

AN INVESTIGATION OF THE REACTIONS OF TRITYL
ESTERS, WITH ALKYL AND ARYL
GRIGNARD REAGENTS

By

NINETTE LATIF DOSS
Bachelor of Science
Cairo University
Cairo, U. A. R.

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Thesis Approved:

K. D. Berlin

Thesis Adviser

O. D. Derner

J. D. Brown

Dean of the Graduate School

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CHAPTER I

INTRODUCTION

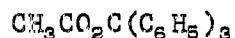
It was anticipated that reactions of trityl esters with Grignard reagents might provide a pathway for the preparation of high molecular weight triphenylmethyl-substituted hydrocarbons. 1,4-Addition on the phenyl ring of the acid portion of trityl benzoate is conceivable since the carbonyl group is hindered. It was therefore of interest to originate a systematic study of the reactions of trityl esters and to investigate the mechanisms of the resulting transformations.

CHAPTER II

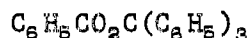
HISTORICAL

Reactions of Hindered Esters with Grignard Reagents

Triphenylmethyl (trityl) esters of carboxylic acids have been synthesized in good yields by the heterogeneous condensation of trityl bromide with salts of carboxylic acids in hydrocarbon solvents. Trityl acetate (I) was prepared (90 per cent) by Berlin and co-workers (7) via the condensation of one mole of silver acetate with 1.02 mole of trityl bromide in boiling anhydrous benzene. Trityl benzoate (II) (92 per cent) was similarly obtained from one mole of trityl bromide and 1.20 mole of potassium benzoate (7). Rathore (43) has recently synthesized trityl β -



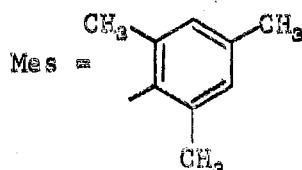
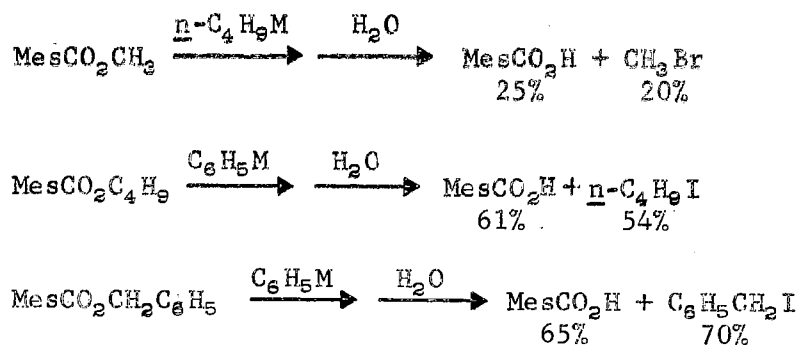
I



II

naphthoate (III) (86.7 per cent) from one mole of trityl bromide with 1.03 mole of sodium β -naphthoate in anhydrous benzene refluxed under nitrogen for thirty-nine hours.

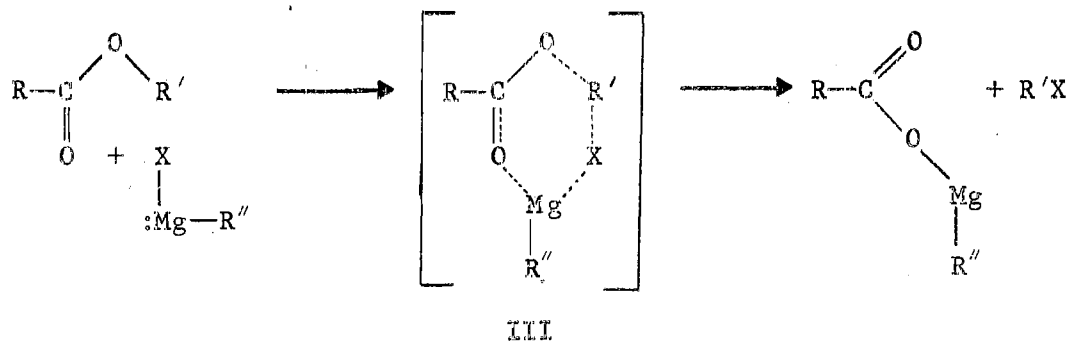
Reactions of hindered alkyl and aryl esters, including I and II, with Grignard reagents have been studied by different investigators. Fuson and co-workers (16) reported that methyl, *n*-butyl, and benzyl mesitoates reacted with alkyl and aryl Grignard reagents to yield mesitoic acid and the halides corresponding to the respective ester alcohols. No mechanism was proposed to explain these transformations.



$\text{n-C}_4\text{H}_9\text{M}$ = n-butyl Grignard reagent

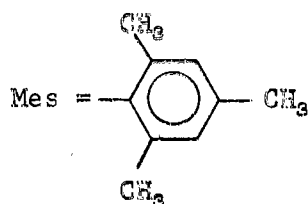
$\text{C}_6\text{H}_5\text{M}$ = phenyl Grignard reagent

Kharasch and Reinmuth (33) suggested a cyclic transition state III formed from one mole of the Grignard reagent and one mole of the ester.



According to this interpretation, the hindered ester portion of the transition state III could not readily react with a second mole of Grignard reagent to effect the first step of the "normal" addition reaction. This reasoning, however, was based on purely theoretical grounds, and its validity needs to be experimentally substantiated. Other energetically less favored reactions could be important in product control.

Aryl mesitoates reacted with Grignard reagents (16) in an entirely different manner. When alkyl Grignard reagents were used, the ester was converted into the corresponding alkyl mesityl ketone and the phenol derived from the aryl group that was removed. In this manner aceto-



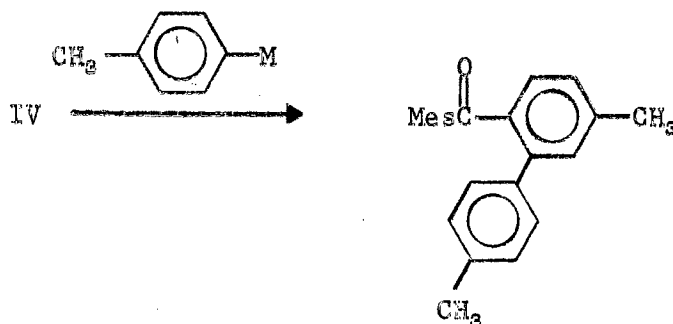
RM = Alkyl Grignard reagent

mesitylene (45 per cent) and propiomesitylene (61 per cent) could be obtained from reaction of *p*-tolyl mesitoate with methyl and ethyl Grignard reagents, respectively.

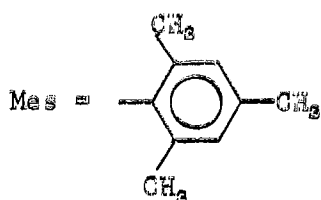
Fuson and co-workers (16) found that aryl mesitoates condensed with aryl Grignard reagents in a more complex fashion. Thus *p*-tolyl reagent reacted with *p*-tolyl mesitoate (IV) (1.2:1) to yield *p*-cresol and 2-*p*-tolyl-4-methylbenzoylmesitylene (V). They explained these results on the



IV



V



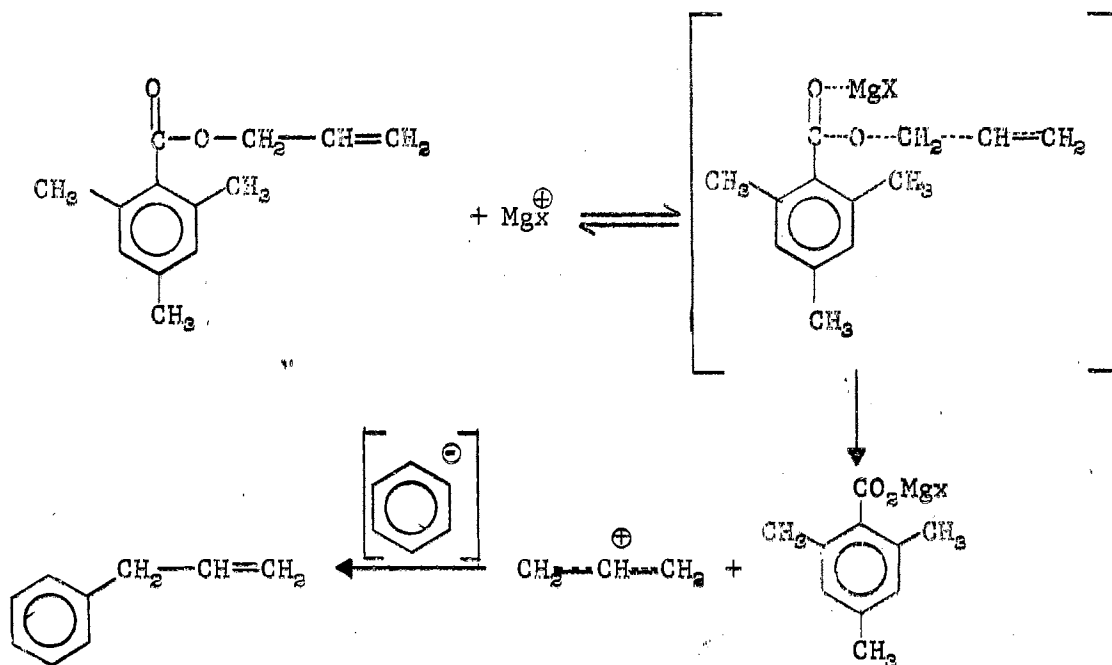
M = Grignard reagent

assumption that the ketone IV was formed initially, as with the alkyl Grignard reagents, and this compound reacted further with another mole of the aryl Grignard reagent in a conjugate addition process (1,4-addition) (15).

Reactions of trityl esters with Grignard reagents were first reported by Fieser and Heymann (13). They observed that when one mole of trityl acetate (I) condensed with 4 moles of methyl Grignard reagent, 1,1,1-triphenylethane (68 per cent) resulted. Formation of the hydrocarbon (rather than the carbinol) was explained as due to the special reactivity of the acyloxy group which resulted in the replacement of the latter by an alkyl radical. Trityl benzoate (II) similarly reacted with excess methyl Grignard reagent to yield 1,1,1-triphenylethane (45 per cent) (26). Fuson and Brasure (17) arrived at the same conclusion about the unusual reactivity of the acyloxy group in trityl acetate (I) which

with excess *t*-butyl Grignard reagent, gave 1,1,1-triphenyl-2,2-dimethylpropane (20 per cent). Some insight concerning this mode of cleavage may be found in two recent papers by Winstein and co-workers (53,54) in which they have carefully studied the importance of ion-pair return in reactions of trityl benzoate (II). Experiments with carbonyl-¹⁸O-labeled ester II in dry and moist acetone at 75° indicated ¹⁸O equilibration, which they postulated to proceed by way of an ion-pair intermediate. They also illustrated that in the presence of lithium azide, the rate of chemical capture was much smaller than the ionization rates. Hence they concluded that ion-pair return phenomenon could cause an exchange of trityl derivatives since the ionization rate was greater than the rate of ion-pair return. They also indicated that ion-pair return became less important as water was added to the acetone solvent. This result may well explain the formation of the hydrocarbon. In the presence of excess Grignard reagents, the medium is somewhat more polar and may promote ion-pair dissociation. Consequently, capture of trityl cations by the Grignard reagent may be more facile.

Substitution at the α -carbon in the alkoxy portion of an ester has also been observed by Arnold and Liggett (2), who obtained substituted allylbenzenes (ca. 70 per cent) by treating allyl mesitoates with excess aryl Grignard reagents. They proposed an ionic, stepwise mechanism to account for the observed products.



The structure of alkyl and aryl Grignard reagents in diethyl ether has been recently examined by Ashby and Smith (5). Rather convincing evidence was presented that whereas alkylmagnesium chlorides were essentially dimeric even at low concentrations (0.05 M), alkyl- and aryl-magnesium bromides and iodides contained essentially monomeric species at low concentrations (0.05 M) and essentially dimeric species at higher concentrations (0.5-1 M). They also indicated that the monomeric species RMgX definitely existed in solution to a considerable degree, and that the dimeric species in solution could be in part described as the symmetrical unit $(\text{RMgX})_2$ as well as the unsymmetrical species $\text{R}_2\text{Mg} \cdot \text{MgX}_2$. They also suggested that addition of Grignard compounds to ketones could be more accurately described in terms of either a monomeric or a dimeric RMgX species (Figure I), or alternatively in terms of an attacking ionic species (Figure II).

Figure I

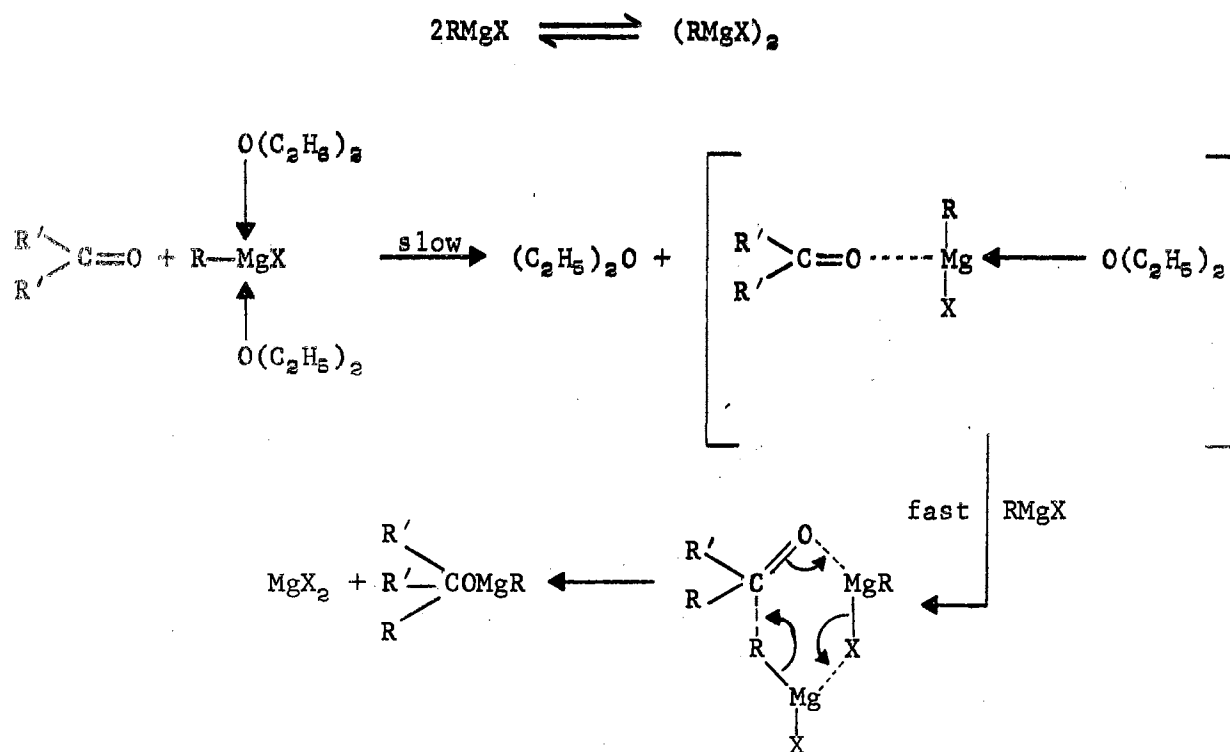
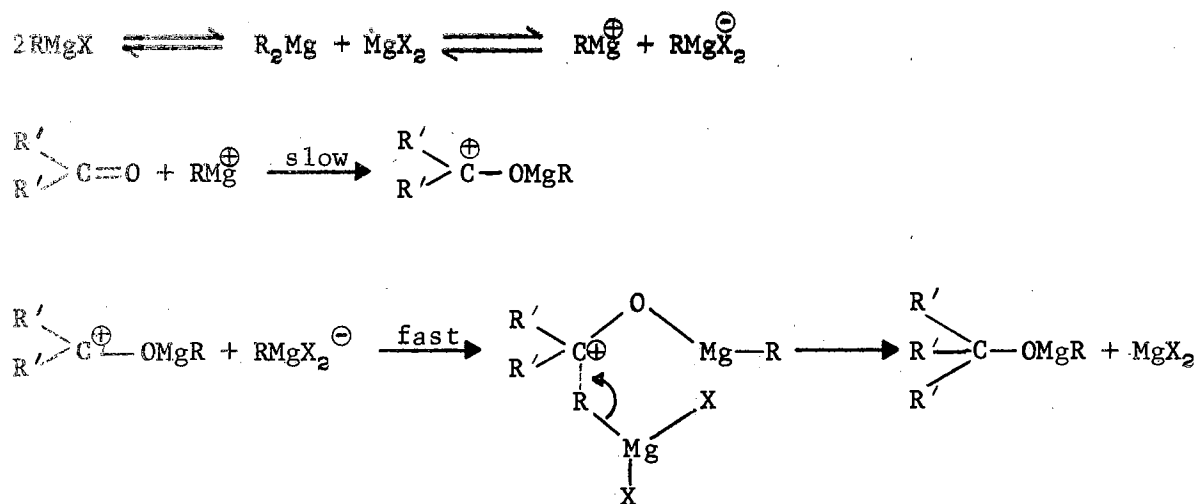
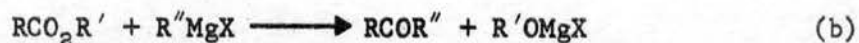
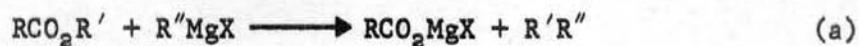


Figure II



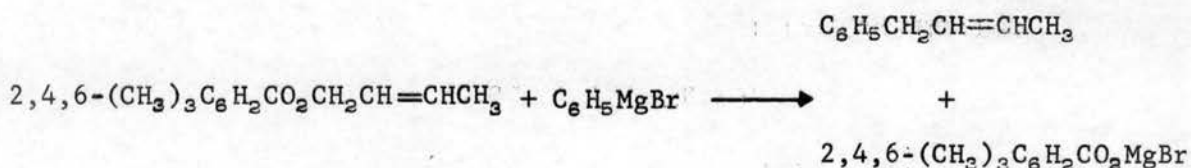
According to Arnold and Liggett (3), hindered esters reacted with Grignard reagents according to either one or both of equations (a) and (b).



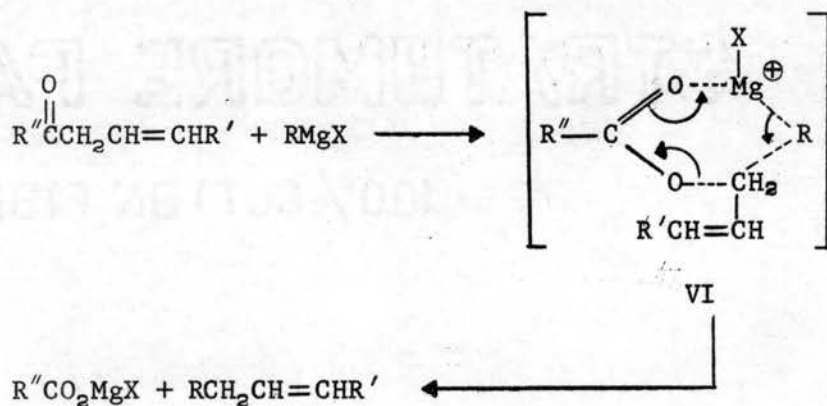
If substituents were present in R which sterically hinder additions to the carbonyl group of ester, and if R' was of such a nature that it had considerable thermodynamic stability as a cation (R'⁺), then cleavage of the ester by the Grignard reagent would take place according to equation (a). If on the other hand R' had little tendency to form a cation and the leaving anion (i.e., Cl⁻, -OC₆H₅⁻, or RCO₂⁻) was readily formed, then an entirely different reaction took place and ketones were produced (1) according to equation (b). Arnold and Liggett further indicated that when the magnitude of the steric factors about the carbonyl group was small, then simple allyl esters of carboxylic acids behaved normally when treated with the Grignard reagent to produce tertiary alcohols. The one exception to this rule was the case in which R' had an extreme tendency to form a cation, as in esters I and II, where only alkyl-oxygen cleavage was observed (12,3). If the steric factors in R were sufficiently great to prevent or inhibit the addition of R''MgX to the carbonyl group, then allyl esters reacted entirely according to equation (a). In a systematic study (2) of the reaction of allyl esters with phenyl Grignard reagents, in which the steric factors in R were varied over a wide range, it was observed that the element of steric hindrance was sufficiently important when R was trityl, 2,2-diphenylethyl, or 2,3-dimethyl-1-naphthyl, that the corresponding alkyl esters underwent complete alkyl-oxygen cleavage with phenyl Grignard reagent. When R was a 3-heptyl or a 3-pentyl group, normal reactions (acyl-oxygen fission) proceeded simultaneously and at comparable

rates. Arnold and Liggett considered additional confirmation for their explanation was realized from the experiment with R as cyclohexyl or 1-ethylcyclohexyl since only the normal reaction occurred between the allyl ester and phenyl Grignard reagent. In these two cases, free rotation was supposedly prevented by the rigidity of the ring structure although this reasoning should be considered untenable by modern theoretical concepts.

In later work (3), Arnold and Liggett found that the olefin produced from phenyl Grignard reagent and n-crotyl mesitoate was pure n-crotylbenzene and apparently contained none of the isomeric isocrotylbenzene.



This seemed of special interest, since it was well known that either of the pure isomeric crotyl halides gives a mixture of isomeric hydrocarbons when treated with the Grignard reagent. In view of their findings, Arnold and Liggett suggested another mechanism to account for the result, by postulating that the reaction proceeds by way of a quasi six-membered ring of the form VI. Since group R is an element of the

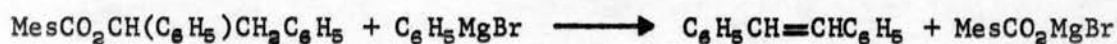


six-membered ring, it is geometrically in a position such that it must attack only the α -carbon atom of the allylic system ($-\overset{\alpha}{\text{C}}\text{H}_2-\overset{\beta}{\text{C}}\text{H}=\overset{\gamma}{\text{C}}\text{H}-\text{R}'$), when the redistribution of electrons is completed. Bond breaking and formation are supposed to occur simultaneously.

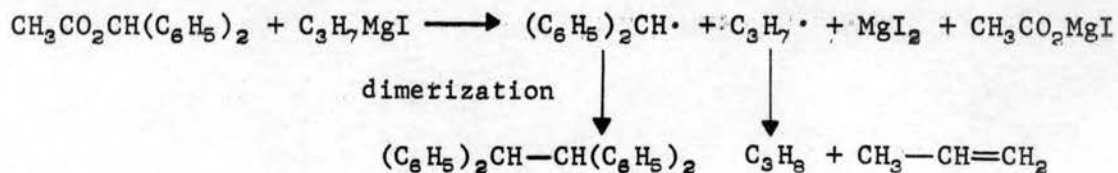
In the condensation of hexen-2-yl 4-mesitoate with phenyl Grignard reagent, Arnold and Searles (4) were able to detect the formation of two isomeric hydrocarbons predicted by the ionic mechanism. The olefinic hydrocarbons were found to be a mixture of the two allylic isomers, 4-phenyl-2-hexene and 2-phenyl-3-hexene, identified by reduction to the corresponding alkylbenzenes and formation of solid diacetamido derivatives of the latter. In view of the new findings, it was suggested that formation of a carbonium ion intermediate would explain the mixture of products obtained. Wilson, Roberts and Young (51) further stated that generation of a carbonium-ion was to be expected via a weakening of the carbon-oxygen bond of the ester through preliminary coordination with the Grignard reagent. They did not consider that a free carbonium ion was formed, but rather that an ion-pair was produced in which the cation was sufficiently free to effectively lose its identity. Arnold and Searles (4) also found that the reaction of t-butyl mesitoate with phenyl Grignard reagent afforded t-butylbenzene (24 per cent) and mesitoic acid (50 per cent), under the usual conditions employed for the cleavage of allylic esters. In trityl acetate (I) the α -carbon of the O-alkyl group is shielded by three phenyl groups, so that formation of a cyclic complex is sterically hindered. The ease of the reaction may well be due to the stability of the trityl cation.

β -Elimination reactions of hindered esters with Grignard reagents were observed during the reaction of one mole of α,β -diphenylethyl

mesitoate with 2 moles of phenyl Grignard reagent in *n*-butyl ether (26). Stilbene and mesitoic acid were isolated (80-90 per cent). With methyl



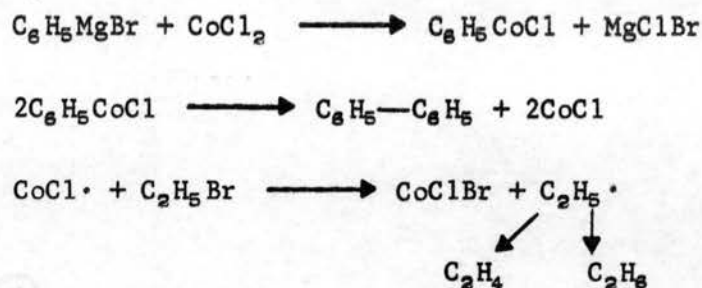
Grignard reagent under similar conditions, the yield of the stilbene was only 30-40 per cent, and another product, 1,2,3,4-tetraphenylbutane, was obtained in 8-9 per cent yield. Hauser and co-workers rationalized the formation of the latter hydrocarbon via dimerization of the intermediate α,β -diphenylethyl radical. This type of reaction has been observed by Stadnikoff (49), who found that benzhydryl acetate reacted with propyl or *n*-butyl Grignard reagent to give sym-tetraphenylethane (VII) (6-10 per cent), along with the corresponding alkane and alkene from the Grignard reagent.



