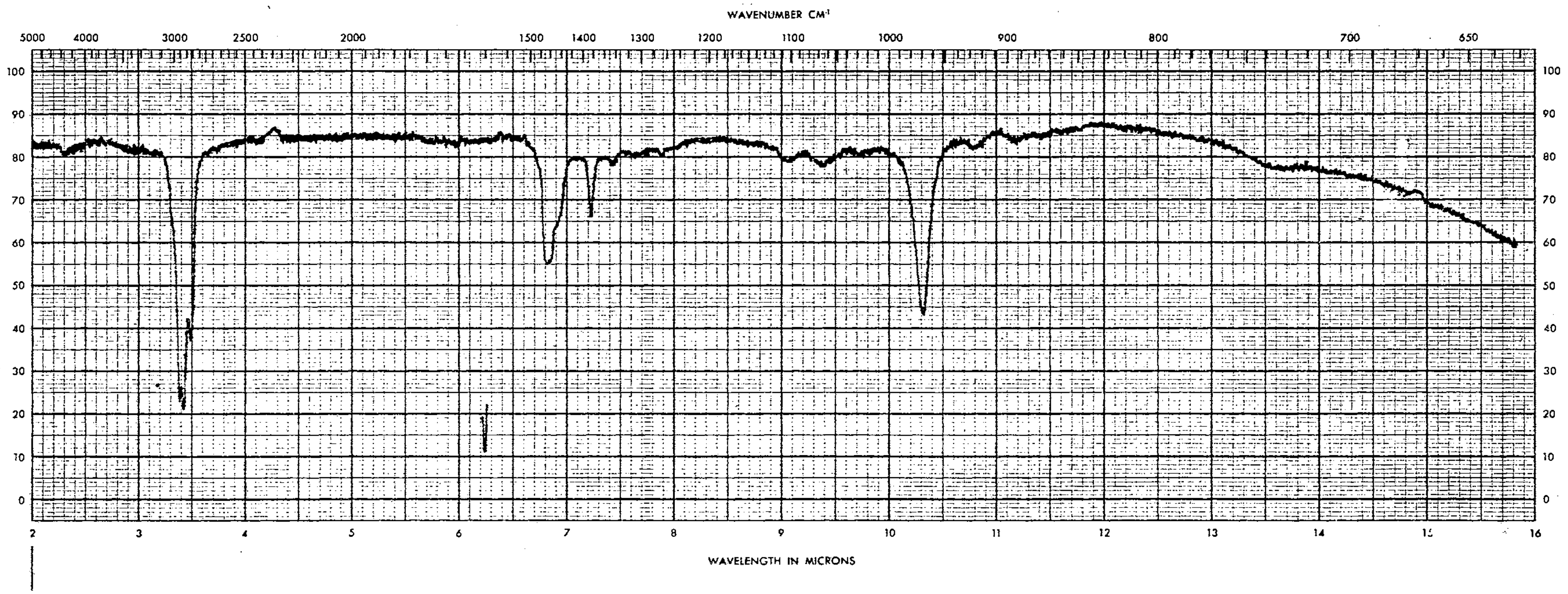


PLATE II

Unknown A, Film on NaCl Crystals

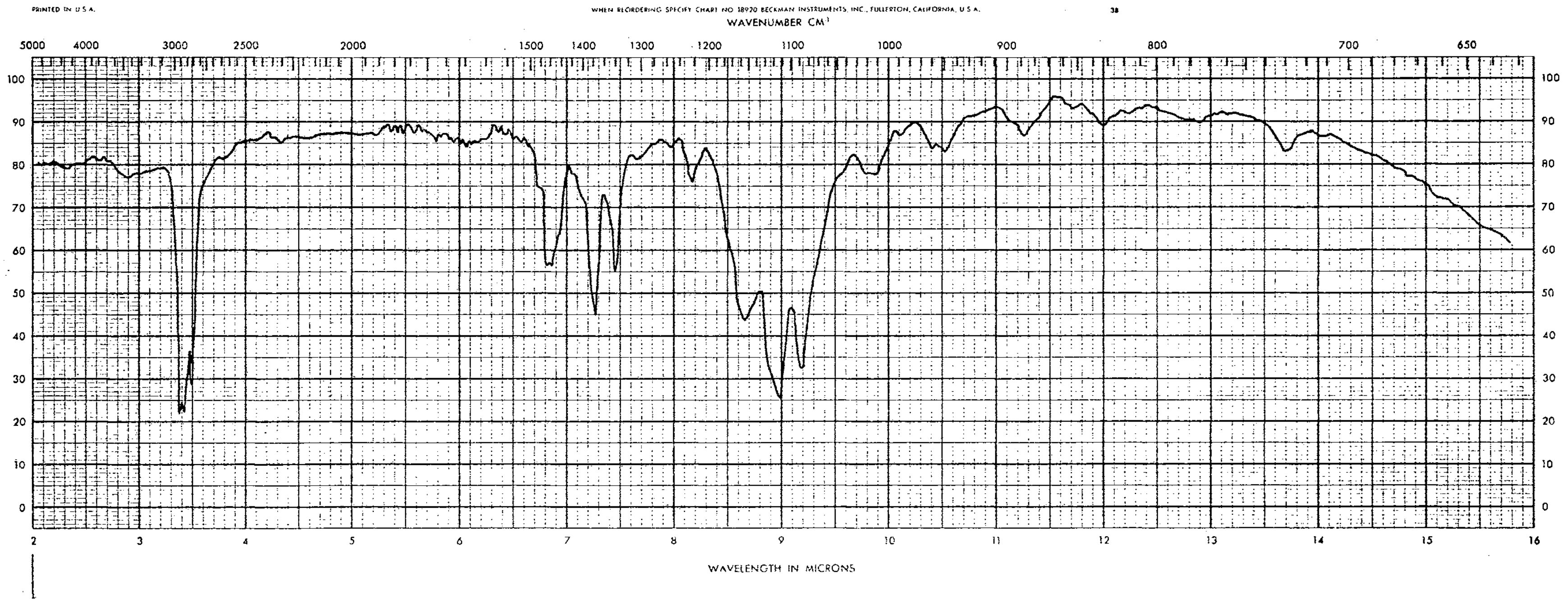


