I. ALKYL-OXYGEN FISSION IN THE REACTION OF TRITYL ACETATE-^{18}O WITH PHENYLMAGNESIUM BROMIDE

II. MASS SPECTRA OF TRITYL-SUBSTITUTED COMPOUNDS--LOSS OF ^{12}C FROM $(C_6H_5)_3{}^{13}CH$ VIA ELECTRON BOMBARDMENT

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INTRODUCTION

This thesis constitutes a report on two independent investigations. Each major part is presented separately, each with individual subsections which are complete within themselves.

A thorough mechanistic examination of the reaction of a hindered ester, trityl acetate, with an aryl Grignard reagent, phenylmagnesium bromide, is discussed. This particular reaction does not parallel, in many respects, the normal course of the reaction of an ester with a Grignard reagent. A free-radical mechanism was postulated in Part I, on the basis of an ^{18}O-labeling study, to account for the abnormal distribution of products detected.

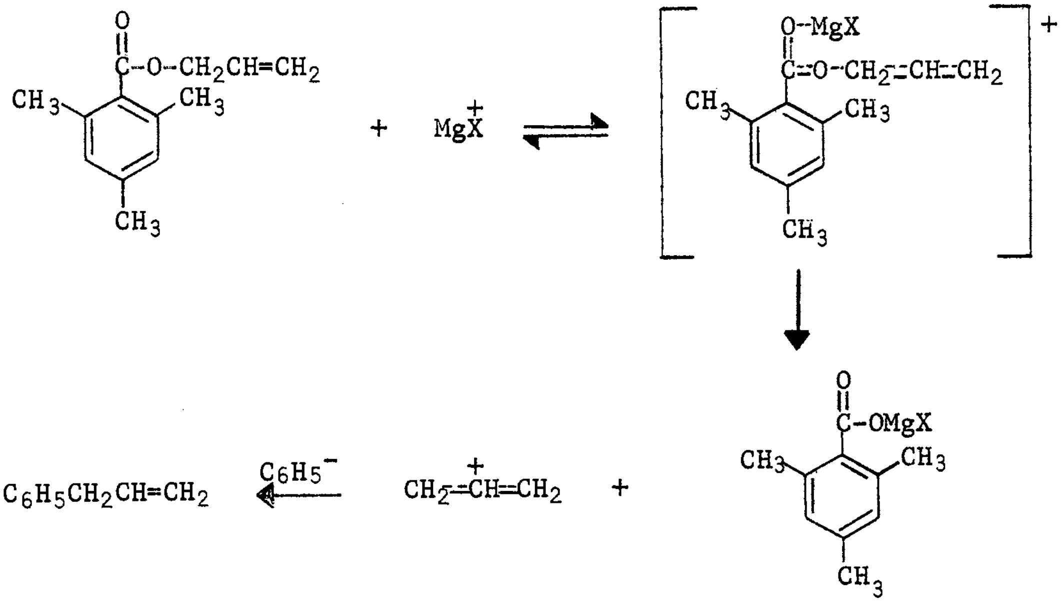
A mass spectral study of five classes of trityl compounds is discussed in Part II. It was found that the trityl portion of these compounds dominate their mass spectra. An examination of triphenylmethane labeled with carbon-13 in the α-position enabled the author to disprove a recently postulated mechanism for elimination of methyl radicals from triphenylmethane, as well as to propose a new mechanism for such an elimination.

CHAPTER I

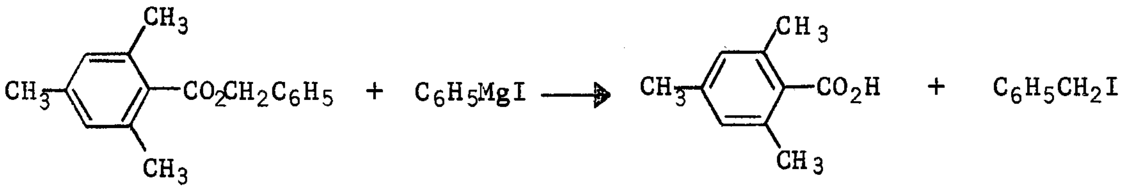
HISTORICAL

Reactions of Hindered Esters With Grignard Reagents

In one of the earliest studies of the reactions of hindered esters with Grignard reagents, Arnold[1] reported that allylic esters with greatly hindered carbonyl groups are cleaved by certain Grignard reagents to give magnesium salts and hydrocarbons. It was believed that the mechanism of this cleavage was comparable to that involved in the reaction of methyl mesityl ketone with the same Grignard reagents (also studied in the aforementioned paper[1]). It was postulated that allyl mesitoate reacted with phenylmagnesium bromide to give allylbenzene (67-70%) and the halomagnesium carboxylate almost quantitatively.



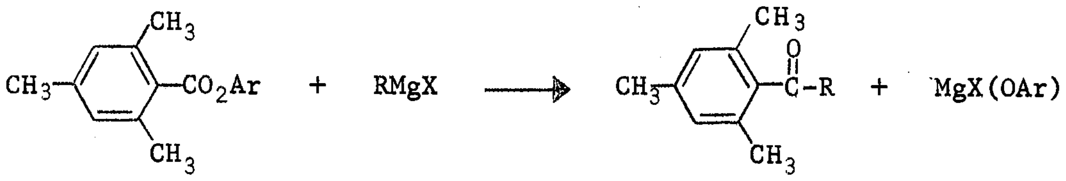
In another study of the reactions of Grignard reagents with highly hindered esters, Fuson[18] found that alkyl mesitoates, when treated with alkylmagnesium halides, yield mesitoic acid and the alkyl halide formed from the alkyl group of the ester and the halogen atom of the Grignard reagent. No hydrocarbon formation was observed in any of the reactions studied but GLC analysis was not available. For example:



65% 70%

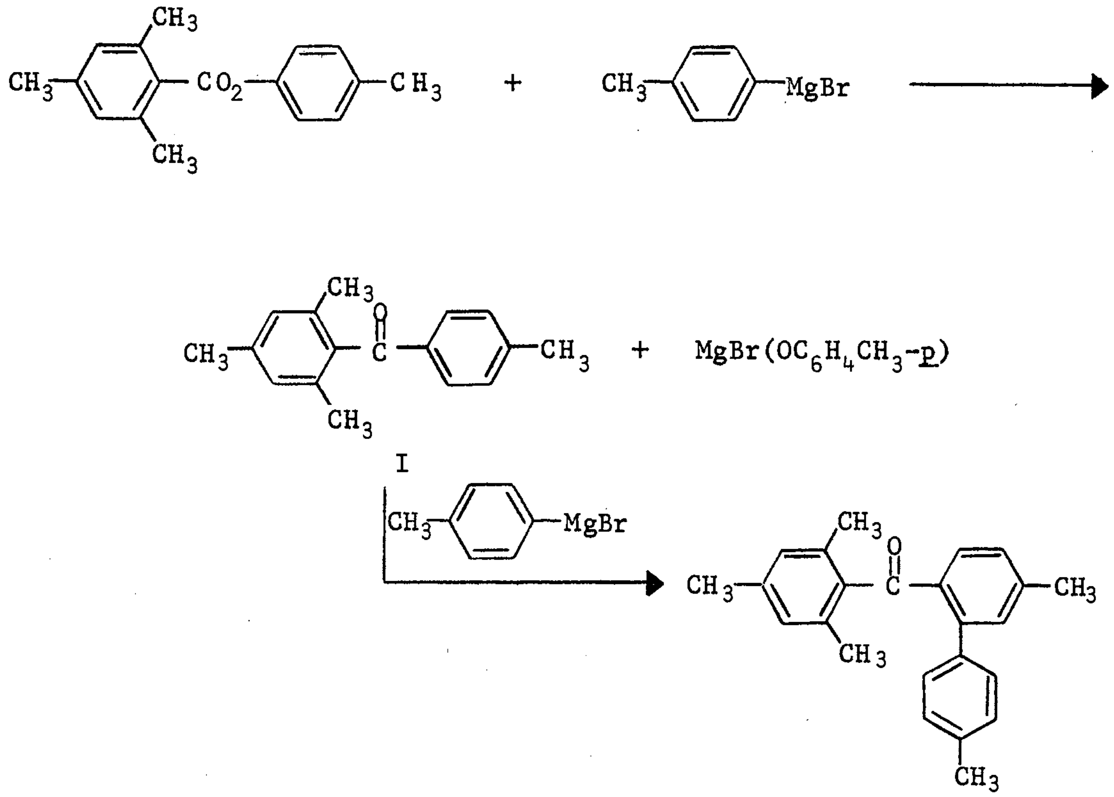
(after hydrolysis)

Aryl mesitoates reacted with the Grignard reagents in an entirely different manner. When alkylmagnesium halides were used, the ester was converted into the corresponding alkyl mesityl ketone and the phenol derived from the aryl moiety that was removed.



In this way high yields of methyl mesityl ketone and p-cresol were obtained from p-tolyl mesitoate and methylmagnesium iodide. In a similar manner p-tolyl 2,4,6-triisopropylbenzoate reacted with methyl- and ethylmagnesium halides to yield, respectively, 2,4,6-triisopropylacetophenone and 2,4,6-triisopropylpropiophenone.[18]

The products obtained by the action[18] of arylmagnesium halides on aryl mesitoates were found to be more complex, but the first step in each case appeared to be the formation of the ketone.



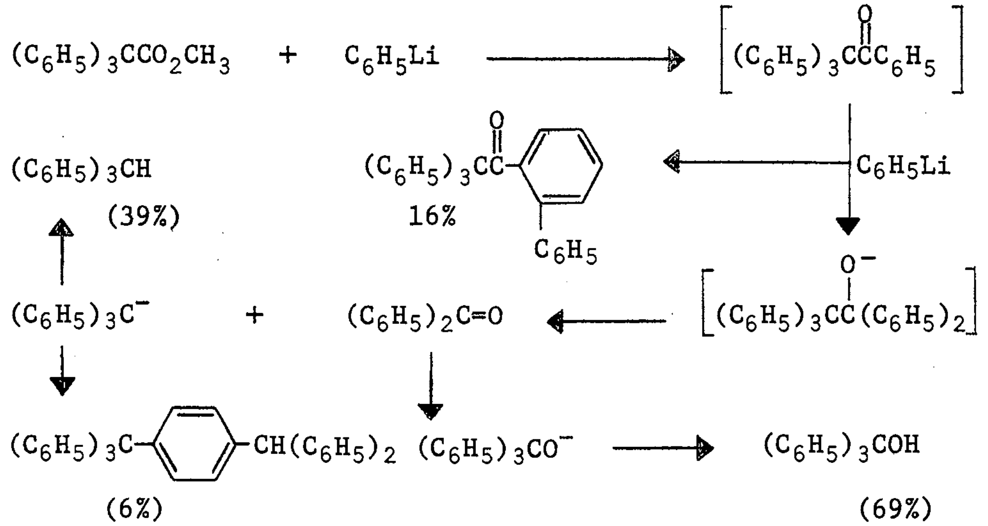
This result may be explained by assuming that the ketone(I) is formed first just as with the alkylmagnesium halides. It had been shown that ketones like I may react with Grignard reagents in such a manner as to undergo arylation in an ortho-position (1,4-addition).

Fieser and Heymann[17] first reported the reaction of a trityl ester of a carboxylic acid with a Grignard reagent. It was found that trityl acetate interacted with methyl Grignard reagent to yield 1,1,1-triphenylethane (68%). This result clearly shows that the replacement of an acetoxy group can occur in such hindered esters.

Doss[14] has recently described the reactions of several trityl esters of carboxylic acids with alkyl Grignard reagents, a reaction which forms trityl hydrocarbons in good yields. The first report, however, of the reaction of a trityl ester $[RCO_2C(C_6H_5)_3]$ with an aryl Grignard reagent did not appear until 1965, in the thesis by Doss.[14] It was later discussed by Shupe[31] and quite recently in a communication by Berlin and co-workers.[8] Trityl acetate was reported to react with phenylmagnesium bromide in ether and at room temperature (8 hrs.). Use of a 1.3:1 molar ratio of Grignard reagent to ester resulted in the isolation of trityl peroxide in yields ranging from 60 to 70 per cent. Analysis of the reaction mixture by GLC and mass spectrometry revealed many products besides trityl peroxide: acetic acid (80.4%), triphenylmethane (22.5%), acetophenone (14%), benzophenone (12%), triphenylmethanol (∿5%), tetraphenylmethane (∿2%), biphenyl (23%) and 1,1-diphenylethanol (∿2-3%). This data is an average of several experiments.

The occurrence of trityl peroxide suggested a trityl radical as a precursor. ESR measurements (for type of spectrometer and techniques used see reference 6) were made on the solution of trityl acetate and phenylmagnesium bromide. Although a strong signal with broad lines was observed a few minutes after the reactants were mixed, a highly resolved complex spectrum was detectable after 1 hr. which was very similar to that reported for trityl radical.[12,24] A <u>para</u>- coupling of 2.77 G was found in toluene at -20°. The total signal range was 21.5 G with a value of 3.4 G for the strongest coupling constant. Neither trityl acetate nor phenylmagnesium bromide in ether gave an ESR signal; the lack of an ESR signal was also reported for freshly prepared <u>n</u>-butyl Grignard reagent in tetrahydrofuran.[29]

Some interesting observations[33] involving the reaction of phenyllithium with methyl triphenylacetate should be interjected here. It was found that with excess phenyllithium the products isolated were triphenylmethane (39%), triphenylmethanol (69%), a hydrocarbon (6%) and a ketone (16%). Presumably a ketone intermediate undergoes both conjugate addition and 1,2-addition. Thus by transposition of the methyl and trityl groups of trityl acetate one obtains a hindered ester which still undergoes simple carbonyl addition with an aryllithium reagent.



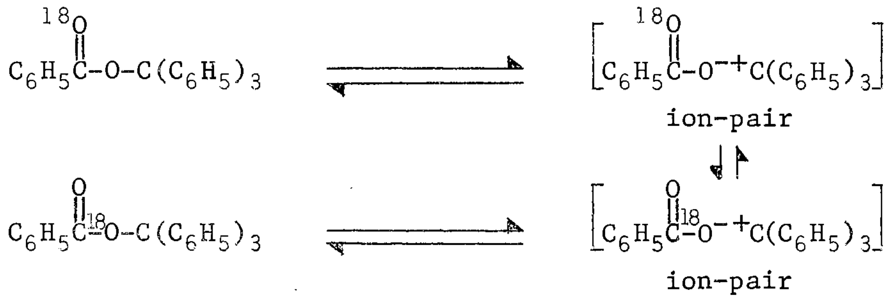
A radical-anion was postulated[33] to give rise directly to triphenylmethane, although it most likely is an anion as would seem obvious from the equations shown. The authors indicate[33] that no significant reaction product has been undetected in the analysis; but it should be pointed out that the material balance is actually quite poor as the triphenylmethanol is derived from the non-trityl portion of the ester and cannot be included with the percentages given for the other products.

Studies Involving Ionization of Trityl Compounds

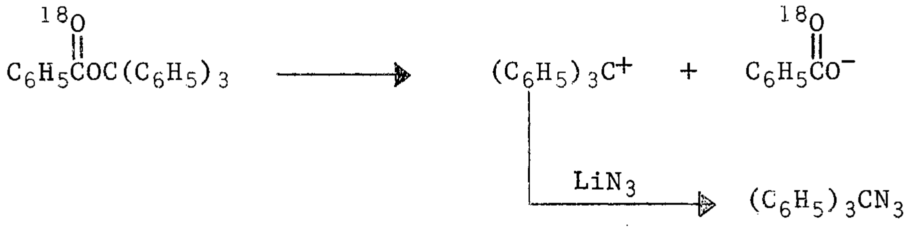
In view of the extensive work concerning the ionization of trityl halides and esters, it was not considered unreasonable to postulate[8] that ionization of the ester occurs to give the trityl cation as the first step in the reaction sequence leading to the formation of trityl peroxide (from trityl acetate and phenylmagnesium bromide).

Hill[22] has reported trapping the trityl cation by the azide ion in acetone and dioxane solutions of trityl halides and trityl acetate. In another study[16] concerning trityl halides (in m-cresol), the effect on ionization of temperature, $(C_6H_5)_3CX$ concentration and halide used (Br or Cl) was examined spectrophotometrically. The greatest ionization reported for a trityl halide was 68 ± 7%. (It was found that tri-p-tolylmethyl chloride ionized 100 ± 10%.)

Trityl benzoate (carbonyl-^{18}O) was examined by Winstein and Appel[35,36] in moist acetone to which had been added various salts, such as $LiClO_4$, LiN_3, $(C_4H_9)_4NN_3$ and $(C_4H_9)_4NO\overset{O}{\overset{\|}{C}}C_6H_5$. It was postulated that ^{18}O-equilibration of trityl benzoate proceeds by way of an ion pair intermediate not easily capturable by added salts or water.



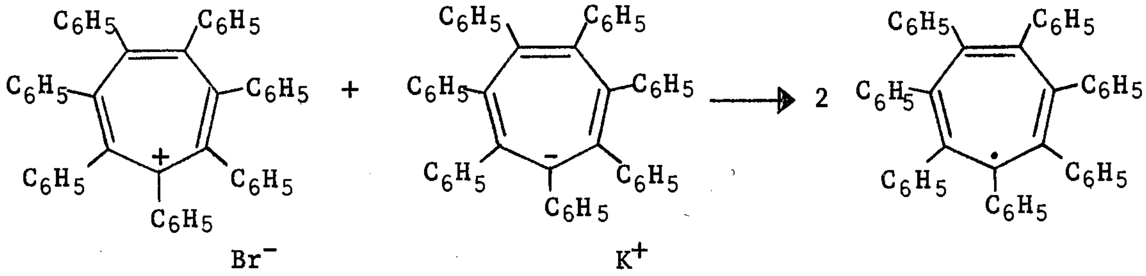
Chemical capture (solvolysis or azide formation) proceeds very predominatly by way of trityl cations which have become free and no longer associated with the $C_6H_5\overset{^{18}O}{\overset{\|}{C}}O-$ portion of the original molecule $(C_6H_5\overset{^{18}O}{\overset{\|}{C}}OC(C_6H_5)_3)$.



Ion pair formation was also suggested by Swain and Tsuchihashi[32] in 1962 in their work concerning the ionization of trityl benzoate, and was deduced from rate studies.

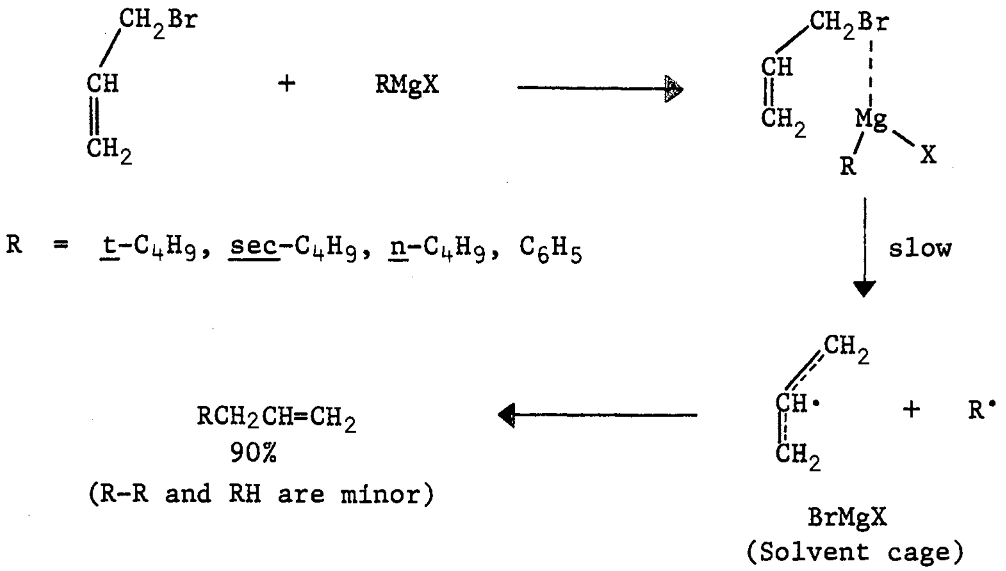
Electron Transfer Involving Organometallic Reagents

Several recent articles have indicated that the occurrence of radical mechanisms in the reactions of organometallic reagents may be more common than previously thought. Breslow[11] has reported an electron transfer from potassium heptaphenylcycloheptatrienide to heptaphenyltropylium cation to give hetaphenylcycloheptatrienyl radical in 1,2-dimethoxyethane.