VII

Some Grignard Reactions in Which Radicals Participate

This review is not intended to be comprehensive but several examples are chosen to illustrate the general phenomena observed. Kharasch and co-workers (34) noted that in the presence of cobaltous chloride, phenyl Grignard reagents reacted with aliphatic halides (methyl, ethyl, propyl, *n*-butyl, and *t*-butyl chlorides) to yield biphenyl and the saturated and unsaturated hydrocarbons derived from the alkyl halide used. A free radical mechanism was postulated to explain these results. Later,

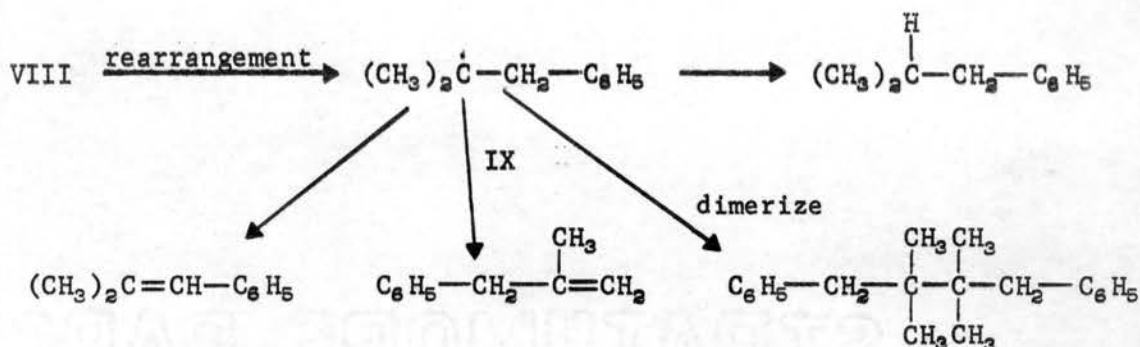


Kharasch and co-workers (31) indicated that bi- α -cumyl (α, α' -dimethyl-dibenzyl, or 2,3-diphenylbutane) was formed by the dimerization of the intermediate cumyl radical when the alkyl Grignard reagent (an alkyl bromide) and cobaltous chloride interacted in the presence of cumene. Vapor phase chromatography was not employed for analysis, however, and the presence of other compounds formed via the postulated intermediate cumyl radical could have been undetected.

The appearance of radicals from Grignard reagents has also been observed by Ruechardt and Trautwein (44), who indicated that during the preparation of the Grignard reagent from 1-chloro-2-methyl-2-phenylpropane, there were also formed 1-phenyl-2-methylpropane (1.3 per cent), 2-methyl-3-phenylpropene (1.1 per cent), and 1-phenyl-2-methylpropene (0.8 per cent). They suggested that these hydrocarbons resulted from rearrangement of intermediate 1-methyl-1-phenylpropyl radicals into 1-phenyl-2-methylpropyl radicals VIII which then disproportionated. The radicals of rearranged structure IX were also observed to dimerize (9.5 per cent dimer).



VIII



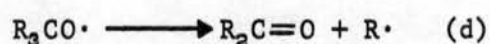
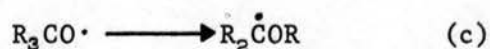
Meyer and Tögel (40) observed early that addition of water during the formation of phenyl Grignard reagent resulted in the synthesis of large amounts of biphenyl. It was argued that this result might be due to the formation of free phenyl radicals which subsequently dimerized. Kharasch and co-workers (30) further stipulated that this mode of reaction was applicable to a variety of Grignard reagents and hydrocarbons. Recently (23), it was established that during the reaction of magnesium with iodobenzene, participation of the phenyl radicals in the medium $\text{C}_6\text{H}_5 - \text{C}_6\text{H}_5\text{D}$, gave $\text{C}_6\text{H}_5\text{D}$ and C_6H_6 in the solvent. A combination method of isotopic studies and mass spectrometer analyses of products was successfully employed.

By means of electron spin resonance (ESR) techniques, Maruyama (39) was able to detect free radicals during the addition of ethyl, phenyl, and *p*-tolyl Grignard reagents to aromatic ketones such as benzophenone, 4-chlorobenzophenone, 4-methoxybenzophenone and acetophenone. The carbonyl compounds and the Grignard reagents were mixed at -25° in the absence of air and moisture. The sample was then inserted into a cavity which had previously been cooled with a stream of boiling liquid nitrogen, and the ESR spectrum was measured. It was observed that although benzophenone and 4-chlorobenzophenone gave well-resolved hyperfine spectra during their reactions with phenyl and *p*-tolyl Grignard reagents (Plate

XIII), the other ketones gave a single line. He suggested that the free radicals detected were of the ketyl type, produced through the reduction of ketones by a species such as $(MgX)_2(RMgX)_{n_1}$ or $(MgR)_2(RMgX)_{n_1}$ which might exist in the Grignard reagent. However, complete analysis of the spectra necessary to determine the value of this important discovery is lacking, and hence the conclusion about a ketyl-type radical is not completely justified.

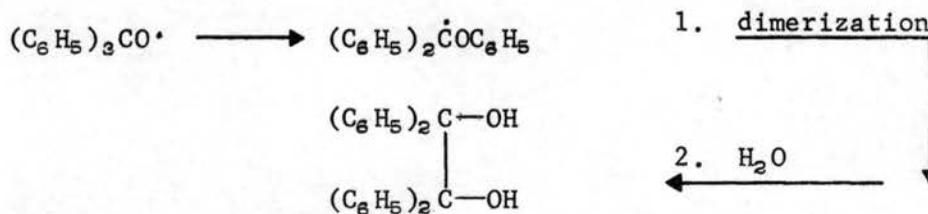
Reactions of Some Alkoxy Radicals

The discussion is not a comprehensive survey of alkoxy radicals but is concerned with model systems most closely related to our work. Among the most important reactions of alkoxy radicals, common transformations such as rearrangement (equation c) and decomposition (equation d) to more stable radicals occur readily. Triphenylmethoxy radicals

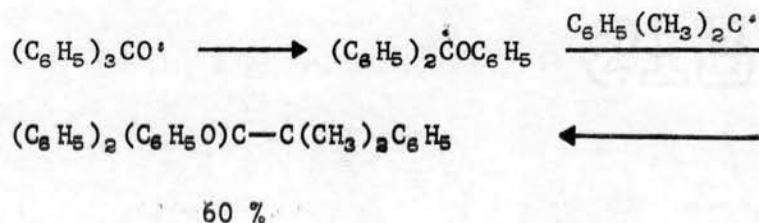


R = Alkyl group or hydrogen atom

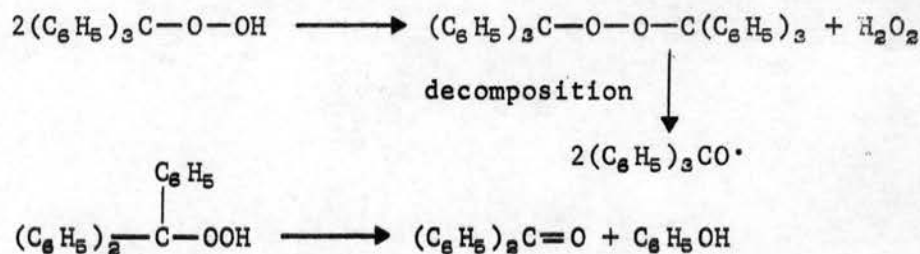
generated in xylene solution by the decomposition of trityl peroxide (50) were found to rearrange and a high yield (70 per cent) of the dimer, benzopinacol, was isolated. This reaction was also studied in cumene



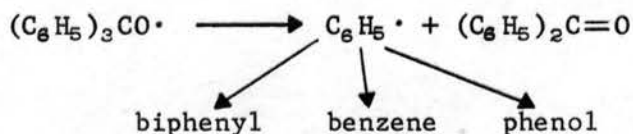
solution at 135-140° by Kharasch and co-workers (32), who obtained the triphenylmethoxyl radical by decomposing t-butyl triphenylmethyl peroxide in cumene. Under these conditions, the rearranged radical coupled with a free α -cumyl radical also produced.



Cristol and co-workers (11) observed that the decomposition products of trityl nitrate at 110° contained benzophenone (83 per cent) and picric acid (minute amount), but they did not report benzopinacol. Similarly Wieland (50) indicated that trityl hydroperoxide yielded benzophenone and phenol, whereas trityl peroxide (41) gave benzophenone and



biphenyl. It was shown that the formation of these products was consistent with the intermediate formation of triphenylmethoxyl radicals and their subsequent decomposition. In view of the above work, it seems that



triphenylmethoxyl radicals can rearrange, couple with another radical,

or dimerize depending on the temperature. The benzyloxy radical, $C_6H_5CH_2O^{\cdot}$, has been generated by pyrolysis of the nitrate (25). Hydrogen abstraction from isopropylbenzene occurred at $100^{\circ}C$ in the liquid phase giving large amounts of benzyl alcohol.

Zimmerman and Somasekhara discovered trityl peroxide in the photolyzate of *p*-acetylphenyl trityl ether (54). It was postulated that triphenylmethoxyl radicals could lead to the peroxide presumably through a coupling mechanism. Triphenylmethanol was also isolated from the photolysis reaction performed at 5° . Thus it seems reasonable that the stability of the triphenylmethoxyl radical is sufficient at or below room temperature to resist rapid decay by hydrogen abstraction or fragmentation to benzophenone and phenyl radical.

ESR Measurements on Radicals

The paramagnetic resonance absorption spectrum of solutions of trityl radical in different solvents has been observed by different investigators. Jarrett and Sloan (29) indicated that the spectrum of 0.001 M trityl radical in benzene consisted of groups of four closely spaced hyperfine structural lines, and that twenty-one such groups of lines were observed. They obtained their measurements at 24 Kmc/sec. at room temperature at a static magnetic field of 0.05 oersted. They concluded that a total of 196 hyperfine structure lines were theoretically possible if it were assumed that hyperfine coupling with a particular hydrogen existed when there was an unpaired electron density on the adjacent carbon atom. It was also assumed that all the ortho-, para-, and meta-positions of the three phenyl rings were equivalent. The first derivative of the resonance absorption of 10^{-3} trityl radical in toluene

was observed by Chesnut and Sloan (plate XIV) (9). They used a Varian x-band spectrometer employing 100 kc field modulation and a Varian 12-inch magnet. The measurements were carried out between -20° and -50°C , since at higher temperatures line broadening began to obscure some of the fine structure. A sweep field of 5×10^{-8} oersted was used through the measurements. Separation of the two most intense lines of the spectrum, which might be considered as a direct measure of the para proton splitting, indicated a para proton coupling constant of 2.77 gauss.

The ESR spectrum of metal ketyls, which are addition products of alkali metals with ketones, have been studied by many investigators. Hirota and Weissman (28) first reported that the ESR spectrum of the potassium ketyl of pentamethylacetone in tetrahydrofuran solvent consisted of seventeen lines evenly spaced at 0.12 oersted. The intensities corresponded to hyperfine interactions with eighteen equivalent protons. They further indicated that nineteen lines were expected, but the two weakest signals were not detected by their spectrometer.

Later, Goto and Maruyama (22) studied the potassium ketyl of benzophenone (plate XV), p-methylbenzophenone, p,p'-dimethylbenzophenone and p-t-butylbenzophenone. A hyperfine structure was obtained in the spectrum of each of these ketyls, and the molecular symmetry of the ketyls was noted to have a considerable influence on the shape of the spectra. The cause of the poor resolution of the spectra of the ketyls of p-methylbenzophenone and p-t-butylbenzophenone, which had different phenyl groups, was attributed to the difference in contributions of the two phenyl groups to resonance stabilization of the free electron.

By analyzing the hyperfine structures in the ESR spectra of various metal ketyls, Kazakova and Syrkin (35) found that the stability of free radicals of a given type was determined by several factors. For aromatic metal ketyls the stabilizing factor was the considerable delocalization of the unpaired electron. In the aliphatic metal ketyls the unpaired electron was mainly localized on the carbonyl carbon atom, and steric factors were more important than delocalization. In mixed ketyls, such as obtained from trimethylacetophenone, both factors were involved to a considerable degree. The work of Maruyama (39), however, seems to be the best to date with ESR in this area since he combined ketones with Grignard reagents and actually detected free radicals.

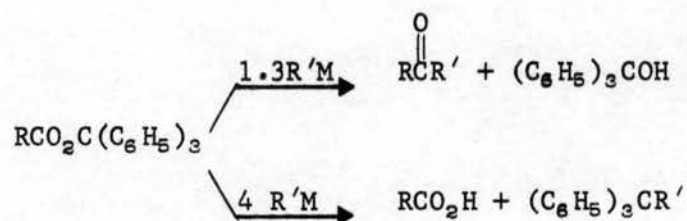
Visible Spectra of Triphenylmethyl Radical

The visible spectrum of the trityl radical was reported by Gilbert and co-workers (18) to consist of seven bands. They performed their experiment at liquid air temperature (90°K) in the EPA solvent (5 parts ether, 5 parts isopentane and 2 parts ethanol by volume). When a solution of trityl radical was cooled to -50°C , it gradually became colorless, owing to almost complete dimerization. When the solution in EPA was cooled by liquid air, however, the color was preserved indefinitely and was not photosensitive. The conclusion was that the photochemical process was at least bimolecular, and bimolecular reactions could not occur in rigid media. This result further illustrated the stability of trityl radicals in EPA solvent.

CHAPTER III

DISCUSSION OF RESULTS AND CONCLUSIONS

The objective of this study was to examine the reaction of trityl esters with Grignard reagents with respect to potential synthetic utility for high molecular weight hydrocarbons and to the mechanism of the resulting transformations. It was discovered that the condensation pathway of alkyl Grignard reagents with such esters was highly dependent upon the concentration of Grignard reagent when R' represented methyl



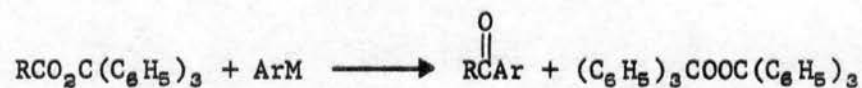
R'M = alkyl Grignard reagent

R' = CH₃, C₂H₅, (CH₃)₂CH, (CH₃)₃C, (CH₃)₃CCH₂, C₆H₁₁

or ethyl groups. For example, with the molar ratio of Grignard reagent:ester (R = CH₃) as 1.3, acetone and triphenylmethanol were obtained in high yields in what appears to be the classical process. However, if the molar ratio was altered to 4, acetic acid and 1,1,1-triphenylethane were isolated, as previously recorded (13). Where a bulky reagent [R' = (CH₃)₂CH] was used under the extremely mild conditions of the reaction (ether solvent at room temperature), no reaction was observed between trityl benzoate (II) and the Grignard reagent. With a

ratio of 4 for these reactants, benzoic acid and 1,1,1-triphenyl-2-methylpropane were produced. Two other new hydrocarbons [$R' = (CH_3)_3CCH_2$ and C_8H_{11}] were synthesized by this method.

Most surprising was the observation that trityl peroxide was a major product from treatment of trityl acetate (I), trityl benzoate (II), or trityl β -naphthoate (III) with aryl Grignard reagents. In addition, with a ratio of Grignard mixture to ester as 1.3, the corresponding ketone was obtained. The reaction of trityl β -naphthoate (III) produced



ArM = Aryl Grignard reagent

R = CH₃, Ar = C₆H₅, *p*-CH₃C₆H₄

R = C₆H₅, Ar = C₆H₅

R = 2-C₁₀H₇, Ar = C₆H₅, *p*-CH₃C₆H₄, *p*-CH₃OC₆H₄

two new ketones (R = 2-C₁₀H₇, Ar = *p*-CH₃C₆H₄, *p*-CH₃OC₆H₄). Alternative synthesis by classic Friedel-Crafts (6) reactions confirmed the identities of these two diaryl ketones.

The reaction of one mole of ester I with 1.3 moles of methyl Grignard reagent at room temperature under nitrogen was investigated. A slightly exothermic reaction occurred during the addition of the ester and the color changed to yellowish green. The formation of triphenylmethanol and acetone as the only products suggested a "normal" addition of either a monomeric, a dimeric (Figure 3), or an ionic species (Figure 4), of the Grignard reagent to the carbonyl carbon atom of the ester. Heterolytic acyl-oxygen bond fission may occur to produce the ketone and the carbinol

in a manner analogous to that proposed by Ashby (5) for the addition of Grignard reagents to ketones.

Figure 3

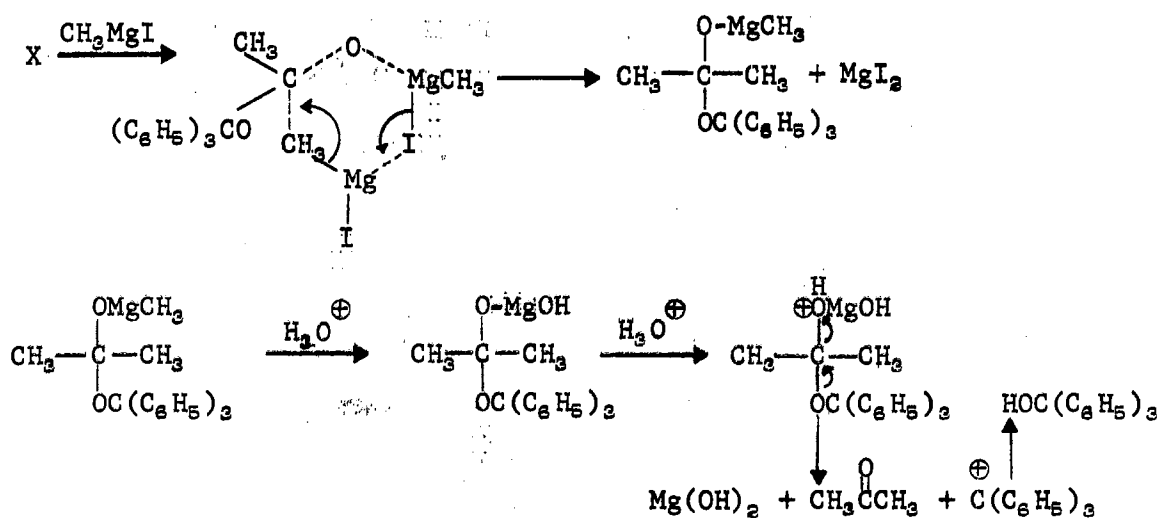
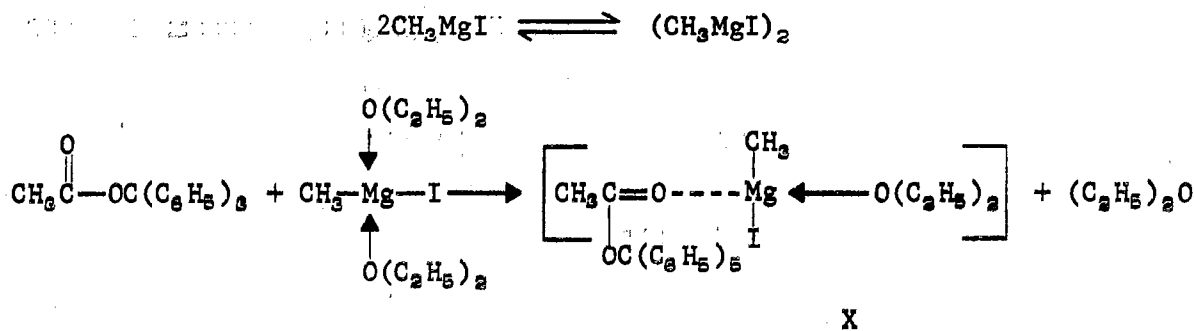
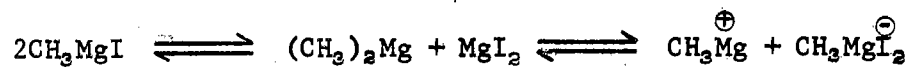
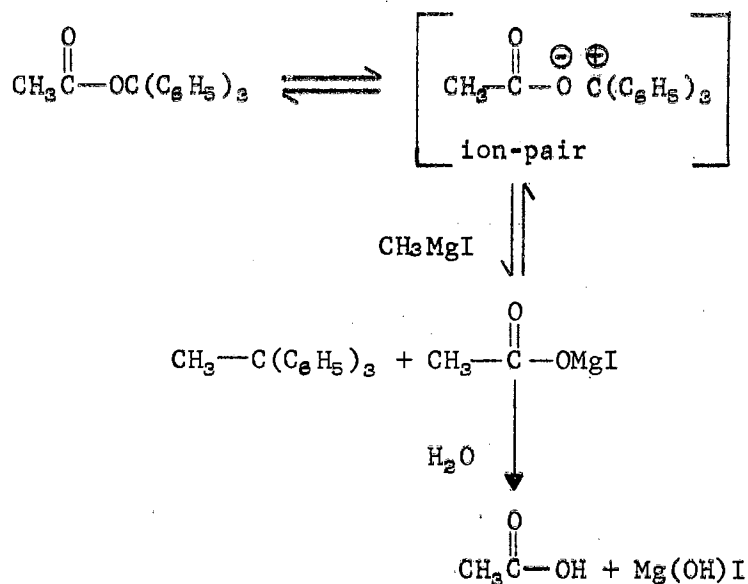


Figure 4



obtained. These results are similar to those reported by Fieser and Heymann (13), although their yield of the hydrocarbon was only 68 per cent. The formation of the hydrocarbon in presence of excess methyl Grignard reagent may indicate that the rate of dissociation of ion-pairs formed from the ester in the more concentrated Grignard reagent was enhanced compared to the rate of ion-pair return, and consequently capture of the trityl cation by methyl Grignard reagent was more favored. The



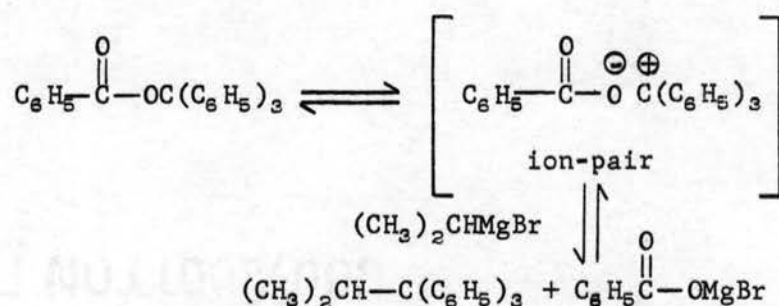
validity of this mechanism is yet to be proved by the inverse addition of excess methyl Grignard reagent to ester I, since ion-pair dissociation should not be as extensive in the absence of a polar medium, and classical addition of the Grignard reagent to the ester might be expected to yield t-butyl alcohol and triphenylmethanol. The reaction of one mole of trityl acetate (I) with 1.3 moles of ethyl Grignard reagent followed the same path, and the formation of triphenylmethanol and methyl ethyl ketone as the sole products may be explained similarly.

The conductivity measurements of Evans and Lee (12) on the ethyl Grignard reagent ($\text{C}_2\text{H}_5\text{MgBr}$) in ether at concentrations above 0.5 M

showed an increase in conductivity with concentration. It has been pointed out that the specific conductances for Grignard reagents, such as C_2H_5MgBr , are small and therefore concentrations of ionic species are probably low. However, this does not rule out the possible importance of small concentrations of ionic species in describing the mechanism of attack of the Grignard reagents on the carbonyl function. With this consideration and the data of Winstein on ion-pair formation from ester II, a tentative explanation for the course of the reaction of alkyl Grignard reagents with trityl esters can be presented. In the experiments with methyl and ethyl Grignard reagents with ester I (molar ratio 1.3:1) the molar concentrations of Grignard reagent ranged from 0.65 to 0.93. After complete addition (20 minutes) of the ester, however, the molar concentration would drop to lows of 0.25 and 0.38 prior to reaction with ester. Since the alkyl iodides were used, monomeric units of the corresponding Grignard reagent may exist, although this is somewhat speculative since the recently published molecular weight data was for concentrations only up to 0.4 M. In any event normal 1,2-attack on the carbonyl group could proceed to give, after hydrolysis, ketone and triphenylmethanol as observed. At higher molar ratios (4:1 reaction) of Grignard reagent to ester I, the molarities in most experiments exceeded 2 initially and could drop only to 0.77 upon addition of ester (assuming little reaction during the addition), a fact which may favor the existence of increased quantities of the Grignard reagent in dimeric or polymeric aggregates. Thus, in view of Evans and Lee work (12), at concentrations of the Grignard reagent between 0.5 and 4 molar and at the higher ratio of reactants, both a structural alteration of Grignard reagent and a slightly improved ionic medium (12) may be generated. The latter situation

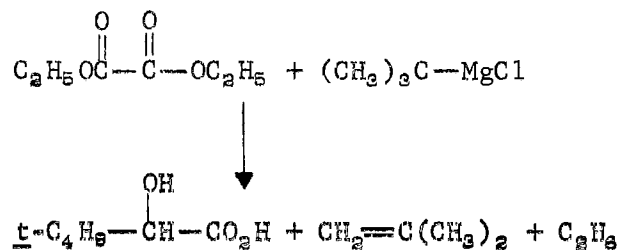
could favor increased ion-pair formation from the ester. With ethylmagnesium bromide at 20° in ether the conductivity measurements varied by a factor greater than 10 for 0.5 M to 2.0 M concentrations (12). In addition, under the mild conditions employed, the polymeric Grignard species might not be as effective in its attack on the hindered carbonyl group. Capture of the trityl ion by the Grignard reagent may thus compete successfully by default.

In larger Grignard reagents, such as from isopropyl bromide, t-butyl bromide, neopentyl bromide, and cyclohexyl bromide, the steric factor alone could prevent the attack on the carbonyl carbon atom. For the isopropyl reagent, no reaction was observed with ester I under the same conditions (1.3:1) used with the smaller alkyl reagents. Only the condensation at higher molar ratios of reagent to ester (4:1) resulted in a condensation which gave benzoic acid and 1,1,1-triphenyl-2-methylpropane, postulated to result from attack of the Grignard reagent on the trityl ion in the ion-pair.