PLATE III

Unknown B, Film on NaCl Crystals

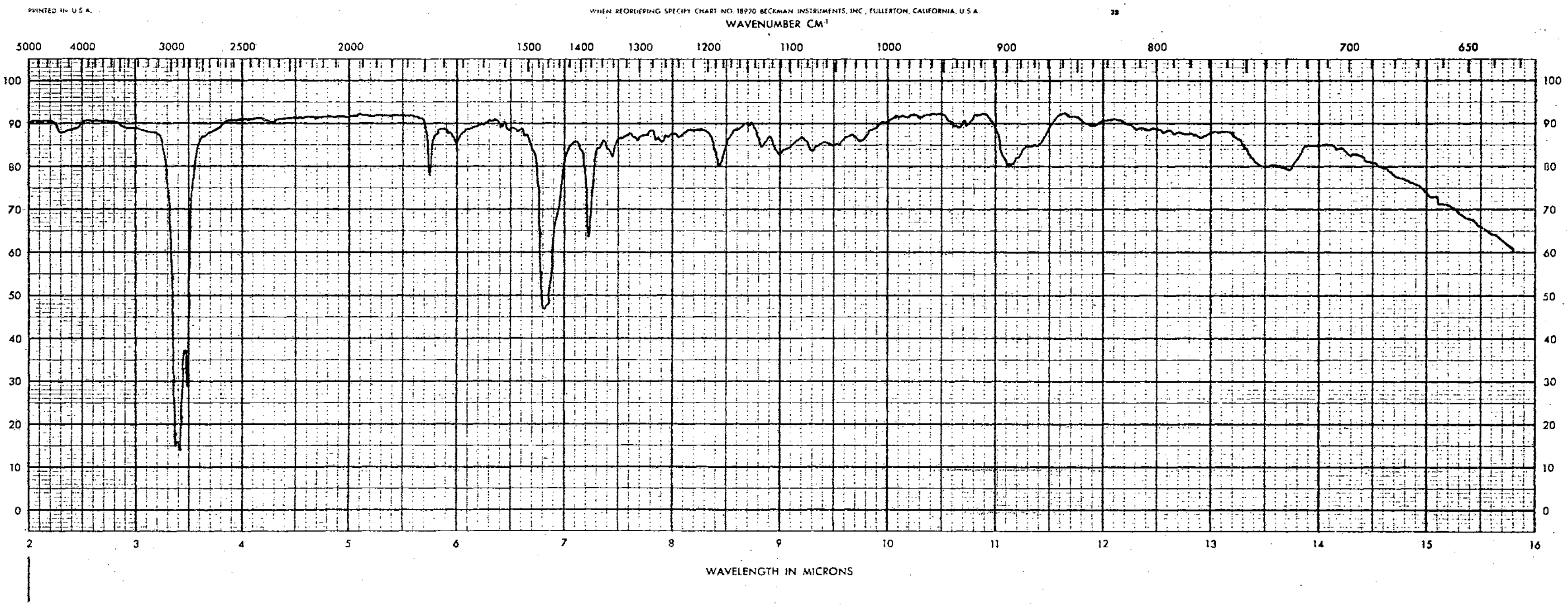


PLATE IV