Bilevitch[9] has summarized various reactions where electron transfer is the first step in nucleophilic substitution reactions. The fact that a great variety of organic and inorganic species (metals, organometallic compounds, anions, Lewis bases, etc.) are capable of electron transfer is now evident.[9] Carbonium ions, aromatic hydrocarbons and molecules containing electronegative substituents are known to accept unpaired electrons with the formation of radicals or anion-radicals.[9]

Free radicals have been detected by ESR in several reactions involving Grignard reagents. Gough and Dixon[20] have suggested radical intermediates based on ESR studies in Grignard coupling reactions with allyl bromide to form hydrocarbons. It is noteworthy that neither reagent by itself gave an ESR signal.

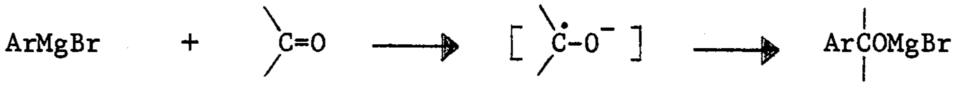


Russell[29] has shown that n-butylmagnesium bromide in tetrahydrofuran will form radical anions with benzophenone, fluorenone, and a variety of non-benzenoid aromatic compounds. He formulates the general reaction as:

$$D^- + A \longrightarrow \underset{\text{solvent cage}}{[\,D^{\cdot -} + A^{\cdot}\,]} \longrightarrow DA^-$$

where D = donor and A = acceptor.

Maruyama[28] has found that arylmagnesium bromides react with ketones to form ketyls, presumably as shown below:



In addition, Lamb[26] demonstrated that a radical mechanism must occur in the reaction of Grignard reagents with oxygen, and Seyferth[30] suggested a free-radical mechanism for the reaction of methylmagnesium bromide with 7,7-dibromobicyclo[4.1.0]heptane.

The overwhelming tendency for the trityl cation to be reduced to the trityl radical is apparently an important property of the former. Simple MO theory predicts[10] that the reduction of the trityl cation results in no loss of resonance energy, although this is of course an approximation. Indeed, it has been observed[23] that trityl cations undergo easy reduction at the dropping mercury electrode. Furthermore, a report[27] is available which indicates that an electron-exchange equilibrium actually exists between trityl cation and trityl radical in acetic-trifluoroacetic acid solution, thus indicating a low energy barrier between the two moieties.

$$(C_6H_5)_3C^+ + (C_6H_5)_3C\cdot \rightleftharpoons (C_6H_5)_3C\cdot + (C_6H_5)_3C^+$$

Specific examples of reduction of the trityl cation by organometallic reagents have been reported.[8,9,15] Trityl perchlorate and trityl chloride react with potassium t-butoxide to form trityl radicals (by ESR detection).[9]

$$(C_6H_5)_3C^+ClO_4^- + (CH_3)_3CO^-K^+ \longrightarrow (C_6H_5)_3C\cdot + (CH_3)_3CO\cdot + K^+ + ClO_4^-$$

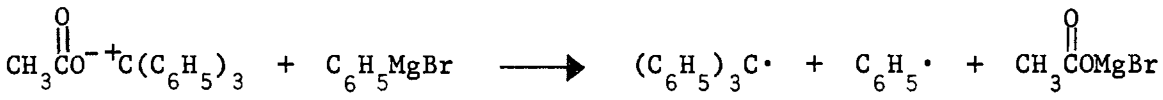
It was also observed[9] that trityl radicals were present in systems containing trityl chloride and sodium phenoxide (in dioxane-THF solution). Indeed this is apparently true also even if the combination of pyridine and phenol are used instead of the phenoxide, although in the latter case the concentration of trityl radicals corresponds to about 0.1% of the total amount of trityl chloride.

Trityl chloride reacts with ethyllithium[15] to form trityl radicals, as well as triphenylmethane, 1,1,1-triphenylpropane, ethylene and ethane.

$$(C_6H_5)_3CCl + CH_3CH_2^-Li^+ \longrightarrow (C_6H_5)_3C\cdot + CH_3CH_2\cdot + LiCl$$

Only about 20% of the trityl radicals result in the formation of hexaphenylethane.

Trityl radicals have also been suggested by Berlin and co-workers,[8] who propose that phenylmagnesium bromide provides an electron to trityl cation (from trityl acetate) to form trityl radical. This trityl radical then reacts with O_2 to form trityl peroxide.



$$CH_3\overset{\overset{O}{\|}}{C}O^{-}\,{}^{+}C(C_6H_5)_3 + C_6H_5MgBr \longrightarrow (C_6H_5)_3C\cdot + C_6H_5\cdot + CH_3\overset{\overset{O}{\|}}{C}OMgBr$$

Interestingly, a careful survey of the review of Kharasch and Reinmuth in 1954[25b] did not reveal one example in which a study was made of reactions of esters with Grignard reagents in the presence of metal ions such as Co^{++}, Cu^{++}, etc. Such metals are known to cause radical formation in reactions of Grignard reagents.[25b] Of course the literature from 1954 to the present needs to be surveyed to ascertain if this area has been examined since the review.

CHAPTER II

DISCUSSION OF RESULTS AND CONCLUSIONS

As has been previously reported from this Laboratory,[8,31] trityl acetate reacts with phenylmagnesium bromide (1:1.3) to yield trityl peroxide and acetic acid as major products. In an attempt to explain the mechanism of this anomalous reaction, it was decided to label the trityl acetate used as starting material with ^{18}O, and then after reaction with the phenyl Grignard reagent, to determine the location of ^{18}O in the products. It should be mentioned that the labeled trityl acetate also contained some ^{2}H (see Experimental). Table I shows the quantitative analysis of percent yields and percent ^{18}O in the products resulting from reaction of trityl acetate-^{18}O(and-^{2}H) and phenylmagnesium bromide (1:1.3).

TABLE I

ANALYSIS OF REACTION OF TRITYL ACETATE-^{18}O[a] WITH PHENYLMAGNESIUM BROMIDE (1:1.3)

Product	Typical Yield %[b]	^{18}O%[c]
Trityl Peroxide	60	0
Acetic Acid	80	50[d]
Acetophenone	14	21[d]
Triphenylmethane	23	--
Benzophenone	12	0
Triphenylmethanol	∿5	2
Biphenyl	23	--
Tetraphenylmethane	∿2	--
1,1-Diphenylethanol	∿2	--[e]
1,1-Diphenylethene	∿2	--
Phenol	∿1	0
Bromobenzene	--[f]	--

---

[a] Trityl acetate used as starting material contained 50 ± 2% ^{18}O and 30 ± 2% ^{2}H (α-position) by mass spectrometry.

[b] Yields based on trityl acetate. Trityl peroxide was actually isolated from the reaction mixture, acetic acid was determined by a NMR study of the water layer after another reaction mixture was decomposed with water[31] and the other products were determined by GLC analysis of the ethereal solution.

[c] Reaction mixture decomposed with anhydrous H_2SO_4 (made anhydrous by adding 1 part fuming H_2SO_4 to 5 parts conc. H_2SO_4) to prevent ^{18}O exchange between acetic acid and water (normally used in workup). Mass spectral analysis used to determine ^{18}O content.

[d] Also contained ^{2}H; no loss of ^{2}H observed.

[e] Mass spectrum of oxygen-containing peak could not be obtained owing to ease of dehydration of this alcohol.

[f] Not determined.

On the basis of the labeling studies in the reaction of trityl acetate-^{18}O (and other experiments described later) with phenylmagnesium bromide in ether, the following mechanism, detailed in Reaction Scheme I, is postulated. As has been suggested earlier,[8,31] the first step is probably the reduction of the trityl cation by the Grignard reagent to yield trityl radical, phenyl radical and bromomagnesium acetate. Similar electron-transfer processes have been reported many times in the literature (see Historical) and have also been observed in this Laboratory[31] in the reaction of trityl bromide with phenyl Grignard reagent. Another trityl cation source, trityl fluoroborate, was also treated with phenylmagnesium bromide in hope of observing the electron-transfer process and producing trityl peroxide. However, no trityl peroxide could be isolated from the reaction mixture; the major product was triphenylmethanol, and other products were triphenylmethane and biphenyl. Triphenylmethane ostensibly arises from hydride transfer from solvent[13] and the alcohol from simple hydrolysis of the trityl salt in the workup. Perhaps the reduction does not occur because of limited solubility of the trityl salt in the ethers used as solvents (ethyl ether, n-butyl ether and tetrahydrofuran).

The bromomagnesium acetate, formed from reaction of trityl acetate with phenyl Grignard reagent, may react with that reagent to form acetophenone and 1,1-diphenylethanol. However, since most of the Grignard reagent is consumed in the electron-transfer step, only a maximum of 0.3 mole excess is available for reaction to form these products. To be sure, most of the bromomagnesium acetate is converted to acetic acid upon acidification of the reaction mixture. Complete ^{18}O and ^{2}H retention is observed in the acetic acid (Table II) as would be expected.

REACTION SCHEME I

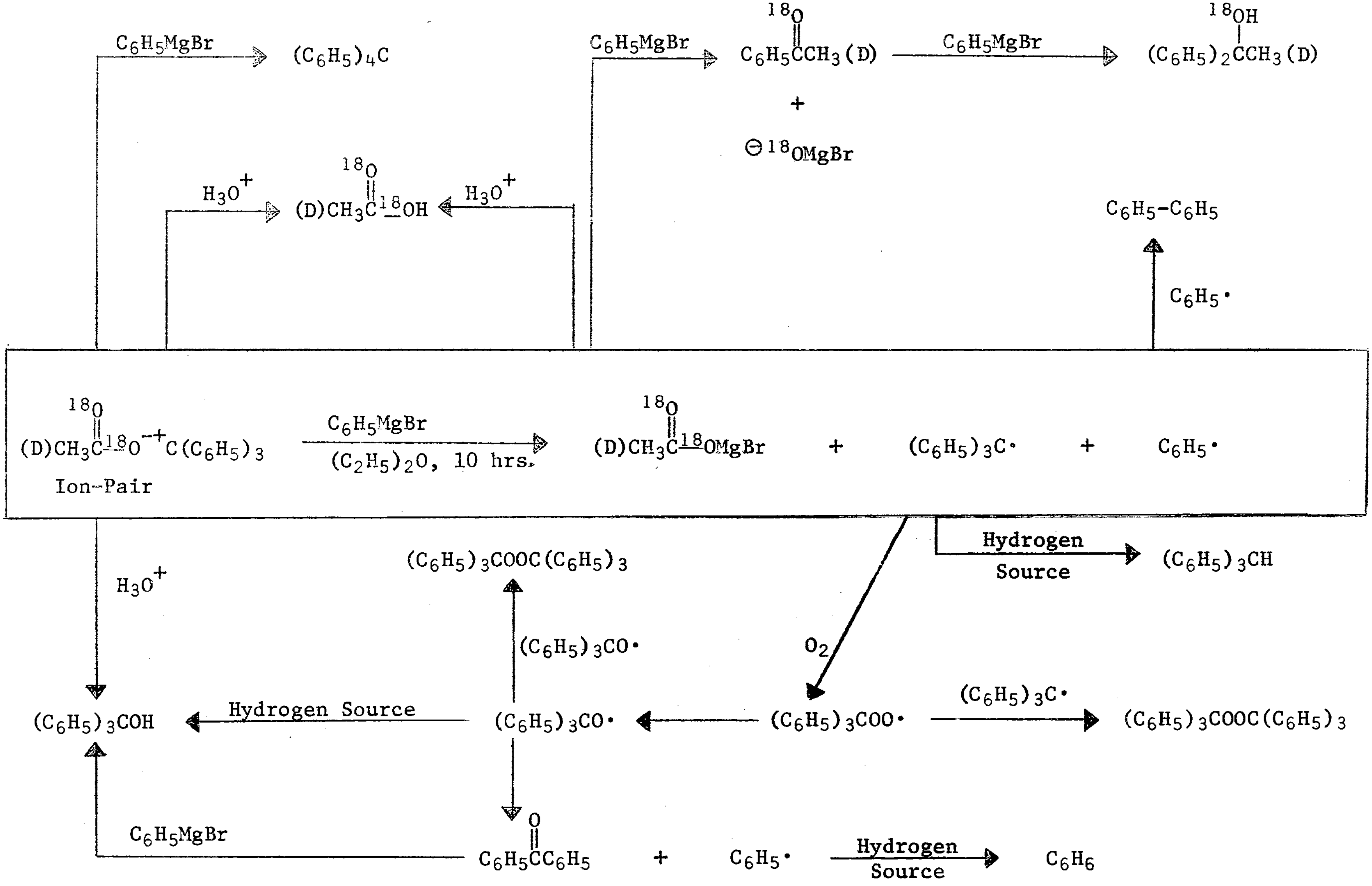


TABLE II

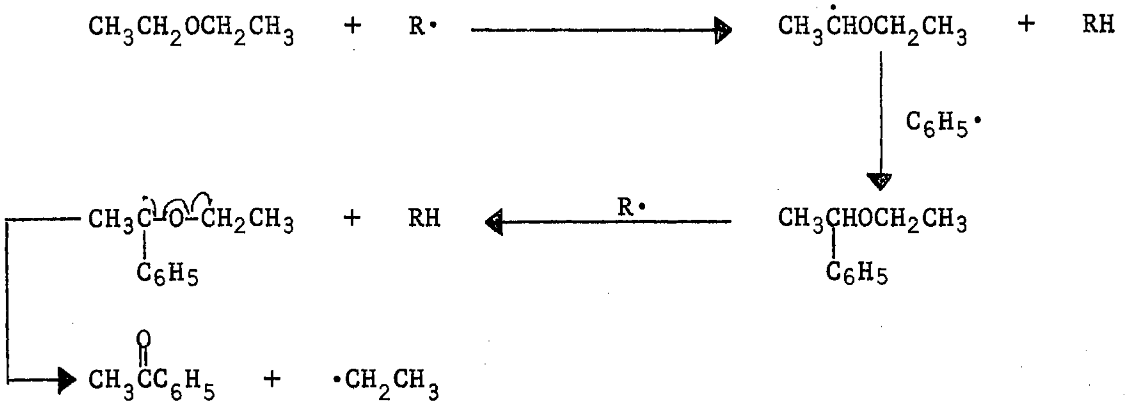
MASS SPECTRAL DATA

m/e	% RI	m/e	% RI	m/e	% RI	m/e	% RI
Acetic Acid-^{18}O and-^{2}H		60	54.0	46	1.7	79	1.1
12	2.1	61	2.4	47	0.97	89	0.8
13	5.3	62	4.6	49	2.0	90	0.45
14	11.0	63	3.4	50	1.5	91	1.5
15	29.0	64	11.5	51	3.4	92	0.9
16	16.0	65	20.0	52	3.5	93	0.45
17	14.0	66	20.0	52.5	1.6	94	12.2
18	18.0	67	8.1	53	1.2	95	1.0
28	32.0	Acetophenone-^{18}O and-^{2}H		55	1.4	103	0.89
29	13.5	28	8.3	59	0.7	104	1.5
30	7.9	29	1.3	60	0.74	105	100.0
31	11.0	30	0.44	61	1.3	106	7.3
32	12.0	31	1.9	62	2.2	107	25.0
41	6.1	32	4.2	63	3.4	108	1.7
42	14.0	37	2.1	64	1.3	120	1.7
43	87.0	38	3.8	65	4.5	121	9.1
44	24.0	39	7.7	66	3.9	122	6.0
45	100.0	40	2.7	73	1.5	123	2.4
46	36.0	41	0.88	74	5.2	124	5.7
47	46.0	42	1.0	75	3.0	Trityl Acetate-^{18}O and-^{2}H	
48	16.0	43	10.5	76	3.7	39	3.5
49	68.0	44	6.0	77	97.5	43	11.0
50	3.7	45	4.7	78	10.8	45	2.6

II (CONTINUED)

m/e	% RI	m/e	% RI	m/e	% RI	m/e	% RI
46	4.2	119.5	6.0	202	4.0	303	1.2
47	4.7	120	3.3	213	4.5	304	0.30
48	2.3	120.5	1.1	214	1.5	305	0.20
50	2.3	121	1.0	215	8.1	306	0.83
51	10.7	139	3.2	216	2.7	307	2.05
63	3.1	150	1.0	226	4.2	308	2.40
74	1.3	151	1.6	227	2.4	309	1.3
75	1.6	152	4.5	228	8.0	310	0.25
76	2.4	153	2.5	229	2.2		
77	37.5	154	3.5	237	2.2		
78	4.3	155	1.7	238	1.6		
89	1.7	163	4.3	239	13.0		
91	3.8	164	4.7	240	5.5		
94.5	3.1	165	81.7	241	16.0		
101	2.4	166	19.0	242	12.0		
105	22.3	167	7.7	243	100.0		
106	2.6	168	1.2	244	27.7		
106.5	2.9	181	4.1	245	3.6		
107	19.0	182	3.3	259	55.0		
107.5	3.0	183	12.0	260	34.0		
108	3.0	184	4.0	261	63.0		
113	3.8	185	4.9	262	25.5		
115	5.2	168	3.3	263	12.0		
118.5	2.0	187	1.5	264	1.8		
119	2.4	189	2.5	302	5.2		

Reference should be made to a model experiment[31] in which acetic acid was treated with phenylmagnesium bromide (1:2.3) and excellent conversion to acetophenone and 1,1-diphenylethanol was observed. The acetophenone formed in the normal reaction (see Table II) contained only 21% ^{18}O, whereas one would expect 50%, the amount present in the trityl acetate. The interpretation of this observation is subject to much debate, although the author feels that the solvent, ethyl ether, is definitely playing a unique role in this process. Evidence for this supposition was provided by two experiments: (a) the reaction of trityl bromide with phenyl Grignard reagent to yield 11% of acetophenone and (b) the detection of 1.63% of acetophenone in the organic layer of the mixture obtained by hydrolysis of phenyl Grignard reagent (the bromobenzene and ether used in the reaction were analyzed for acetophenone before use and none was present). It is possible that radicals present in the reaction mixture abstract α-hydrogen atoms from the ether solvent[25c] to initiate the formation of acetophenone.



This process is only of very minor importance in a solution of Grignard reagent, as evidenced by the low yield of acetophenone, presumably because only small amounts of radicals are present in the Grignard solution and then only during the preparation. On the other hand, in the reaction of trityl bromide with phenyl Grignard reagent many radicals are present owing to the electron-transfer process and an appreciable yield (11%) of acetophenone is detected. It is postulated here that the production of acetophenone (via the solvent) in the reaction of trityl acetate-^{18}O with phenyl Grignard accounts for the ^{18}O dilution effect that is observed.

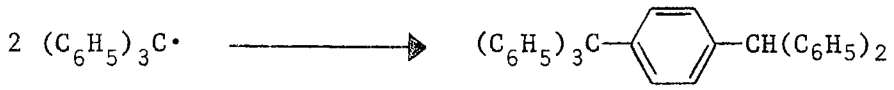
Phenyl radical may, besides its aforementioned role in acetophenone production, (a) couple to produce biphenyl, (b) couple with trityl radical to produce tetraphenylmethane (a minor pathway as evidenced by product analysis) or (c) abstract hydrogen from a hydrogen source.

It is noteworthy that the amount of biphenyl (23%) produced is greater than that produced in a blank run with only phenyl Grignard reagent and ether. This is taken as additional evidence that phenyl radicals are being generated in the reaction, presumably via the electron-transfer process and perhaps other pathways.