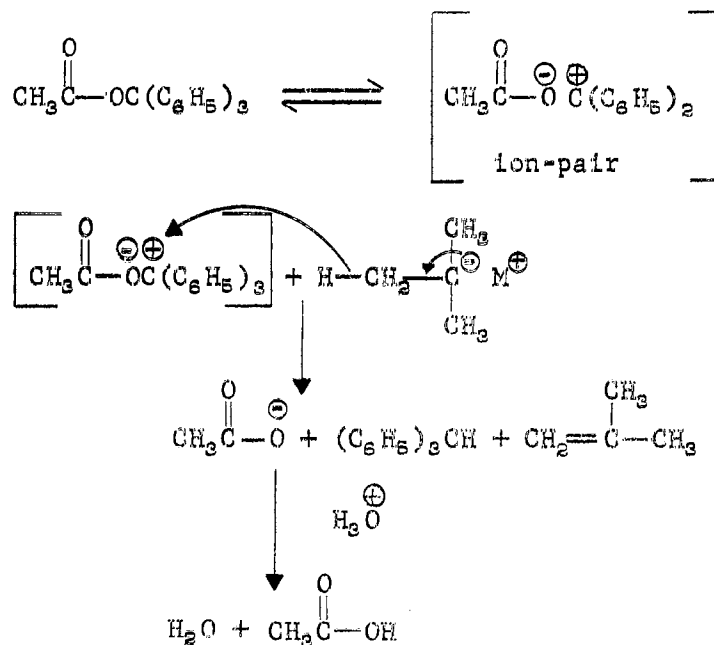


The formation of 1,1,1-triphenyl-2,2-dimethylpropane and acetic acid from the reaction of excess t-butyl Grignard reagent with ester I was explained by Fuson and Brasure (17) as due to the special reactivity of the acyloxy group, which resulted in the replacement of the latter by an alkyl radical. An improved interpretation might include the mechanism just postulated for the reaction of excess isopropyl Grignard reagent with ester II. It would have been proper in this case to try

the same reagents under more mild conditions to ascertain if any reaction could occur. The condensation of excess t-butyl Grignard reagent with ester I also gave rise to a small amount (12 per cent based on ester) of triphenylmethane. Formation of this hydrocarbon is not unusual since t-butyl Grignard reagent is known to be a strong reducing agent (27).



Similarly the t-butyl anion can easily lose a hydride ion to the trityl cation in the following fashion. Attempts should be made to



find isobutylene among gases evolved, which would lend credibility to this suggestion.

The absence of triphenylmethanol and 2,2,4,6,6-pentamethyl-4-heptanol among the products of reaction of excess neopentyl Grignard reagent with ester I suggests that attack at the carbonyl group of the ester by the large neopentyl carbanion is inhibited. The formation of 1,1,1-triphenyl-3,3-dimethylbutane and acetic acid as the only two products indicates extensive ion-pair formation in the ester and carbonium ion capture by the neopentyl Grignard reagent.

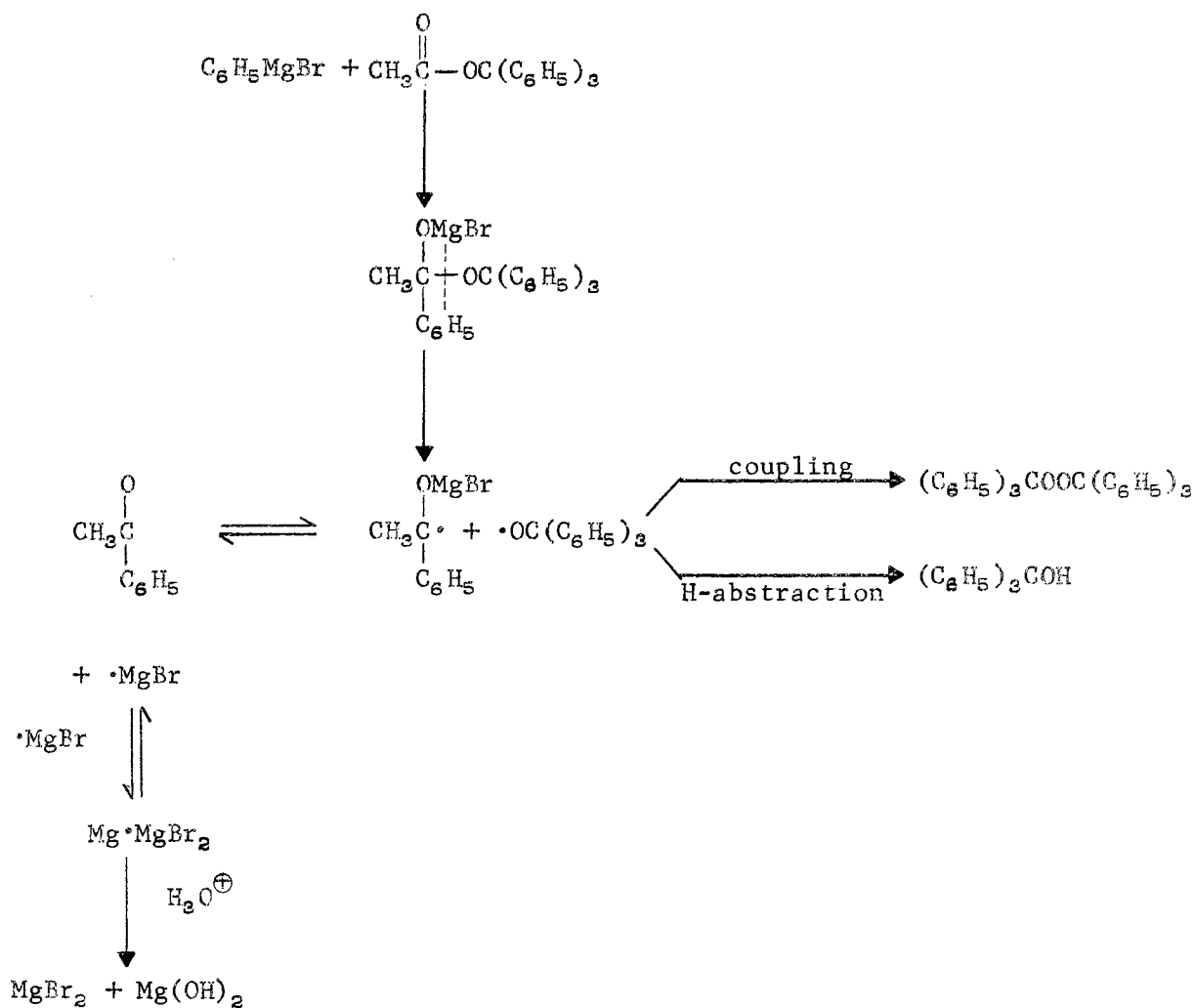
The reaction of ester I with excess cyclohexyl Grignard reagent was conducted primarily to determine whether the geometry of the cyclohexyl ring would hinder capture of the ion-pair intermediate by the cyclohexyl reagent. The formation of cyclohexyltriphenylmethane, as well as acetic acid, from the above reaction suggests that ion-pair capture is again facile with the cyclohexyl Grignard reagent.

During the reaction of ester I with ethereal phenyl Grignard reagent at room temperature under nitrogen, there was a distinct change in color from yellow to blood red and finally to yellowish green. A high yield (ca. 70 per cent) of trityl peroxide was obtained, along with acetophenone and a small quantity of triphenylmethanol, detected by gas chromatography. These results suggest an initial attack of a phenyl reagent on the carbonyl carbon atom of the ester, followed by homolytic fission of the acyl-oxygen bond to yield triphenylmethoxyl radicals. Coupling of two alkoxy radicals in this case could give trityl peroxide, although abstraction of hydrogen (perhaps from ether) would lead to triphenylmethanol. In either case, acetophenone would result via the decay of the magnesium ketyl as represented in Figure 5. The formation of the peroxide in high yield indicates that at room temperature, coupling of triphenylmethoxyl radicals was favored over hydrogen

abstraction, and this seems to be in agreement with previous work (25). The findings of Lorand and Reese (37) constitute an example of alkoxy radical dimerization.



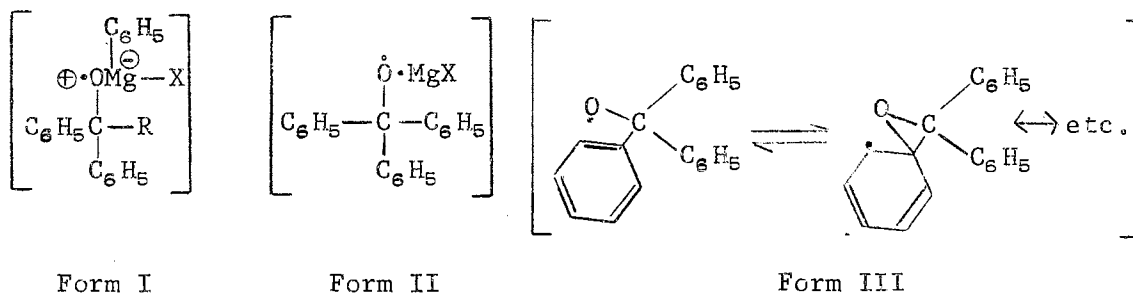
Figure 5



Electron spin resonance measurements made on two samples of phenyl Grignard reagent (a freshly prepared sample, and another prepared the previous day) verified the absence of radicals in the Grignard mixture,

as no signal was observed. This fact does not exclude the possibility of radical participation in the attack of the Grignard reagent on the carbonyl carbon atom of the ester. The failure of ester I to give any signal in ESR further suggests that radical pair formation was probably not important. However, ESR measurements on successive aliquots of the reaction mixture of the ester I with phenyl Grignard reagent (within the first hour) gave a spectrum composed of seventeen broadened lines (Plate XVI). Sharp, well-resolved signals were obtained after the first hour of reaction (Plate XVIII). It was also noted that the best-resolved signals were obtained when the temperature was lowered to -30° . In any case, however, there were always seventeen peaks in the unresolved spectra, and seventeen groups of peaks (they appeared to have four lines per group) in the resolved spectra. The separation of the two most intense lines of the spectrum, which might be considered as a direct measure of the maximum coupling of the electron with a proton of another atom, was 3.4 ± 0.2 gauss. It was also noted that the ESR spectrum obtained from the reaction mixture of ester II with phenyl Grignard reagent had the same features as that obtained with ester I and essentially the same number of peaks. Likewise it was observed that ESR signals were detected after twenty hours of reaction of the ester with the phenyl Grignard reagent in the quartz tube in the ESR cavity which indicated the presence of stable radicals. In order to exclude the possibility of formation of the peroxide via oxidation of trityl radicals by the small amount of oxygen which might be present in the regular nitrogen, the same reactions were carried under highly decxygenated nitrogen. Identical products were obtained.

Although the results of ESR measurement indicated beyond doubt the presence of free radicals in the reaction mixtures of trityl esters with the phenyl Grignard reagent, definite conclusions as to the nature of these radicals can not be stated. The possibility exists that they are ketyl-type radicals, similar to that obtained by Gato and Maruyama (22) from the reaction of benzophenone and phenyl Grignard reagent. This data may be applicable in the interpretation of our ESR spectra although different solvents are used but further work is needed with an ESR examination over a variety of temperatures for reaction and concentration ranges of reactants. In the single experiment acetophenone failed to give an ESR signal when treated with the binary mixture Mg-MgBr₂. This should be repeated. Interpretation of the spectrum and determination of products obtained from the reaction of benzophenone and phenyl Grignard reagent (39) would have been valuable in determining the nature of the radicals obtained. A radical anion of form I is conceivable, but a radical-pair of form II is also likely. In our case, triphenylmethoxyl radicals may be stabilized by delocalization of the unpaired electrons. Thus mesomeric form III may contribute to stabilization of the hybrid, and the association of the electron with the protons on the ring may be responsible for the spectrum.



In our effort to ascertain if triphenylmethoxyl radicals were intermediates n-butyl ether was added to the reaction mixture (fifteen minutes after addition of ester I to phenyl Grignard reagent was complete) and the temperature was raised to 120-22°. Regular workup afforded benzophenone and acetophenone as major products. The presence of benzophenone strongly supports the presence of triphenylmethoxyl radicals in the reaction mixture (11). This observation lends further endorsement to the homolytic fission of the acyl-oxygen bond and the formation of trityl peroxide via coupling of the intermediate triphenylmethoxyl radicals.

In view of the bright red color of the reaction mixture, alkyl-oxygen fission to yield trityl radicals which might undergo oxidation to the peroxide was suspected. However, the visible spectrum (quartz cells - Plate XII) of the species present during the reaction of ester I with phenyl Grignard reagent was different from that reported for the trityl radical (18) and might be due to absorption of the triphenylmethoxyl radical. Unfortunately, the visible spectrum of the latter has not been reported.

To be sure, the formation of benzophenone at high temperature from the reaction of trityl esters with phenyl Grignard reagent is circumstantial evidence for the acyl-oxygen homolytic fission. Absolute proof that the oxygen atom in trityl peroxide came from the ester is yet to be supplied. It is anticipated that ¹⁸O-labelling in the alcohol part of the ester should permit this, since the ¹⁸O-labelled triphenylmethoxyl radicals would give rise to ¹⁸O in trityl peroxide which could be determined by mass spectrometry.

The reactions of phenyl, *p*-tolyl and *p*-anisyl Grignard reagents with

ester III seem to follow the same path as observed in the reaction of phenyl Grignard reagent with ester I and II. Trityl peroxide was isolated in high yield in each case along with the corresponding ketones. p-Tolyl and p-anisyl β -naphthyl ketones are two new ketones prepared by this route.

For proof of structure p-tolyl β -naphthyl ketone was prepared by an alternative method which involved the classic Friedel-Crafts reaction (6). β -Naphthoyl chloride was first prepared in a quantitative yield by the chlorination of β -naphthoic acid with thionyl chloride. The acid chloride was then treated with a molar amount of anhydrous aluminum chloride and excess toluene at the reflux temperature of the solvent. The reaction was highly exothermic and evolution of hydrogen chloride gas was observed. The p-tolyl β -naphthyl ketone obtained was identified by its infrared and nuclear magnetic resonance spectrum, as well as its 2,4-DNP derivative, which gave satisfactory analytical results. By means of an analogous procedure to that described above, p-anisyl β -naphthyl ketone was obtained (75 per cent) and similarly characterized.

In summary, reactions of trityl esters with excess alkyl Grignard reagents provide a convenient path for the preparation of 1,1,1-triaryl-substituted alkanes. The reaction mechanism seems to include capture of the trityl cation by the Grignard reagent. Aryl Grignard reagents appeared to react with trityl esters by means of a free radical mechanism in part. ESR and chemical evidence support this conclusion. These reactions produced two new β -naphthyl aryl ketones.

CHAPTER VI

EXPERIMENTAL^{1,2,3,4,5,6,7}

Preparation of Trityl Acetate (I). The procedure was essentially that developed in this laboratory (7). A 1-l., three-necked, round-bottom flask equipped with a mechanical stirrer, an addition funnel fitted with a nitrogen inlet tube, and a reflux condenser was charged with 22.4 g. (0.06 mole) of trityl bromide. Anhydrous, reagent-grade benzene (200 ml.) was added through the addition funnel, and stirring was started. After all the trityl bromide had dissolved, 13.6 g.

¹ All melting points are corrected.

² The infrared spectra were determined on Beckman IR-5 and IR-5A spectrometers with sodium chloride cells as potassium bromide pellets or films.

³ The microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

⁴ The proton magnetic resonance spectra were determined by Dr. M. Khayat and D. M. Hellwege, using a Varian Model A-60 high resolution spectrometer with a field-sensing stabilizer ("super Stabilizer"). Tetramethylsilane was used as an internal standard.

⁵ Gas chromatographic analyses were performed using a thermal unit A-350 B and an Aerograph Hy-Fi Model A-550 with a hydrogen flame ionization detector from Wilkens Instrument and Research, Inc.

⁶ Visible Spectral Analysis were performed on a Beckman DK-1 Model Spectrometer by Dr. M. Nagabhushanam and Mr. L. A. Wilson.

⁷ Electron Spin Resonance Analyses were performed on a conventional Bridge-type X-Band Spectrometer utilizing a 6-inch Varian Electromagnet (3300 Gauss), by Dr. M. D. Bell and Mr. J. P. King.

(0.08 mole) of silver acetate was added in small portions to the stirred mixture. The temperature of the mixture rose until the solvent began to reflux (79°). When the addition was complete, the mixture was heated at reflux 4 hours under nitrogen. The mixture was filtered while hot to remove the silver bromide and unreacted silver acetate, and the filtrate was concentrated under aspirator pressure to one-third its original volume. A viscous liquid remained which soon solidified on standing in a vacuum desiccator. The pale yellow solid was filtered under vacuum, and recrystallized from cyclohexane to yield 21.0 g. (91.5 per cent) of trityl acetate (I), m.p. 82-3°, which was shown to be pure by mixture melting point. Yields averaged 90.1 per cent on several runs.

Preparation of Trityl Bromide. The procedure was essentially that followed by Rathore (43). The reagents used were triphenylmethanol (150.0 g.; 0.50 mole), anhydrous benzene (75 ml.), and acetyl bromide (56 ml.; 0.75 mole). The yield of the trityl bromide was 154.0 g. (96 per cent), m.p. 153-5° (lit. m.p. 152-4°) (43).

Preparation of Trityl Benzoate (II). The procedure was essentially that found in the literature (7). To 1-l., three-necked, round-bottom flask equipment with a mechanical stirrer, an addition funnel fitted with a nitrogen inlet tube, and a reflux condenser was added 40.0 g. (0.124 mole) of trityl bromide and 400 ml. of anhydrous, reagent-grade benzene. After all the trityl bromide had dissolved, sodium benzoate (18.0 g.; 0.124 mole) was added in small portions to the stirred mixture. The temperature of the mixture rose until the solvent began to reflux (80°). When the addition was complete, the mixture was heated under

nitrogen at reflux for 5 hours. The mixture was filtered while hot to remove the sodium bromide and unreacted sodium benzoate, and the filtrate was concentrated under aspirator pressure to about one-third its original volume. A viscous liquid remained which soon solidified to a pale yellow solid. The solid was filtered under vacuum and recrystallized twice from methyl ethyl ketone; yield 40.0 g. (90.0 per cent); m.p. 169-70° (lit. m.p. 169°) (7). Yields averaged 91.0 per cent on several runs.

Preparation of Sodium β -Naphthoate. A solution of sodium hydroxide (10.1 per cent) was added to a mixture of 40.0 g. (0.23 mole) of β -naphthoic acid in 200 ml. absolute ethanol until pH 7.6 was attained (checked by pHDrion paper). The white precipitate was isolated by filtration, and the filtrate was concentrated under vacuum where another crop of the salt was isolated. A yield of 40.0 g. (99.0 per cent) was obtained, m.p. above 300° (45), and the compound was used without further purification.

Preparation of Trityl β -Naphthoate (III). The procedure used was essentially that followed by Rathore (8) with 30.3 g. (0.15 mole) of trityl bromide, anhydrous benzene (210 ml.), and sodium β -naphthoate (32.7 g.; 0.18 mole). The pale yellow solid obtained was washed with 25 ml. of isopropyl ether containing 2 ml. of triethylamine. Trityl β -naphthoate (III) was purified from isopropyl ether, yield 50.0 g. (80 per cent); m.p. 148-9° (lit m.p. 149-50°) (43).

Preparation of β -Naphthoyl Chloride. A 250-ml., round-bottom flask was charged with 27.0 g. (0.016 mole) of β -naphthoic acid and 45.2 ml. (0.63 mole) of thionyl chloride, and the mixture was heated at reflux 5

hours. A vigorous reaction occurred and a large evolution of hydrogen chloride and sulfur dioxide was observed for two hours. Excess thionyl chloride was distilled under vacuum; pale yellow needles remained. The yield of the acid chloride was 29.4 g. (quantitative), and the compound was used directly in the next step without further purification (46).

Preparation of p-Tolyl β -Naphthyl Ketone. The method used was a modification of that reported in the literature for the preparation of p-anisyl α -naphthyl ketone (6). A 500-ml., 3-necked, round-bottom flask equipped with a mechanical stirrer, an addition funnel, and a reflux condenser fitted with a calcium chloride tube was charged with 7.2 g. (0.05 mole) of anhydrous powdered aluminum chloride. Toluene (100 ml.) was added and stirring was initiated. A solution of 10 g. (0.05 mole) of β -naphthoyl chloride in 50 ml. toluene was added dropwise by means of the addition funnel over a period of 30 minutes. Rapid evolution of hydrogen chloride took place from the exothermic reaction. When addition was complete, the mixture was stirred at room temperature for 12 hours. The mixture was then cooled in an ice bath and decomposed by pouring it over crushed ice. Layers were separated and washed in the same manner as previously described. The ether-toluene solvent was distilled under aspirator pressure to leave a yellow solid. Purification from 95 per cent ethanol gave 7.7 g. (61 per cent) of a white solid, m.p. 91-5°. The infrared spectrum of the solid (Plate VI) showed strong absorption at 1650 (conjugated carbonyl group) and 805 cm^{-1} (p-disubstituted benzene).

Anal. Calcd. for $C_{18}H_{14}O$:

C, 87.77; H, 5.73

Found: C, 86.58; H, 5.55

The nuclear magnetic resonance spectrum of the solid (Plate IX) showed a singlet centered at delta 2.45 (methyl hydrogens) and a multiplet centered at delta 7.5 (aromatic hydrogens). The above data is consistent with the structure of *p*-tolyl β -naphthyl ketone.

Preparation of *p*-Anisyl β -Naphthyl Ketone. The method used was a modification of that found in the literature (6) for the preparation of *p*-anisyl α -naphthyl ketone, and essentially that followed to prepare *p*-tolyl β -naphthyl ketone. Anhydrous aluminum chloride (7.2 g.; 0.05 mole), anisole (100 ml.), and β -naphthoyl chloride (10.0 g.; 0.05 mole) were allowed to react in the same manner as described in the previous analogous experiment. The mixture was stirred at room temperature for 12 hours and then decomposed in the manner described. Distillation of the organic solvent under vacuum left a white solid which was purified from 95 per cent ethanol to yield 10.0 g. (72 per cent) of a white solid, m.p. 93-4°. The infrared spectrum of the ketone (Plate V) showed strong bands at 1650 (conjugated carbonyl group) and 805 cm^{-1} (*p*-disubstituted benzene). The NMR spectrum (Plate X) showed a singlet

Anal. Calcd. for $C_{18}H_{14}O_2$:

C, 82.42; H, 5.38

Found: C, 81.84; H, 5.11

centered at delta 3.95 (methoxy protons) and two multiplets centered at delta 6.95 and 7.7 (aromatic hydrogens).

Preparation of p-Tolyl β -Naphthyl Ketone 2,4-Dinitrophenylhydrazone.

The general procedure found in the literature (47) was followed. A solution of 2,4-dinitrophenylhydrazine was freshly prepared by cautiously adding concentrated sulfuric acid (2 ml.) to 0.4 g. of 2,4-dinitrophenylhydrazine. Water (3 ml.) was added dropwise with stirring until solution was complete. Ethanol (10 ml.; 95 per cent) was then added to the warm mixture. p-Tolyl β -naphthyl ketone (0.5 g.; 0.002 mole) was dissolved in 20 ml. of 95 per cent ethanol and added to the freshly prepared solution of 2,4-dinitrophenylhydrazine, and the resulting mixture was allowed to stand at room temperature. Crystallization of an orange hydrazone took place within 5 minutes. The mixture was filtered on a Buchner funnel, mixed with 30 ml. of 95 per cent ethanol, and heated on a steam cone. Ethyl acetate was added drop by drop to the hot mixture until solution of the hydrazone was attained. The hot solution was filtered on a fluted filter paper, and was allowed to stand at room temperature until crystallization was complete. The orange crystals were filtered on a Buchner funnel and dried under vacuum; yield, 0.6 g. (75 per cent), m.p. 248-9°.

Anal. Calc. for $C_{24}H_{18}N_4O_4$:

C, 67.60; H, 4.24; N, 13.14

Found: C, 67.18; H, 4.27; N, 13.09.

Preparation of p-Anisyl β -Naphthyl Ketone 2,4-Dinitrophenylhydrazone.

The procedure was essentially that followed for the preparation of the

2,4-dinitrophenylhydrazone of *p*-tolyl β -naphthyl ketone. The yield of the dark red hydrazone was 0.7 g. (87.5 per cent).

Anal. Calcd. for $C_{24}H_{18}N_4O_5$:

C, 65.15; H, 4.10; N, 12.66

Found: C, 64.75; H, 4.00; N, 12.31

Preparation of Phenyl Grignard Reagent. A 1-l., three-necked, round-bottom flask fitted with a reflux condenser, a mechanical stirrer, and an addition funnel fitted with a nitrogen inlet tube, was charged with 0.90 g. (0.037 g. atom) of magnesium. By means of the addition funnel, a solution of 6.4 g. (0.037 mole) of bromobenzene dissolved in 50 ml. of anhydrous ether was added dropwise to the magnesium in such a way as to maintain a gentle reflux in the mixture. When addition was complete, the mixture was heated to reflux under nitrogen for 15 minutes. Stirring was stopped, and the Grignard reagent was cooled to room temperature. Two 1-ml. aliquots of the mixture were withdrawn by a 1-ml. pipet and added to excess standard hydrochloric acid and titrated to the phenolphthalein end point with standard sodium hydroxide (20). The yield calculated by this method was 93.0 per cent. The phenyl Grignard reagent was always titrated prior to immediate use in the next step in the same apparatus.

Reaction of Phenyl Grignard Reagent with Ester I (1.3:1). Trityl acetate (I) (10.0 g.; 0.033 mole) was dissolved in 80 ml. of anhydrous ether and added dropwise to the stirred Grignard mixture. Addition required 20 minutes, after which time the reaction mixture was stirred under nitrogen at room temperature for 8 hours. The color of the mixture

changed from yellow to dark orange and finally to blood red within approximately 20 minutes. The reaction appeared to be only slightly exothermic under these conditions. At the end of 8 hours, the mixture was cooled in an ice bath, and decomposed with 300 ml. of ice-cold 6 N hydrochloric acid which was added dropwise through the addition funnel. After complete addition, the mixture was stirred for 15 minutes and was then poured into a separatory funnel. Two layers separated, and the organic phase was observed to contain a pale yellow solid. Two ether extracts (20-ml. portions) of the water layer were combined with the organic layer. The combined organic extract, together with the yellow solid, was washed once with 20 ml. of water, once with 20 ml. of 10 per cent sodium bicarbonate solution, once again with 20 ml. of water, and was finally dried over anhydrous calcium chloride for 2 hours. The yellow solid (9.1 g.; 68 per cent, m.p. 183-4°) was filtered and recrystallized from benzene. Infrared analysis of the solid showed it to be trityl peroxide (lit. m.p. 186°) (21). The organic layer was concentrated under aspirator pressure to one-third its original volume. Qualitative analysis of the ether residue by gas chromatography was performed using a 12-ft. column composed of 10 per cent silicone rubber on acid-washed Chromosorb W, with the thermal unit A- 350 B of Wilkens Instrument and Research, Inc. The nitrogen flow rate was 66 ml. per minute, and the column temperature was 180°. Three peaks were found and identified as due to bromobenzene, biphenyl and acetophenone by comparing the retention times and mixed injections with those of authentic samples. The results were reproducible in three other experiments.