Unknown C, KBr Pellet

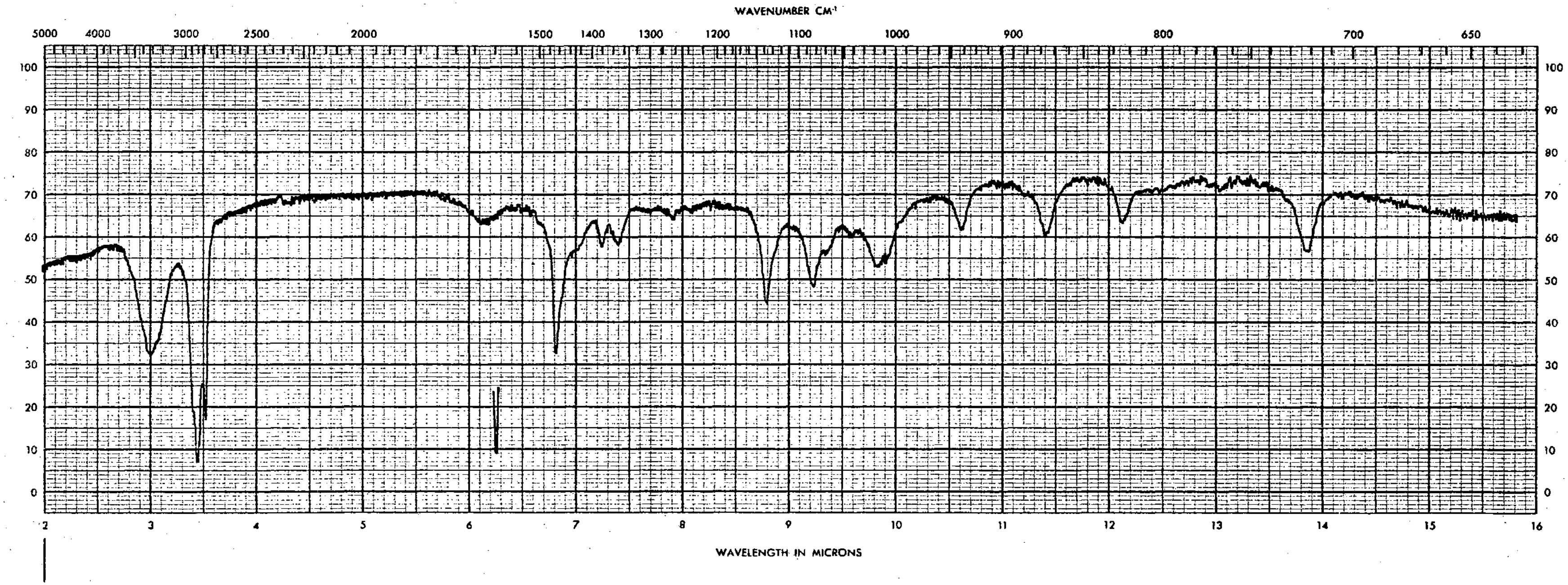
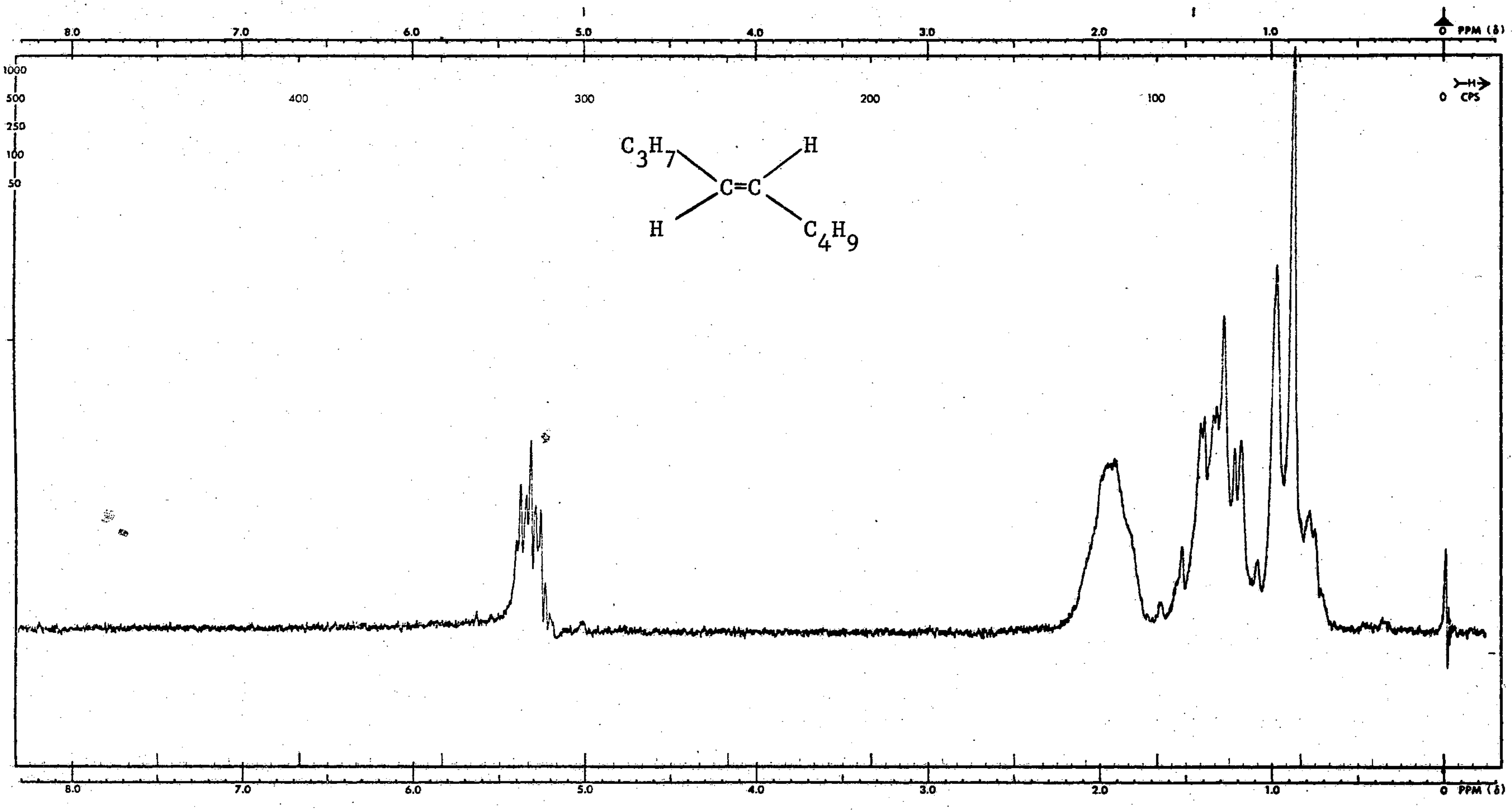