The trityl radical is postulated to be the origin of several of the observed reaction products. Triphenylmethane is probably formed by hydrogen abstraction from ether, although this process is surely secondary to the reaction of trityl radical with oxygen as the high yield of trityl peroxide indicates. Two observations appear to be pertinent to this point: (1) the acetic acid-^{18}O and ^{2}H (Reaction Scheme I) suffered no loss of ^{2}H, thus indicating that trityl radical does not, to any appreciable extent, abstract hydrogen from trityl acetate or any intermediates derived therefrom and (2) upon carrying out the reaction of trityl acetate with phenylmagnesium bromide in a dry box, with great care taken to make the system as oxygen-free as possible, the trityl radicals actually survived the workup stage (H_2O/HCl) (clear organic layer) as evidenced by the immediate precipitation of trityl peroxide upon allowing air to enter the system.

Trityl radical (Reaction Scheme I) may also react with oxygen to yield tritylperoxy radical (evidently a reversible process as reported by Ayers and co-workers[3,4]), which may then react with another trityl radical to form trityl peroxide.

Apparently in a regular run without deoxygenated N_2 ($\sim$1% O_2), trityl radical reacts very rapidly with the trace of O_2.[5] It is reported[5] that this process is much faster than that of irreversible dimerization.



or, from our own results, hydrogen abstraction leading to triphenylmethane.

The tritylperoxy radical may also give rise to trityloxy radical as discussed by Shupe[31] previously. The trityloxy radical may then (a) abstract hydrogen from a hydrogen source to form triphenylmethanol (b) couple to form trityl peroxide or, most likely, (c) undergo β-cleavage which would give rise to benzophenone (detected) and phenyl radical[21,34] (leading to biphenyl among other products previously mentioned). The benzophenone thus formed would not be expected to contain ^{18}O since the oxygen in it supposedly came from O_2 dissolved in the solvent. Triphenylmethanol appears to contain some (2-3%) ^{18}O above natural abundance and although this is somewhat unexpected, the most likely source is hydrolysis of trityl acetate.

CHAPTER III

EXPERIMENTAL[a-e]

Preparation of ^{18}O- and ^{2}H-Labeled Trityl Acetate. The preparation was essentially the same as that reported earlier.[31] The reagents used were 1.70 g. (0.00526 mole) of trityl bromide, 0.50 g. (0.0030 mole) of silver acetate (87.6% ^{18}O-labeled and 61% ^{2}H-labeled in the α-position), 0.09 g. (0.00054 mole) of silver acetate (70.0% ^{18}O-labeled) and 0.46 g. (0.00276 mole) of unlabeled silver acetate. The mixture was allowed to react for 15 hrs. The yield was 1.2 g. (0.004 mole, 76%) of trityl acetate, m.p. 82-4°C, lit.[7] m.p. 82-4°C. Mass spectral analysis of the ester indicates the presence of 50 ± 2% ^{18}O and 30 ± 2% deuterium (see Table II).

Reaction and Product Analysis of ^{18}O- and ^{2}H-Labeled Trityl Acetate With Phenylmagnesium Bromide (1:1.3). The procedure was similar to that

---

[a] Gas chromatographic analyses were performed using a Varian-Aerograph Hy-Fi Model 1520 with a hydrogen flame ionization detector.

[b] Mass spectral analyses were performed on two instruments: (1) a Bendix Time-of-Flight mass spectrometer at the Continental Oil Company, Ponca City, Oklahoma and (2) an LKB-9000 prototype, magnetic sector, GLC-mass spectrometer, Biochemistry Department, Oklahoma State University.

[c] Nitrogen gas used in this work was dried by passing it through concentrated sulfuric acid and then through three Linde 3A molecular sieve traps.

[d] Silver acetate (87.6% ^{18}O and 61% ^{2}H) was obtained from the Weizmann Institute of Science, Rehovoth, Israel.

[e] Nitrogen gas used in a special experiment (see discussion) was deoxygenated with a system designed by Arthur.[2]

reported earlier[31] with the exception of the workup. Labeled trityl acetate, 1.0 g. (0.0033 mole) dissolved in ether, was added dropwise to 0.0043 mole of phenylmagnesium bromide solution. After the mixture was stirred for 12 hrs., the solution was cooled and 0.5 ml. of H_2SO_4 (made anhydrous by the addition of 20% fuming H_2SO_4) was added to acidify the reaction mixture. The anhydrous conditions were desirable in order to minimize ^{18}O exchange between water and any ^{18}O-acetic acid formed. The magnesium salts and the trityl peroxide were filtered from the reaction mixture, and the ethereal solution was analyzed on the GLC-mass spectrometer. The acetic acid was analyzed on a 6' glass column of 6% FFAP on Chromosorb W, acid-washed and treated with DMCS. The other products were analyzed on a metal column (6' x 1/8") of 6% SE-30 on Chromosorb G, acid-washed and treated with DMCS. The mass spectra of the two major oxygen-containing products, acetic acid and acetophenone, are listed (along with the trityl acetate used as starting material) in Table II. The acetic acid was found to contain labeling essentially identical to the trityl acetate used as starting material. The acetophenone was found to contain 21 ± 2% of the ^{18}O labeling contained in the original trityl acetate. The triphenylmethanol contained $\sim$2-3% ^{18}O, but no other oxygen-containing compound was found to contain ^{18}O above natural abundance.

Reaction of Trityl Bromide With Phenylmagnesium Bromide (1:1.3). The procedure was essentially the same as that reported previously.[31] Trityl bromide, 3.0 g. (0.0093 mole) dissolved in ether, was added slowly to 0.0121 mole of phenylmagnesium bromide. Dry oxygen was periodically (i.e. every hr.) bubbled through the reaction mixture for a few seconds. The total reaction time was 6 hrs. After hydrolysis, the trityl peroxide was filtered from the ether layer; the yield was 47% (1.10 g., 0.00212 mole). Other products, observed by GLC analysis, were benzene, bromobenzene, phenol, acetophenone (11%), biphenyl, benzophenone (17%), triphenylmethane (26%), triphenylmethanol (7%) and tetraphenylmethane (3%). It is assumed that the acetophenone arises in some manner from reaction of the solvent, diethyl ether.

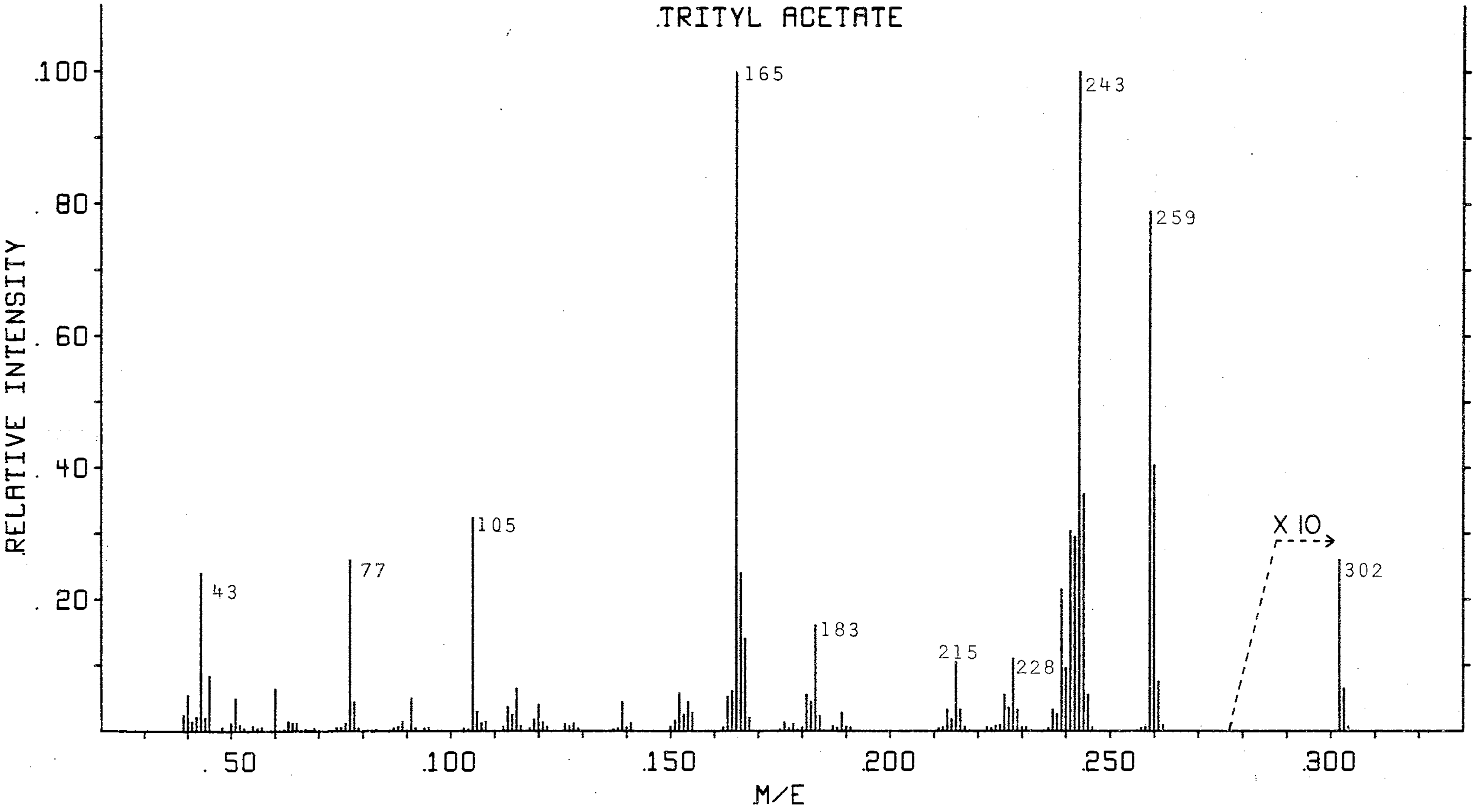
Product Analysis of Hydrolyzate of Phenylmagnesium Bromide With 6N HCl. Phenyl Grignard reagent was prepared in the usual manner.[25a] Reagents used were magnesium (1.21 g., 0.05 g. atom) and bromobenzene (7.0 g., 0.0446 mole). After the mixture was heated for 5 hrs., the excess magnesium was filtered from the Grignard solution. The Grignard reagent was then hydrolyzed with 6N HCl and the organic layer separated and analyzed by GLC.

Product	% Yield
benzene	83.0
phenol	8.65
biphenyl	5.96
acetophenone	1.61
bromobenzene	trace
	99.22 (total)

Preparation of Trityl Fluoroborate. The procedure was essentially the same as reported by Dauben and co-workers.[13] Reagents used were: triphenylmethanol (10.0 g., 0.0384 mole), propionic anhydride (100 g., 0.77 mole) and 10 ml. of 48% HBF_4. Yield was 9.0 g. (72%) of trityl fluoroborate after 5 washings with anhydrous ether; the m.p. was 214°C (decomp.), lit.[13] m.p. 207-10°C(decomp.).

Reaction of Phenylmagnesium Bromide With Trityl Fluoroborate (1.3:1). The reaction was carried out similarly to that reported[31] for phenyl Grignard reagent and trityl acetate. Trityl fluoroborate, (2.0 g., 0.00605 mole) dissolved in 100 ml. ether, was added dropwise to 0.008 mole of phenylmagnesium bromide. After 10 hrs. the reaction mixture was hydrolyzed with 2N HCl. Trityl peroxide was not observed in the reaction mixture and GLC analysis showed triphenylmethane, triphenylmethanol and biphenyl to be major products with the alcohol being by far the major one. Minor products were acetophenone, bromobenzene and phenol. No products indicative of a trityl radical intermediate were found. Other solvent systems (tetrahydrofuran and n-butyl ether) were also used but with similar results.

Plate I


TRITYL ACETATE
RELATIVE INTENSITY
100
80
60
40
20
50
100
150
200
250
300
M/E
43
77
105
165
183
215
228
243
259
X 10
302

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PART II

MASS SPECTRA OF TRITYL-SUBSTITUTED COMPOUNDS--LOSS OF ^{12}C FROM $(C_6H_5)_3{}^{13}CH$ VIA ELECTRON BOMBARDMENT

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CHAPTER I

HISTORICAL

General Synthetic Methods for Trityl Amines, Esters, Ethers, Hydrocarbons and Sulfides

The preparation of N-tritylamines was first reported by Elbs.[23] Basically, the procedure was to combine a trityl halide with a monoamine in a boiling benzene-alcohol solution. This method was employed by van Alphen[45] several years later in his studies concerning the migration of the trityl group in N-tritylaniline (and derivatives thereof). A more comprehensive examination of the preparation of N-trityl derivatives of aromatic primary amines was reported in 1952.[46] These workers are quick to point out that alcohol should not be employed in the reaction solvent, since it reacts readily with trityl halides to form trityl ethers. It is deduced, therefore, that the N-tritylarylamines can best be prepared by allowing a boiling solution of a monoamine and a trityl halide to react in the molar ratio of 2:1. Excess amine provides the necessary base for the absorption of the hydrogen halide which is liberated. The amine hydrohalide can easily be taken up in water in the reaction workup. Over 25 N-tritylarylamines were obtained in good (i.e., 78-97%) yield by using this method.[46]

The preparation of carboxylic esters of triphenylmethanol has been studied extensively by Berlin.[6] The general procedure is to treat trityl bromide with the sodium, silver or potassium salt of the carboxylic acid necessary to yield the desired product. Since these esters are hydrolyzed very rapidly, great care must be exercised to minimize the water content of the system both during and after the reaction. The esters can usually be recrystallized from either cyclohexane or methyl ethyl ketone; however, no recrystallization is necessary if the moisture content of the system is maintained at an extremely low level.

Synthesis of trityl alkyl ethers may be achieved via reaction of a trityl halide with an alcohol in a benzene-pyridine solvent[30] (the pyridine serves to fix the hydrogen halide produced during the reaction). Alternatively, reaction of a trityl halide with a sodium alcoholate was used by Norris and Young[35] to prepare eleven ethers of triphenylmethanol in yields ranging from 10 to 60%. Later, Smith and Smith[44] found a different route to the trityl alkyl ethers from triphenylmethanol. This procedure involved the reaction of 100% sulfuric acid with triphenylmethanol forming presumably the trityl cation. An alcohol was then added and the trityl alkyl ether formed immediately.

$$(C_6H_5)_3COH + 2H_2SO_4 \longrightarrow (C_6H_5)_3C^+ + H_3O^+ + 2HSO_4^-$$

$$(C_6H_5)_3C^+ + ROH \longrightarrow (C_6H_5)_3COR + H^+$$

This procedure is, however, incapable of producing the s-butyl, t-butyl and benzyl ethers. The failure of such alcohols to give ethers by reaction with the carbonium ions may be due to one of three processes:

1. The effect of these branched-chain alcohols may be such as to materially decrease the rate of reaction.[43]

2. An equilibrium of the type

$$(C_6H_5)_3COR + H_2O \rightleftharpoons (C_6H_5)_3COH + ROH$$

may exist in solution, and the effect of increased complexity of the alkyl group may be of such a nature as to shift the equilibrium toward the formation of triphenylmethanol.

3. It should be recalled that not only triphenylmethanol but certain other alcohols can form stable cations in strong acid. For example:

$$(CH_3)_3COH \; + \; H^+ \longrightarrow (CH_3)_3C^+ \; + \; H_2O$$

The generation of the tert-butyl cation would hinder further formation of an ether and would itself lead to the formation of isobutylene.

Assuredly, the best synthetic method for the trityl alkyl ethers is merely to treat triphenylmethanol with an alcohol in the presence of only a trace (ca. 10^{-4} M) of HCl or H_2SO_4.[17,29]

$$(C_6H_5)_3COH \; + \; H^+ \rightleftharpoons (C_6H_5)_3C\overset{+}{O}H_2 \rightleftharpoons (C_6H_5)_3C^+ \; + \; H_2O$$

$$(C_6H_5)_3C^+ \; + \; ROH \rightleftharpoons (C_6H_5)_3COR \; + \; H^+$$

The regeneration of the hydrogen ion insures that the processes are truly acid-catalyzed. This method was employed in our Laboratory to prepare our trityl alkyl ethers. It should be noted that the trityl t-butyl ether could not be prepared by this route, supposedly owing to steric reasons. Furthermore, this ether could not be prepared by the reaction of trityl bromide with potassium t-butoxide as a result of the electron transfer tendency of the latter.[12]

$$(C_6H_5)_3CBr \; + \; K^{+-}OC(CH_3)_3 \longrightarrow (C_6H_5)_3C\cdot \; + \; \cdot OC(CH_3)_3 \; + \; KBr$$

The trityl aromatic ethers were not employed in this study but it should be pointed out for completeness that the reaction of trityl chloride with phenol yields 4-hydroxytetraphenylmethane.[15] Thus, alkylation occurs at the para position of phenol. Condensation of alkali phenoxide with trityl chloride does produce the phenyl ether of triphenylmethanol.

Trityl hydrocarbons can best be obtained by taking advantage of the coupling reactions of Grignard reagents with alkyl halides.[32b] For example, reaction of tritylmagnesium bromide with an appropriate alkyl halide is the method of Bachmann.[1] When elimination can easily occur (e.g., in t-butyl halide or cyclohexyl halide), the method of choice is the reaction of trityl bromide with the alkyl Grignard reagent. It is noteworthy also that trityl esters ionize sufficiently in solution[49,50] to react with alkyl Grignard reagents to form trityl hydrocarbons.[21a,24] It is interesting that when methylmagnesium iodide is combined with trityl acetate in an inverse addition, a 12% yield of trityl peroxide is formed,[21c] probably via reduction of the trityl cation to the trityl radical which then reacts with oxygen to form the peroxide. Although, under normal addition techniques, quantitative yields of trityl hydrocarbons are formed via reaction of trityl bromide with certain alkyl Grignard reagents, the reaction of aryl Grignard reagents with trityl halides gives very poor yields of trityl hydrocarbons[27,39] (trityl peroxide is the major product). For example, trityl chloride in ether-benzene solution reacts with phenylmagnesium bromide to yield tetraphenylmethane[39] (∿6-7%) and para-biphenyldiphenylmethane (45%). The trityl peroxide is presumably formed via a trityl radical intermediate which arises from reduction of the trityl cation by the phenyl Grignard reagent.[5]

The preparation of trityl sulfides are reported in the literature.[28,40] Whereas phenol reacts with trityl bromide to give 4-hydroxytetraphenylmethane,[15] the more nucleophilic thiophenol reacts with trityl bromide to yield only trityl phenyl sulfide. This compound is insensitive to acid and base and no elaborate synthetic procedures are necessary to prevent rearrangement of the trityl phenyl sulfide. The general method of preparation of alkyl or aryl trityl sulfides, then, involves the reaction of a trityl halide with a mercaptan in a benzene-pyridine solvent. After a short reaction time, the reaction mixture is poured into water and, in most cases, the trityl sulfide immediately crystallizes out.

General Review of Important Theory Related to Mass Spectrometry

In the past few years mass spectrometry has developed into one of the most important tools used by organic chemists. The mass spectrometer provides a method to vaporize a compound under high vacuum, ionize the resulting gas with an electron beam emitted from a hot filament, accelerate the positive ions through a series of focusing slits (and a stable magnetic field), collect and amplify the ion beam by a vacuum-tube electrometer or an electron multiplier, and finally record the signal with a suitable recording system. Mass spectra are routinely obtained at an electron beam energy of 70 electron volts. The simplest event that occurs is removal of a single electron from the molecule by an electron of the electron beam to form a molecular (parent) ion.

$$R{:}R' \xrightarrow{e} R\overset{+}{\cdot}R' \quad + \quad 2e$$

Many of these parent ions disintegrate to give, in the simplest case, a positively charged fragment and a radical. A number of fragment ions are thus formed, and each of these can cleave in turn to give smaller fragments.

$$R\overset{+}{\cdot}R' \longrightarrow R^{+} \quad + \quad \cdot R'$$

Thus, a mass spectrum is a presentation of the masses of the positively charged fragments (including the parent ion) versus their relative concentrations. The most intense peak in the spectrum, called the base peak, is assigned a value of 100%, and the intensities of the other peaks, including the parent peak, are reported as percentages of the base peak. Of course, the parent peak may sometimes be the base peak.