By careful manipulation with the washings from recrystallization of trityl peroxide, it was possible to obtain a concentrate. Gas

chromatographic analyses of the filtrate (Hy Fi A-556 unit), using a 6 ft. x 1/8 in. column composed of 10 per cent silicone rubber on acid-washed Chromosorb W confirmed the structure as that of triphenylmethanol. The column temperature was 240°, and the flow ratio of hydrogen and nitrogen gas were 26 and 29 ml. per minute, respectively.

Retention time: Triphenylmethanol (240°) 4 min. 0 sec.

Preparation of 1,1-Diphenylethanol. The phenyl Grignard reagent was prepared as described previously from 3.3 g. (0.138 g. atom) of magnesium, 30 ml. of dry ether, and 21.7 g. (0.138 mole) of bromobenzene. The yield was 88 per cent by titration. To the stirred phenyl Grignard mixture was added dropwise, over a period of 30 minutes, a mixture of 15.0 g. (0.124 mole) of reagent-grade acetophenone in 100 ml. of ether. After complete addition, the mixture was heated at reflux for 12 hours under nitrogen. When cooled to ice-bath temperature the mixture was decomposed with 500 ml. of ice-cold 6 N hydrochloric acid. The two layers were separated, and the water layer was washed once with a 30-ml. portion of ether, and the washings were combined with the organic layer. The combined organic extract was washed once with a 30-ml. portion of water, once with a 30-ml. portion of 10 per cent sodium bicarbonate solution, once again with a 30-ml. portion of water, and finally dried for 2 hours over anhydrous calcium chloride. Distillation under aspirator pressure removed the ether, leaving a yellow solid. The solid was recrystallized twice from Skellysolve F (boiling range 34-45°), to yield 22.0 g. (91.0 per cent) of 1,1-diphenylethanol, m.p. 60-1° (lit. m.p. 61-2°) (19). Infrared analysis showed strong peaks at 3350 cm⁻¹ (O-H) and 700 cm⁻¹ (monosubstituted benzene). Other prominent peaks are present

at 2585, 1425, and 758 cm^{-1} .

Reactions of Methyl, Ethyl, Phenyl, p-Tolyl and p-Anisyl Grignard Reagents with Ester I. In each experiment the Grignard reagent was prepared and allowed to react with ester I in the same manner as described for the reaction of phenyl Grignard reagent with ester I (1.3:1). The results of condensations and analyses of reaction mixtures are given in Tables I, II, III, IV and V.

Reaction of Methyl Grignard Reagent with Ester I (4:1). The method used is essentially that reported by Fieser and Heymann (13). The methyl Grignard reagent was formed from 4.0 g. (0.166 g. atom) of magnesium, 50 ml. of dry ether, and 23.3 g. (0.166 mole) of methyl iodide (94 per cent yield). Trityl acetate (I) (10.0 g.; 0.033 mole) was dissolved in 80 ml. of dry ether and added dropwise over a period of 20 minutes to the stirred Grignard mixture. No change in color was observed. After complete addition, the mixture was stirred under nitrogen at room temperature for 8 hours. The reaction mixture was decomposed and worked up in the usual fashion. The ether was removed under aspirator pressure to leave a white solid. The solid (3.5 g.; 83 per cent) was purified by two recrystallizations from 95 per cent ethanol and was identified as 1,1,1-triphenylethane, m.p. 95-6° (lit. m.p. 94-5°) (14). The infrared spectrum was identical to that of an authentic sample. The water layer was boiled to expel excess hydrochloric acid, and a concentrated solution of silver nitrate was added dropwise until no further precipitation of silver acetate was visible. The salt was filtered and dried by pressing it between two sheets of filter papers. Dilute nitric acid was added dropwise to the silver salt to liberate the free acid. The infrared

spectrum of the acetic acid obtained was identical to that of an authentic sample.

Reaction of Isopropyl Grignard Reagent with Ester II (4:1). The isopropyl Grignard reagent was prepared from 2.7 g. (0.113 g. atom) of magnesium, 50 ml. of dry ether, and 12.0 g. (0.113 mole) of isopropyl bromide (yield, 94 per cent). A mixture of trityl benzoate (II) (10.0 g.; 0.028 mole) in 80 ml. of anhydrous benzene was added dropwise to the stirred Grignard over a period of 20 minutes. The gray mixture was heated at reflux for 8 hours and was worked up in the regular manner. Distillation of the ether-benzene solvents under aspirator pressure left a yellow solid. The solid was dissolved in the smallest possible amount of anhydrous benzene and was then chromatographed on an acid-washed alumina column (15 in. x 1.25 in.). Fractions of approximately 25 ml. each were collected. A solution of cyclohexane-benzene (1:1) was used as eluant for the first 12 fractions, followed by a solution of benzene-ether (1:1) for the next 15 fractions. Pure ether was the solvent for the following 13 fractions and finally absolute ethanol was added as eluant for the last 7 fractions. Fractions 1-13 were blank, but the next three fractions (14-16) contained a viscous liquid on evaporation of the solvent. After standing, the oil solidified, and the resulting solid was recrystallized from ether to yield 4.0 g. (50.0 per cent) of a white solid, m.p. 96-7°. Infrared analysis of the solid (Plate I) showed recognizably strong peaks at 3050 (C-H stretch) and 700 cm^{-1} (monosubstituted benzene), and other prominent bands were present at 1850, 1425, 1045, and 758 cm^{-1} . The nuclear magnetic resonance spectrum of the compound (Plate VI) showed a doublet centered at δ 0.83 (methyl

hydrogens) with $J = 6$ c.p.s., a quintet centered at δ 3.53 (tertiary hydrogen) with $J = 7.0$ c.p.s., and a multiplet centered at δ 7.16 (aromatic hydrogens). This data is consistent with the structure of 1,1,1-triphenyl-2-methylpropane. Fractions 17-23 were blank, but fractions 24-27 left a white solid (1.7 g.; 48.0 per cent), which was purified from 95 per cent ethanol, m.p. 120-21°. This material was identified as benzoic acid by comparing its infrared spectrum with that of an authentic sample. Fractions 28-30 were blank, but fractions 31-37 left a pale yellow solid (4.8 g.; 48.0 per cent) identified as trityl benzoate (II) by its infrared spectrum. In an experiment with the molar ratio of Grignard reagent to ester II at 1.3, the ester was recovered in yield exceeding 90 per cent.

Reaction of *t*-Butyl Grignard Reagent with Ester I (4:1). The same procedure found in literature (17) was followed. The *t*-butyl Grignard reagent was made in the usual manner from 3.2 g. (0.13 g. atom) of magnesium, 50 ml. of dry ether, and 17.9 g. (0.13 mole) of *t*-butyl bromide; yield 90 per cent. Trityl acetate (I) (10.0 g.; 0.033 mole) dissolved in 80 ml. of dry ether was added dropwise over a period of 20 minutes to the stirred mixture. The mixture was stirred under nitrogen at room temperature for 8 hours. Trityl peroxide was not obtained as an insoluble material in the organic layer. Distillation under vacuum removed the ether to leave a yellow solid. The material was dissolved in a minimum quantity of anhydrous benzene and was then chromatographed on an acid-washed alumina column (15 in. x 1.25 in.). A total of 32 fractions (25 ml. each) were collected. The first 9 cuts were collected, with cyclohexane-ether (1:1) as eluant, and were found to be blank. The

next 4 fractions were eluted with benzene-ether (1:1) and were found to contain a white solid which was purified from ethanol to yield 0.9 g. (12 per cent) of triphenylmethane, m.p. $92.5-3^{\circ}$ (lit. m.p. 92.5°) (17), identified by the infrared and nuclear magnetic resonance spectra. The following 7 fractions were eluted with dry ether and contained a yellow solid which was purified from ethanol to yield 2.4 g. (25 per cent) of a white solid, m.p. $185-6^{\circ}$. The nuclear magnetic resonance spectrum showed a singlet at δ 0.51 (methyl hydrogens) and a multiplet centered at δ 7.15 (aromatic hydrogens), which supports the structure of 1,1,1-triphenyl-2,2-dimethylpropane (lit. m.p. $185-7^{\circ}$) (17). The next 6 fractions eluted with ether were blank, but the next 6 fractions eluted with absolute ethanol contained a yellow solid. The solid was purified from cyclohexane to yield 6.0 g. (60 per cent) of ester I, m.p. $83-4^{\circ}$, identified by its infrared spectrum. The water layer was worked up as described previously [reaction of methyl Grignard reagent with ester I (4:1)], and acetic acid was identified by its infrared spectrum as the only other product.

Reaction of Neopentyl Grignard Reagent with Ester I (4:1). The neopentyl Grignard reagent was made in the usual manner from 3.1 g. (0.13 g. atom) of magnesium, 50 ml. of dry ether, and 13.9 g. (0.13 mole) of 1-chloro-2,2-dimethylpropane (87 per cent). Ester I (10.0 g.; 0.033 mole) dissolved in 80 ml. of dry ether was added dropwise to the stirred mixture over a period of 20 minutes. The mixture was stirred under nitrogen at room temperature for 8 hours. The usual procedure was then followed. Trityl peroxide was not obtained as an insoluble material in the organic layer. Distillation under aspirator pressure removed the ether, and a yellow solid remained. The solid was dissolved

in the smallest amount possible of anhydrous benzene and was then chromatographed on acid-washed alumina column (17 in. x 1.25 in.). A total of 35 fractions, 25 ml. each, were collected. The first 11 fractions were eluted with a mixture of cyclohexane-ether (1:1), and were found to be blank. The next 5 fractions eluted from the column with a solution of benzene-ether (1:1) contained a white solid which was purified from 95 per cent ethanol to yield 4.2 g. (41 per cent) of a white solid, m.p. 102-3°. The nuclear magnetic resonance spectrum of the compound (Plate VII) showed a singlet centered at δ 0.59 (methyl hydrogens), another singlet centered at δ 2.8 (methylene hydrogens), and a multiplet centered at δ 7.25 (aromatic hydrogens). Infrared spectrum (Plate II) indicated prominent bands at 3010, 1480, 780, 750 and 700 cm^{-1} . The

Anal. Calcd. for $\text{C}_{24}\text{H}_{26}$:

C, 91.67; H, 8.33

Found: C, 92.02; H, 8.06

above data are consistent with the structure of 1,1,1-triphenyl-3,3-dimethylbutane.

The next 6 fractions were eluted with pure benzene and were found to be blank. Absolute ethanol was used to elute the next 8 fractions, which contained a yellow solid. Purification from cyclohexane gave 5.6 g. (56 per cent) of trityl acetate (I), m.p. 83-4°, which was identified by its infrared spectrum. The last 5 fractions eluted with absolute ethanol were blank.

The water layer was worked up as described for the 4:1 molar reaction of methyl Grignard reagent with ester I, and acetic acid was obtained and identified by its infrared spectrum.

Reaction of Cyclohexyl Grignard Reagent with Ester I (4:1). The cyclohexyl Grignard reagent was prepared in the usual manner from 3.1 g. (0.13 g. atom) of magnesium, 50 ml. of dry ether, and 21.2 g. (0.13 mole) of cyclohexyl bromide (91 per cent yield). Ester I (10.0 g.; 0.033 mole) was dissolved in 80 ml. of dry ether and added dropwise over a period of 20 minutes to the stirred Grignard mixture. The mixture was then stirred under nitrogen at room temperature for 8 hours, decomposed and worked up as usual. No trityl peroxide was isolated. The ether was distilled under aspirator pressure to yield a viscous oil which solidified on standing to a yellow solid. Infrared spectrum (Plate III) indicated absorption at 2590, 1490, 1445, 760 and 715 cm^{-1} . No carbonyl peaks were detected in the spectrum. The solid was purified from absolute ethanol to yield 3.7 g. (35 per cent) of a white solid, m.p. 139-40°.

Anal. Calcd. for $\text{C}_{25}\text{H}_{28}$:

C, 92.02; H, 7.97

Found: C, 92.05; H, 8.07

Nuclear magnetic resonance spectrum of the compound (Plate VIII) showed a broad multiplet centered at delta 1.6 (cyclohexyl hydrogens), and another multiplet centered at delta 7.25 (aromatic hydrogens). The above data are consistent with the structure of cyclohexyltriphenylmethane. The water layer was worked up as previously described, and acetic acid was obtained and identified by its infrared spectrum.

Reaction of Phenyl Grignard Reagent with Ester II (1.3:1). The phenyl Grignard reagent was made in the usual manner from 0.84 g. (0.035 g. atom) of magnesium, 50 ml. of dry ether, and 5.6 g. (0.035 mole) of

bromobenzene; yield 90 per cent. Ester II (10.0 g.; 0.025 mole) dissolved in 80 ml. of anhydrous benzene was added dropwise over a period of 20 minutes to the stirred Grignard reagent. The usual procedure was then followed. Trityl peroxide (9.1 g.; 68.0 per cent) was isolated and identified by infrared analysis, and biphenyl and benzophenone were found by gas chromatography (same column as used previously) as the only other products in the mixture. When the column temperature was raised to 280°, no other component was detected.

Retention time: benzophenone (180°) 4 min. 15 sec.

Reaction of p-Tolyl Grignard Reagent with Ester II (1.3:1). The p-tolyl Grignard reagent was prepared in the customary manner from 0.80 g. (0.034 g. atom) of magnesium, 50 ml. of dry ether, and 6.2 g. (0.034 mole) of p-bromotoluene; yield 85 per cent. Ester II (10.0 g.; 0.028 mole) dissolved in 80 ml. of anhydrous benzene was added dropwise to the stirred Grignard mixture over a period of 20 minutes. Trityl peroxide (9.0 g.; 65.0 per cent), p-bromotoluene, and p-tolyl phenyl ketone were identified as the only three products. An authentic sample of p-tolyl phenyl ketone was prepared by an alternate route (Friedel-Crafts reaction). Gas chromatography on the same column used previously at 180° showed the two materials to be identical.

Retention time: p-bromotoluene (180°) 1 min. - 0 sec.

p-tolyl phenyl ketone (180°) 4 min. - 50 sec.

Preparation of Phenyl p-Tolyl Ketone. The procedure followed was essentially that found in the literature (16). A 1-l., three-necked, round-bottom flask, equipped with a mechanical stirrer, a reflux condenser

fitted with a calcium chloride tube, and an addition funnel, was charged with 73.5 g. (0.55 mole) of powdered anhydrous aluminum chloride. Toluene (100 g.; 1.08 mole) was added by means of the addition funnel and stirring was started. Benzoic anhydride (56.5 g.; 0.25 mole) was added dropwise over a period of 1 hour to the heterogeneous mixture. A vigorous exothermic reaction took place and a rapid evolution of hydrogen chloride was observed. When addition was complete, the mixture was heated at reflux for 1 hour. When cooled in an ice bath the mixture was decomposed by pouring it over crushed ice. Two layers separated and were washed and dried in the usual manner. The solvent was distilled under aspirator pressure and the residue was subjected to vacuum distillation to yield 37.2 g. (80 per cent) of phenyl p-tolyl ketone, b.p. 155-60°/4 mm. The compound solidified on standing, m.p. 150-2° (lit m.p. 152°) (38), and was further identified by its infrared spectrum.

Reaction of Phenyl Grignard Reagent with Ester III (1.3:1). The phenyl Grignard reagent was prepared in the usual manner from 0.75 g. (0.031 g. atom) of magnesium, 50 ml. of dry ether, and 4.9 g. (0.031 mole) of bromobenzene; yield 90 per cent. Ester III (10.0 g.; 0.024 mole) dissolved in 80 ml. of anhydrous benzene was added dropwise over a period of 20 minutes. The mixture was stirred under nitrogen at room temperature for 8 hours, decomposed and worked up as previously described. Trityl peroxide precipitated in the organic layer and was removed by filtration and was purified from benzene, yield 8.6 g. (65 per cent), m.p. 182-4°. Infrared analysis confirmed the structure. Distillation of ether-benzene solvent under aspirator pressure left a white solid which was purified from 95 per cent ethanol to yield 3.7 g. (65 per cent)

of phenyl β -naphthyl ketone, m.p. 81.5-2° (lit. m.p. 82°) (36), which was identified by its infrared spectrum. Analysis of the filtrate by gas chromatography was performed using the same column under the same conditions as described for the 1.3:1 molar reaction of phenyl Grignard reagent with ester I. No other components than those described were detected.

Reaction of *p*-Tolyl Grignard Reagent with Ester III (1.3:1). The *p*-tolyl Grignard reagent was prepared in the usual manner from 0.74 g. (0.03 g. atom) of magnesium, 50 ml. of dry ether, and 5.3 g. (0.031 mole) of *p*-bromotoluene; yield was 86 per cent. Ester III (10.0 g.; 0.024 mole) was dissolved in 80 ml. of anhydrous benzene and added dropwise to the stirred mixture over a period of 20 minutes. The mixture was stirred under nitrogen at room temperature for 8 hours, decomposed and worked up as previously described. Trityl peroxide was obtained by suction filtration and purified from benzene, yield 8.0 g. (64 per cent), m.p. 183-4°. Distillation of the ether-benzene solvent under vacuum left a gray solid which was purified from 95 per cent ethanol to yield 3.5 g. (63 per cent) of *p*-tolyl β -naphthyl ketone, m.p. 91-2°, which had an infrared spectrum identical with that of the authentic ketone prepared by the Friedel-Crafts reaction. Analysis of the filtrate by gas chromatography under the same conditions as described for the 1.3:1 molar reaction of phenyl Grignard reagent with ester I indicated the presence of only benzene under these conditions.

Reaction of *p*-Anisyl Grignard Reagent with Ester III (1.3:1). The *p*-anisyl Grignard reagent was prepared as previously described from 0.76 g. (0.032 g. atom) of magnesium, 50 ml. of dry ether, and 5.8 g.

(0.032 mole) of p-bromoanisole; yield 88 per cent. Ester III (10.0 g.; 0.024 mole) was dissolved in 80 ml. of anhydrous benzene, and the solution was added dropwise to the stirred Grignard mixture over a period of 20 minutes. The mixture was stirred under nitrogen at room temperature for 8 hours, decomposed and worked up as previously described. Trityl peroxide was isolated and purified, yield 8.8 g. (70 per cent), m.p. 182-4°. Distillation of the solvent left a pale yellow solid which was purified from 95 per cent ethanol to yield 4.2 g. (66 per cent) of p-anisyl β -naphthyl ketone, m.p. 93-4°, which had an infrared spectrum identical with that of the ketone prepared by reaction of β -naphthoyl chloride with anisole. Analysis of the filtrate by gas chromatography under the same conditions described for the 1.3:1 molar reaction of phenyl Grignard with ester I indicated the presence of benzene as the only compound under these conditions.

Reaction of Phenyl Grignard Reagent with Ester II (1.3:1) Followed by Treatment with Bromine. The Grignard reagent was made as usual from 0.84 g. (0.035 g. atom) of magnesium, 50 ml. of dry ether, and 5.6 g. (0.035 mole) of bromobenzene; yield 88 per cent. Ester II (10.0 g.; 0.028 mole) was dissolved in 80 ml. of anhydrous benzene and added dropwise to the stirred Grignard mixture over a period of 20 minutes. The mixture was stirred under nitrogen at room temperature for 1 hour. Bromine (1.5 ml.; 0.028 mole) was slowly added to the stirred mixture over a period of 15 minutes. After addition was complete, the mixture was stirred under nitrogen at room temperature for 3 hours. The mixture was cooled in an ice bath, treated with 5.0 g. (0.031 mole) of sodium thiosulfate, and stirred for 15 minutes to destroy unreacted bromine.

The pale yellow mixture was filtered and concentrated under vacuum to a viscous oil. The oil was chromatographed on a column of neutral alumina (15 in. x 1.25 in.). A total of 25 fractions (25 ml. each) were collected. Although the first 7 fractions eluted with cyclohexane-benzene (1:1) were found to be blank, the next 3 fractions, eluted with ether, contained a pale yellow solid which was purified from Skellysolve B. Trityl bromide (1.5 g., 16.6 per cent) was identified by its infrared spectrum. The following 10 fractions eluted with ether were blank, but the next 5 fractions eluted with absolute ethanol contained a gray solid. Recrystallization from methyl ethyl ketone gave 5.0 g. (50 per cent) of ester II, m.p. 169-70°, identified by its infrared spectrum.

Bromination of Ester II. A 500 ml., 3-necked, round-bottom flask equipped with a mechanical stirrer, an addition funnel fitted with a nitrogen inlet tube and a reflux condenser, was charged with 10.0 g. (0.028 mole) of trityl benzoate. Anhydrous benzene (80 ml.) was added and stirring was started. After all the trityl benzoate (II) had dissolved, bromine (1.5 ml.; 0.028 mole) was slowly added to the stirred ester over a period of 15 minutes. The mixture was then stirred under nitrogen at room temperature 3 hours. The mixture was cooled, treated with 5.0 g. (0.031 mole) of sodium thiosulfate, stirred for 15 minutes and then filtered. The mixture was concentrated under aspirator vacuum to an oil, which was chromatographed on a neutral alumina column. A total of 27 fractions, 25 ml. each, were collected. The first 10 fractions eluted with cyclohexane-benzene (1:1) were blank. The next 2 fractions were eluted with ether and contained trityl bromide (1.0 g.;

11.0 per cent) which was identified by its infrared spectrum, m.p. 154-5°. The next 10 fractions were eluted with ether and were found to be blank, while the last 5 fractions eluted with absolute ethanol contained 8.5 g. (85.0 per cent) of ester II, which was purified from methyl ethyl ketone, m.p. 169-70°, and identified by its infrared spectrum.

Reaction of Phenyl Grignard Reagent with Ester I (1.3:1) with n-Butyl Ether. The phenyl Grignard reagent was prepared in the usual manner from 0.9 g. (0.037 g. atom) of magnesium, 50 ml. of dry ether, and 6.4 g. (0.037 mole) of bromobenzene (92 per cent). Ester I (10.0 g.; 0.033 mole) dissolved in 80 ml. of dry ether was added dropwise to the stirred Grignard mixture over a period of 20 minutes. The mixture was stirred at room temperature under nitrogen for 10 minutes. At this time n-butyl ether (80 ml.) was added directly by means of the addition funnel, and the temperature was immediately raised to 120-22° by raising the Powerstat to 85 v. and measuring the pot temperature by means of a thermometer. The reaction mixture was stirred in this temperature range for 3 hours under nitrogen. Decomposition, workup, and removal of trityl peroxide was performed in the usual manner. Qualitative analysis of the mixture was performed at 156° with the aid of the Hy Fi A-500 gas chromatography unit with a hydrogen flame detection cell. A 6-ft. x 1/8-in. column composed of 10 per cent silicone rubber on acid-washed Chromosorb W was used. Hydrogen and nitrogen gas flow rates were 26 and 29 ml. per minute, respectively. Acetophenone and benzophenone were found as the only two compounds in the mixture under these conditions. They were identified by comparing the retention times and mixed injections with those of authentic samples. The temperature was

lowered to 80°, where n-butyl ether was also detected.

Retention time: acetophenone (156°) 1 min. 0 sec.
benzophenone (156°) 5 min. 30 sec.
n-butyl ether (80°) 1 min. 0 sec.

Electron Spin Resonance Analysis of Reaction Mixtures of Phenyl Grignard Reagent with Ester I. The phenyl Grignard reagent was made for each run from 0.037 g. atom of magnesium, 0.037 mole of bromobenzene and 50 ml. of dry ether. In each experiment the Grignard reagent was heated for 15 minutes, titrated, and then treated with 0.033 mole of ester I in 80 ml. of ether, added dropwise over a period of 20 minutes. Several aliquots were withdrawn by means of a Pasteur's pipet for electron spin resonance analysis. Dilution when required was made in the reaction vessel. The results of the analyses are shown in Tables VI, VII and VIII.

Electron Spin Resonance Analysis of the Reaction Mixture of Phenyl Grignard Reagent With Ester I (benzene added). The phenyl Grignard reagent was made from 0.037 g. atom of magnesium, 0.037 mole of bromobenzene and 50 ml. of dry ether, heated for 15 minutes and treated with 0.033 mole of ester I dissolved in 50 ml. of dry ether over a period of 20 minutes. After complete addition, anhydrous benzene (100 ml.) was immediately added to the reaction vessel and the temperature was raised rapidly to 50° by turning the Variac to 65 volts. The pot temperature was measured by means of a thermometer, and was kept at 50° ± 2 for 8 hours. Several aliquots were withdrawn for analysis by means of a Pasteur's pipet. The results of the electron spin resonance analyses are shown in Table IX.

Electron Spin Resonance Analysis of Reaction Mixtures of Phenyl Grignard Reagent with Ester II. The phenyl Grignard reagent for each run was made from 0.035 g. atom of magnesium, 0.035 mole of bromobenzene and 50 ml. of dry ether. In each run the Grignard reagent treated with 0.028 mole of ester II dissolved in 80 ml. of anhydrous benzene by dropwise addition over a period of 20 minutes (in one run, all the ester was added in 5 minutes). Several aliquots were withdrawn for analyses by means of a Pasteur's pipet. The results of the electron spin resonance analyses are shown in Table X.

Electron Spin Resonance Analysis of the Reaction Mixture of Phenyl Grignard Reagent with Ester II (cooled to -30°). The phenyl Grignard reagent was prepared from 0.18 g. atom of magnesium, 0.018 mole of bromobenzene and 25 ml. of dry ether. Ester II (0.014 mole) was dissolved in 40 ml. of anhydrous benzene and added dropwise over a period of 10 minutes to the stirred mixture. The mixture was stirred at room temperature under deoxygenated nitrogen for 15 minutes. An aliquot was immediately withdrawn, by means of a Pasteur's pipet, cooled to -30° and the electron spin resonance spectrum determined. A highly resolved signal (Plate XXVII) was obtained.