PLATE V

trans-4-Nonene



Solvent: CCl_4

R.F. Field: 0.22 mG

S.W.: 500 cps

S.A.: 3.2

F.B.: 2 cps

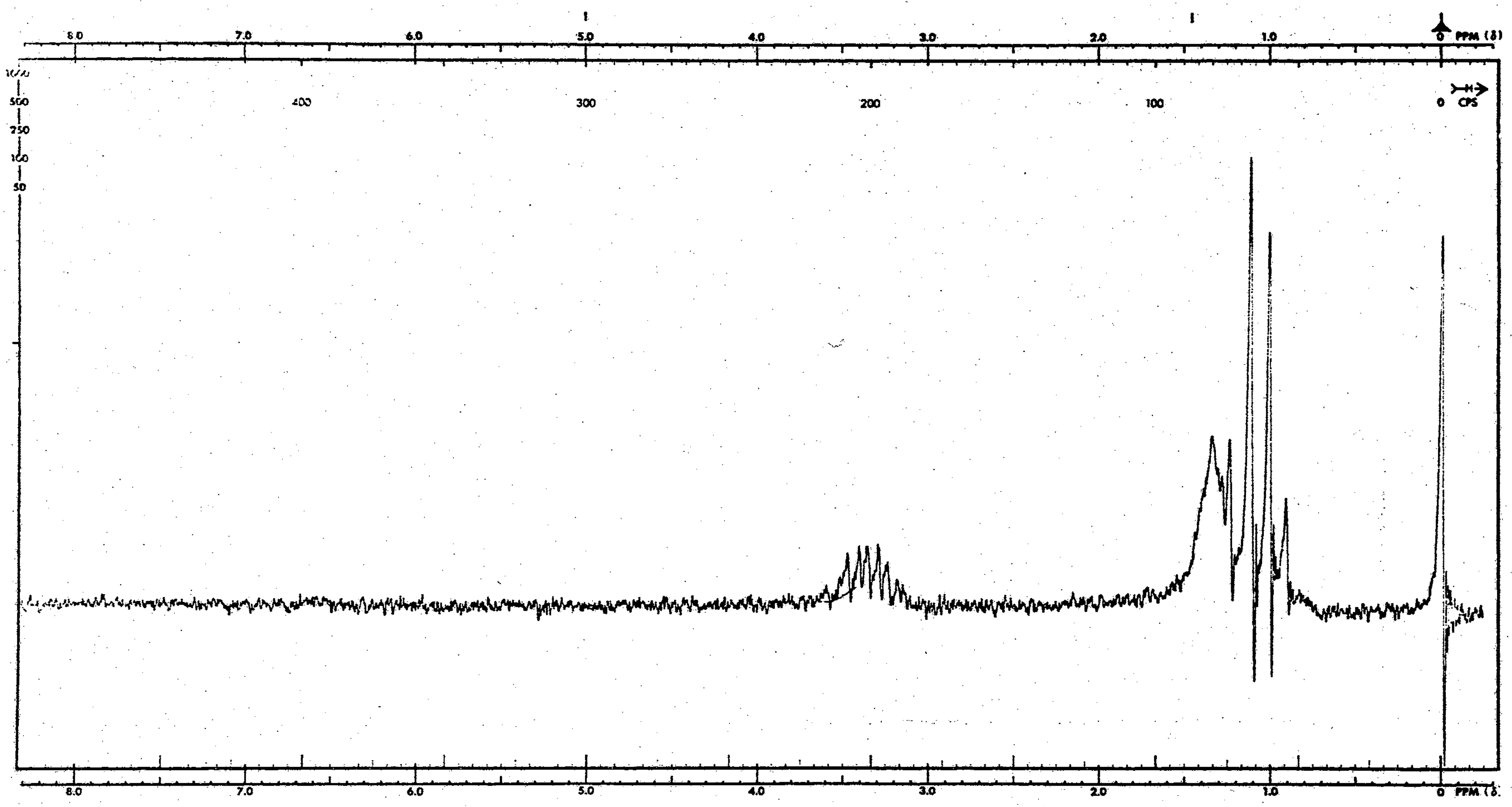
S.T.: 250 sec

S.O.: 0 cps

I.A.: Off

PLATE VI

Unknown A

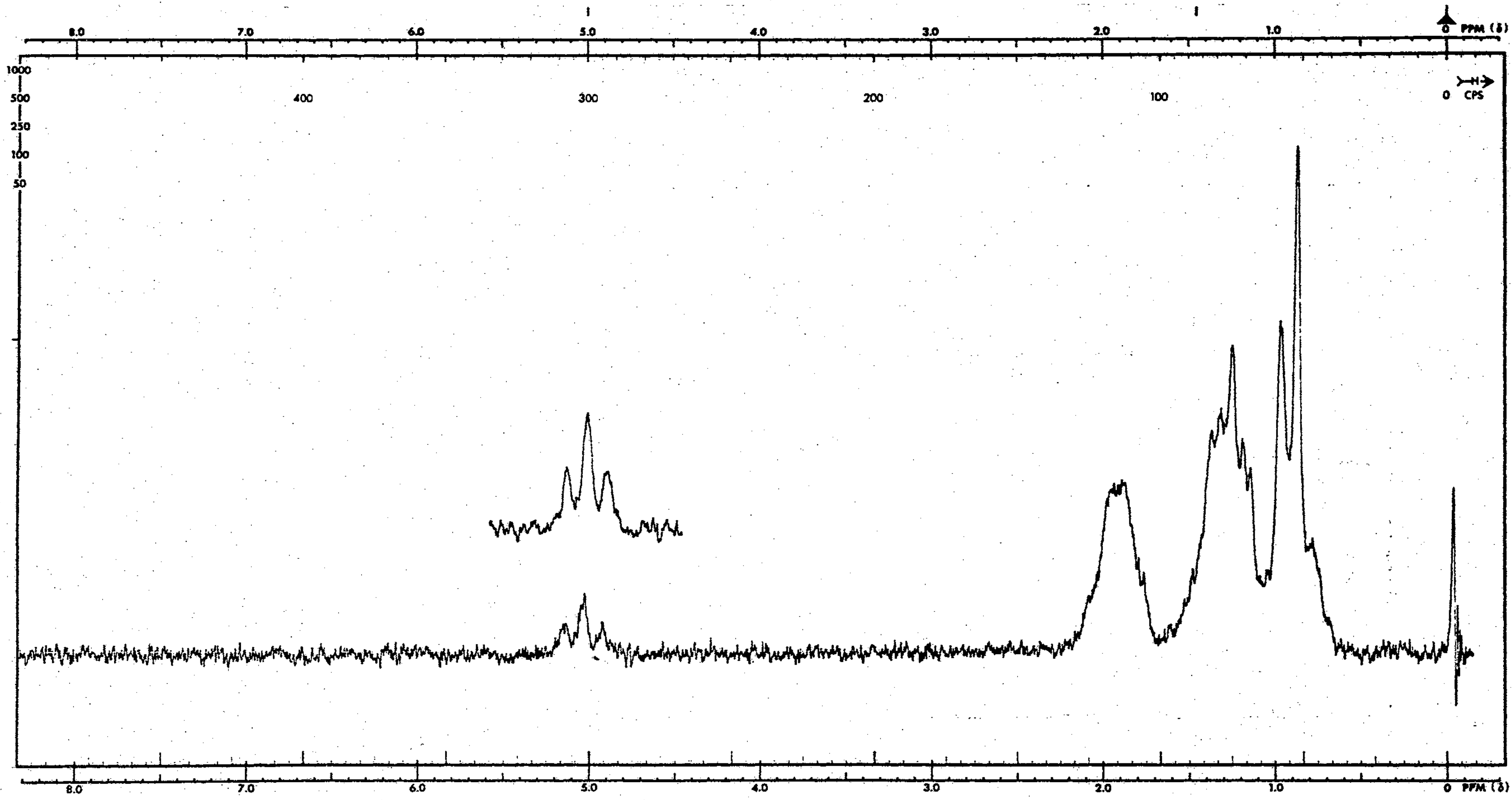