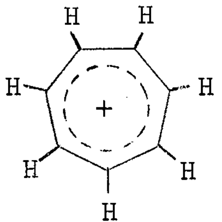
The energy required for the production of a certain fragment from the parent ion will depend primarily on the energy of the bond to be broken. In addition there is a dependence upon the energy content (stabilization) of the positive ion formed, upon the energy content (stabilization) of the neutral fragment, which may be a radical or a neutral molecule, and finally upon the steric arrangement of the atoms in the molecule, a factor which is significant mainly for rearrangement processes. The most important of these factors is often the stabilization of the positive charge of the fragment. Its formation will be enhanced even further if in the fragmentation process a particularly stable radical or, better, a neutral molecule is produced.

Some of the simple, common, cleavage mechanisms can be summarized as follows:

1. Formation of tropylium ions via carbon-carbon bond cleavage.

$$[C_6H_5CH_2CH_2OH]^{+\cdot} \longrightarrow \cdot CH_2OH + C_6H_5CH_2^+$$

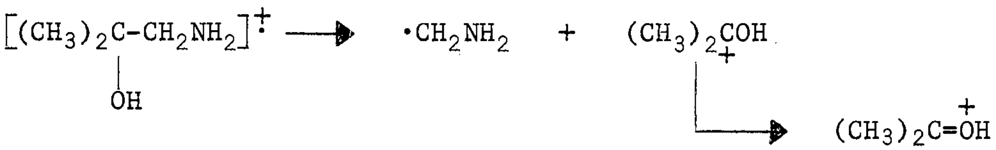
$$C_6H_5CH_2^+ \longrightarrow$$



2. Loss of a neutral fragment to form a stable cation via carbon-heteroatom bond cleavage.

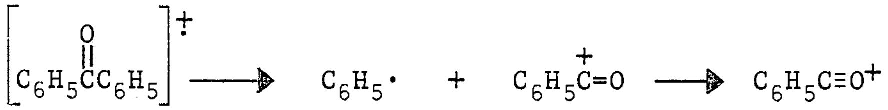
$$[(C_6H_5)_3C{-}X]^{+\cdot} \longrightarrow (C_6H_5)_3C^+ + X\cdot$$

3. Heteroatom (with its free electron pair) stabilization of a positive charge on an adjacent carbon atom, resulting from rupture of a carbon-carbon bond.



$$[(CH_3)_2\underset{OH}{C}-CH_2NH_2]^{+\cdot} \longrightarrow \cdot CH_2NH_2 + (CH_3)_2\underset{+}{C}OH \longrightarrow (CH_3)_2C=\overset{+}{O}H$$

4. Stabilization of the positive charge on a carbon atom by a heteroatom attached to it by a double bond, after carbon-carbon bond cleavage.



$$\left[C_6H_5\overset{O}{\overset{\|}{C}}C_6H_5\right]^{+\cdot} \longrightarrow C_6H_5\cdot + C_6H_5\overset{+}{C}=O \longrightarrow C_6H_5C\equiv O^+$$

Present-day chemists are using mass spectrometry, not only for its obvious utility in identification of compounds, but also as an aid in examining mechanisms. Mechanistic studies are frequently advanced by the use of isotopes. For example, two mass spectra of the same compound are obtained but one of the samples is labeled in known positions with stable isotopes. By comparing the two spectra it is often possible to learn enough about the fragmentation to disprove a proposed mechanism or postulate a new one. The isotopes most frequently used by the organic chemist are ^{13}C, ^{15}N, ^{18}O and ^{2}H.

Another aid to the organic chemist in the study of fragmentation mechanisms is a consideration of metastable peaks. The term "metastable peak" is somewhat misleading, because it is, of course, not the peak in the spectrum which is unstable and would disappear. Rather it is the primary ion which is considered metastable and may decompose into other fragments before it is deflected into the collector.

When a molecule becomes ionized upon electron impact, the positively charged molecular ion will, under the influence of the potential gradient in the ion source, begin to travel toward the accelerating region, owing to the slightly more positive charge on the repeller plates. If the decomposition of this molecular ion into fragments is very fast, nearly all such ions will decompose before reaching the first accelerating plate, and only the fragments will be accelerated and deflected by the magnetic field. The spectrum then usually consists primarily of fragment peaks, with no peak for the molecular ion, a situation which is common for branched alcohols, for example. If on the other hand, the molecular ion is a very stable one with little tendency to decompose, as in the case of aromatic hydrocarbons, virtually all molecular ions originally formed will be accelerated as such, and the mass spectrum will exhibit a very strong peak for the molecular ion. Molecular ions which decompose at an intermediate rate will, in part, pass intact through the accelerating region and, in part, decompose earlier. In such a case, intense peaks will occur both for the molecular ion and for the fragments.

Obviously there will be some primary ions which happen to decompose into fragments while traversing the accelerating region. They will be accelerated first as mass m_1. At the point of decomposition, part of the achieved kinetic energy will be carried off by the neutral fragment, while mass m_2 will continue to be accelerated and deflected as such, and as a result the particle will be recorded neither as m_1 nor as m_2 but will give rise to a broad peak of low intensity with a maximum at m*. Mass m*, at which such ions are recorded, can be simply related to the mass of the original ion m_1 and the mass of the product ion m_2 by the following equation:

$$m^* = \frac{(m_2)^2}{m_1}$$

If a metastable peak with a maximum at mass m^* is present in the spectrum which can be related by the above equation to the masses of two other intense peaks, m_1 and m_2, it can be assumed with reasonable certainty that the fragment of mass m_2 arises in a one-step decomposition from the species of mass m_1.

Consideration of metastable peaks is important not only for studies concerned with the mechanism of fragmentation of ions formed in the mass spectrometer but the peaks also have considerable value in the general interpretation of mass spectra. From the occurrence of the metastable peak relating two peaks of the spectrum, it follows that those two peaks must be derived from one and the same substance and cannot be due to two different compounds present as a mixture. It also follows that the smaller fragment of the two arising from a single fragmentation step must necessarily be composed entirely of atoms present in the larger fragment from which it arose. Such considerations are extremely valuable if the structure of the molecule is to be reconstructed from the fragments.

Another useful, but more restrictive, phenomenon which is sometimes helpful in the interpretation of mass spectra is multiply charged ions. The majority of the ions formed in the mass spectrometer under normal conditions bear a single positive charge. However, it is possible to obtain doubly charged ions if in the initial ionization process two electrons are removed from the molecule. The resulting ion then may decompose into neutral fragments and doubly charged fragments:

$$AB \xrightarrow{e} AB^{++} + 3e$$

$$AB^{\dot{+}+} \longrightarrow A^{++} + B\cdot$$

although the decomposition of a singly charged ion into a doubly charged fragment plus a negative ion

$$AB^{+} \longrightarrow A^{++} + B^{-}$$

cannot be ruled out as an alternative process. The particle bearing two positive charges will be collected and recorded at the mass-to-charge ratio which corresponds to half its weight.

The removal of two electrons from a molecule is facilitated by the presence of a high π-electron density and by the absence of bonds which can undergo fragmentation with great ease. It is for this reason that saturated aliphatic hydrocarbons have a very slight tendency to yield doubly charged ions, while their abundance increases in the series monoolefins, polyolefins, aromatic molecules and heterocyclic molecules. The absolute intensity of doubly charged ions is, of course, much lower than for singly charged particles. In general the intensity of doubly charged ions is of the order of about 1 per cent of the most intense singly charged peak.

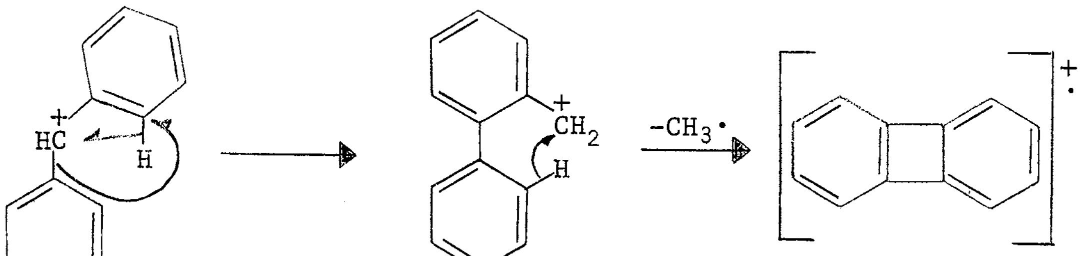
The importance of doubly charged peaks in the interpretation of mass spectra lies in the relationship between their abundance and molecular type to which the compound belongs. If a considerable number of peaks at half mass numbers (therefore due to doubly charged ions) are present in the mass spectrum, the compound is probably highly unsaturated or aromatic. With some experience it is thus possible to deduce from the abundance of such peaks whether the compound is saturated, olefinic or aromatic.

Normally, the atoms encountered in organic molecules are not monoisotopic. Carbon, for example, is predominately of isotope 12, but 1.107% of all carbon atoms are of isotope 13. This means that a compound of molecular weight 300 will contain some molecules which weigh 301 mass units due to the presence of a ^{13}C, or a hydrogen atom of isotope 2. Some molecules may contain two ^{13}C atoms or one carbon atom ^{13}C and one hydrogen of isotope 2. This combination would produce a molecule of 302 mass units. Thus, if we let P represent the parent ion, then the P + 1 ion will be the ion of mass 301 and the P + 2 ion will be the ion of mass 302. Naturally, the P + 1 will be more intense than the P + 2 since there is more chance for the presence of one heavy isotope than for two. Tables are available in the literature[9] which tabulate the P + 1 and P + 2 values for any molecular formula. It should be noted that if the P + 1 and P + 2 values are known with considerable accuracy, the molecular formula may be ascertained from the same tables.

Mass Spectra of Trityl Derivatives and Related Compounds

At least 3 papers have recently appeared in the literature which strongly imply that the loss of a methyl group from the diphenylmethyl cation occurs in such a manner that the central carbon atom is lost.[22,31,41] Johnstone and Millard[31] attempt to demonstrate loss of internal carbon from diphenylmethyl, 1,2-diphenylethyl and stilbene ions by means of ^{2}H and ^{13}C labeling. For the diphenylmethyl system it is stated that CH_3 radical could be lost, with hydrogen being supplied from two ortho positions of one phenyl ring or one ortho position of each ring. Since the labeling experiments do not support either of these possibilities, it is stated that the observed data mean that two mechanisms are operating simultaneously. The present author feels that no conclusive evidence is given to disprove the formation of an intermediate tropylium ion which could explain the results of the reported labeling studies.

Sheikh, Duffield and Djerassi[41] also propose a mechanism for loss of the central carbon atom in the diphenylmethyl system but they have no labeling work to support their mechanism.

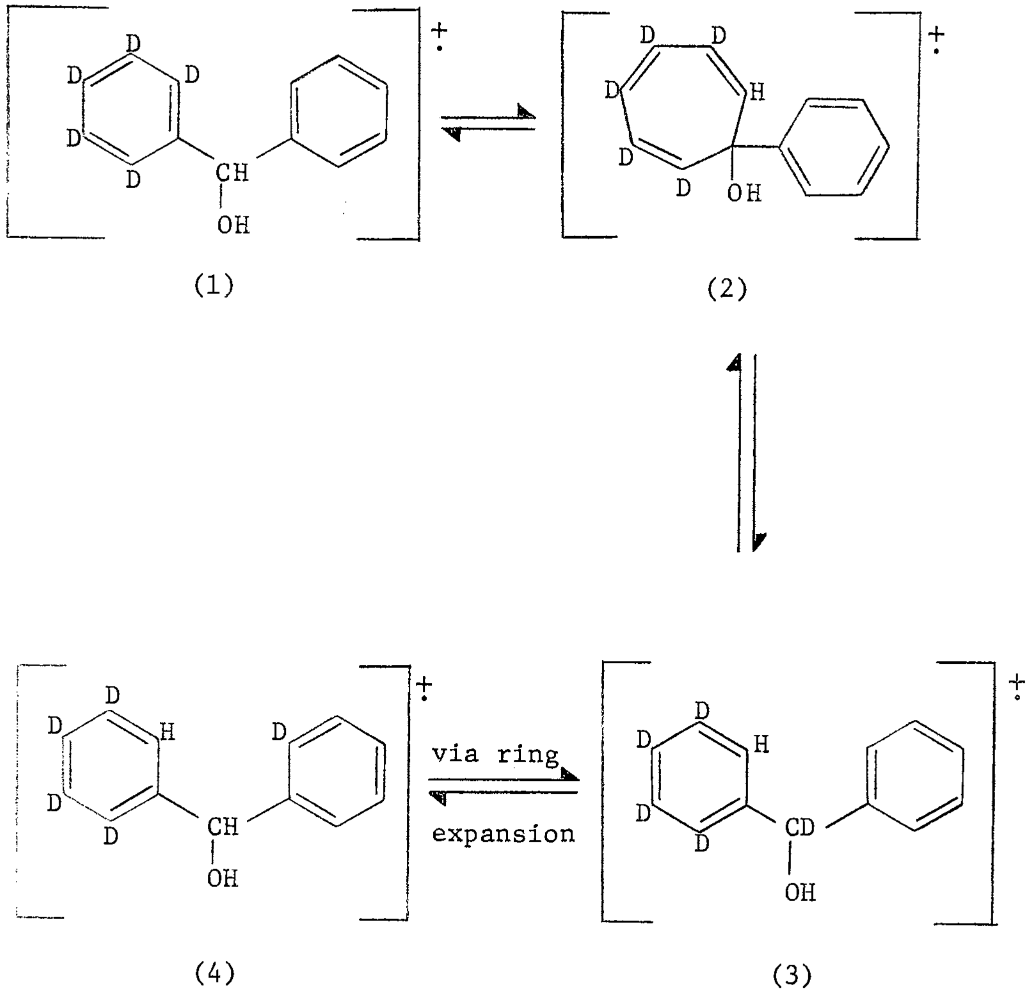


m/e 167

m/e 152

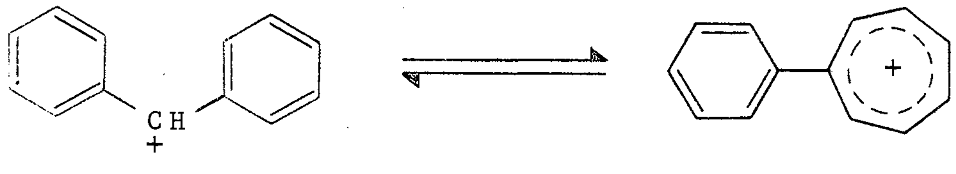
Eland and Danby[22] have studied ten diphenyl compounds ($C_6H_5\cdot X\cdot C_6H_5$, where X is ·NH·, ·O·, ·S·, ·N:N·, ·CO·, ·N(Me)·, $\cdot CH_2\cdot$, ·C⋮C·, ·CH:CH· and $\cdot CH_2\cdot CH_2\cdot$) in which it is assumed that a central group is lost to form a fragment at m/e 152. While the central group is probably lost in most of the above examples, it should not be assumed that this occurs in systems which can form a tropylium ion intermediate, such as the diphenylmethyl system.

Recent work by Williams, Ward and Cooks[48] shows from the mass spectra of deuterated analogs of diphenylmethanol that partial hydrogen scrambling between phenyl rings occurs in the molecular ion of diphenylmethanol itself. Expansion to a seven-membered ring is thought to occur and therefore it should be, in principle, possible to transfer a deuterium atom from a fully deuterated ring of diphenylmethanol into a second phenyl ring which did not originally contain deuterium [e.g. (1) $\rightleftharpoons$ (2) $\rightleftharpoons$ (3) $\rightleftharpoons$ (4)].



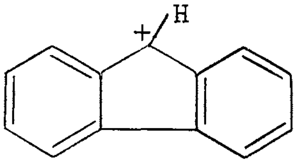
The appearance of the $[C_6H_4DC{\equiv}O]^+$ ion proves (along with other evidence presented in the paper) conclusively that some kind of scrambling is occurring. The additional observation that in the spectrum of $[^2H_5]$ benzophenone (completely deuterated in one phenyl ring) no exchange occurs between phenyl rings prior to benzoyl ion formation, very strongly supports the suggestion that exchange between rings takes place through the reversible ring expansion shown.

The diphenylmethyl cation (formed from loss of chlorine from diphenylmethyl chloride) decomposes in part by loss of a methyl radical. On the basis of deuterium labeling evidence, it was concluded[22] that the loss of a methyl radical from $C_{13}H_{11}^+$ (the diphenylmethyl cation) involves the loss of the central CH unit with the extra hydrogens being provided in part from the two ortho positions of one phenyl ring and in part from one ortho position of each ring. However, in an extremely important experiment, Williams, Ward and Cooks[48] have shown that the (M - Cl) ion from $C_6D_5CHClC_6H_5$ decomposes by loss of CD_3, CD_2H, CDH_2 and CH_3 to give m/e 154, 155, 156 and 157 peaks in the ratio 16:51:66:32 (after correction for 3% $[^2H_4]$-contaminant and ^{13}C isotope peaks). The expected peak heights at these m/e values for complete randomization of hydrogens and deuteriums in m/e 172 prior to expulsion of a methyl radical are 10:60:75:20. Also, appropriate metastable peaks are observed for the loss of CD_3, CD_2H, CDH_2 and CH_3, and the relative intensities of these metastable peaks are close to those calculated on a statistical basis. In the absence of a correction for an isotope effect, the agreement between the calculated and observed figures is sufficiently close to warrant the conclusion that randomization of hydrogens and deuteriums does occur in the (M - Cl) ion from diphenylmethyl chloride prior to its decomposition by loss of a methyl radical. One mode through which the randomization could occur involves rapid reversible equilibration between the diphenylmethyl cation and the phenyl tropyluim ion.

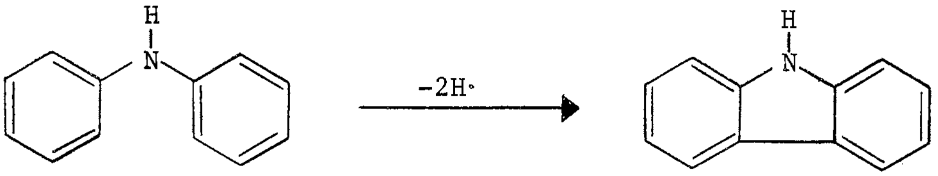


It is obvious, however, that in either of the above species, further hydrogen shifts (and perhaps rearrangement of the carbon skeleton also) would be necessary prior to expulsion of a methyl radical. Such subsequent rearrangements could also play a role in the hydrogen-scrambling process.

The m/e 165 ion ($C_{13}H_9$) has been noted in the mass spectra of a variety of heterocyclic systems containing at least two phenyl substituents.[13] This skeletal-rearrangement fragment is most prominent in the spectra of certain substituted oxazoles, imidazoles and thiazoles. A pronounced $C_{13}H_9$ peak is not characteristic of the $C_6H_5{-}\underset{|}{C}{=}\underset{|}{C}{-}C_6H_5$ moiety but is generally derived only from 5-membered heterocyclic systems containing two heteroatoms (normally in 1,3 positions) and from isolated compounds, including diphenylmethane, stilbene, dihydrophenanthrene and systems containing the trityl group.[41] Even though structures drawn for fragment ions are nominal only, it is argued that the most plausible structure for m/e 165 corresponds to the fluorene cation. It



should be mentioned that diphenyl systems in which the central atom is not carbon also form ions which are similar to the fluorene cation in many cases. For example, diphenylamine is converted partially to carbazole upon electron bombardment.[19]



Bublitz and Baker[16] have shown that this ortho ring closure also occurs in systems where the central atom is phosphorus, arsenic or antimony.[16] The stability must be high for an ion with the general structure of the fluorene cation in view of the many types of molecules which give rise to an ion of this type.