Visible Spectral Analysis of the Reaction Mixture of Phenyl Grignard Reagent with Ester II. The Grignard reagent was made from 0.035 g. atom of magnesium, 0.035 mole of bromobenzene, and 20 ml. of dry ether. Ester II (0.028 mole) dissolved in 40 ml. of anhydrous benzene was added dropwise over a period of 15 minutes. The mixture was stirred under nitrogen at room temperature and samples were withdrawn by means of a Pastuer's pipet for visible spectral analysis. The results are shown in Table XI.

Visible Spectral Analysis of the Reaction Mixture of Phenyl Grignard Reagent with Ester II (ethanol-isopentane solution added). The Grignard reagent was made from 0.035 g. atom of magnesium, 0.035 mole of bromobenzene, and 50 ml. of dry ether (yield 92 per cent). Ester II (0.028 mole) was dissolved in 80 ml. of benzene and added dropwise to the Grignard mixture over a period of 20 minutes. The mixture was stirred under oxygen-free nitrogen at room temperature for 1 hour. Isopentane (50 ml.) and 16 ml. of absolute ethanol were added to the reaction flask, and the resulting mixture was stirred for another hour, at the end of which the stirrer was stopped for 10 minutes. By means of a 10-ml. pipet fitted with a propipette, a 20-ml. aliquot of the supernatant liquid was transferred to a 50-ml., two-necked, round-bottom flask fitted with an oxygen-free nitrogen inlet and a calcium chloride tube. Oxygen-free nitrogen was slowly bubbled through the liquid for 1 hour in order to concentrate the solution. An aliquot was then taken by means of a Pasteur's pipet for visible spectral analysis. Strong absorption in the region 400-2400 $m\mu$ was observed (Plate XII).

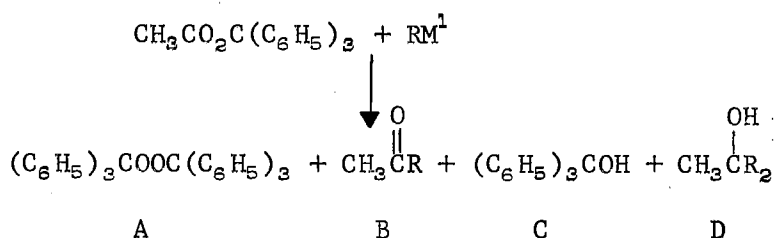
Electron Spin Resonance Analysis of the Reaction Mixture of Acetophenone with Magnesium - Magnesium Bromide Binary Mixture. The procedure was essentially that followed by Bowers (8). A 500-ml., three-necked, round-bottom flask equipped with a mechanical stirrer, a reflux condenser and an addition funnel fitted with a nitrogen inlet tube, was charged with 4.9 g. (0.2 g. atom) of powdered magnesium. By means of the addition funnel, 60 ml. of anhydrous benzene and 30 ml. of dry ether were added at once and stirring was started. Bromine (3 ml.; 0.1 mole) was added dropwise over a period of 15 minutes. A highly exothermic



reaction took place. When addition was complete, the reaction mixture was stirred under nitrogen at room temperature for 15 minutes. Acetophenone (12.0 g.; 0.1 mole) was added dropwise over a period of 30 minutes and the resulting mixture was heated at reflux for 1 hour. An aliquot was taken by means of a Pasteur's pipet for electron spin resonance analysis, and no signal was observed. The rest of the reaction mixture was cooled, decomposed and worked up in the usual fashion. The mixture was then subjected to vacuum distillation to yield 10.0 g. (85 per cent) of acetophenone (b.p. $80-2^{\circ}/2$ min.) as the only product which was identified by its infrared spectrum. This needs to be repeated and gas chromatographic analysis should be used to detect any pinacol present.

Reaction of Phenyl Grignard Reagent with Ester I (1.3:1). The phenyl Grignard reagent was prepared in the usual fashion from 0.90 g. (0.037 g. atom) of magnesium, 50 ml. of dry ether, and 6.4 g. (0.037 mole) of bromobenzene. Ester I (10.0 g.; 0.033 mole) dissolved in 80 ml. of dry ether was added dropwise and the mixture was stirred under nitrogen for 8 hours, decomposed and worked up in the usual fashion. Trityl peroxide was removed by filtration and recrystallized twice from benzene. The filtrate remaining after purification of the peroxide was carefully concentrated one-third of its original volume. Gas chromatography analyses of the filtrate (performed on hydrogen flame detection cell, using a 6 ft. x 1/8 in. column composed of 10 per cent silicone rubber on acid washed Chromosorb W) confirmed the structure as that of triphenylmethanol. The column temperature was 240° , and the flow rates of hydrogen and nitrogen gas were 26 and 29 ml. per minute, respectively.

TABLE I

CONDENSATION OF ESTER I WITH GRIGNARD REAGENTS



Exp.	RX	RM/ester (molar)	Products %			
			A	B	C	D
I	CH ₃ I	1.3:1	0	²	76 ³	0
II	C ₂ H ₅ I	1.3:1	0	⁴	60 ⁵	0
III	C ₆ H ₅ Br	4:1	70	0	0	70.5 ⁶
IV	CH ₃ -  -Br	1.3:1	71	⁷	0	0
V	CH ₃ O-  -Br	1.3:1	69	⁸	0	0

¹RM = Grignard reagent.

²Qualitatively determined by gas chromatography along with triphenylmethanol. The ketone was the only major product; yield of ketone assumed equal to or less than that of triphenylmethanol.

³Qualitatively determined by gas chromatography along with acetone and ester I (53 per cent).

⁴Qualitatively determined by gas chromatography along with triphenylmethanol and ester I.

⁵Qualitatively determined by gas chromatography along with methyl ethyl ketone. These were the only major products; yield of methyl ethyl ketone is assumed equal to or less than that of triphenylmethanol.

⁶Purified from Skellysolve F; melting point 60-1° (lit. m.p. 61-2°) (19).

⁷Qualitatively determined by gas chromatography along with small amounts of p-bromotoluene and ester I. The yield of p-methylacetophenone assumed to be equal to or less than that of triphenylmethanol.

⁸Qualitatively determined by gas chromatography. The ketone was the only major product. The yield of p-methoxyacetophenone is assumed equal to or less than that of triphenylmethanol.

TABLE II

QUALITATIVE GAS CHROMATOGRAPHIC ANALYSIS OF
ORGANIC LAYER FROM EXPERIMENT I

Column: Silicone rubber 10% on Chromosorb W, 6 ft.

Conditions: H_2 flow = 20 ml./min; N_2 flow = 23 ml./min., Temp. 230°C;
Hy Fi unit; hydrogen flame cell.

Compound	Retention Time
Trityl acetate (I)	2 min. 0 sec.
Triphenylmethanol	4 min. 30 sec.

Column: U-con Polar 5%, 12 ft.

Conditions: N_2 flow = 67 ml./min., Temp. 50°, A-350 B unit.

Compound	Retention Time
Acetone	1 min. 15 sec.

TABLE III

QUALITATIVE GAS CHROMATOGRAPHIC ANALYSIS
OF ORGANIC LAYER FROM EXPERIMENT II

Column: Silicone rubber 10% on Chromosorb W, 6 ft.

Conditions: H_2 flow = 20 ml./min; N_2 flow = 23 ml./min., Temp. 230°C;
Hy Fi unit; hydrogen flame cell.

Compound	Retention Time
Trityl acetate (I)	2 min. 0 sec.
Triphenylmethanol	4 min. 30 sec.

Column: U-con Polar 5%, 12 ft.

Conditions: N_2 flow = 70 ml./min., Temp. 70°C, A-350 B unit.

Compound	Retention Time
Methyl ethyl ketone	3 min. 0 sec.

TABLE IV
 QUALITATIVE GAS CHROMATOGRAPHIC ANALYSIS
 OF ORGANIC LAYER FROM EXPERIMENT IV

Column: Silicone rubber 10% on Chromosorb W, 12 ft.
 Conditions: N₂ flow = 66 ml./min., Temp. 180° and 230°; A-350 B Unit.

Compound (Temp. °C)	Retention Time
p-Bromotoluene (180°)	1 min. 0 sec.
p-Tolyl methyl ketone (180°)	1 min. 43 sec.
Trityl acetate (I) (230°)	2 min. 53 sec.

TABLE V
 QUALITATIVE GAS CHROMATOGRAPHIC ANALYSIS
 OF ORGANIC LAYER FROM EXPERIMENT V

Column: Silicone rubber 10% on Chromosorb W, 12 ft.
 Conditions: N₂ flow = 66 ml./min., Temp. 180°, A-350 B unit.

Compound	Retention Time
p-Bromoanisole	1 min. 25 sec.
p-Anisyl methyl ketone	1 min. 47 sec.

TABLE VI
ESR SPECTRA OF RM¹ + TRITYL ACETATE REACTION MIXTURE

Sample ^{2,3}	Experiment	Dilution with Ether	Reaction Time, hrs.	Signal Type, Plate
1a	RM + Ether	none	-	none
1b	Trityl Acetate and Ether	none	-	none
1c	RM + Trityl Acetate and Ether	none	0.25	XVI
1d	RM + Trityl Acetate and Ether	none	1.0	XVII
1e	RM + Trityl Acetate and Ether	none	3.5	XVII
1f	RM + Trityl Acetate and Ether	none	20.0	XVIII

¹RM = Phenyl Grignard reagent.

²Reactions were run at room temperature.

³High-purity dry nitrogen (Linde Inc.) was used.

TABLE VII
ESR SPECTRA OF RM¹ + TRITYL ACETATE REACTION MIXTURES

Sample ^{2,3}	Experiment	Dilution with Ether	Reaction Time, hrs.	Signal Type, Plate
2a	RM + Trityl Acetate and Ether	none	~0	XVI
2b	RM + Trityl Acetate and Ether	none	3.56	XVII
2c	RM + Trityl Acetate and Ether	2X	5.06	XIX
2d	RM + Trityl Acetate and Ether	20X	5.6	XX

¹RM = Phenyl Grignard reagent.

²Reactions were run at room temperature.

³High-purity dry nitrogen (Linde Inc.) was used.

TABLE VIII
ESR SPECTRA OF RM¹ + TRITYL ACETATE REACTION MIXTURES

Sample ^{2,3}	Experiment	Dilution with Ether	Reaction Time, hrs.	Signal Type, Plate
3a	RM + Trityl Acetate and Ether	none	~0	XVI
3b	RM + Trityl Acetate and Ether	none	0.5	XVI
3c	RM + Trityl Acetate and Ether	2X	1.0	XVII
3d	RM + Trityl Acetate and Ether	10X	1.5	XIX
3e	RM + Trityl Acetate and Ether	100X	2.0	none

¹RM = Phenyl Grignard reagent.

²Reactions were carried out at room temperature.

³The nitrogen used was deoxygenated by passing it through zinc amalgam-sodium chromite mixture. Thanks are extended to Dr. P. Arthur for his help in setting up the deoxygenation system.

TABLE IX
ESR SPECTRA OF RM¹ + TRITYL ACETATE REACTION MIXTURES

Sample ^{2,3}	Experiment	Dilution with Ether	Reaction Time, hrs.	Signal Type, Plate
4a	RM + Trityl Acetate and Ether	none	~0	XVI
4b	RM + Trityl Acetate and Ether	none	0.67	XVI
4c	RM + Trityl Acetate and Ether	none	1.0	XVII
4d	RM + Trityl Acetate and Ether	none	3.5	XVII
4e	RM + Trityl Acetate and Ether	none	4.0	XIX

¹RM = Phenyl Grignard reagent.

²Reactions were carried out at 50°.

³Deoxygenated nitrogen was used.

TABLE XI
ESR SPECTRA OF RM¹ + TRITYL BENZOATE REACTION MIXTURES

Sample ^{2,3}	Experiment	Dilution	Reaction Time, hrs.	Signal Type, Plate
5a	RM + Trityl Benzoate	none	2.0	XXI
5b	RM + Trityl Benzoate	none	4.5	XXII
6a	RM + Trityl Benzoate	none	0.25	XXIII
6a	RM + Trityl Benzoate	none	2.0	XXIV
7a	RM + Trityl Benzoate	none	1.0	XXV
7b	RM + Trityl Benzoate	none	2.0	XXIV
8a	RM + Trityl Benzoate	none	0.5	XXIII
8b	RM + Trityl Benzoate	none	1.5	XXVI

¹RM = Phenyl Grignard reagent.

²Reactions were all carried out at room temperature.

³Regular nitrogen was used for experiments 5, 6, 7 and deoxygenated nitrogen was used for experiment 8.

TABLE XI.
VISIBLE SPECTRA OF RM¹ + TRITYL BENZOATE REACTION MIXTURES

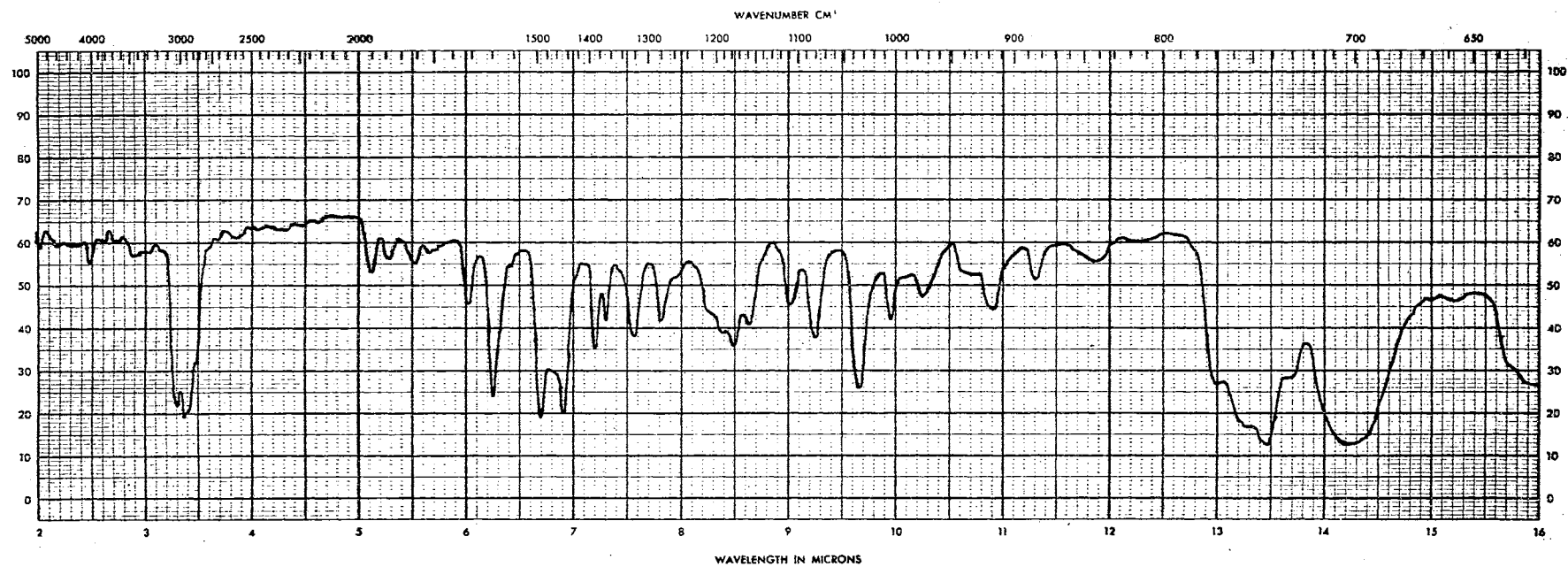
Sample ^{2,3}	Experiment	Dilution	Reaction Time, hrs.	Absorption in Visible Region, Plate
9a	RM + Trityl Benzoate	none	1.5	XI
9b	RM + Trityl Benzoate	none	4.5	XI
9c	RM + Trityl Benzoate	none	6.5	XI

¹RM = Phenyl Grignard reagent.

²Reactions were carried out at room temperature.

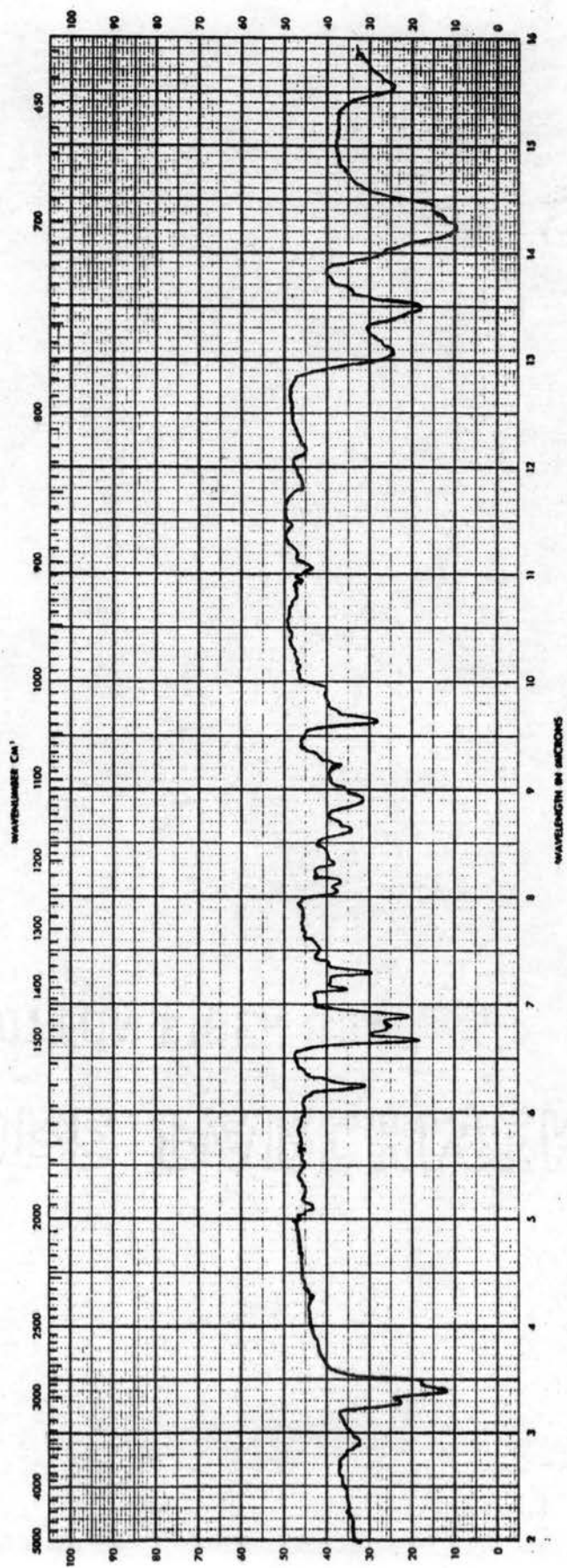
³Regular nitrogen was used.

Plate I



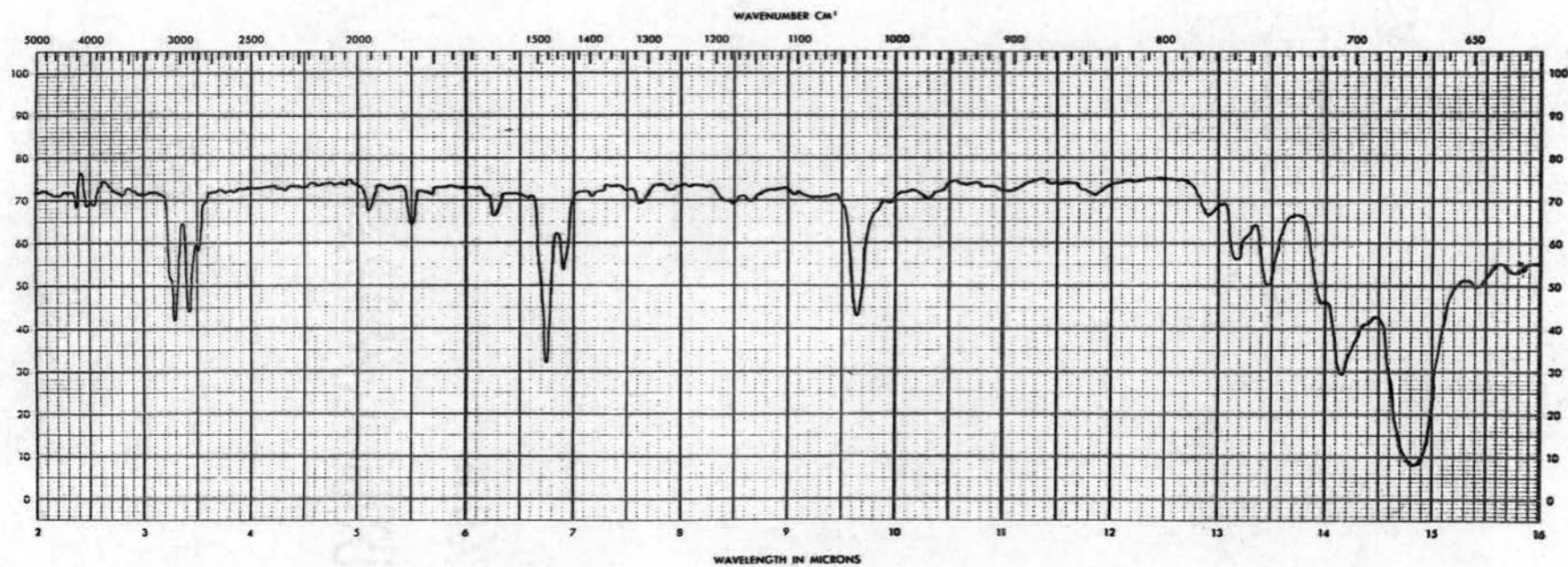
1,1,1-Triphenyl-2-methylpropane, KBr Pellet

Plate II



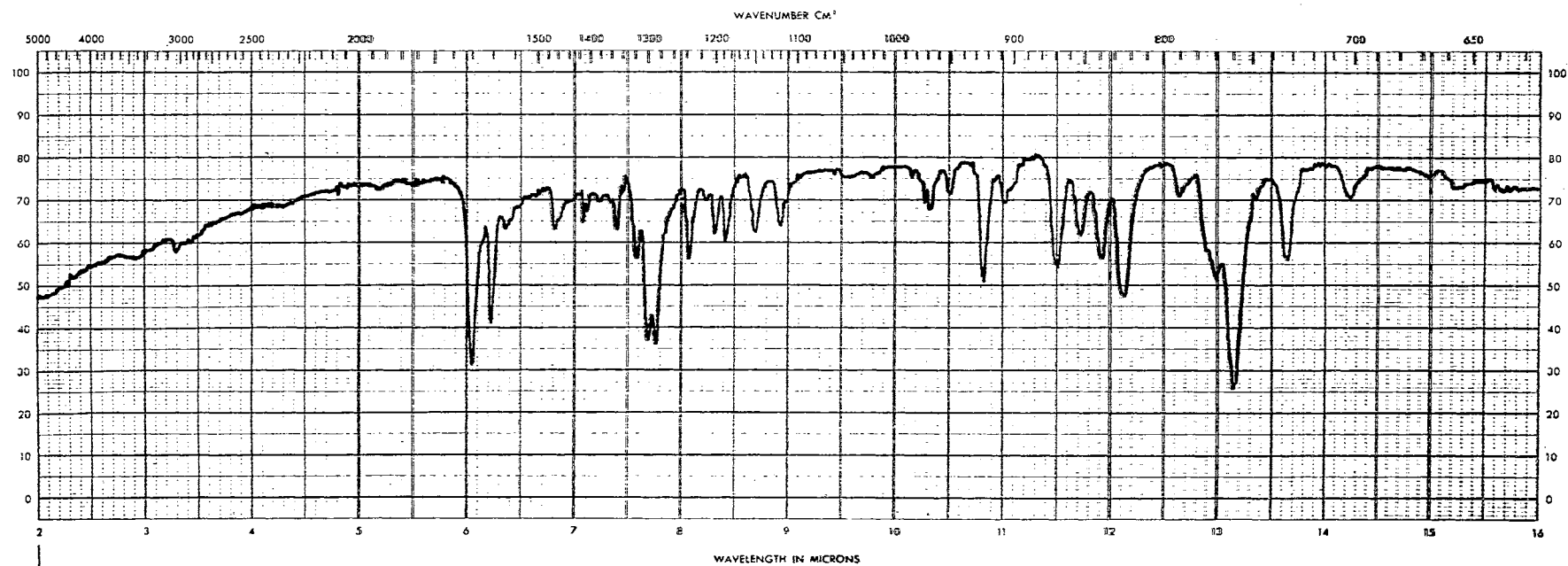
1,1,1-Triphenyl-3,3-dimethylbutane, KBr Pellet