Solvent: CCl_4 R.F. Field: 0.2 mG S.W.: 500 cps S.A.: 8.0

F.B.: 2 cps S.T.: 250 sec S.O.: 0 cps I.A.: Off

PLATE VII

Unknown B

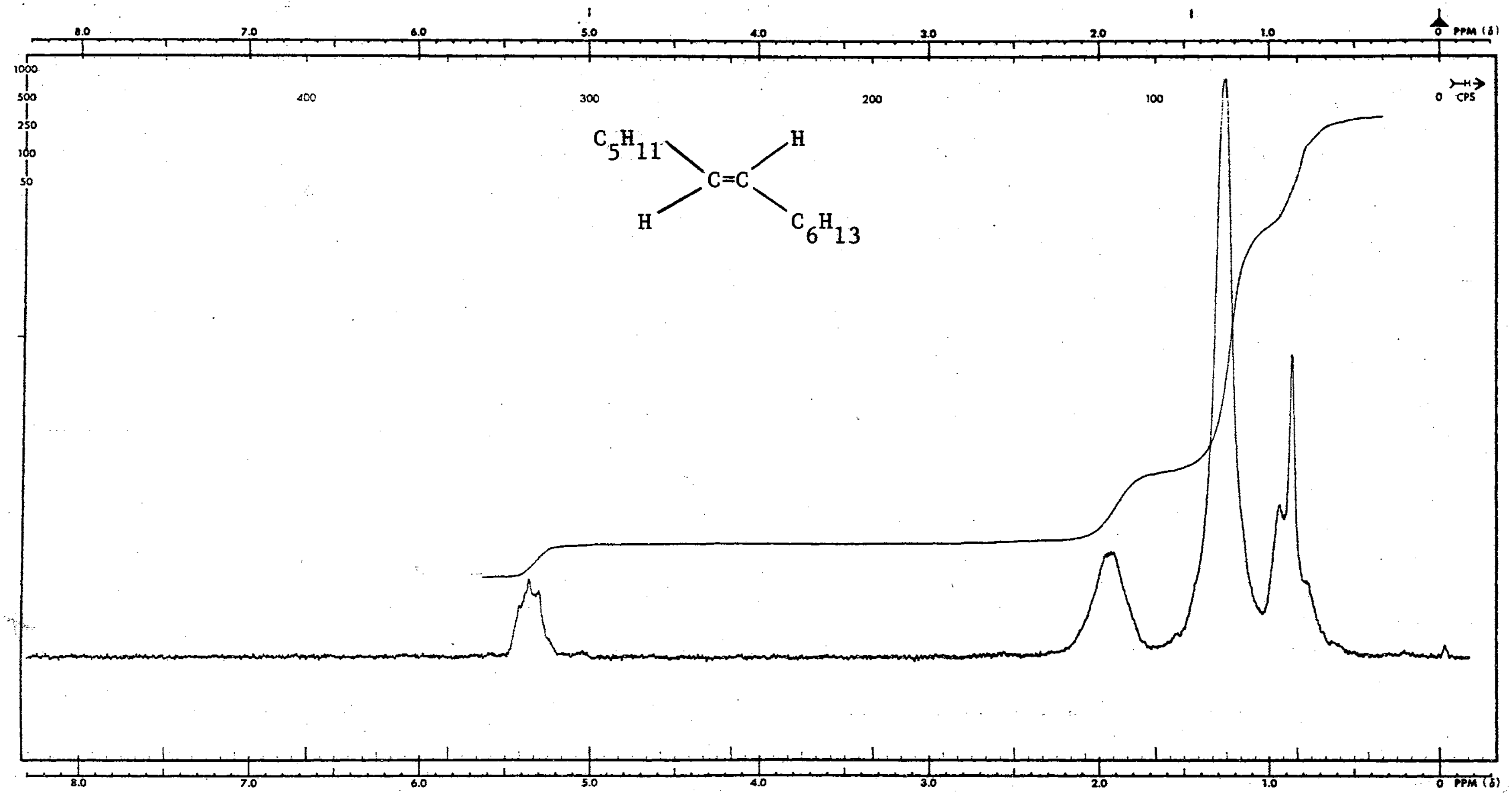


Solvent: CCl_4 R.F. Field: 0.25 mG S.W.: 500 cps S.A.: 10