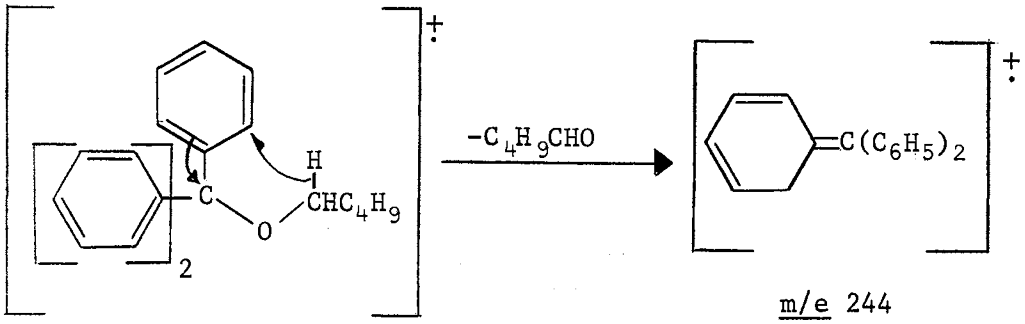
The mass spectra of trityl compounds heretofore reported in the literature are quite limited.[18,36,37] The only extensive study of trityl systems is reported by Sheikh, Duffield and Djerassi[41] in which they examined several trityl ethers and sulfides. The major peak in all the ethers studied occurred at m/e 243, albeit a major peak was observed at m/e 244. This, of course, necessitates a hydrogen transfer from the non-trityl portion of the ether. Deuterium transfer in the deuterated derivatives of n-pentyl trityl ether (Table I) established that no specific

TABLE I

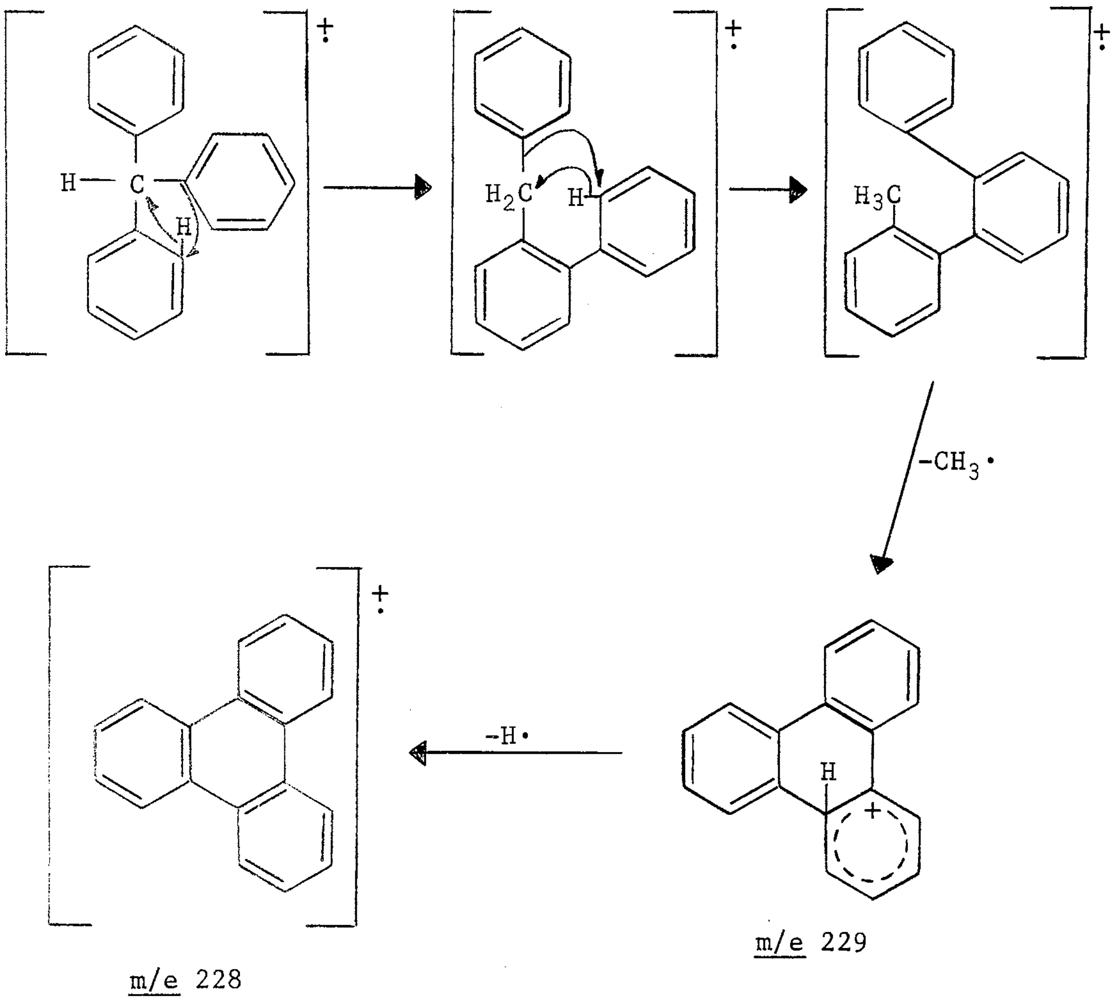
SPECIFICITY OF HYDROGEN TRANSFER IN REARRANGEMENT ION FORMATION IN n-PENTYL TRITYL ETHER

Compound	Isotopic Purity	% Transfer m/e 244
1,1 - d_2	98%	70%
2,2 - d_2	95%	10%
3,3 - d_2	98%	10%
4,4 - d_2	95%	10%

carbon atom was associated with this hydrogen-transfer process. It should be noted that the principal donor of hydrogen in the rearrangement process is C-1 of the alkyl chain, with smaller but equal contributions from C-2, C-3 and C-4. The following rationalization invoking hydrogen transfer from C-1 through a six-membered intermediate to the ortho position of a benzene ring is postulated to account for the bulk of the m/e 244 peak in the spectra of alkyl trityl ethers.



A very interesting rearrangement must occur to give rise to a m/e 228 peak (from systems in which the trityl cation is the base peak), and a m/e 229 peak (from systems in which the base peak is m/e 244) is postulated to arise in the following manner (triphenylmethane itself was examined to support this mechanism):


H
C
H
H_2C
H
H_3C
$-CH_3\cdot$
$-H\cdot$
H
+
m/e 229
m/e 228

CHAPTER II

DISCUSSION OF RESULTS AND CONCLUSIONS

The mass spectral analyses obtained in this study were performed on an LKB-9000 single focusing mass spectrometer featuring sample introduction by three different inlet systems. The instrument is specially designed for operation with a GLC inlet, but the array of high capacity vacuum pumps and valves enables the operator to change quickly from one inlet system to another. The direct probe was the inlet system of choice for this study since all of the trityl compounds are solids. The source of electrons necessary for electron bombardment is provided by a rhenium filament. The filament is heated to the point at which it emits a substantial stream of electrons which are accelerated by a suitable electrode and then collected by an electron trap. A small but representative group of the molecules are ionized and then accelerated towards the analyzer tube by three pairs of plates. As the ions pass between the plates (extraction, focusing and deflection), each of decreasing positive voltage, the ion beam is collimated and accelerated. After traversing the 60° magnetic sector, in which groups of ions are deflected according to their individual m/e ratios, a particular group of ions of equal m/e ratio is focused to impinge on a collector plate of an electron multiplier. The signal thus produced is amplified and its intensity recorded on the high-speed recording oscillograph. By varying the magnetic field strength, one can scan a wide range of masses and thereby obtain a recording of the m/e ratio of all fragment ions from a particular sample and the abundance of each type. The central section of the analyzer tube contains the exit slits as well as the magnet. These slits (and also the collector slits) are adjustable by micrometer controls outside the vacuum. For correct alignment with the ion beam the collector slit can be rotated at right angles to the ion beam 6° in either direction. The slit openings will determine the degree of resolution and intensity. By continuous variation of the magnetic field the entire spectrum of ions is allowed to enter the collector slits in order. Provision is made for scanning any selected portion of the mass range as well as for selecting the rate of scanning. The electron multiplier, preamplifier, galvanometer, amplifier and oscillograph function together to amplify and record an electrical signal resulting from the impingement of ions of a selected m/e. Each peak is recorded simultaneously by three galvanometers of different gains and the reading is made from the tracing of the most sensitive galvanometer remaining on the photographic paper.

The mass spectrometer is equipped with two high-capacity, high-vacuum systems which are described more technically in the specifications list of the LKB-9000 which follows:

Technical Specifications

Mass Range	Automatic scanning (continuously variable): m/e 2-1000 at 3.5 kV accelerating voltage m/e 2-1150 at 3.0 kV " " m/e 2-1400 at 2.5 kV " " Manual adjustment (continuously variable): m/e 2- 600 at 3.5 kV " " m/e 2- 700 at 3.0 kV " " m/e 2- 850 at 2.5 kV " "
Resolution	$M/\Delta M = 1000$ (10 % valley definition).
Sensitivity (at optimal performance)	The required sample amount is less than 0.01 μg (capillary column) and 0.1 μg (packed column).
Scanning	Magnetic scan, the range of which can be pre-set to any suitable value by means of limit controls. Scanning speeds 1-960 seconds in 9 steps for full scan. Examples: m/e 12 - 100 in 2.5 sec. m/e 12 - 400 in 4.2 sec. m/e 24 - 800 in 4.2 sec. m/e 48 - 1000 in 3.6 sec. $M/\Delta M = 1000$ m/e 12 - 100 in 1.0 sec. m/e 12 - 400 in 1.7 sec. m/e 24 - 800 in 1.7 sec. m/e 48 - 1000 in 1.5 sec. $M/\Delta M = 400$
Magnetic Field	
Accelerating Voltage	3-step selector for 2.5, 3.0 and 3.5 kV. Stability better than 0.01 % per 10 min.
Magnetic Field	0-13 kilogauss continuously variable. Stability better than 0.01 % per 10 min.
Electron Energy	10-100 eV. Automatic switching to preselected value during scan, e.g. from 20 to 70 eV.
Ion Source Exit Slit	0-0.4 mm. Continuously adjustable from outside the vacuum.
Collector Slit	0-0.8 mm and rotatable ± 5°. Continuously adjustable from outside the vacuum.
Electron Multiplier	14 dynodes, variable gain $10^3 - 10^7$. The multiplier is fed by a high-voltage D.C. power supply (stability better than 0.01 % per 10 min.), 1.7 - 3.7 kV in 10 steps.
Recording	A collector electrode, located just after the exit slit of the ion source is connected through an electrometer amplifier to a strip-chart recorder. With GLC- typical chromatograms are produced by continuous recording of total ion current in the spectrometer. With other inlet systems the recorder serves to indicate optimal ion intensity for mass spectral analysis. Mass spectra are recorded at 3 sensitivities on a multichannel UV recording oscillograph, the operation of which is automatically synchronized with the automatic scan.
Inlet Systems	Gas chromatograph and all-glass system for alternative use. Provision for connection of optional inlet systems. (A direct inlet system has been installed.)
Gas Chromatograph	The cylindrical oven with a circulating air bath accepts coiled columns of variable length but maximum dimensions of 140 mm (5½") coil diameter and 100 mm (4") height. Column temperatures are regulated by proportional control (25-350° C) for isothermal operations, and can be programmed linearly at rates up to 15°/min. A carrier gas flow meter and flow control regulator are included with the standard instrument.
Molecule Separator*	2-step jet separator of the Becker-Ryhage type, column temperature regulated by proportional control. 50 % to 75 % of the sample injected into the column passes through the separators and reaches the ion source of the mass spectrometer but only 0.5 % to 1 % of the carrier gas. The total enrichment factor is between 50 and 150.

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* The principles of the molecule separator are protected by patents in USA, West Germany, France, Great Britain, Italy, Canada and Japan.

Vacuum System	Two separate pumping assemblies are provided: one for the analyzer tube and one for the inlet systems, with two separate high capacity pumps.		
	Analyzer tube:	Fore pump	2.5 m^3/h
		Oil diff. pump	550 ltrs/sec.
		Cold trap for liquid N_2 or CO_2. Ultimate vacuum 10^{-7} mm Hg (closed dual valve).	
	Inlet system:	Fore pump	9.5 m^3/h
		Oil diff. pump	150 ltrs/sec.
		Mercury booster pump	2 ltrs/sec.
	Gauges:	Pirani and Penning type vacuum gauges.	
Bake-Out	Analyzer tube and other high vacuum parts can be out-gassed at 300-400° C by indirect heating.		
Mains Connection	220/380 V (220 V to ground, 380 V between phases) 3-phase A.C. Other voltages are suitable, but require a separate transformer, optionally available.		
Power Consumption	Approx. 8 kVA, unsymmetrical load, max. 15 A/phase (at 220/380 V).		
Cooling Water Consumption	Approx. 3 ltrs/min., temperature max. 25° C (77° F).		
Dimensions and Weights	Analyzer Unit		125 cm (4 ft 1 in) = h
			85 cm (2 ft 9 in) = w
			165 cm (5 ft 5 in) = l
		Approx. weight	600 kg (1,300 lb)
	Control Unit		150 cm (4 ft 11 in) = h
			105 cm (3 ft 5 in) = w
			105 cm (3 ft 5 in) = l
		Approx. weight	250 kg (550 lb)

For a schematic diagram of the LKB-9000 GLC-mass spectrometer see Figure 1.

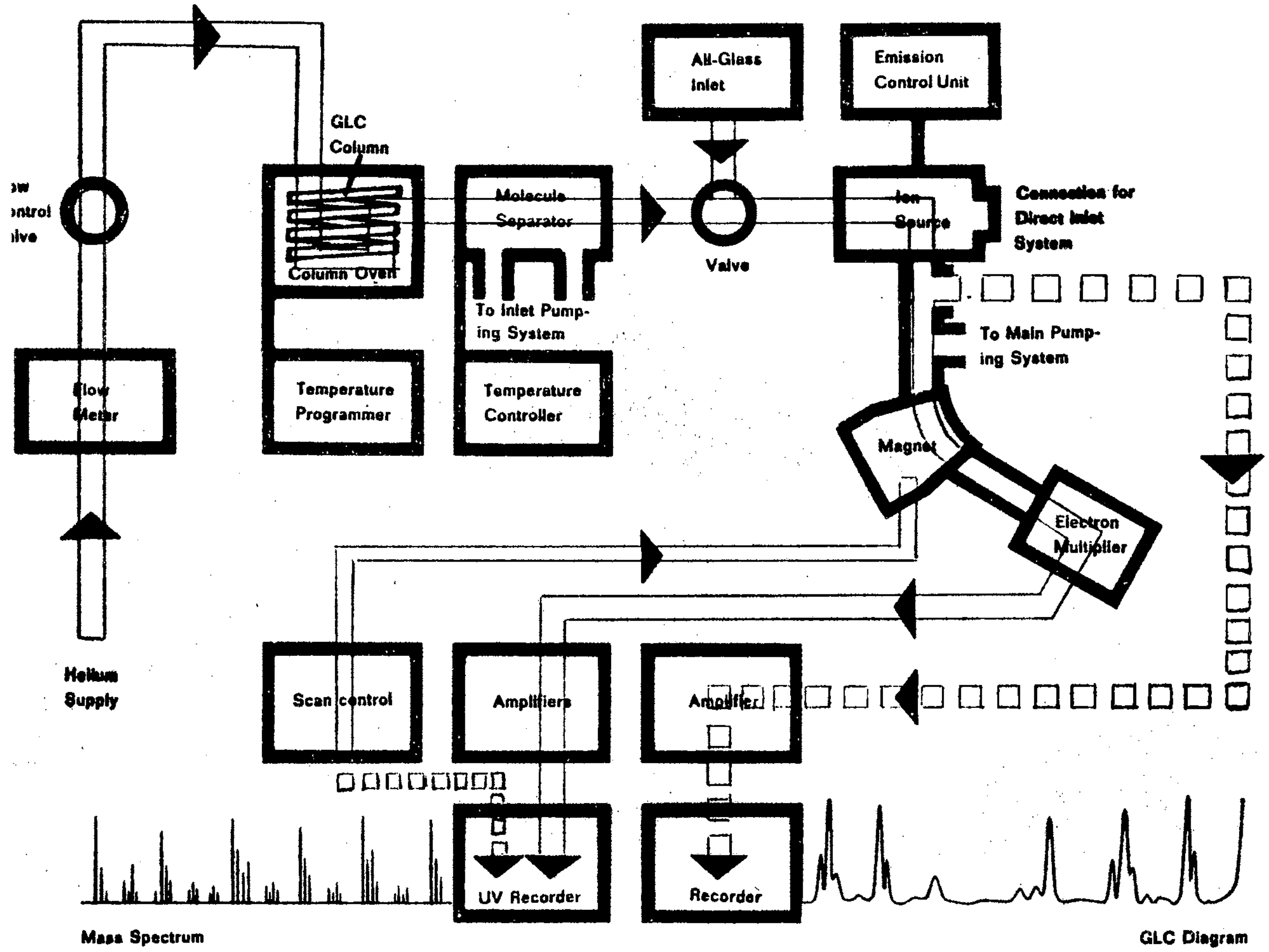


Figure 1. Block diagram of LKB-9000 Gas Chromatograph-Mass Spectrometer.

The NMR spectra of some trityl compounds are quite interesting, particularly in the aromatic (i.e. trityl) region, and should be examined more carefully at high and low temperatures. The aromatic protons in N-tritylaniline (Plate XXXVII) split into two groups, a multiplet at δ 7.2 (15H) and a series of singlets at δ 6.2-6.9 (5H). In o-trityltoluene (Plate XXXI), the aromatic protons are observed as a singlet at δ 7.15 (15H) and a singlet at δ 7.06 (4H); thus it is possible that the four aromatic protons on the ring containing the methyl group are slightly shielded with respect to the other aromatic hydrogens. Three tritylamines (Plates XXXVII, XXXIX and XL) showed multiplets centered at δ 7.15 and 7.50 which are difficult to integrate but are of the correct order of magnitude to be the six ortho hydrogens (δ7.5) with the remaining aromatic protons at δ 7.15. Trityl phenyl sulfide (Plate XLI) has a multiplet at δ 7.17 (15H) and a singlet at δ 6.9 (5H), thus indicating nonequivalence of the aromatic protons. A hydrocarbon, 1,1,1,2-tetraphenylethane (Plate XXVIII), showed nonequivalent aromatic hydrogens with a singlet at δ 7.17 (15H) and a multiplet from δ 6.5-7.0 (5H). Thus, from these few examples it is apparent that alterations in shielding of certain ring protons of the trityl system occur with a variation in substituents attached to the alpha-carbon. One case which could well be examined by a high and low temperature study via NMR analysis is that involving N-tritylaniline. Assuming that the C-N-C bond angle is less than 109° one might expect restricted rotation around the C_6H_5-N bond at room temperature. Thus certain protons (probably the ortho hydrogens) on the phenyl rings of the trityl system could experience a marked difference in magnetic shielding because of the position of the phenyl ring attached to nitrogen. At high temperature the ease of rotation around the C_6H_5-N bond would be increased and the shielding of the _ortho_ protons in the rings of the trityl system would change.

The trityl compounds used in this study were prepared as exemplified by the following reaction equations:

1. $(C_6H_5)_3CMgBr \quad + \quad RX \xrightarrow[\text{benzene}]{\text{ether}} (C_6H_5)_3CR \quad + \quad MgBrX$

R = $CH_2C_6H_5$ (VIII) and $CH_2CH{=}CH_2$ (VII)

2. $(C_6H_5)_3CBr \quad + \quad RMgX \xrightarrow[\text{benzene}]{\text{ether}} (C_6H_5)_3CR \quad + \quad MgBrX$

R = CH_3 (VI), $(CH_3)_3C$ (IX) and _c_-C_6H_{11} (XI)

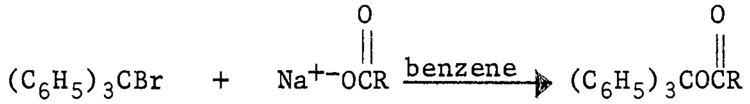
3. $(C_6H_5)_3CBr \quad + \quad C_6H_5C{\equiv}C^-Na^+ \xrightarrow[\text{benzene}]{\text{ether}} (C_6H_5)_3CC{\equiv}CC_6H_5 \quad + \quad NaBr$

4. $(C_6H_5)_3COH \quad + \quad ROH \xrightarrow[H_2O]{\text{trace } H_2SO_4} (C_6H_5)_3COR \quad + \quad H_3O^+ \quad + \quad HSO_4^-$

R = CH_3 (XIV) and CH_2CH_3 (XV)

5. $(C_6H_5)_3CBr \quad + \quad CH_2{=}CHCH_2OH \xrightarrow[\text{benzene}]{\text{pyridine}} (C_6H_5)_3COCH_2CH{=}CH_2$

$+ \quad C_5H_5\overset{+}{N}H\ Br^-$

6.