Plate III



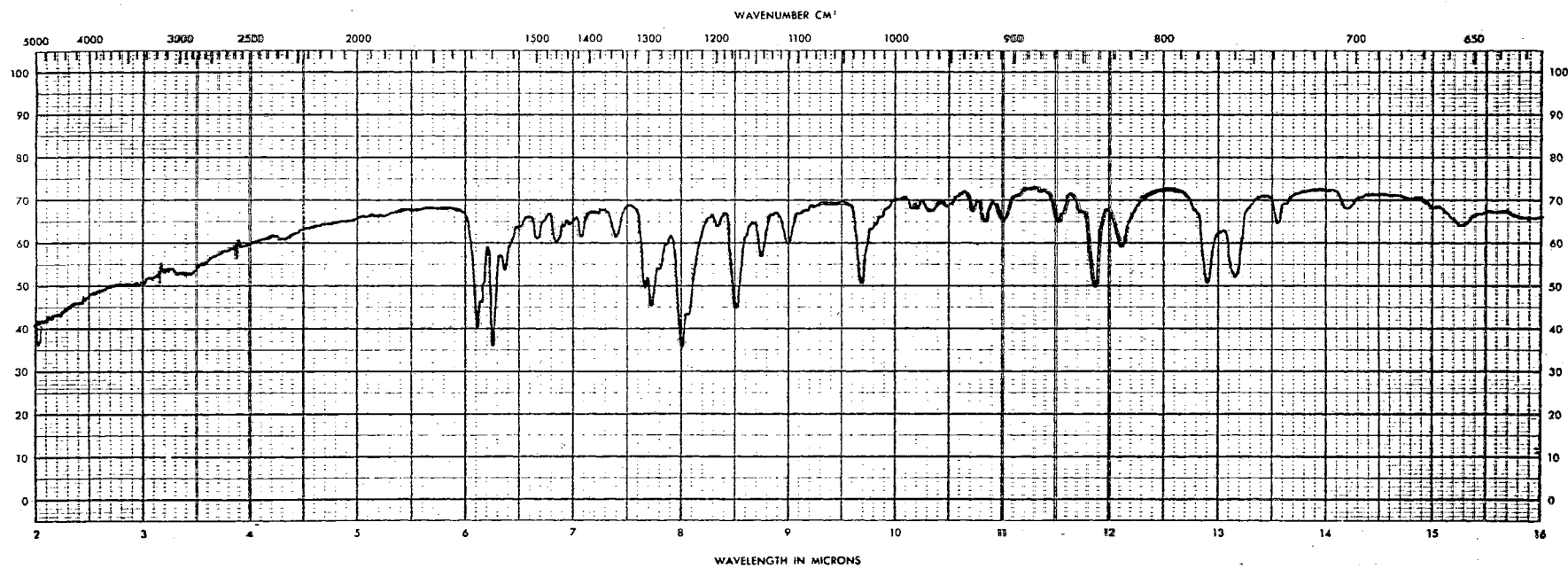
Cyclohexyltriphenylmethane, KBr Pellet

Plate IV



p-Tolyl β -Naphthyl Ketone, KBr Pellet

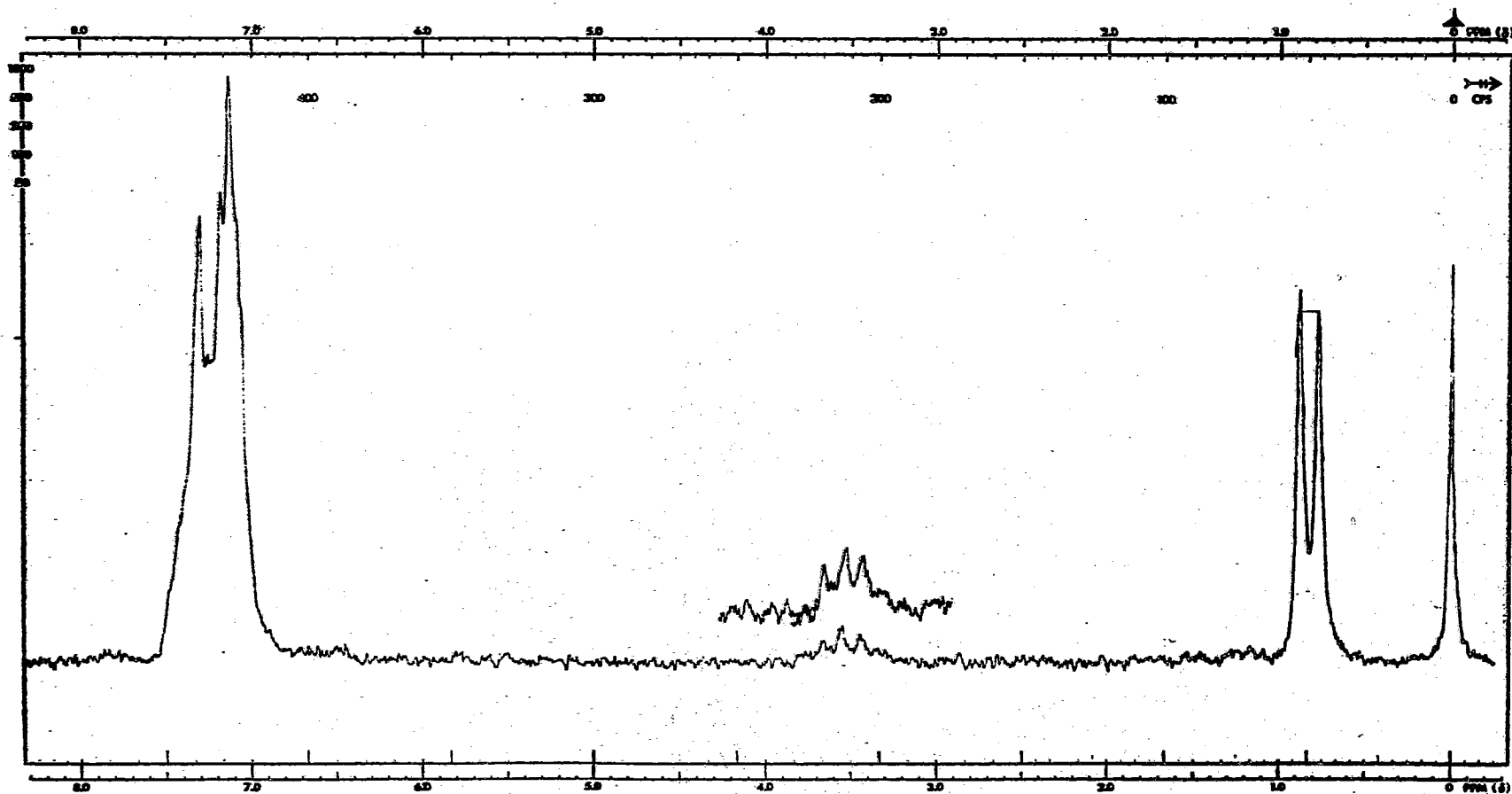
Plate V



p-Anisyl β -Naphthyl Ketone, KBr Pellet

Plate VI

1,1,1-Triphenyl-2-methylpropane



Solvent: CCl_4
F.B.: 1 cps

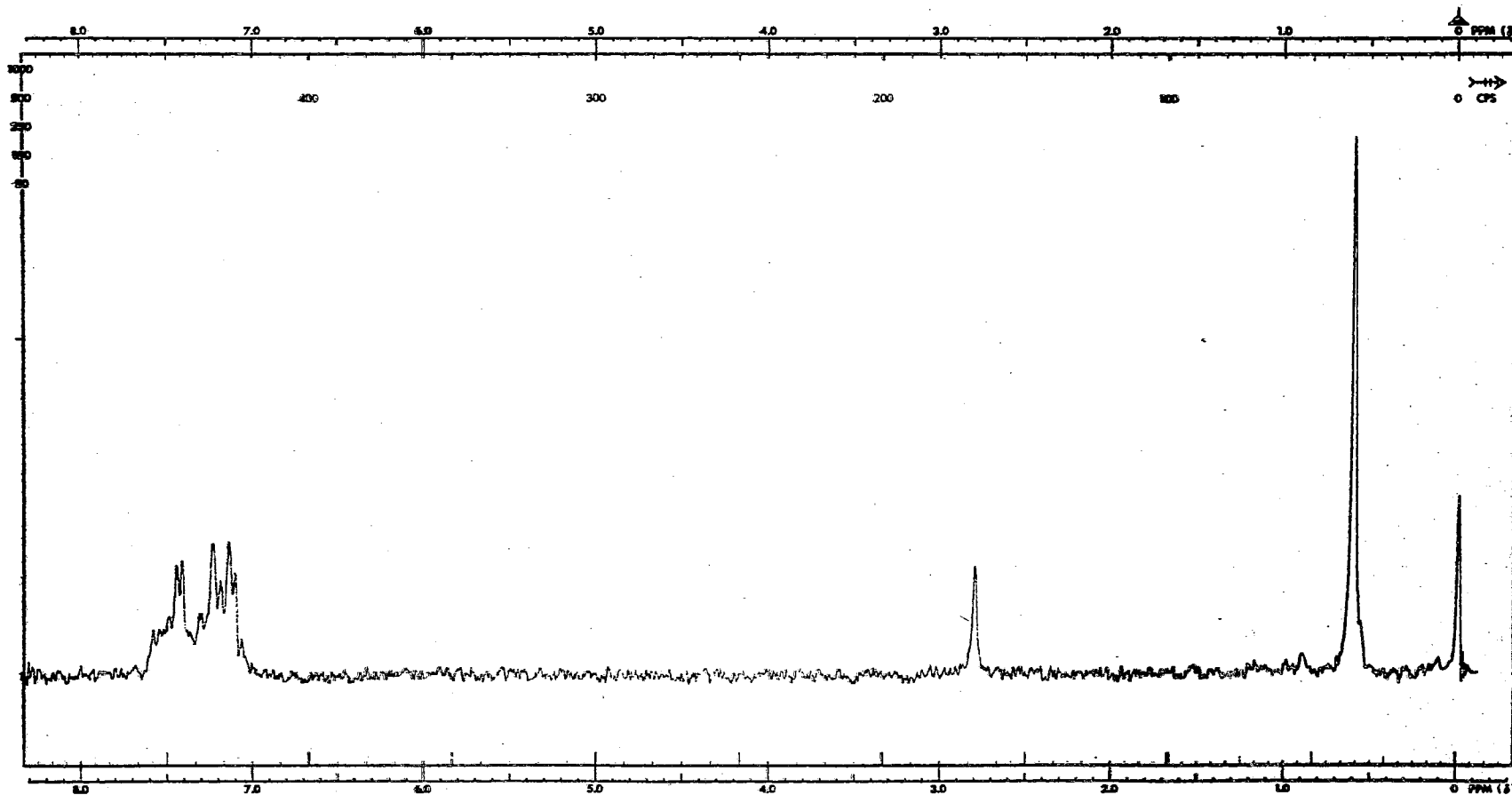
R.F. Field: 0.2 mG
S.T.: 250 sec

S.W.: 500 cps
S.O.: 0 cps

S.A.: 8 and 20
I.A.: off

Plate VII

1,1,1-Triphenyl-3,3-dimethylbutane



Solvent: CCl_4
F.B.: 1 cps

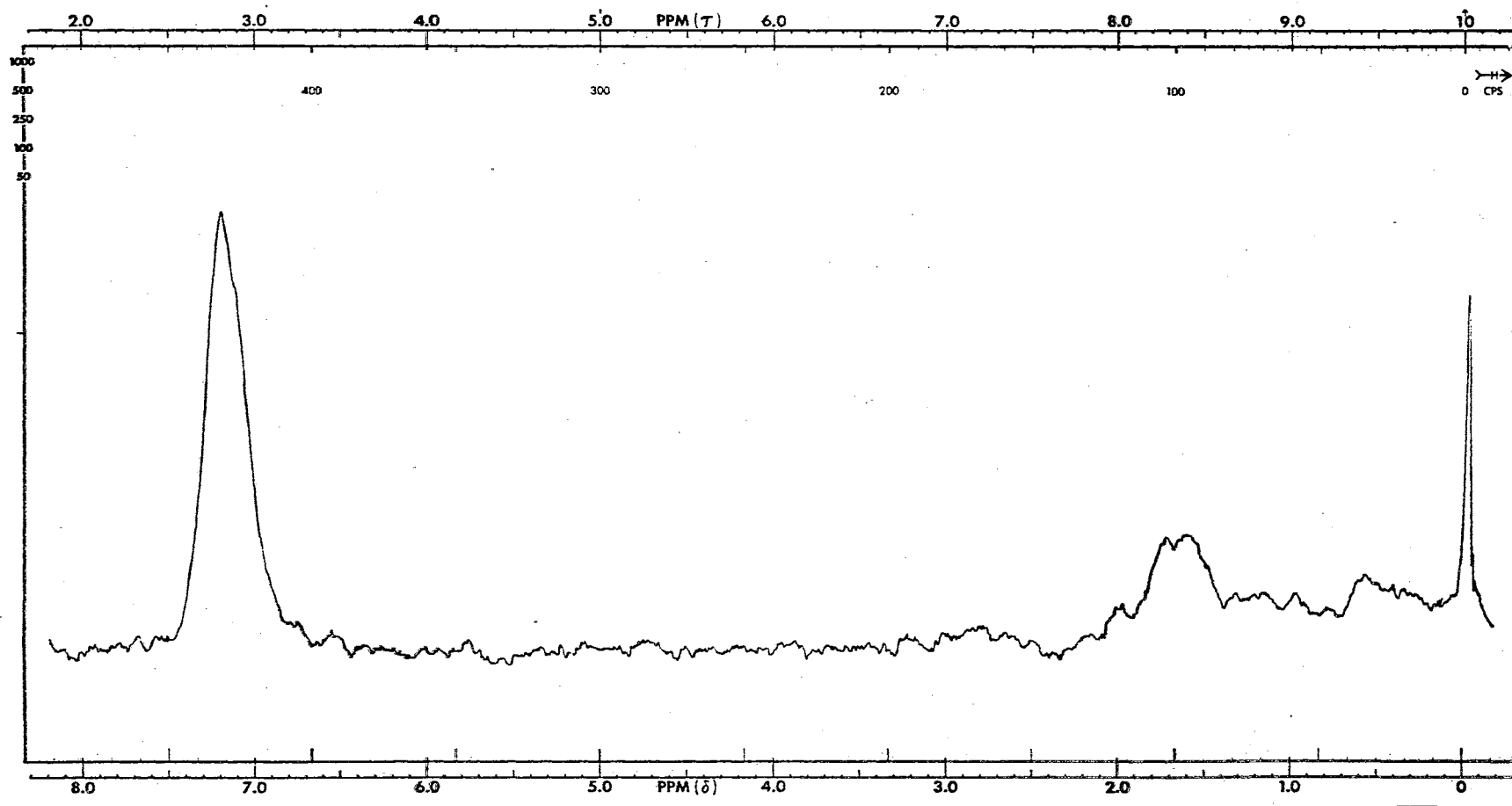
R.F. Field: 0.2 mG
S.T.: 250 sec

S.W.: 500 cps
S.O.: 44 cps

S.A.: 10
I.A.: off

Plate VIII

Cyclohexyltriphenylmethane



Solvent: CCl_4
R.E.: 0.1 cps

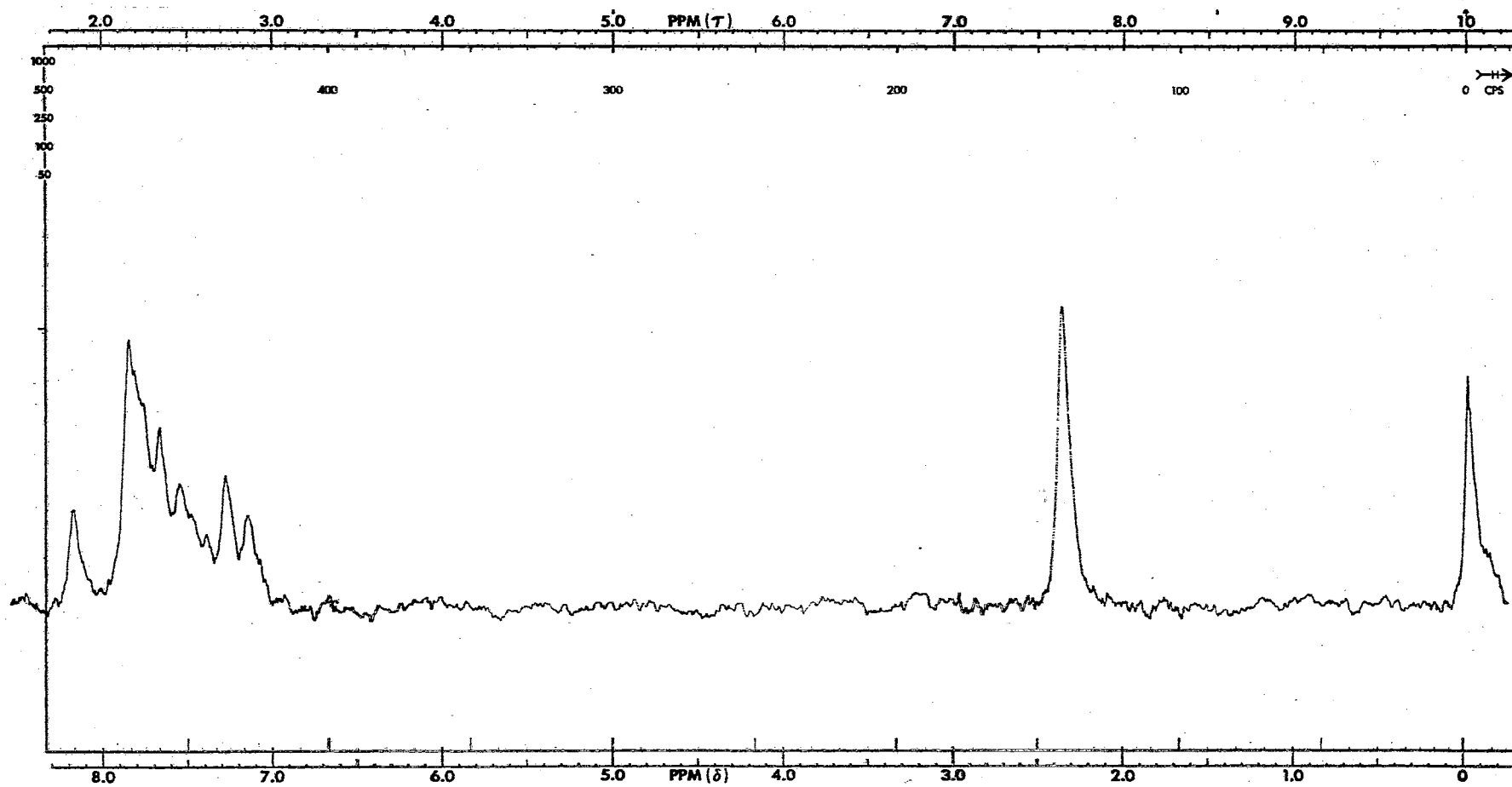
R.F. Field: 0.2 mG
S.T.: 500 sec

S.W.: 500 cps
S.O.: 0 cps

S.A.: 50
I.A.: off

Plate IX

p-Tolyl β -Naphthyl Ketone



Solvent: CCl_4
F.B.: 0.1 cps

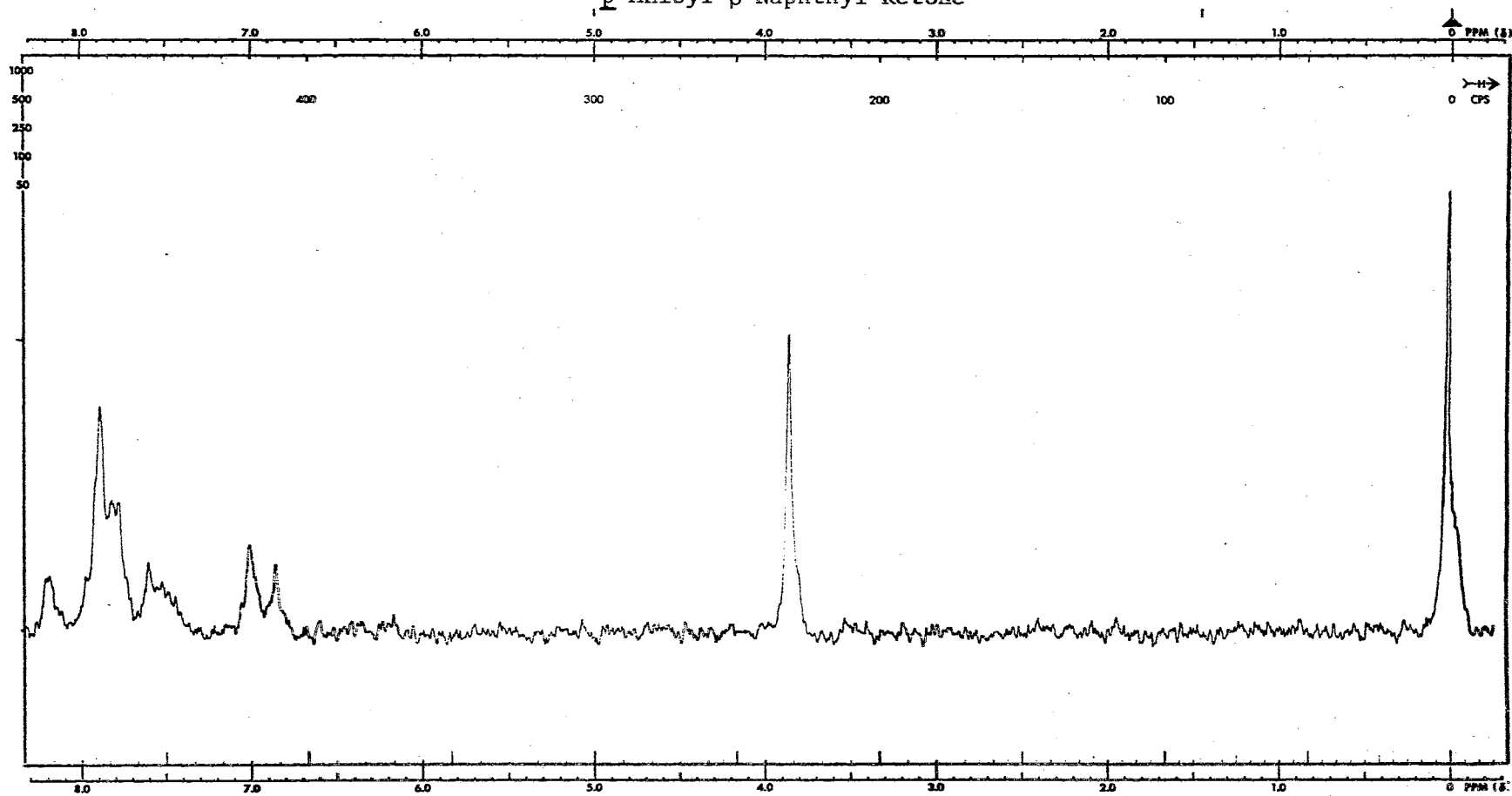
R.F. Field: 0.2 mG
S.T.: 500 sec

S.W.: 500 cps
S.O.: 0 cps

S.A.: 50
I.A.: off

Plate X

p-Anisyl β -Naphthyl Ketone



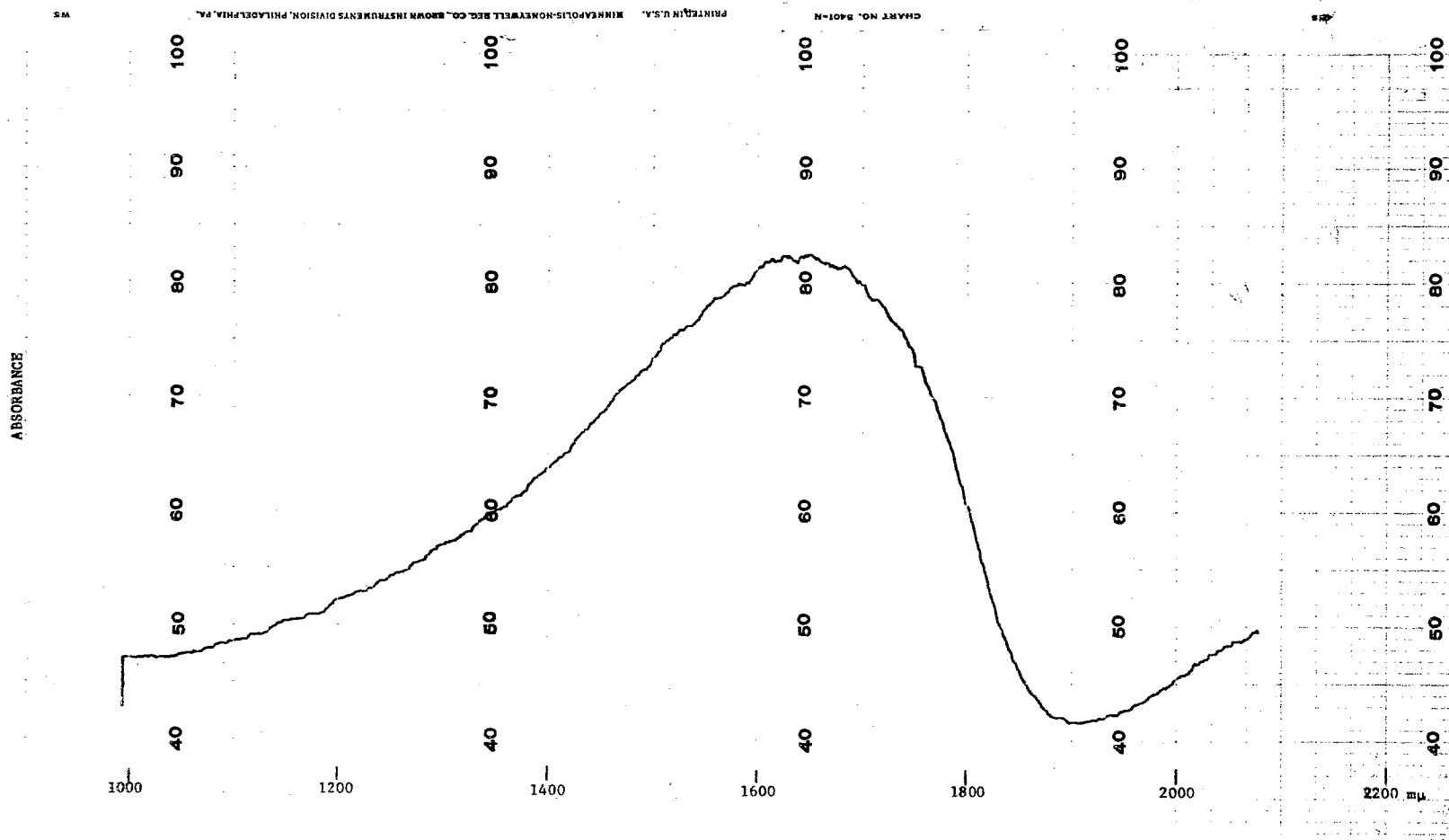
Solvent: CCl_4
F.B.: 0.4 cps

R.F. Field: 0.2 mG
S.T.: 250 sec

S.W.: 500 cps
S.O.: 0 cps

S.A.: 20
I.A.: off

Plate XI



Visible Spectrum of Reaction Mixture of Trityl Benzoate and Phenyl Grignard Reagent (1:1.3)

Plate XIII

Visible Spectrum of Reaction Mixture of Triethyl Benzoate and Phenyl Grignard Reagent (1:1.3), in Ethanol-Isopentane Solution