F.B.: 2 cps S.T.: 250 sec S.O.: 0 cps I.A.: Off

PLATE VIII

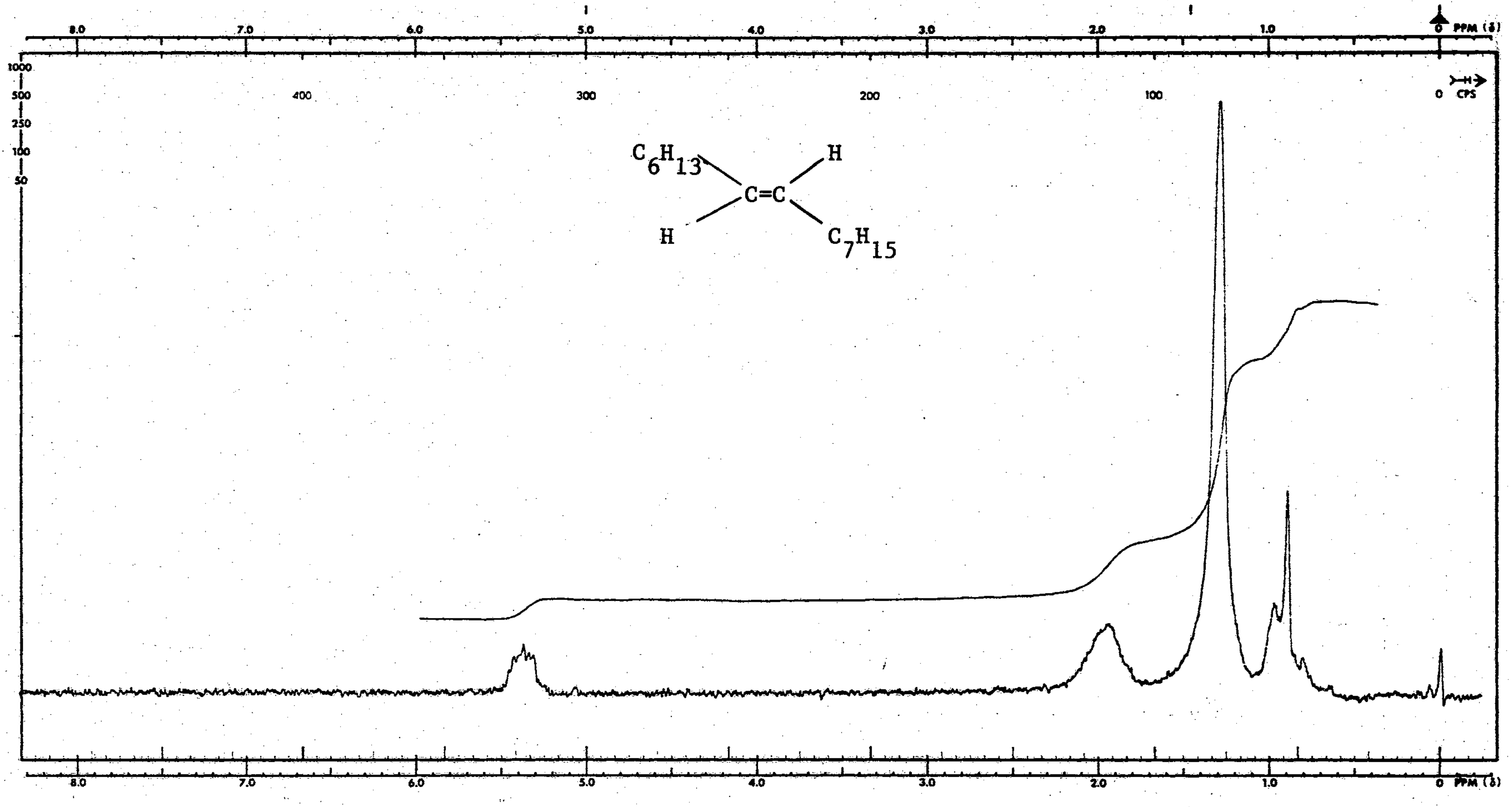
trans-6-Tridecene



Solvent: CCl_4
F.B.: 4 cps
R.F. Field: 0.22 mG
S.T.: 250 sec
S.W.: 500 cps
S.O.: 0 cps
S.A.: 2.0
I.A.: 8.0