$(C_6H_5)_3CBr \quad + \quad Na^{+-}O\overset{\overset{O}{\|}}{C}R \xrightarrow{\text{benzene}} (C_6H_5)_3CO\overset{\overset{O}{\|}}{C}R$

R = CH_3 (XVIII), C_6H_5 (XX) and $(CH_3)_3C$ (XIX)

7. $(C_6H_5)_3CBr \quad + \quad RNH_2 \xrightarrow[\text{benzene}]{\text{pyridine}} (C_6H_5)_3CNHR \quad + \quad C_5H_5\overset{+}{N}H\ Br^-$

R = C_6H_5 (XXVI), $C_6H_5CH_2$ (XXVII), _c_-C_6H_{11} (XXIX)

and CH_3CH_2 (XXVIII)

8. $(C_6H_5)_3CBr \quad + \quad RSH \xrightarrow[\text{benzene}]{\text{pyridine}} (C_6H_5)_3CSR \quad + \quad C_5H_5\overset{+}{N}H\ Br^-$

R = C_6H_5 (XXI), $C_6H_5CH_2$ (XXII) and $CH_3CH_2CH_2$ (XXIII)

In addition to the above compounds, other trityl derivatives and related substances examined in the study were: $(C_6H_5)_3CH$, $(C_6H_5)_3{}^{13}CH$, $(C_6H_5)_3COH$, $(C_6H_5)_3CBr$, $(C_6H_5)_2CH_2$, $(C_6H_5)_3CCH_2C(CH_3)_3$, c-$C_6H_{11}C(C_6H_5)_3$, $(C_6H_5)_4C$, c-$C_6H_{11}OC(C_6H_5)_3$ and 9-phenylfluorene. Another compound, o-trityltoluene, was found to be slightly impure as evidenced by elemental analysis but was included in Table VII for the sake of completeness.

All of the trityl compounds examined, except 1,3,3,3-tetraphenylpropyne, give rise to a high intensity peak at m/e 243 in the mass spectrometer. This fragment must certainly be the trityl cation and it is the decay of this moiety which provides much of the interesting chemistry of these compounds. The above-named acetylenic compound does not fragment to an appreciable extent to yield a major peak at m/e 243 (0.8%) and thus, being an anomaly, will be discussed separately. One very interesting fragment occurs at m/e 228 (or at m/e 229 when the base peak is m/e 224). This would require loss of CH_3 from the trityl cation, a transition which is supported by a metastable peak, as are all major transitions postulated in this thesis (see Table II). Since it was previously thought[41] that the carbon atom being lost was the central carbon of the trityl system (it was also believed[31] that the central carbon was lost in diphenylmethyl systems upon electron bombardment), we decided to study the mass spectrum of triphenylmethane α-^{13}C (Plate III). A comparison of this compound with unlabeled triphenylmethane (Plate II) made it immediately obvious that the ^{13}C was retained in all major fragment ions to a rather high degree. The m/e 228 and 229 fragments were chosen for accurate calculations concerning ^{13}C retention in the

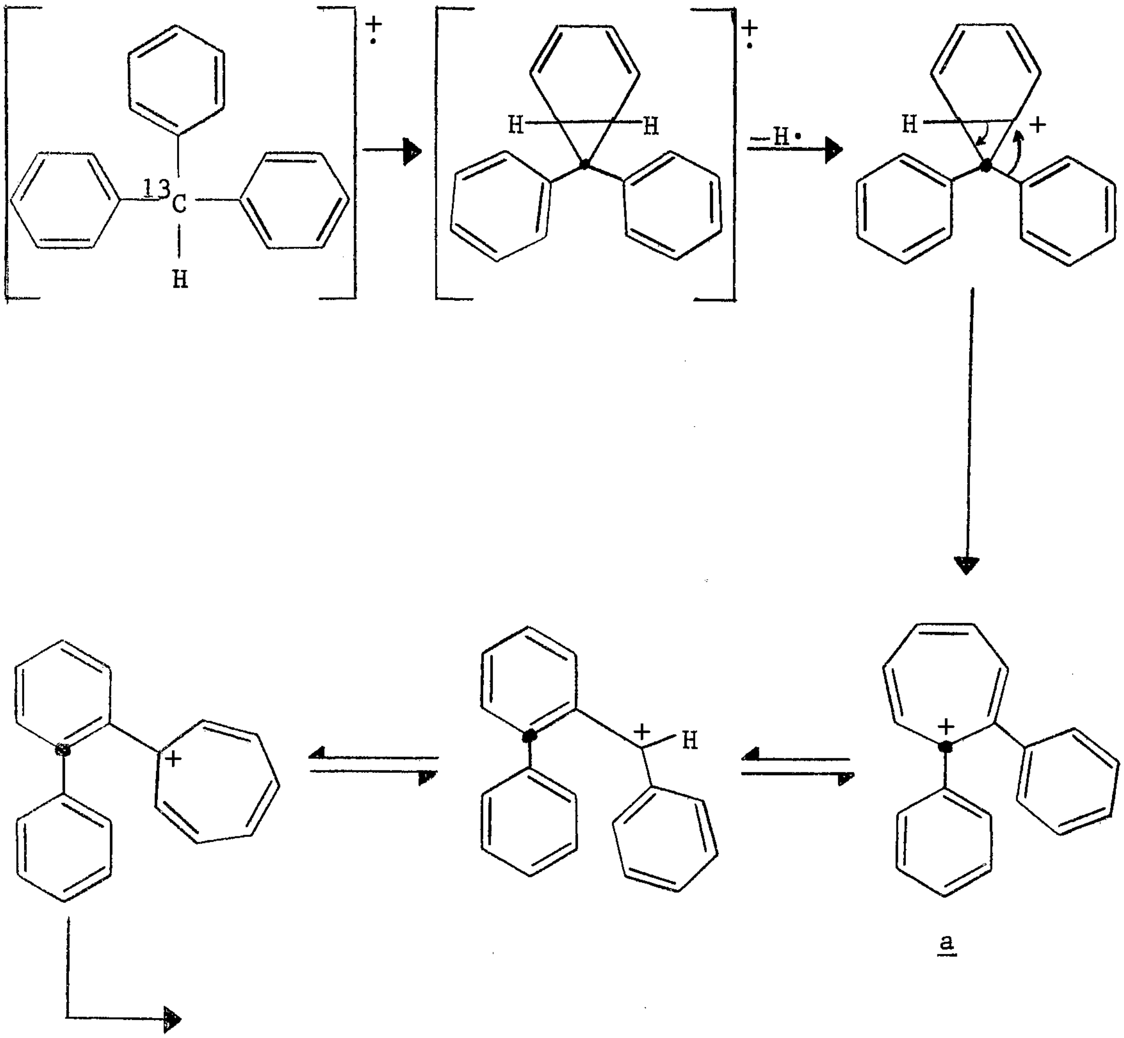
TABLE II

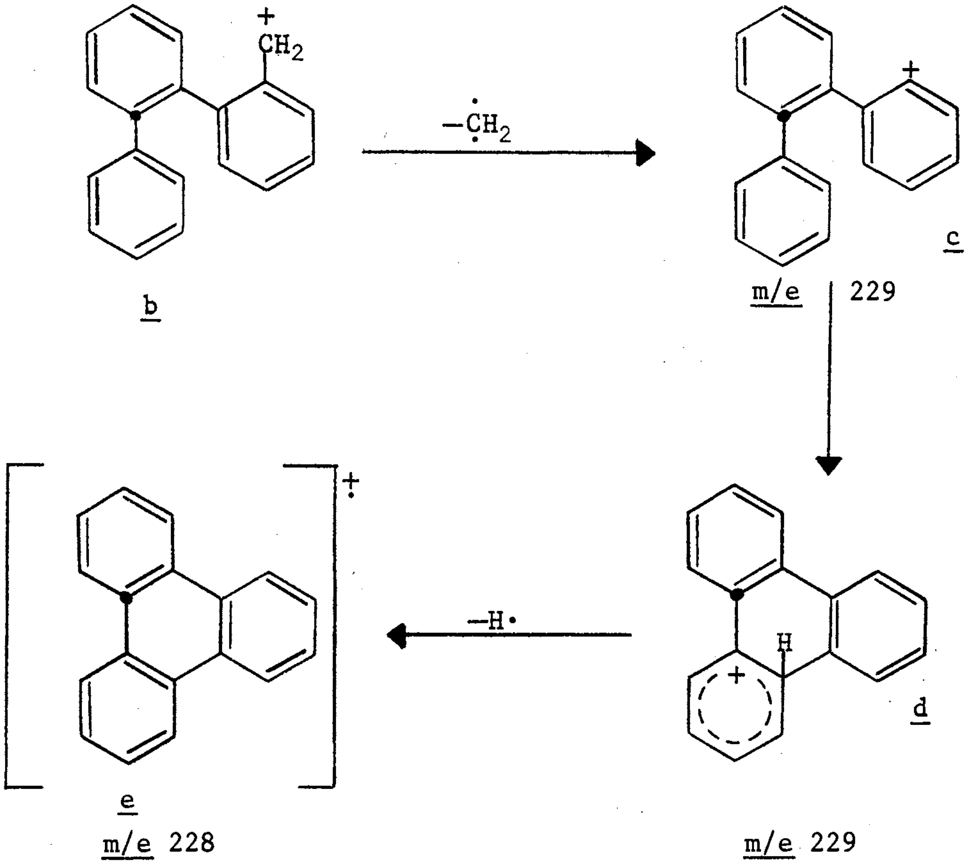
IMPORTANT METASTABLE TRANSITIONS OBSERVED IN SYSTEMS CONTAINING THE TRITYL GROUP

A, approximate (m/e) position of observed metastable peak
B, transition implied
C, calculated value[10] (m/e) for metastable peak of B

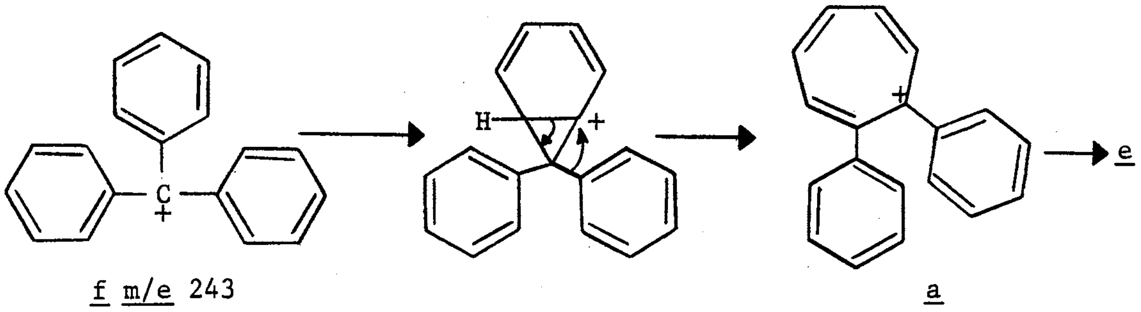
A	B	C
164	166 → 165 + H•	164.01
163	167 → 165 + H_2	163.02
215	244 → 229 + CH_3•	214.29
242	244 → 243 + H•	242.00
138	167 → 152 + CH_3•	138.35
214	243 → 228 + CH_3•	213.93
113	243 → 166 + C_6H_5•	113.40
192	241 → 215 + C_2H_2	191.80

labeled triphenylmethane (57.5% ^{13}C in α-position). In order to make these calculations one must consider the m/e range 226-231 because of natural abundance ^{13}C and ^{2}H content which must be taken into consideration when calculating the ^{13}C distribution. The calculations (see Table III) confirmed a high level of ^{13}C retention, 95.0% in m/e 229 and 96.5% in m/e 228. Since the α-carbon atom is not lost (within experimental error), we postulate a tropylium ion intermediate in the formation of the m/e 229 peak from triphenylmethane (or m/e 228 peak from trityl cation). Note: the ^{13}C is labeled as a black dot in the formulas.





A similar mechanism can easily be envisioned for the formation of m/e 228 from the trityl cation, m/e 243 (see Plate I for the mass spectrum of the simplest trityl cation, trityl bromide).



It seems reasonable that the increased amount of d (m/e 229), which occurs when the base peak is m/e 244, is due to some kind of minor energy difference in the rearrangement of $[(C_6H_5)_3CH]^{+\cdot}$ as compared with

TABLE III

CALCULATIONS OF ^{13}C DISTRIBUTION IN $(C_6H_5)_3{}^{13}CH$ IN THE FRAGMENTS *m/e* 226-231

m/e	$(C_6H_5)_3CH$		$(C_6H_5)_3{}^{13}CH$	
226	33.5[a]	0.1313[b]	18.2[a]	0.0641[b]
227	23.6	0.0925	31.6	0.1112
228	79.7	0.3125	53.6	0.1887
229	100.0	0.3921	100.0	0.3520
230	18.2	0.0714	69.5	0.2446
231			11.2	0.0394

	$(C_6H_5)_3CH$[c]	$(C_6H_5)_3{}^{13}CH$[c]	^{12}C in $(C_6H_5)_3{}^{13}CH$	^{13}C in $(C_6H_5)_3{}^{13}CH$
226	0.1596	0.0778	0.0778	0.0
227	0.0810	0.1198	0.0370	0.0818
228	0.3607	0.2042	0.1602	0.0440
229	0.4039	0.3852	0.1847	0.2005
230	0.0007	0.2177	-0.0015	0.2192
231		-0.0016		

$$^{13}C \text{ content in } \underline{m/e}\ 229 = \frac{0.2192}{0.2192 + 0.1847} = 54.5\%. \quad \text{Retention} = 95.0\%.$$

$$^{13}C \text{ content in } \underline{m/e}\ 228 = \frac{0.2005}{0.2005 + 0.1602} = 55.5\%. \quad \text{Retention} = 96.5\%.$$

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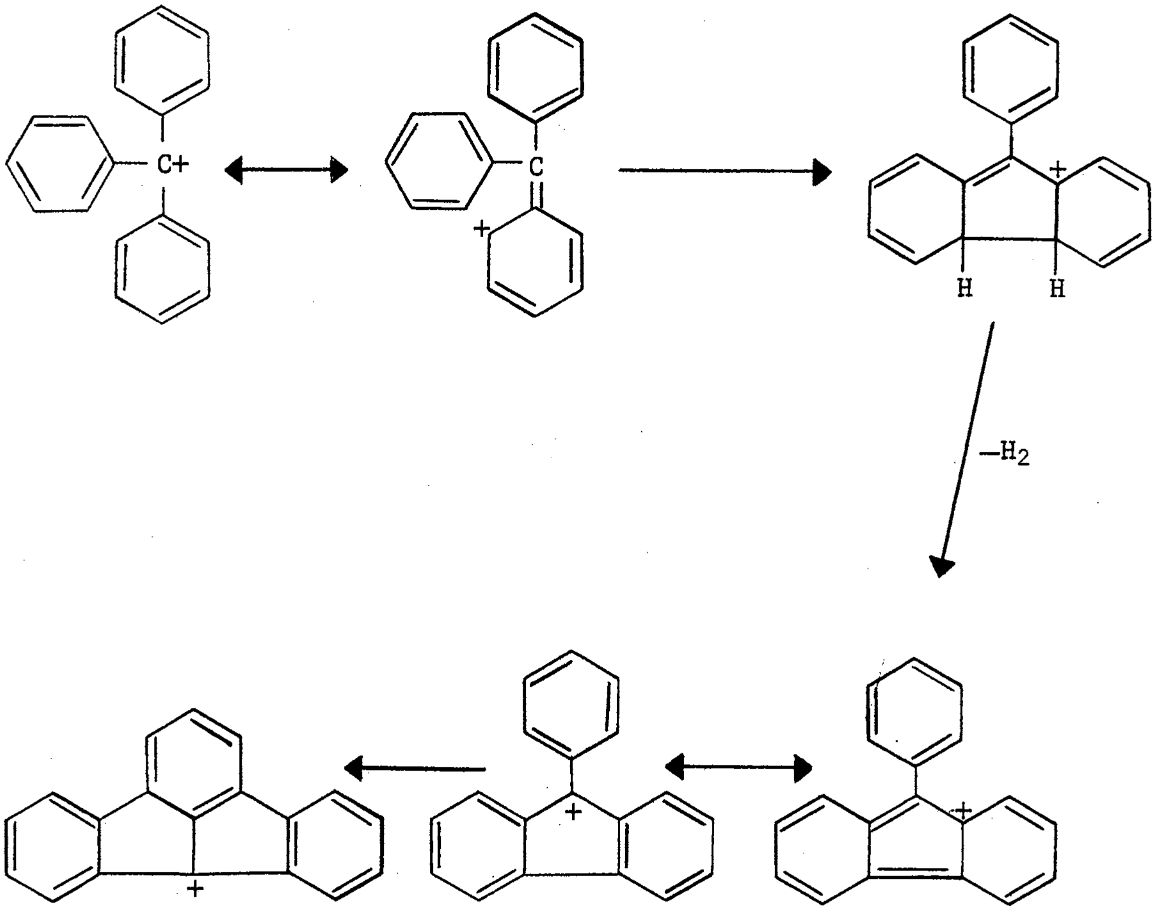
[a] Relative intensities based on *m/e* 229 = 100%, each an average value of nine scans across the *m/e* range in question.

[b] Relative intensities based on $\sum_{226-231} = 1.0$.

[c] Relative intensities corrected for natural abundance of ^{13}C and ^{2}H, based on $\sum_{226-231} = 1.0$.

$(C_6H_5)_3C^+$. Of course, the answer may be more subtle than this explanation.