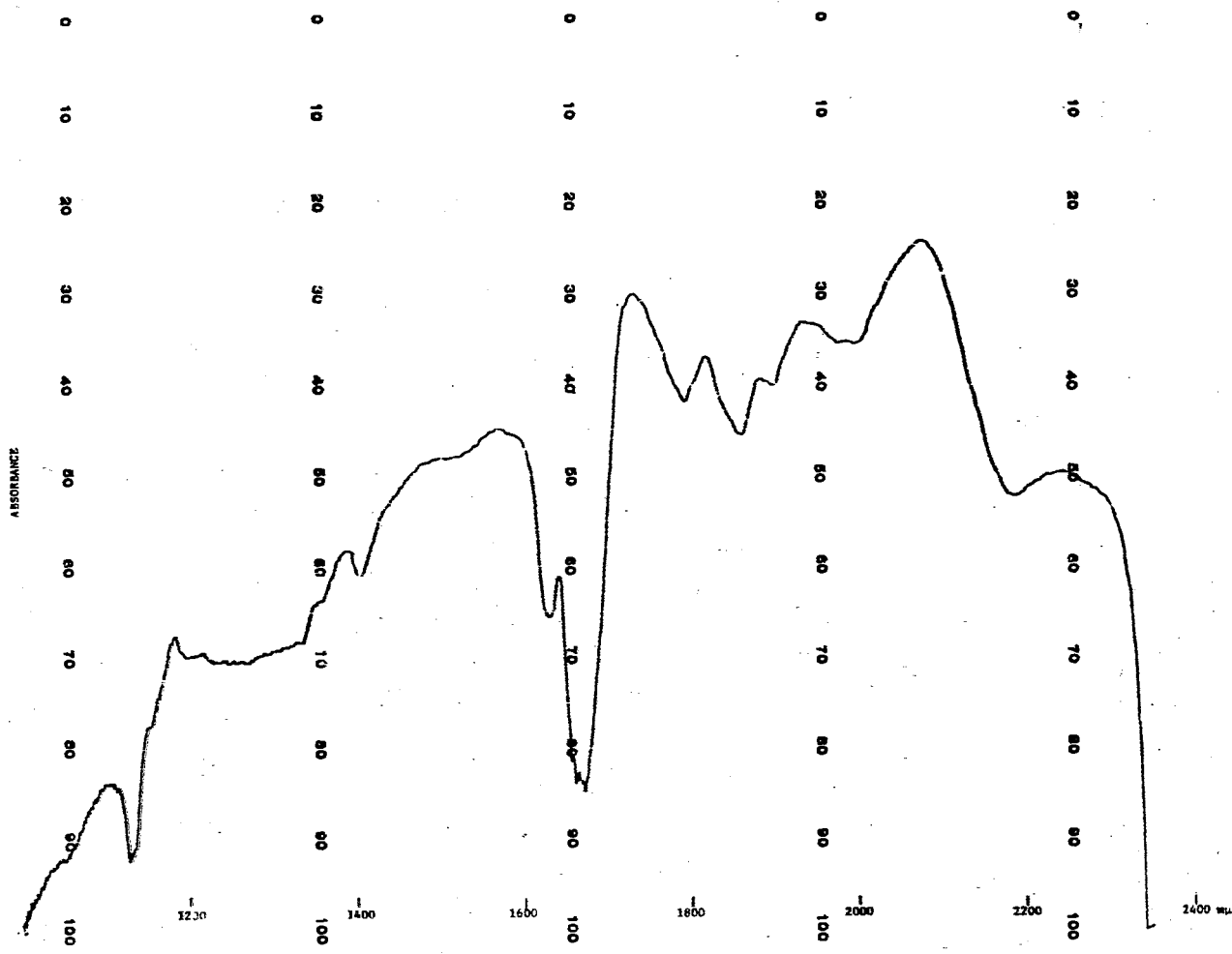
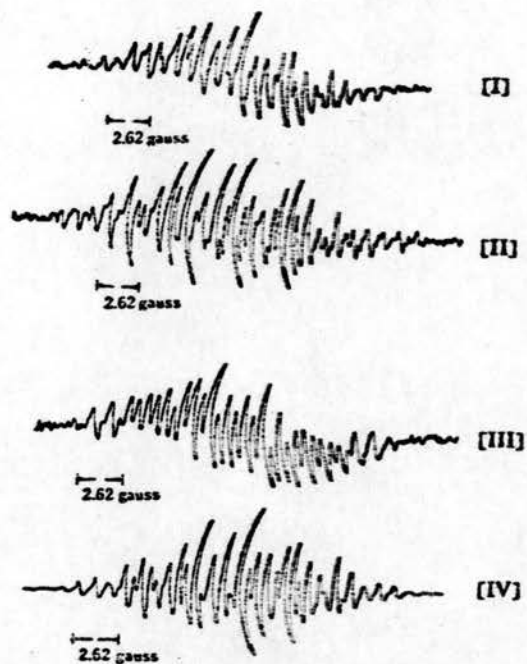
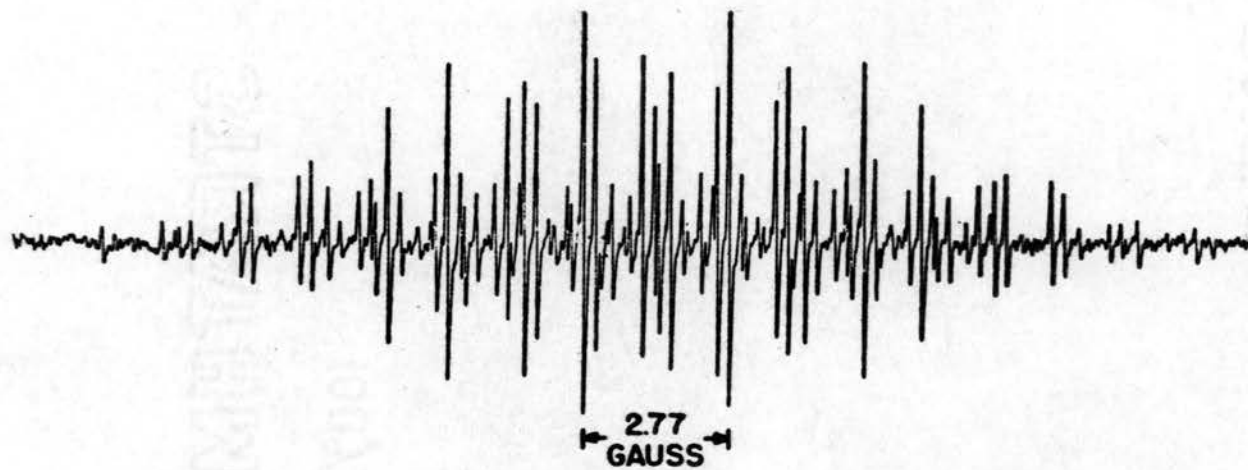


Plate XIII



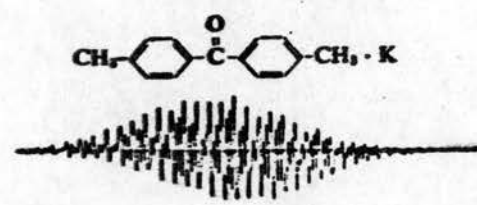
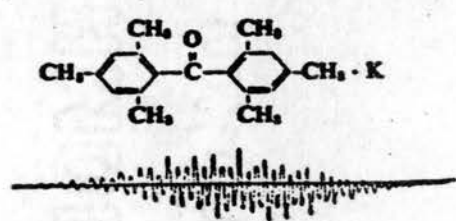
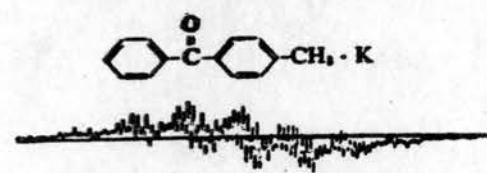
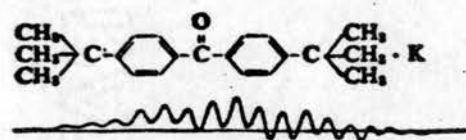
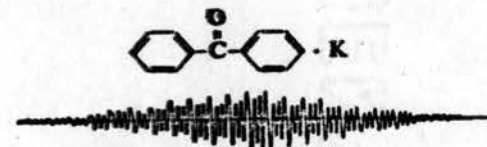
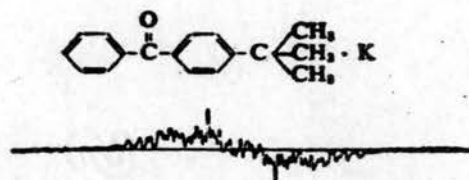
- The ESR spectra obtained during the course of some Grignard reaction.
- [I] Benzophenone/phenylmagnesium bromide reacting system at -25°C
 - [II] Benzophenone/*p*-tolylmagnesium bromide reacting system at -25°C
 - [III] *p*-Chlorobenzophenone/phenylmagnesium bromide reacting system at -20°C .
 - [IV] Benzophenone-magnesium ketyl at -20°C

Plate XIV



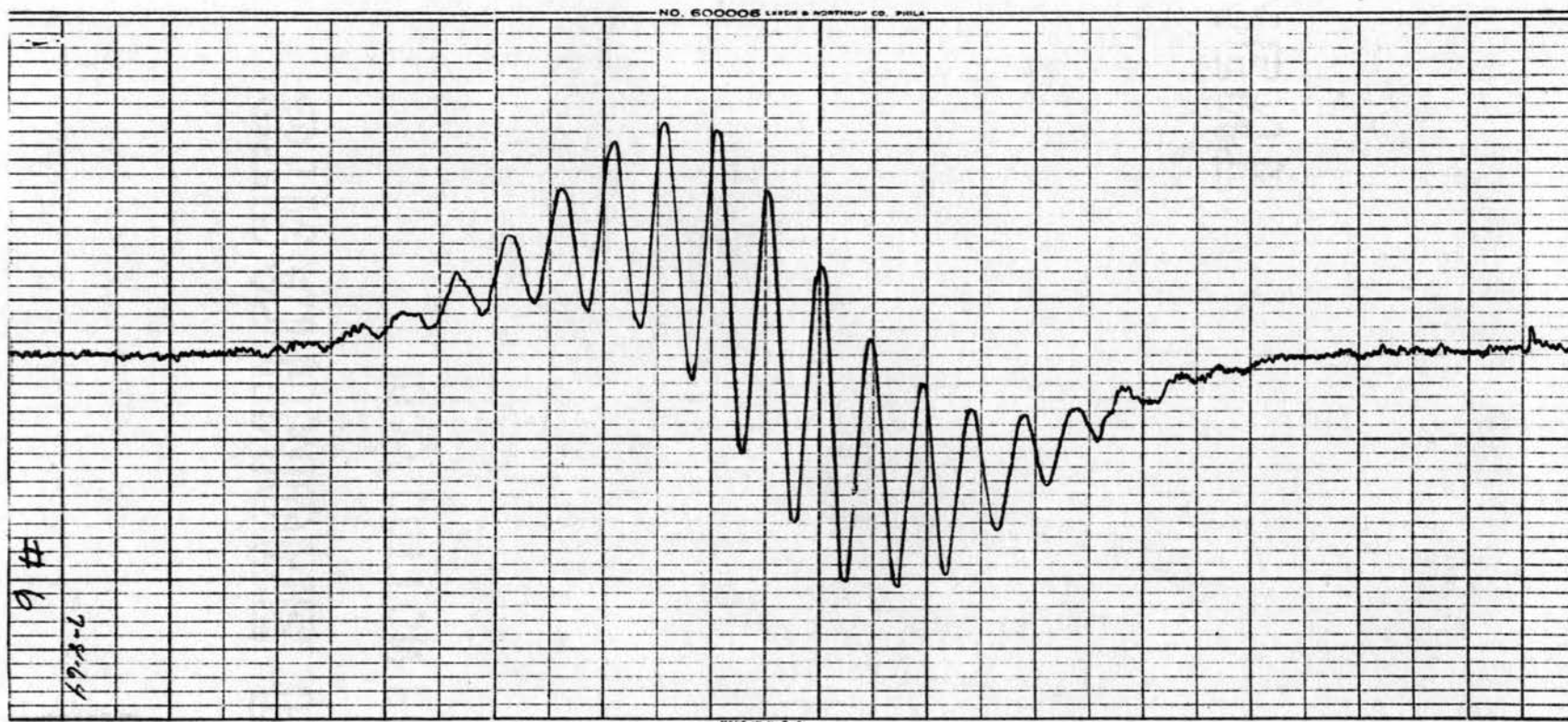
ESR Spectrum of a 10^{-3} Molar Solution of Trityl Radical in Toluene at -20°

Plate XV



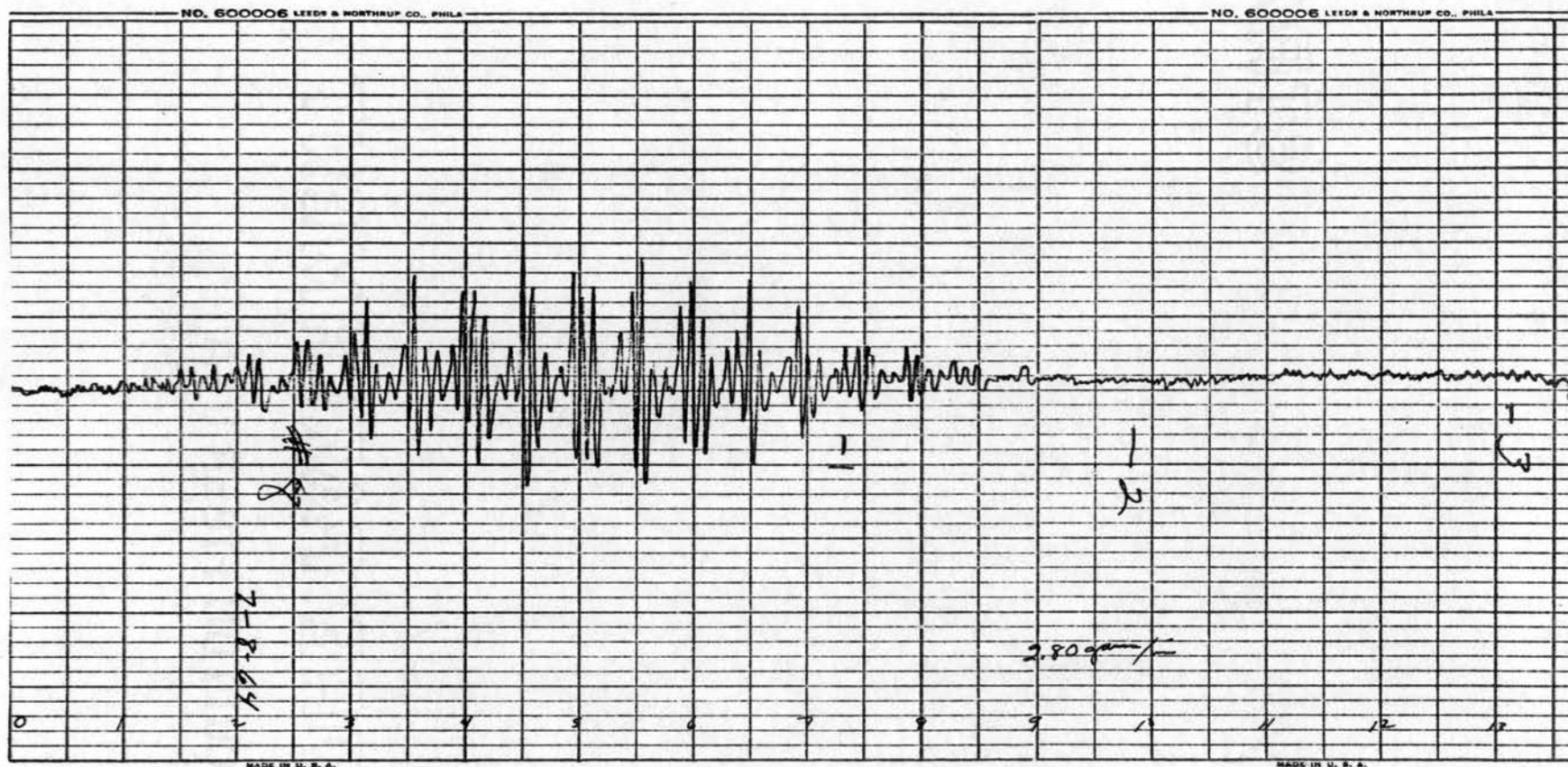
ESR Spectra of Several Substituted Benzophenone Derivatives

Plate XVI



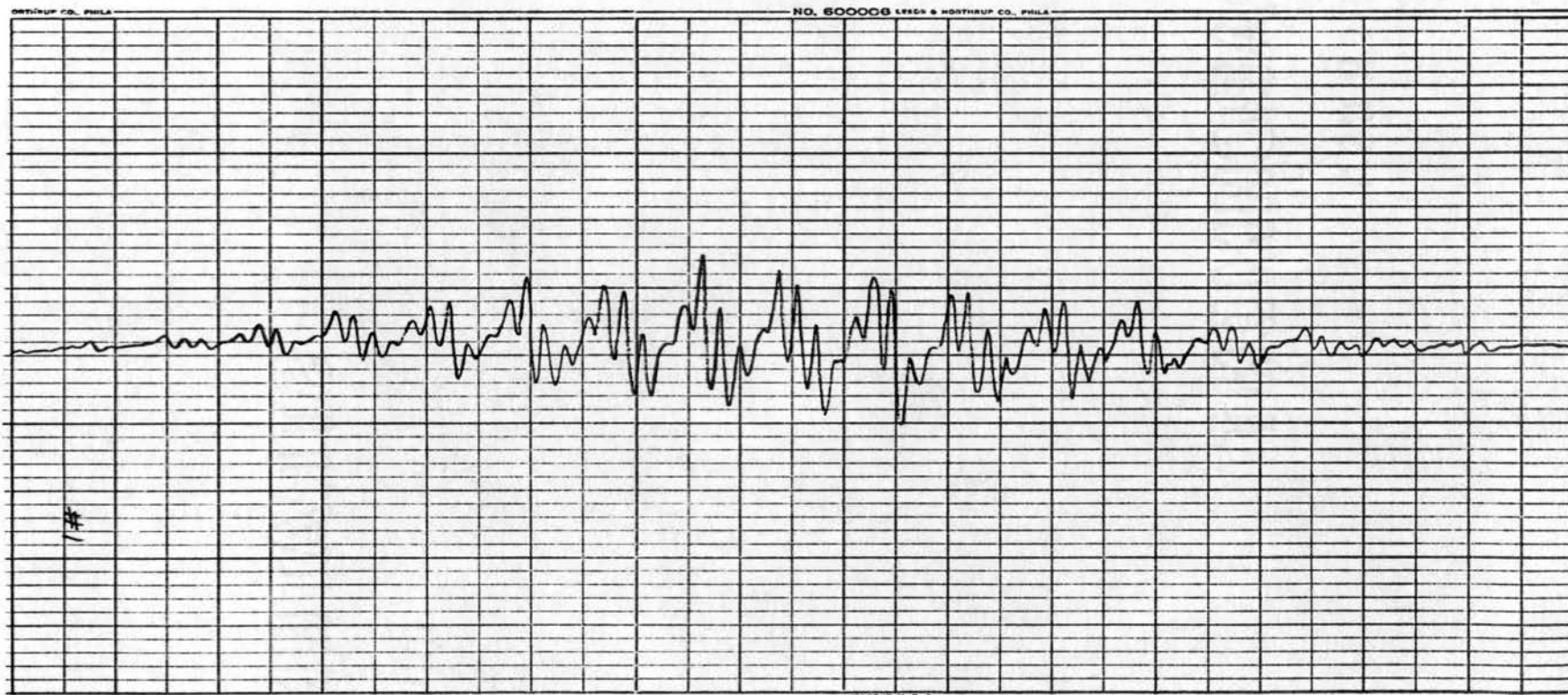
Broad, Unresolved Signal of Reaction Mixture of Trityl Acetate and Phenyl Grignard Reagent (1:1.3)

Plate XVII



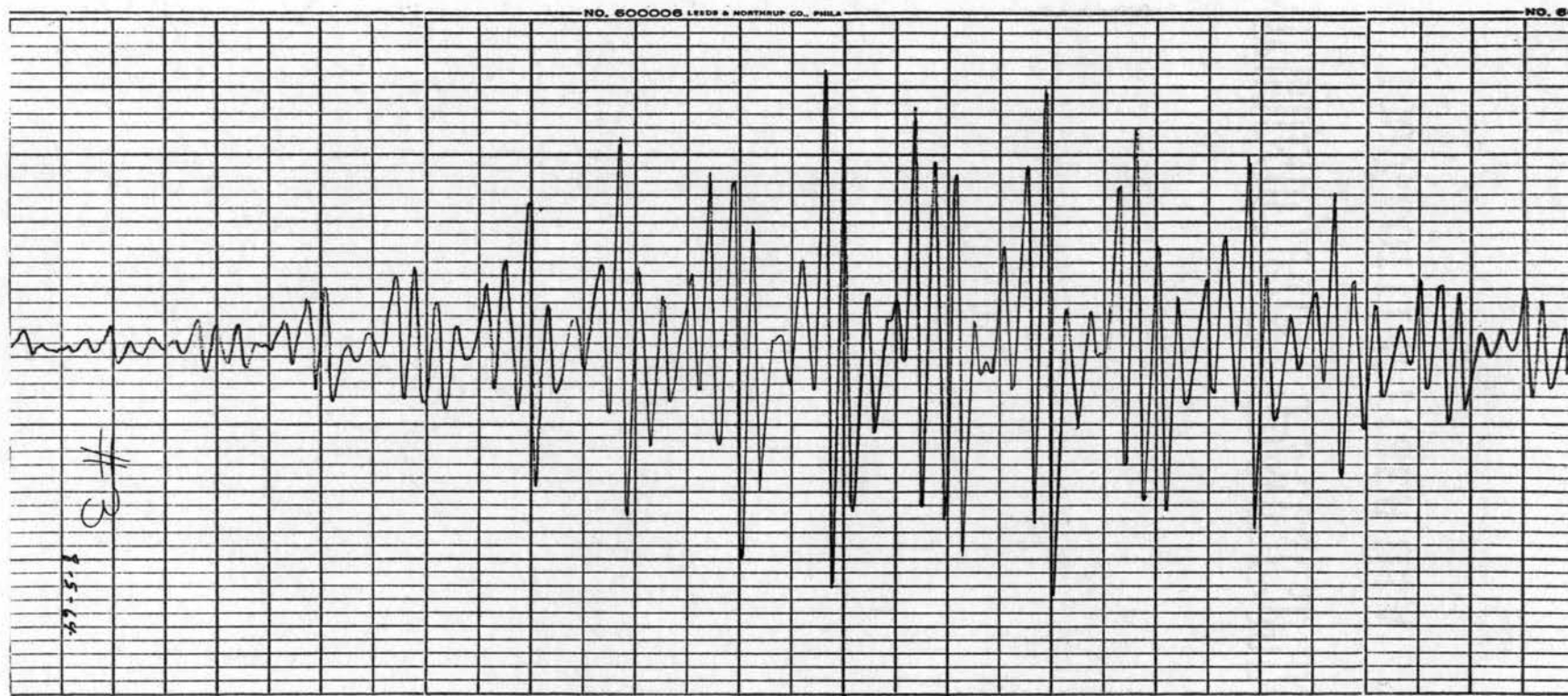
Strong, Resolved Signal of Reaction Mixture of Trityl Acetate and Phenyl Grignard Reagent (1:1.3) (1 hr.)

Plate XVIII



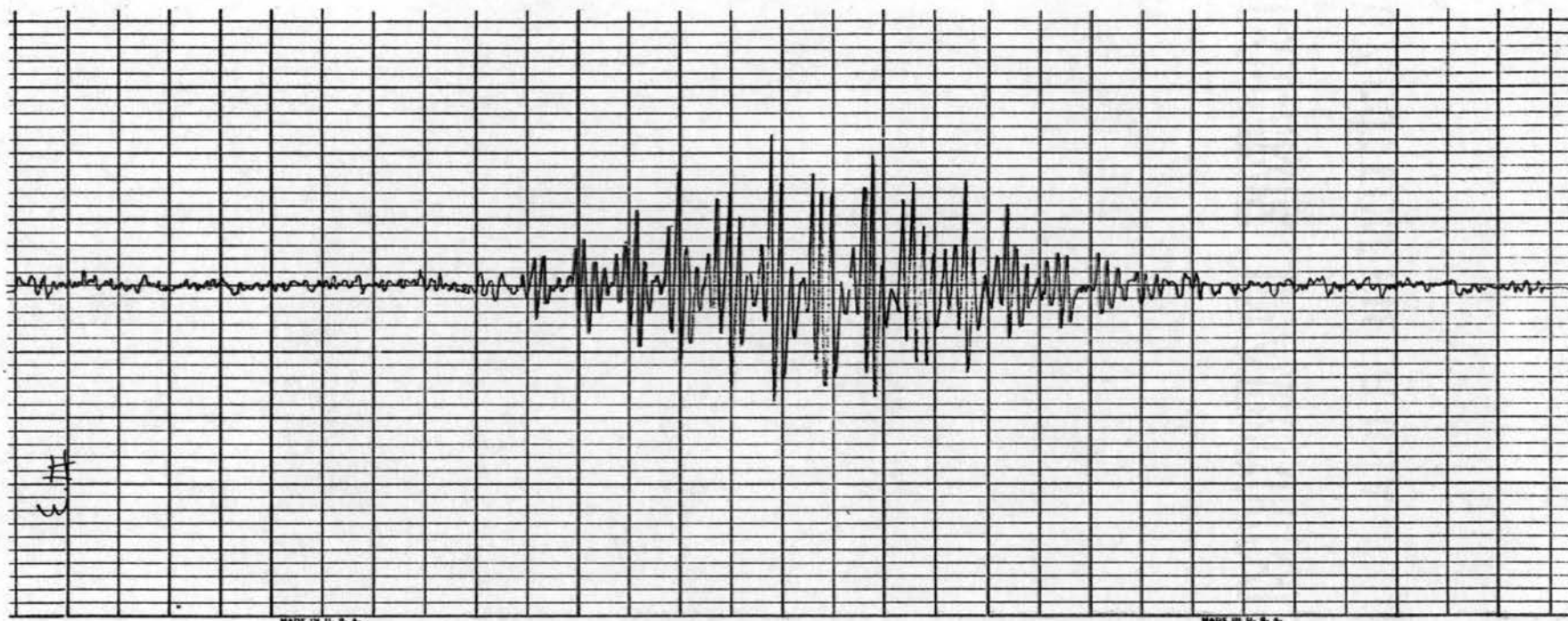
Weak, Resolved Signal of Reaction Mixture of Trityl Acetate and Phenyl Grignard Reagent (1:1.3) (20 hrs.)