PLATE IX

trans-7-Pentadecene



Solvent: CCl_4

R.F. Field: 0.2 mG

S.W.: 500 cps

S.A : 3.2

F.B.: 2 cps

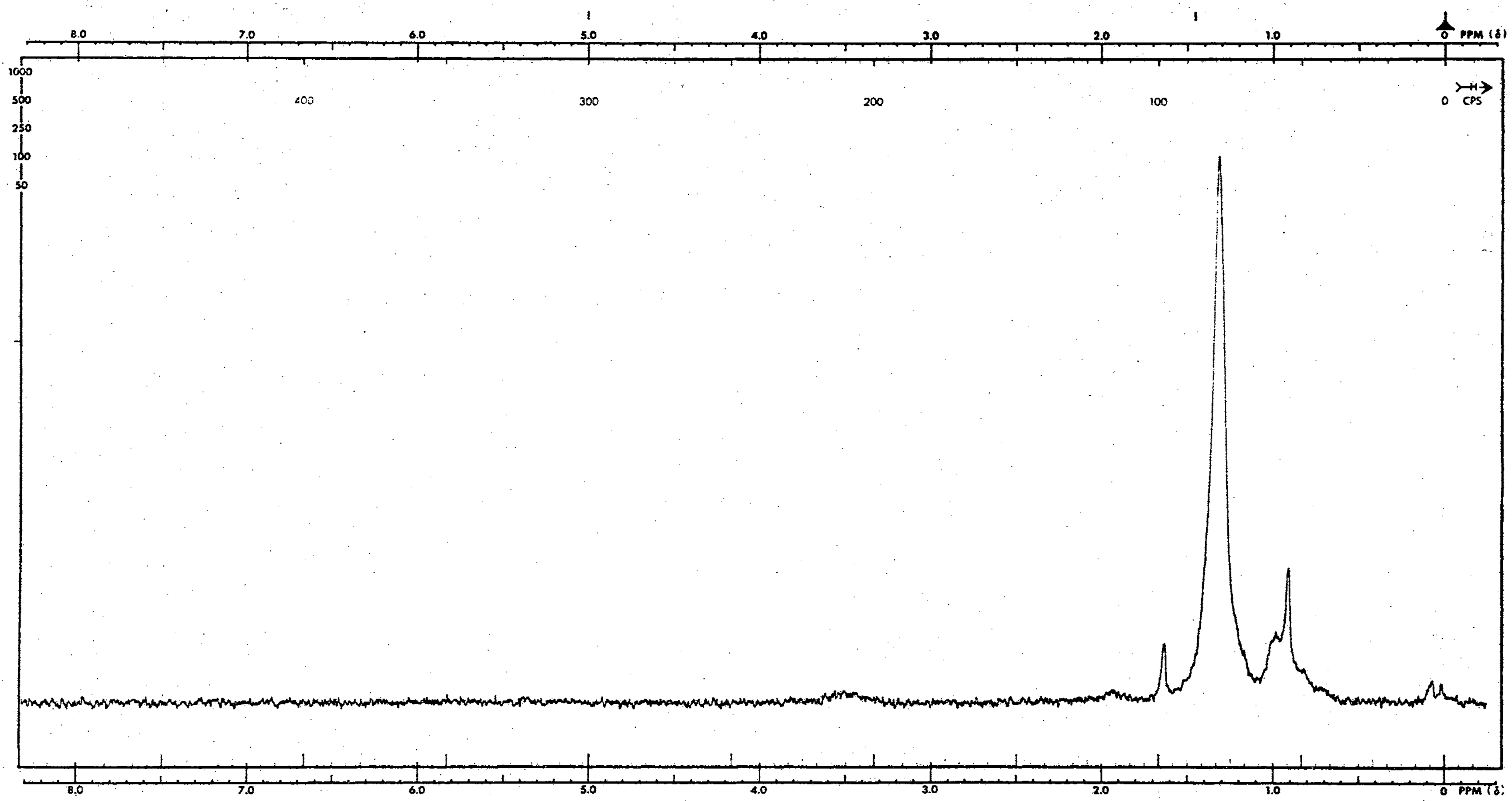
S.T.: 250 sec

S.O.: 0 cps

I.A.: 3.2

PLATE X

Unknown C

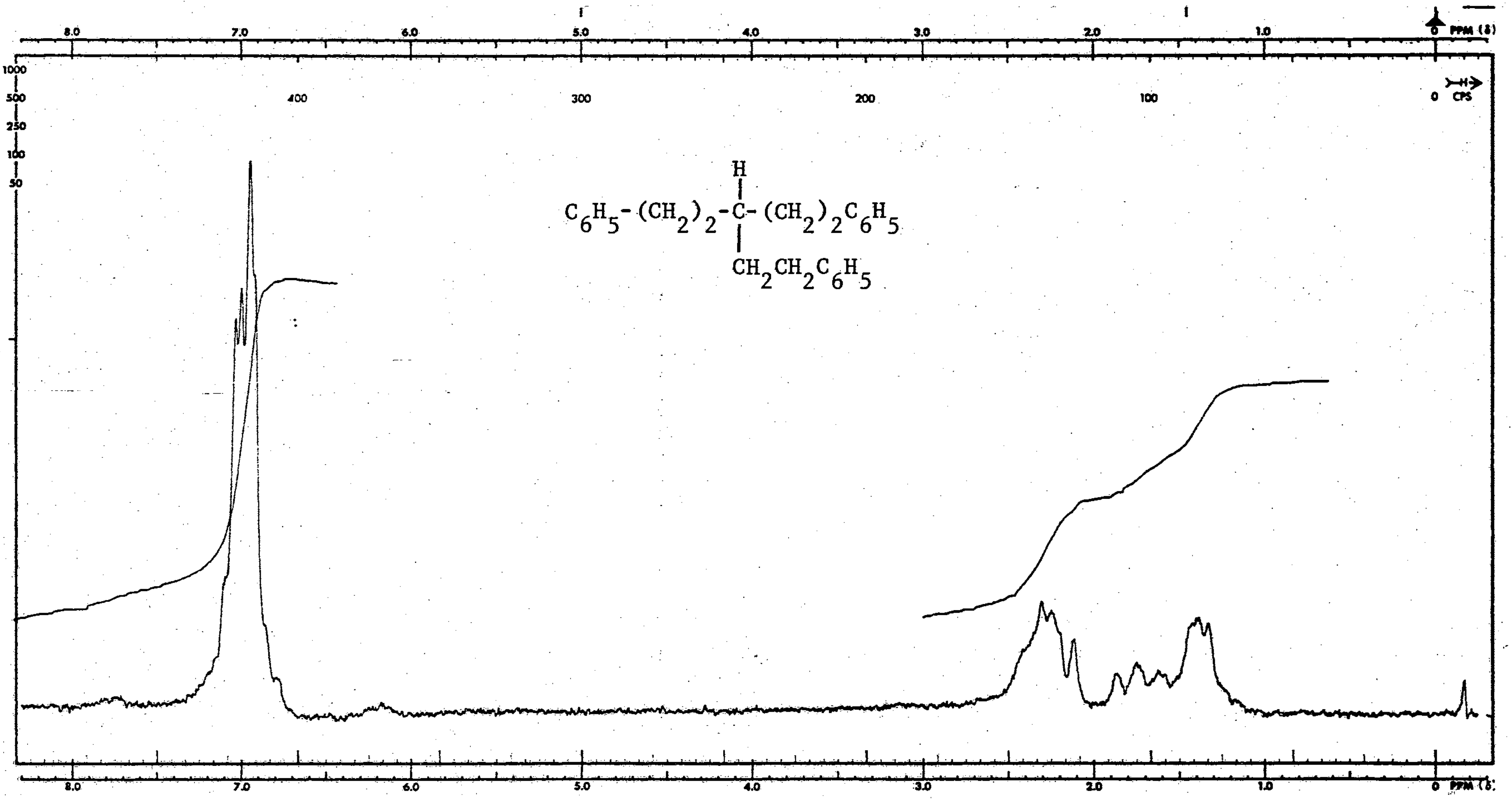


Solvent: CCl_4 R.F. Field: 0.25 mG S.W.: 500 cps S.A.: 5.0

F.B.: 2 cps S.T.: 250 sec. S.O.: 0 cps I.A.: Off

PLATE XI

3-β-Phenethyl-1,5-diphenylpentane



Solvent: CCl_4

F.B.: 2 cps

R.F. Field: 0.25 mG

S.T.: 250 sec

S.W.: 500 cps

S.O.: 0 cps

S.A.: 4.0

I.A.: 8.0

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