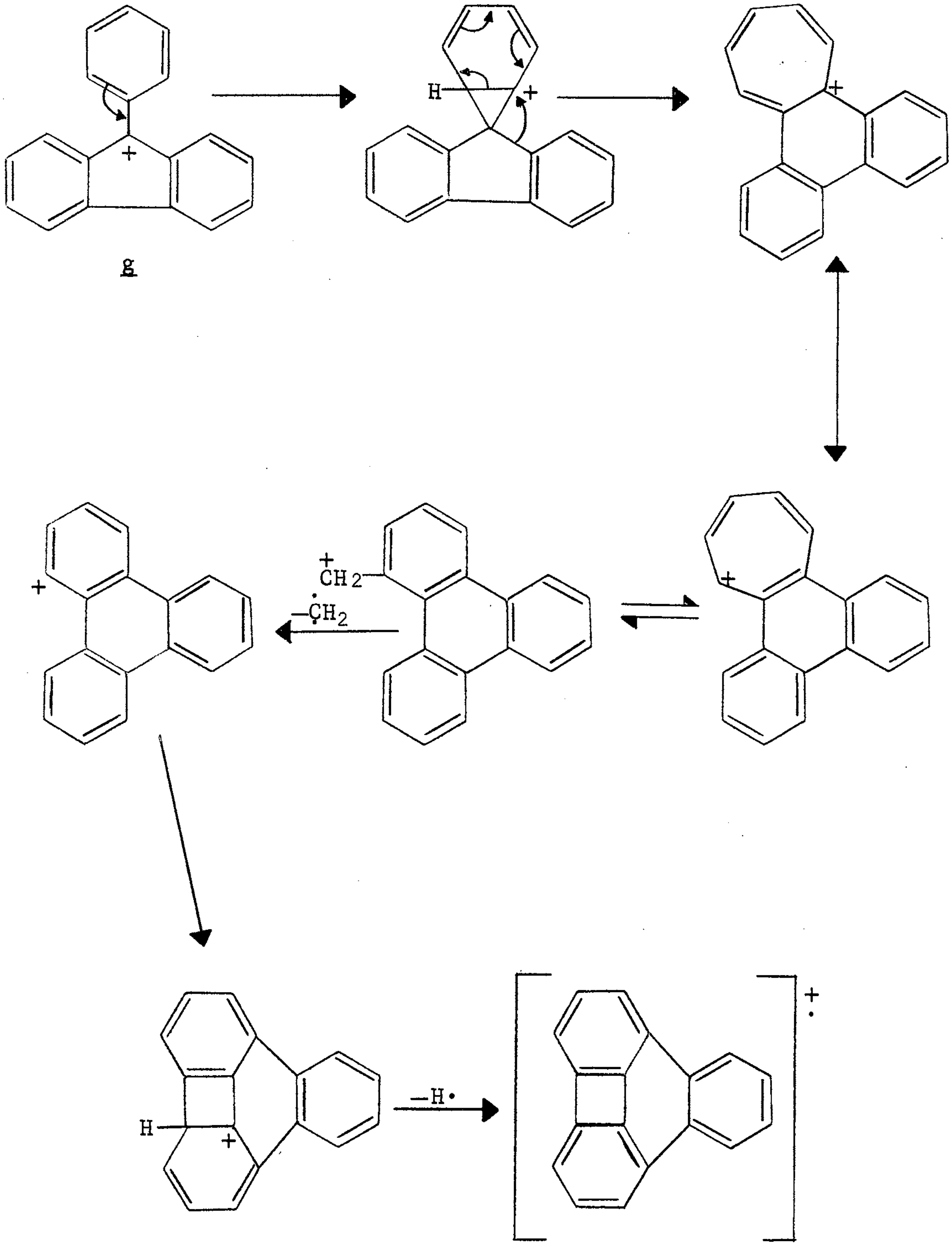
Low abundance peaks at *m/e* 241 and 239 are always observed in the rearrangement of the trityl group and are possibly due to *g* and *h*. The mass spectrum of 9-phenylfluorene gives rather intense peaks at *m/e* 241 and 239, which supports the postulate that *ortho* coupling occurs in 9-phenylfluorene to give a *m/e* 239 (*h*), and in the trityl cation to give *g* and *h*. The mass spectrum of 9-phenylfluorene also gives a low intensity peak at *m/e* 226 (with nothing at *m/e* 228 and 229), thus lending



h *m/e* 239

g *m/e* 241

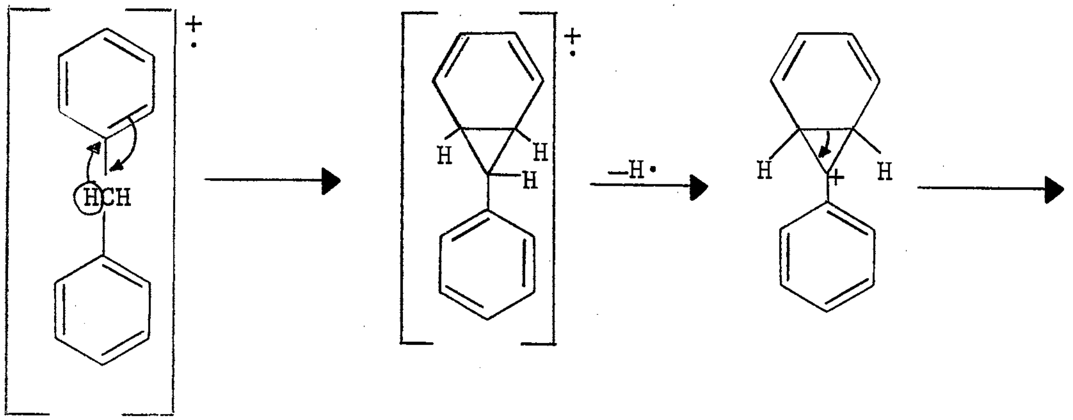
credence to the supposition that the m/e 226 peak (i) is triphenylmethane arises from the 9-phenylfluorenyl cation (g). We cannot, however, rule

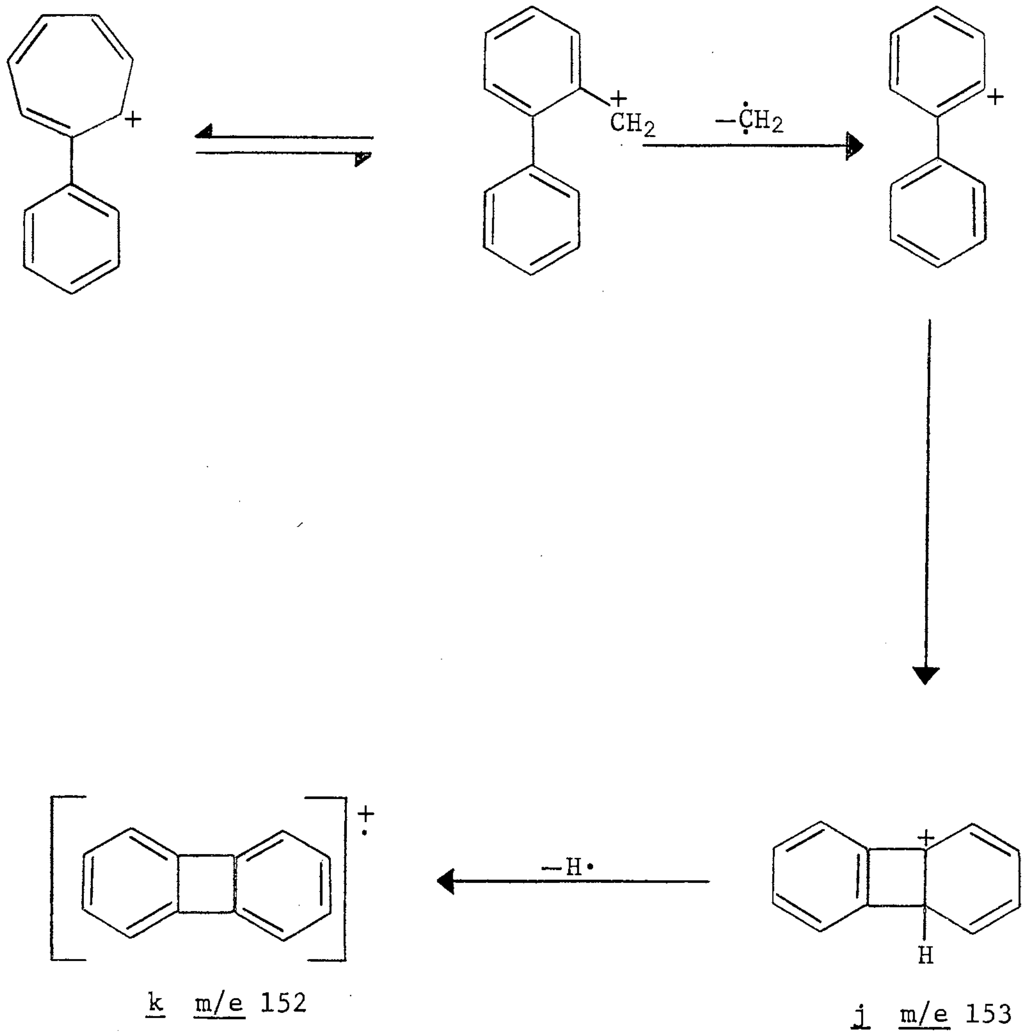


i m/e 226

out the possibility that the m/e 226 peak (i) arises from the m/e 228 fragment (e). Compound (e), 9,10-benzophenanthrene, itself loses a pair of hydrogen atoms[11] from the parent ion (100%) to give an ion of mass 226 (22%). No structure is proposed for this ion, but it could be a benzyne derivative or possibly a structure corresponding to (i). This, admittedly, is a strained moiety but other similar strained systems have been postulated in the literature.[4]

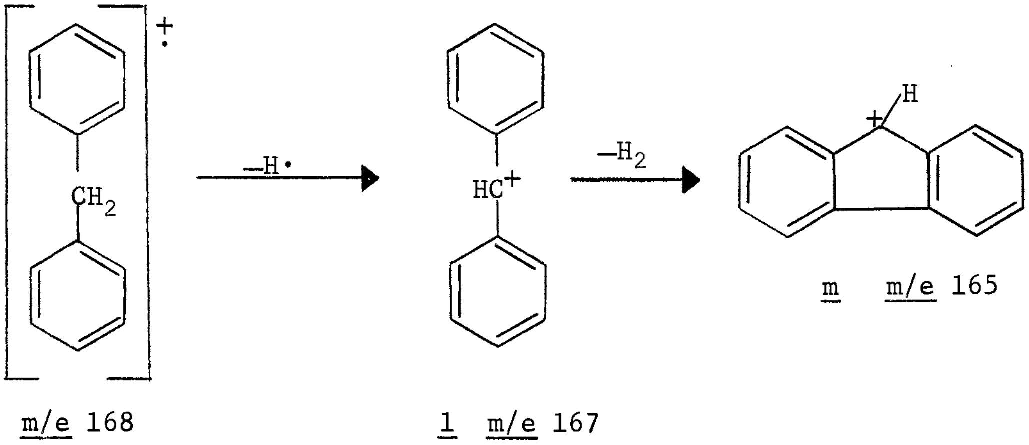
Biphenylene, which is formed from the diphenylmethyl cation, must decay without the loss of the central carbon atom as evidenced by the ^{13}C retention in the m/e 152 peak in triphenylmethane-$\alpha^{13}C$. Thus, a tropylium ion intermediate is suspected in the rearrangement m/e 167 (diphenylmethyl cation) to m/e 152 (k, biphenylene). Supporting evidence for this is given by the fact that diphenylmethyl systems are well known to undergo tropylium ion formation as evidenced by a deuterium scrambling study (see Historical, page 45). The mass spectrum of diphenylmethane shows rather intense ions at m/e 168, 167, 165, 153 and 152, which may be formed in the following manner:



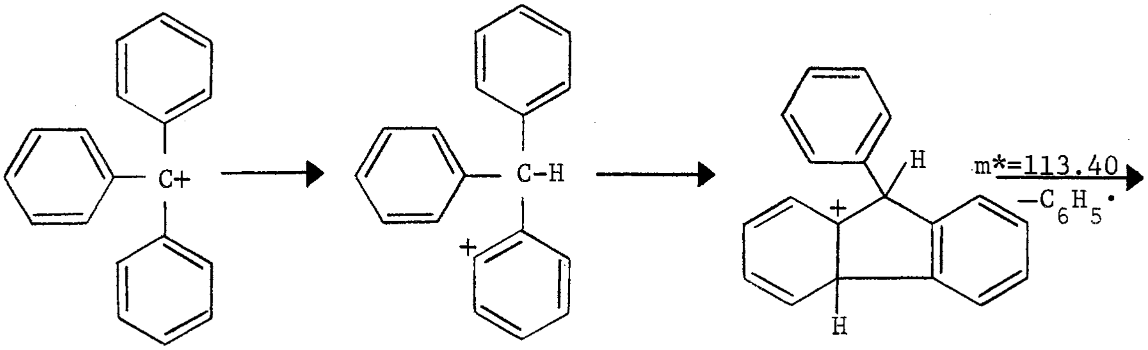


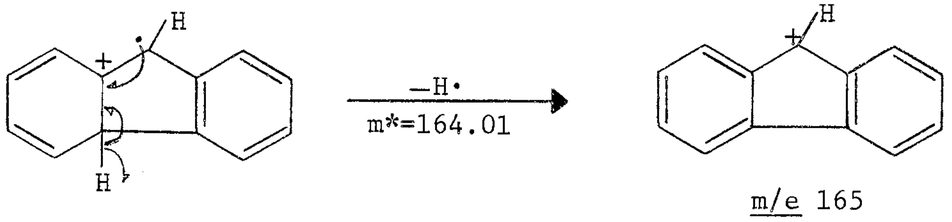
It should be noted that this mechanism is quite similar to the one postulated for the transition (f) to (e) in which the α-carbon atom is not lost.

The diphenylmethyl cation can give rise to the fluorenyl cation (m) in a mechanism similar to the one postulated for the formation of the 9-phenylfluorenyl cation from trityl cation:



It is quite possible that the fluorenyl cation (m/e 165) is formed from the trityl cation, as well as the above mentioned ortho ring closure of the diphenylmethyl cation. In either case appropriate metastable peaks are observed (see Table II).





It should be noted that whatever the reason for the unexpectedly large amount of m/e 229 (d) in the mass spectrum of triphenylmethane (as compared to other trityl systems), a similar explanation may be valid for the increased amount of m/e 153 (j) in the mass spectrum of diphenylmethane (as compared to other diphenylmethyl systems).

Other peaks which are present in all trityl derivatives but seldom exceed 5% of the base peak are at m/e 77, 89, 115, 139, 202 and 215. They can be rationalized[41] by loss of phenyl radicals or acetylene from the more intense ions in the spectra. These transitions are summarized in Table IV.

Doubly[18] and triply[33] charged ions have been reported previously in studies involving trityl systems and were also observed in this study with the major doubly charged ions being observed at m/e 94.5, 106.5, 107.5, 118.5, 119.5, 120.5 and 121.5. Of these, the doubly charged ion observed at m/e 119.5 is always the major one and is assumed to have the basic structure of h.

TABLE IV

MINOR FRAGMENTS IN THE MASS SPECTRA OF TRITYL COMPOUNDS

$$\text{f, m/e } 243^{+} \xrightarrow{-2\ C_6H_5\cdot} \text{m/e } 89^{+}$$

$$\text{l, m/e } 167^{+} \xrightarrow{-2\ C_2H_2} \text{m/e } 115^{+}$$

$$\text{m, m/e } 165^{+} \xrightarrow{-C_2H_2} \text{m/e } 139^{+}$$

$$\text{e, m/e } 228^{+} \xrightarrow{-C_2H_2} \text{m/e } 202^{+}$$

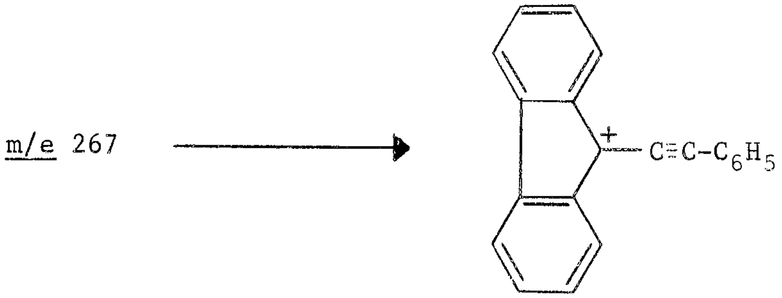
$$\text{g, m/e } 241^{+} \xrightarrow{-C_2H_2} \text{m/e } 215^{+}$$

An anomaly among the mass spectra of trityl hydrocarbons is that of 1,3,3,3-tetraphenylpropyne (Plate VI). The trityl cation itself contributes an extremely small part of the total ion current while the molecular ion is the base peak. This irregularity is presumably due to increased s character of the trityl-alkynyl bond (the mass spectrum of diphenylacetylene also yields a large molecular ion[22]) and is observed also in systems containing trityl functions attached to alkene groups.[36] A peak at m/e 267 suggests loss of phenyl group.

$$(C_6H_5)_2\text{-}\underset{+}{C}\text{-}C{\equiv}C\text{-}C_6H_5 \quad (\text{or } (C_6H_5)_3C\text{-}C{\equiv}C^{+})$$

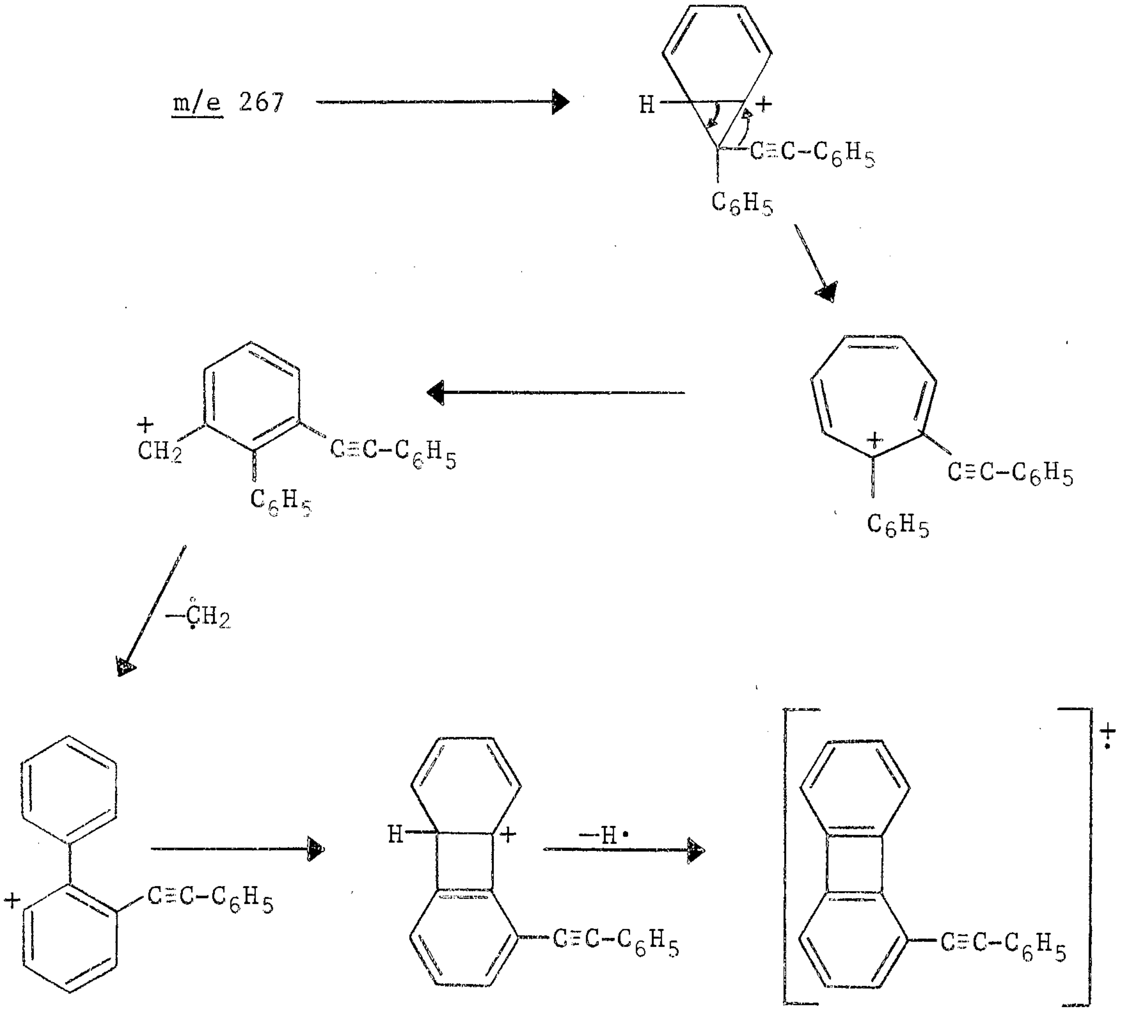
m/e 267

Ring closure to give the fluorenyl system is reminiscent of the pathways proposed previously.



m/e 265

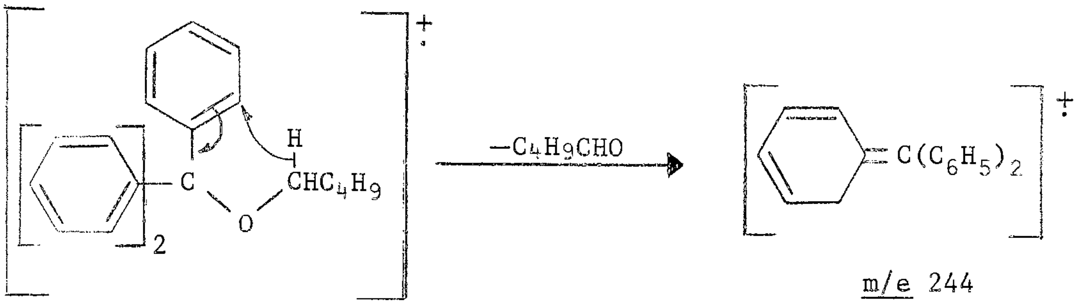
A route to m/e 252 could involve a tropylium ion as suspected in the trityl compounds already discussed.



m/e 252

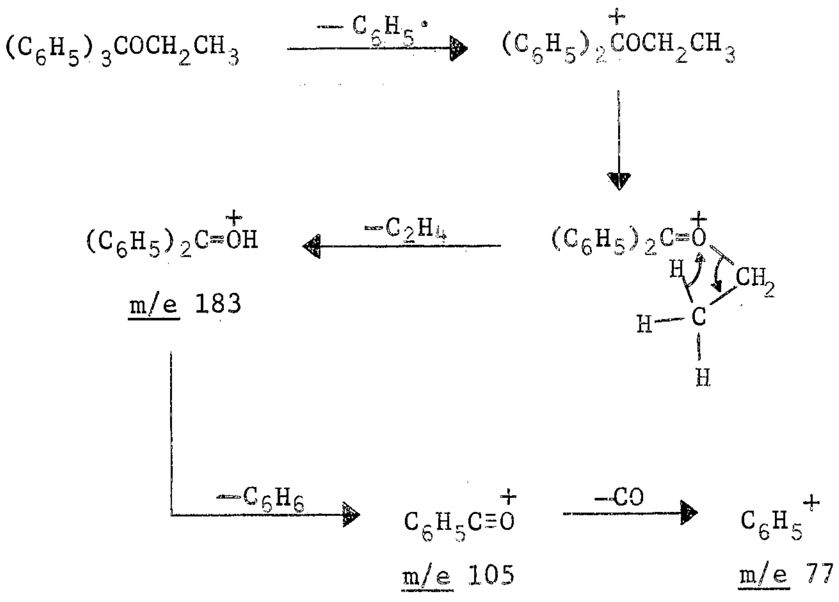
Interestingly, a m/e 343 peak of fair intensity (11%) is apparently due to loss of one hydrogen from an aromatic ring. This unusual transformation and that relating to the generation of m/e 165 (15% of the base peak) is not immediately discernible.