Plate XIX



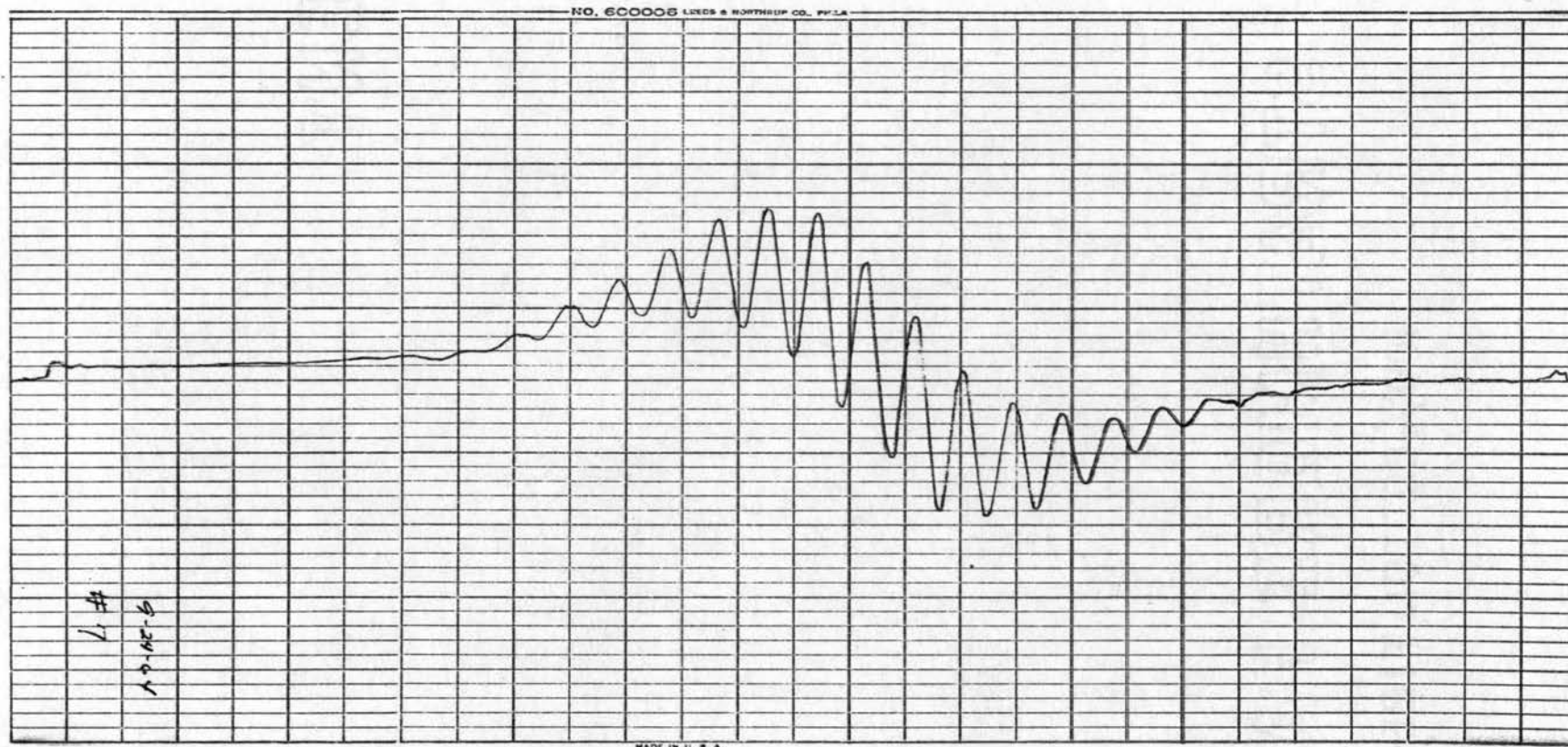
Strong, Resolved Signal of Reaction Mixture of Trityl Acetate and Phenyl Grignard Reagent (1:1.3)
(diluted with 5 cc. of ether)

Plate XX



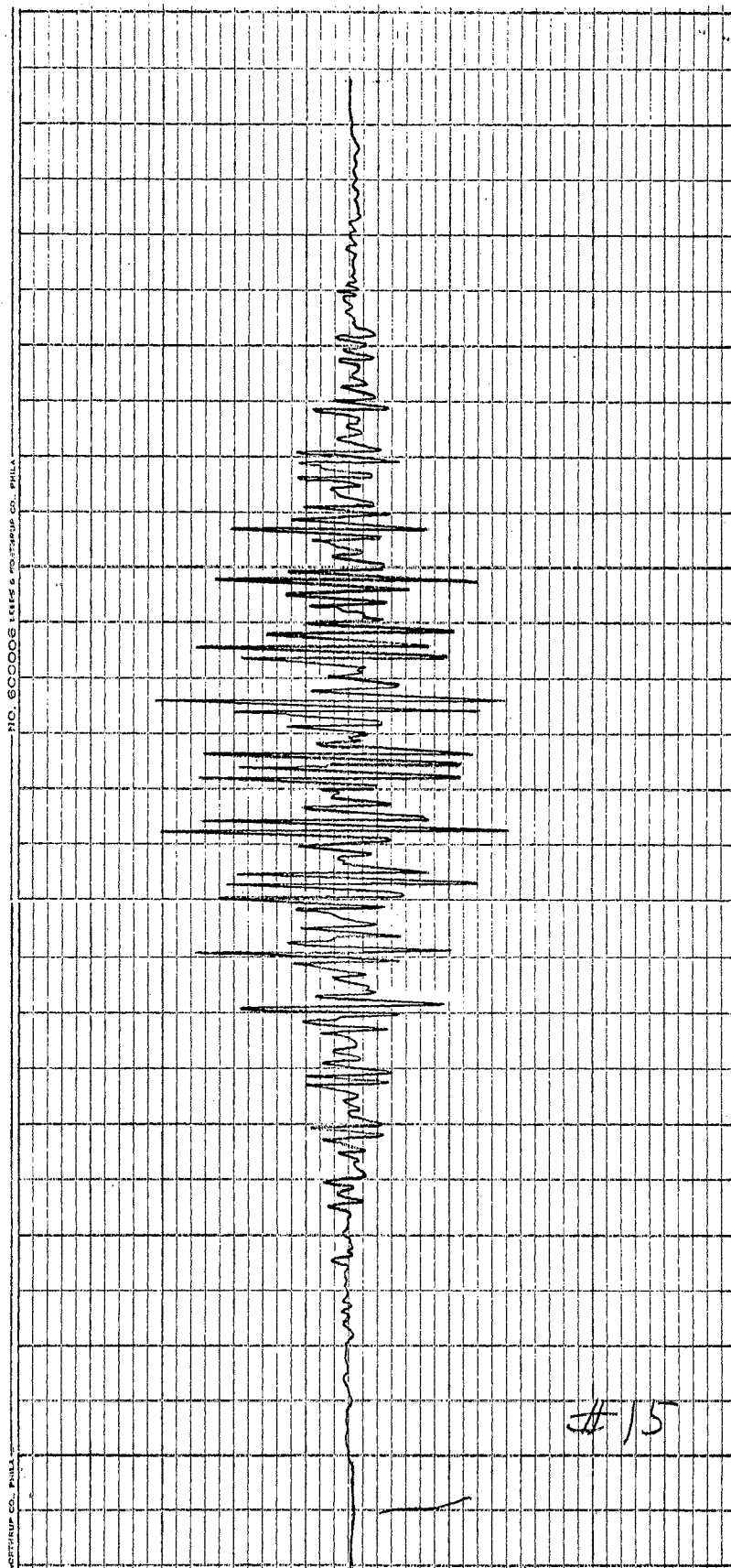
Strong, Resolved Signal of Reaction Mixture of Trityl Acetate and Phenyl Grignard Reagent (1:1.3)
(diluted with 20 cc. of ether)

Plate XXI



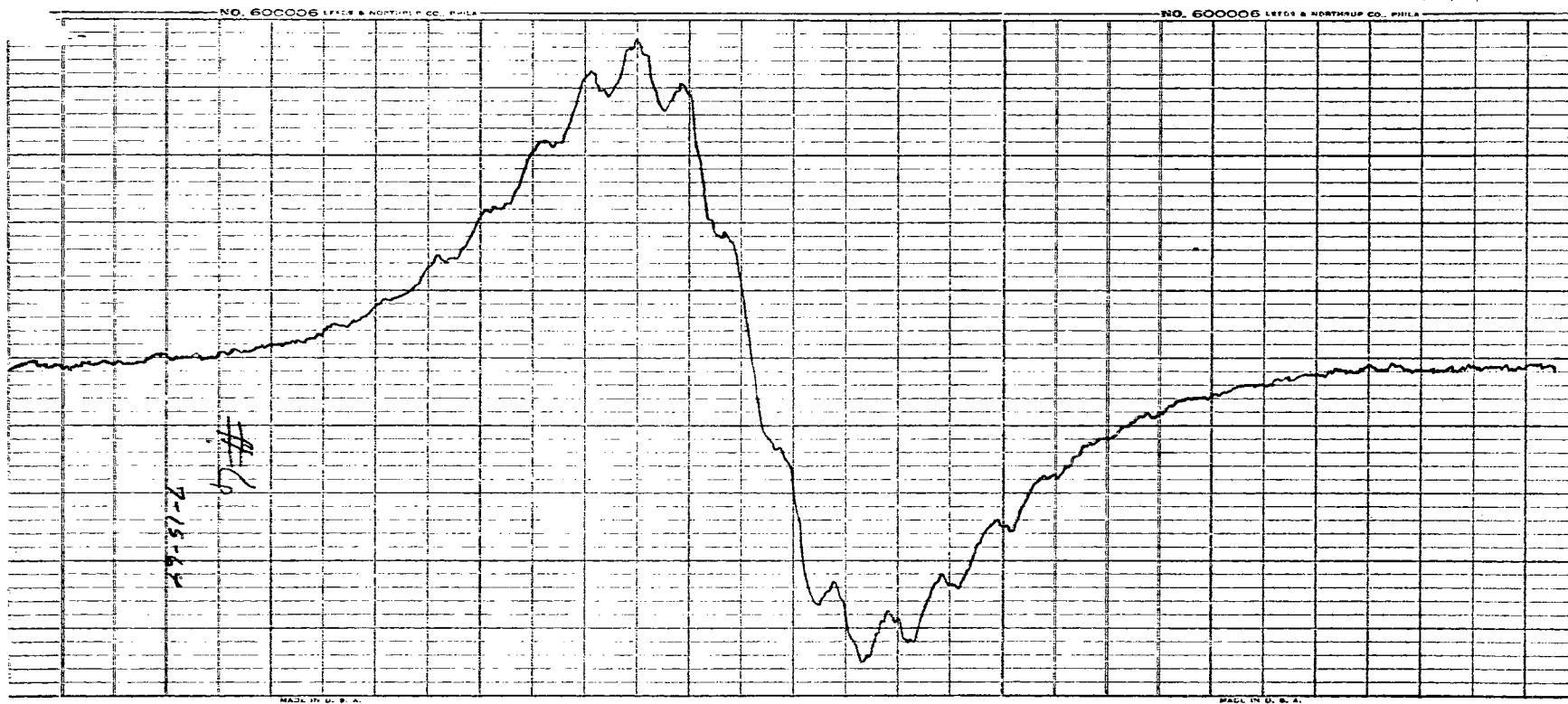
Broad, Unresolved Signal of Reaction Mixture of Trityl Benzoate and Phenyl Grignard Reagent (1:1.3) (2 hrs.)

Plate XXII



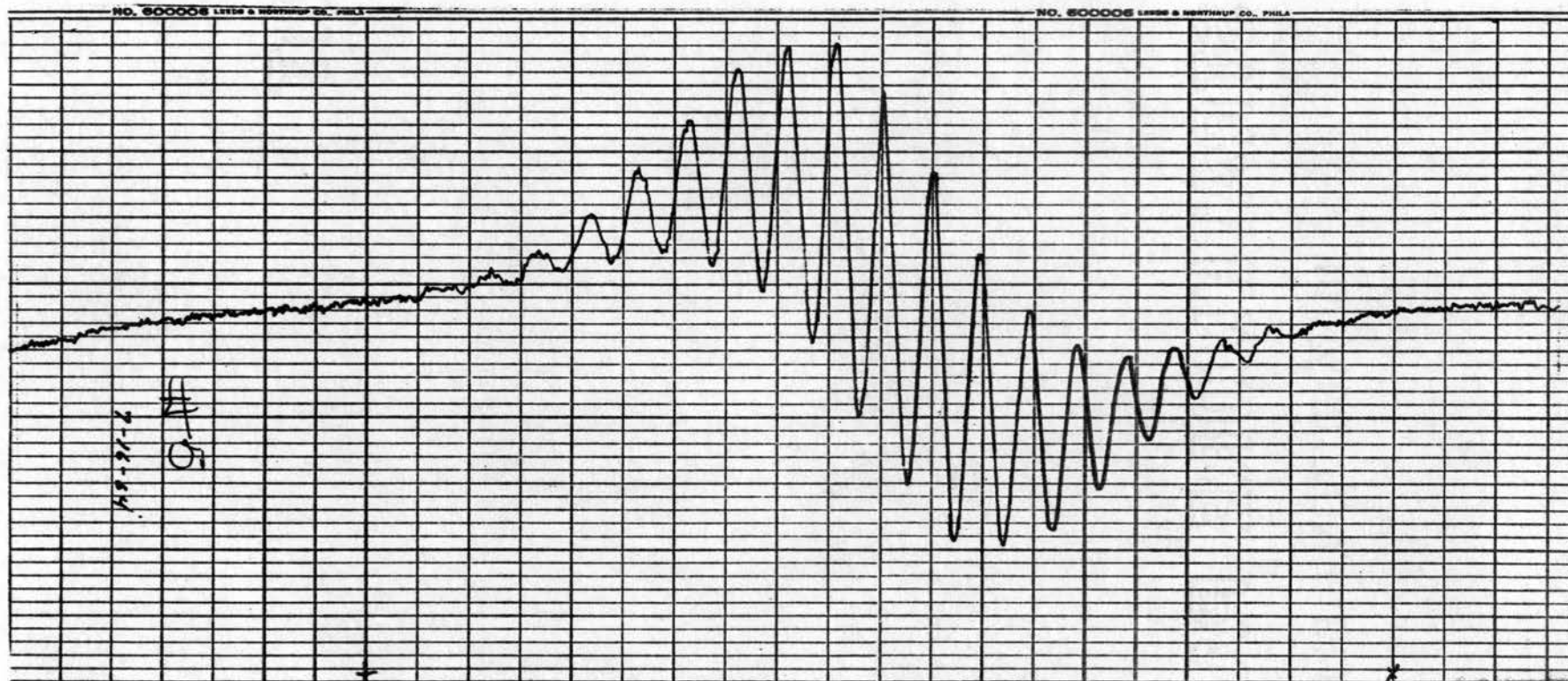
Strong, Resolved Signal of Reaction Mixture of Trityl Benzoate and Phenyl Grignard Reagent (1:1.3)
(4.5 hrs.)

Plate XXIII



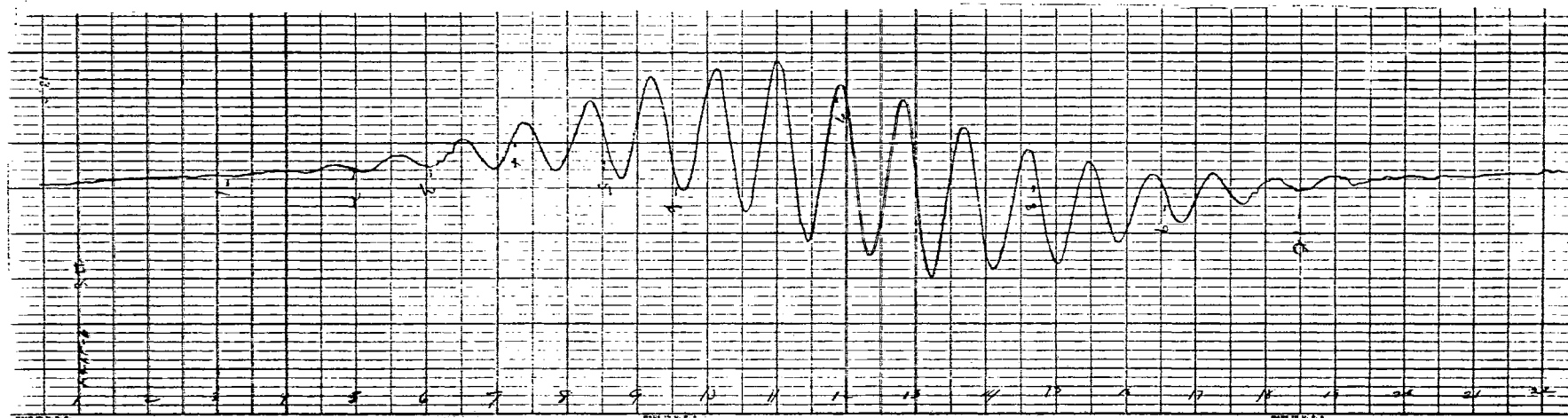
Broad, Unresolved Signal of Reaction Mixture of Trityl Benzoate and Phenyl Grignard Reagent (1:1.3)
(0.25 hrs.)

Plate XXIV



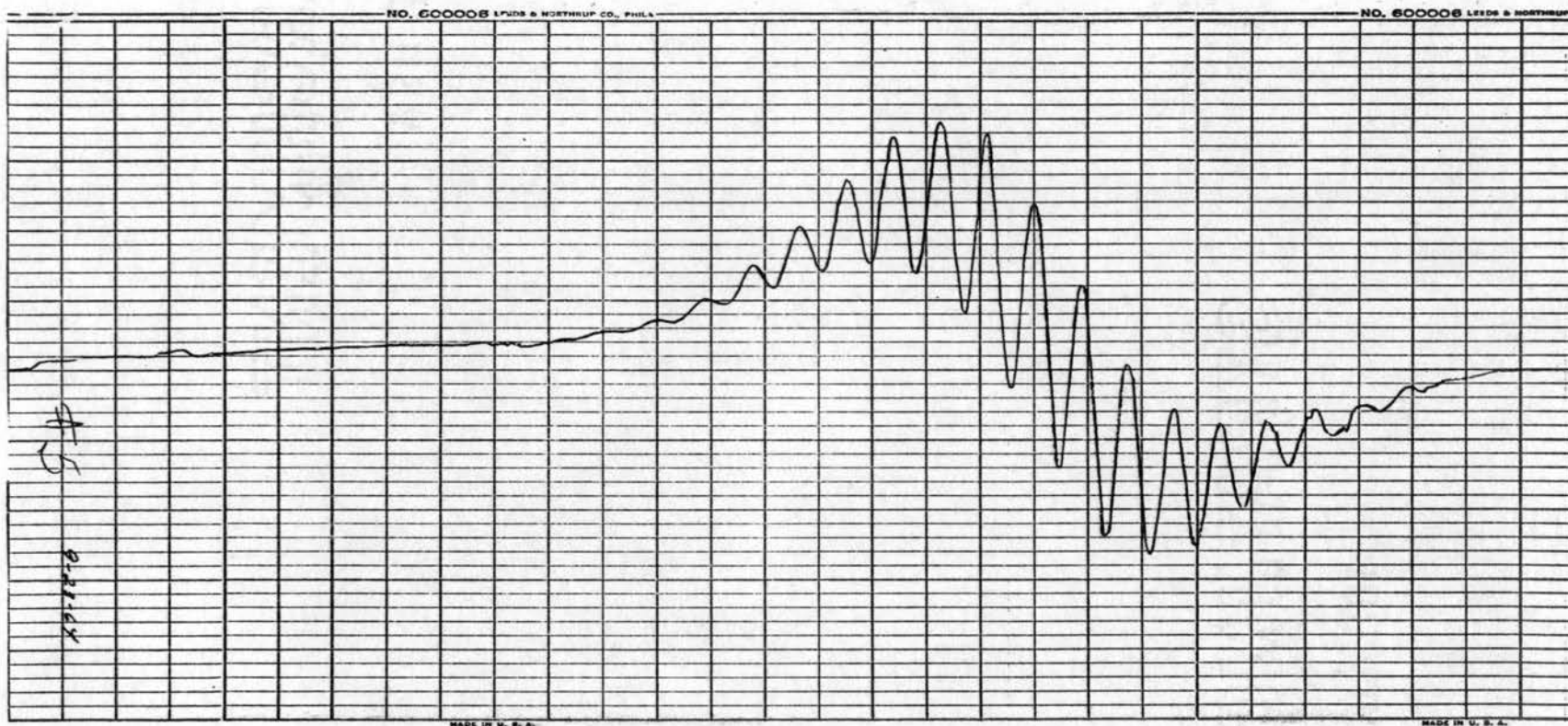
Broad, Unresolved Signal of Reaction Mixture of Trityl Benzoate and Phenyl Grignard Reagent (1:1.3) (1.5 hrs.)

Plate XXV



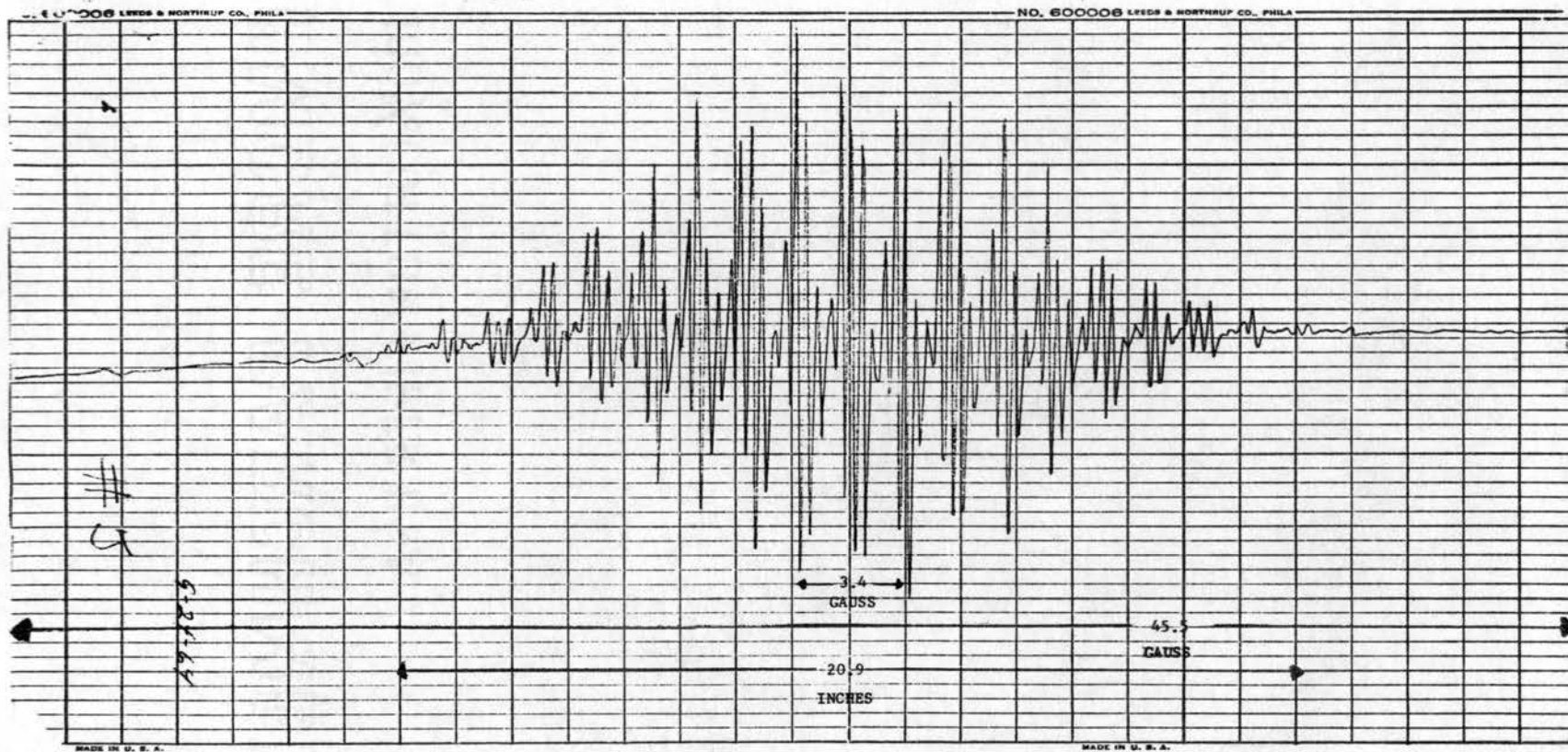
Weak, Unresolved Signal of Reaction Mixture of Trityl Benzoate and Phenyl Grignard Reagent (1:1.3)

Plate XXVI



Broad, Unresolved Signal of Reaction Mixture of Trityl Benzoate and Phenyl Grignard Reagent (1:1.3)

Plate XXVII



Strong, Highly Resolved Signal of Reaction Mixture of Trityl Benzoate and Phenyl Grignard Reagent (1:1.3) at -30°

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VITA

Ninette Latif Doss

Candidate for the Degree of

Master of Science

Thesis: AN INVESTIGATION OF THE REACTIONS OF TRITYL ESTERS WITH ALKYL
AND ARYL GRIGNARD REAGENTS

Major Field: Organic Chemistry

Biographical:

Personal data: The author was born in Cairo, U. A. R., on October 16,
1936, the daughter of Latif Doss and Agnes Zakhari.

Education: the author graduated from Amira Fawzia High School, Cairo,
in 1953. She received the Bachelor of Science degree from Cairo
University, Cairo, U. A. R. in May 1957..

Professional experience: The author was employed by the National
Research Center, at Cairo as a research scholar from December
1956 to December 1959. She was Teaching Assistant from
September 1963 to August 1964, and Research Foundation as-
sistant from September 1964 to February 1965 at Oklahoma
State University, Stillwater.