The mass spectra of some trityl ethers have been very recently published.[41] Peaks at m/e 243 and 244 are both large, but the peak at m/e 244 is the base peak (for the mass spectrum of a typical trityl ether see Plate V, trityl benzyl ether). This was rationalized by a hydrogen transfer from the carbon atom adjacent to the oxygen atom through a six-membered intermediate to the ortho position of a benzene ring[41] (illustrated below with n-pentyl trityl ether).



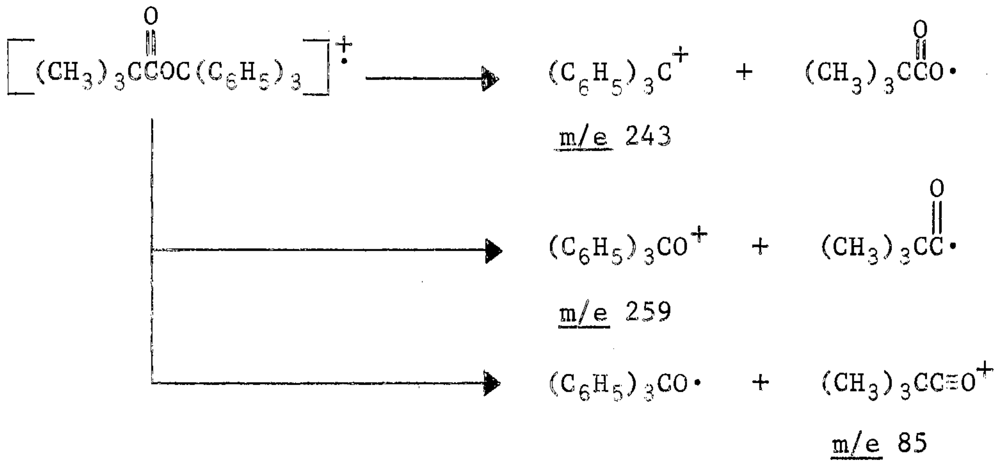
We wish to point out that trityl ethers are subject to pyrolysis[34] between 200-300° or below 200° in the presence of catalysts[35] (the metal surface of the ion source may cause early pyrolysis) as unpublished results from this Laboratory have confirmed.[8] Thus, fragmentation in the ion source may be due, in part, to pyrolysis instead of electron bombardment, giving rise to considerable quantities of triphenylmethane, m/e 244.

Other fragmentation pathways are more classical and are briefly summarized below using trityl ethyl ether as an example.

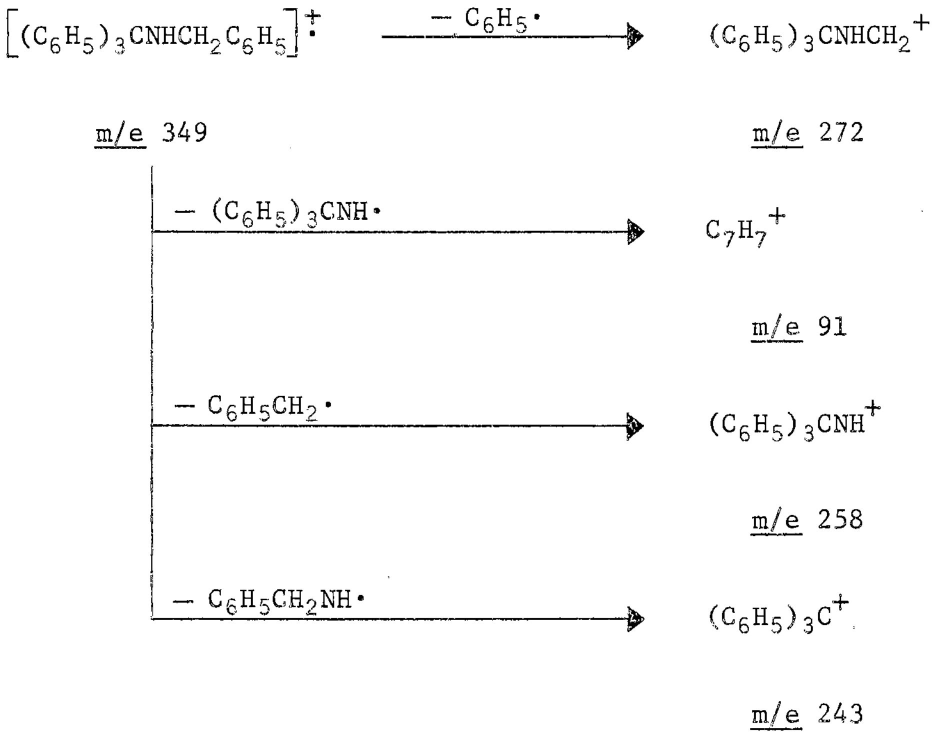


The β-hydrogen transfer to oxygen prior to the formation of the m/e 183 fragment is supported by the fact that the m/e 183 peak is absent in trityl ethers containing no available β-hydrogen.

Trityl esters, such as trityl pivalate (Plate VII), result in major peaks at m/e 243 and 259 upon electron bombardment. The peak at m/e 243 is formed via trityl-oxygen bond cleavage and the one at m/e 259 via acyl-oxygen bond cleavage. Again the fragment at m/e 244 is quite intense, possibly because of pyrolysis before electron bombardment. Such pyrolysis is well known to yield triphenylmethane[7] (m/e 244).



Tritylamines show low intensity molecular ions with major peaks occurring at m/e 243, 258 and 244. Tritylbenzylamine (Plate VIII) has as its base peak m/e 272; the molecular ion probably decays in the following manner:



Once again it is possible that the peak at m/e 244 is due to triphenylmethane formed from pyrolysis of the parent amine.

Three trityl sulfides examined gave only an extremely small molecular ion (i.e., less than 0.03%) and only two fragments with charge retention on sulfur. Trityl phenyl sulfide gives a peak at m/e 109 ($C_6H_5S^+$, 7.8%), and trityl benzyl ether a peak at m/e 123 ($C_6H_5CH_2S^+$, 9.7%). The trityl cation is the base peak from all three trityl sulfides and the previously discussed rearrangements and decompositions of the trityl system account for the majority of the total ion current in the trityl sulfides.

To summarize: 30 trityl derivatives (or related compounds) were subjected to mass spectral analysis. It was observed that the trityl portion of most of the compounds studied presented the most interesting and dominating feature in the mass spectra. Trityl cations and diphenylmethyl cations showed a strong tendency to undergo ortho ring closure between the phenyl rings, and it also was noted that these two species gave rise to a fragment which indicates loss of CH_3. The spectrum of $(C_6H_5)_3{}^{13}CH$ was examined in order to ascertain whether or not the α-carbon was being lost in this rearrangement; it was found that it was retained. Therefore, we have postulated a mechanism consistent with this observation. The mass spectrum of one hydrocarbon, 1,3,3,3-tetraphenylpropyne, was not dominated by the trityl portion of this molecule but was instead found to fragment in a rather unusual manner. A mechanism was postulated in an attempt to explain the cleavage of a C_6H_5-C bond rather than loss of the trityl group to give $(C_6H_5)_3C^+$.

CHAPTER III

EXPERIMENTAL[a-i]

Preparation of Triphenylmethanol (XIII). The method used was that found in Organic Syntheses.[2] Reagents used were 3.0 moles phenylmagnesium bromide and 200.0 g. (1.33 moles) ethyl benzoate. The yield of

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[a] The mass spectra were determined on an LKB-9000 prototype, single-focusing magnetic sector instrument (see Experimental for details).

[b] The proton nuclear magnetic resonance spectra were measured on a Varian A-60 high resolution spectrometer.

[c] The infrared spectra were determined with a Beckman IR-5A spectrophotometer in potassium bromide pellets.

[d] Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

[e] Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected.

[f] All solvents used in the reactions were distilled and stored over Linde 3-A molecular sieve as were all reagents used in making Grignard reagents.

[g] The nitrogen used to flush the reaction vessel during reaction was passed through a concentrated sulfuric acid trap and three traps filled with Linde 3-A molecular sieve.

[h] Tetraphenylmethane was purchased from Columbia Organic Chemicals Co., Inc. Triphenylmethane α-^{13}C was supplied by Dr. Richard Waack of the Dow Chemical Company, Midland, Michigan. o-Trityltoluene and 1,1,1-triphenyl-3,3-dimethylbutane were prepared by Mrs. N. L. Doss, a previous worker in this Laboratory.

[i] Mass spectral bar graph representations were provided by Miss Jo Green using an IBM 1620 computer and a computer program designed by Mr. Hsiao Yuan Li.

crude triphenylmethanol was 88%. The product was recrystallized from carbon tetrachloride. The m.p. was 161-2°C, lit.[2] m.p. 161-2°C.

Preparation of Trityl Bromide (I). Procedure was essentially that of Rathore.[38] Reagents used: 200 g. (0.78 mole) of triphenylmethanol, 117 g. (0.95 mole) of acetyl bromide and 120 ml. of benzene. The yield was 275 g. (85%), m.p. 153.5-4.3°C, lit.[38] m.p. 152-4°C.

Preparation of 1,1,1-Triphenylethane (VI). The preparations of most of the trityl hydrocarbons are exemplified by the following procedure: a 200-ml., three-necked, round-bottom flask was oven-dried at 110°C for several hours and then fitted with a nitrogen inlet tube, a condenser, and an addition funnel. Methyl iodide, 8.8 g. (0.062 mole), dissolved in 50 ml. of anhydrous ether, was added dropwise to 1.50 g. (0.062 g. atom) of magnesium, which was covered with 20 ml. of anhydrous ether. After stirring the Grignard solution for 2 hrs., it was filtered under nitrogen through glass wool. Trityl bromide, 10.0 g. (0.031 mole), dissolved in 50 ml. of benzene-ether (2:1 solution) was added dropwise to the Grignard reagent. After being stirred overnight, the reaction mixture was cooled in an ice bath and 70 ml. of 6N HCl was slowly added. The organic layer was stirred with the aqueous layer for 1 hour, then washed successively with 100 ml. of H_2O, 100 ml. of 5% $NaHCO_3$, and 100 ml. of H_2O. The organic layer was then separated and the solvent stripped off in a flash evaporator. The resulting oil was recrystallized from ethanol to yield white crystals which were dried in the vacuum oven for 4 hrs.; yield 2.04 g. (79%), m.p. 94-5°C, lit.[26] m.p. 95°C.

Preparation of 1,1,1,2-Tetraphenylethane (VIII). Trityl Grignard reagent was prepared according to the method of Bachmann.[1] Reagents used were 1.0 g. (0.041 g. atom) of magnesium, 10.0 g. (0.031 mole) of trityl bromide and 75 ml. of benzene-ether solvent (2:1). Then 7.0 g. (0.055 mole) of benzyl chloride was added slowly and the mixture stirred for 10 hrs. After workup, the oil was recrystallized from ether-hexane containing small amounts of benzene; yield 0.87 g. (26%), m.p. 143.5-4°C, lit.[26] m.p. 143-4°C.

Preparation of 4,4,4-Triphenyl-1-butene (VII). Trityl Grignard reagent was prepared as usual.[1] Reagents used were: 1.0 g. (0.041 g. atom) of magnesium, 10.0 g. (0.031 mole) of trityl bromide and 75 ml. of benzene-ether solvent. Allyl bromide, 8.5 g. (0.07 mole), was added to the Grignard reagent, and the mixture stirred for 12 hrs. The yield was 1.13 g. (40%) of 4,4,4-triphenyl-1-butene after four recrystallizations from 1-propanol, m.p. 68.5-9.5°C, lit.[1] m.p. 69.5-70.5°C.

Preparation of 2,2-Dimethyl-1,1,1-triphenylpropane (IX). Tertiary butylmagnesium chloride was prepared according to Kharasch[32a] (see also ref.47). Reagents used were: 1.88 g. (0.077 g. atom) of magnesium and 7.15 g. (0.077 mole) of tert-butyl chloride. To the filtered Grignard reagent was added 5.0 g (0.0155 mole) of trityl bromide dissolved in 50 ml. of benzene-ether. The yield of crude product was 2.9 g. (97%). After several recrystallizations from ethanol:1-propanol the yield was reduced to 55%, m.p. 185-8°C, lit.[25] m.p. 185-7°C.

Preparation of Cyclohexyltriphenylmethane (XI). Cyclohexyl Grignard reagent was prepared by treating 0.97 g. (0.04 g. atom) of magnesium with 4.9 g. (0.03 mole) of cyclohexyl bromide. Trityl bromide, 5.0 g. (0.0155 mole), disolved in benzene-ether, was added to the filtered Grignard reagent. After several recrystallizations from ethanol, the yield was 1.14 g. (35%), m.p. 138-40°C, lit.[21b] 139-40°C.

Preparation of 1,3,3,3-Tetraphenylpropyne (XXV). Sodium phenylacetylide was prepared by the reaction of 3.6 g. (0.035 mole) phenylacetylene with 0.69 g. (0.03 g. atom) sodium in 50 ml. of anhydrous benzene. After stirring for 4 hrs., 5.0 g. (0.0155 mole) of trityl bromide was added and this mixture stirred overnight. Water was added to the cooled solution and then the organic layer separated and taken to dryness. After two recrystallizations from ethanol:ethyl acetate (7:3), the yield of 1,3,3,3-tetraphenylpropyne was 60% (2.06 g.); m.p. 137.5-9.5°C, lit.[51] m.p. 138.5-40°C.

Preparation of Trityl Allyl Ether (XVI). The preparation was essentially that of Helferich.[30] Allyl alcohol, 1.1 g. (0.019 mole), was dissolved in 15 ml. of anhydrous pyridine, and to this solution was added all at once, 5.0 g. (0.0155 mole) of trityl bromide. The reaction was stirred for 25 hrs. at room temperature and then 300 ml. of H_2O was added. In 10-15 minutes, white crystals formed from the original oil-water mixture. The crystals were washed with H_2O, then dissolved in ether and the ether solution was dried ($MgSO_4$). Recrystallization from methanol yielded crystals 2.7 g. (90%) which melted at 75-6°C, lit.[30] m.p. 76°C.

Preparation of Trityl Ethyl Ether (XV). The procedure was essentially that of Smith,[44] except that it was necessary to add only a trace of H_2SO_4 to obtain an excellent yield of the desired product. Triphenylmethanol, 1.0 g. (0.0038 mole), was added to an excess of absolute ethanol (20 ml.) with a trace of H_2SO_4. The solvent was evaporated to leave a pure product (2.8 g., 95%). The m.p. was 83°C, lit.[44] m.p. 82.5-3°C.

Preparation of Trityl Acetate (XVIII). The usual procedure is described in Part I of this thesis. Reagents used were: 1.0 g.

(0.0031 mole) of trityl bromide, 0.41 g. (0.005 mole) of sodium acetate and 50 ml. of anhydrous benzene; yield 2.4 g. (80%), m.p. 82.1-3°C, lit.[6] m.p. 82-4° C.

Preparation of Trityl Pivalate (XIX). The procedure was the same as for trityl acetate. Sodium pivalate, 0.65 g. (0.005 mole), was added to 1.0 g. (0.0155 mole) of trityl bromide dissolved in 50 ml. of anhydrous benzene. The yield was 2.85 g. (83%), m.p. 92-3°C, lit.[6] m.p. 91-3°C.

Preparation of Trityl Benzoate (XX). The procedure was the same as for trityl acetate. Sodium benzoate, 0.72 g. (0.005 mole), was added to 1.0 g. (0.0031 mole) of trityl bromide dissolved in 50 ml. of anhydrous benzene; yield 3.1 g. (85%), m.p. 168-70° C, lit.[6] m.p. 168-70° C.

Preparation of N-Tritylbenzylamine (XXVII). Trityl bromide, 5.0 g. (0.0155 mole) dissolved in 50 ml. of anhydrous dioxane, was added to 3.5 g. (0.033 mole) of benzylamine, and the mixture stirred for 3 hrs. The benzylamine hydrochloride was filtered from the cold reaction mixture and the dioxane then removed with a flash evaporator. After two recrystallizations from ethanol, the yield was 2.62 g. (75%), m.p. 93.5-4° C, lit.[3] m.p. 91° C.

Preparation of Tritylcyclohexylamine (XXIX). Cyclohexylamine, 3.3 g. (0.037 mole) in 50 ml. of dioxane, was added to 5.0 g. (0.0155 mole) of trityl bromide and the mixture boiled for 4 hrs. The cyclohexylamine hydrochloride was filtered off and the resulting crystals were recrystallized three times from ethanol. The yield was 2.05 g. (60%), m.p. 124.5-5.5°C, lit.[42] m.p. 126-7°C.

Preparation of N-Tritylaniline (XXVI). Aniline, 2.0 g. (0.021 mole) dissolved in 20 ml. of anhydrous pyridine, was added to 5.0 g. (0.0155 mole) of trityl bromide. The reaction mixture was stirred at room temperature for 10 hrs., and then 500 ml. of cold H_2O was added to the reaction mixture. Crystals soon formed which were filtered out and recrystallized twice from ethanol:chloroform (5:1 mixture) containing small amounts (∿5%) of pyridine. The yield was 1.8 g. (54%), m.p. 149-50°C, lit.[46] m.p. 150-1°C.

Preparation of N-Tritylethylamine (XXVIII). Excess ethylamine (10 ml.) was added to 15 ml. of pyridine at 0°C followed by 5.0 g. (0.0155 mole) of trityl bromide. After stirring for 24 hrs., the reaction mixture was poured into 600 ml. of H_2O. The crystals formed were recrystallized twice from ethanol to give N-tritylethylamine 2.4 g. (83%), m.p. 78-9°C, lit.[14] m.p. 75-7°C.

Preparation of Trityl Phenyl Sulfide (XXI). Benzenethiol, 1.8 g. (0.016 mole), dissolved in 15 ml. of pyridine, was added to 5.0 g. (0.0155 mole) of trityl bromide. The reaction mixture was stirred 8 hrs., then heated for 1 hour and poured into 600 ml. of cold water. The resulting oil was recrystallized from ethanol twice; weight 2.1 g. (66%); m.p. 105.5-6°C, lit. m.p. 106-7°C[40] and 104-6°C.[28]

Preparation of Trityl n-Propyl Sulfide (XXIII). To 20 ml. of anhydrous pyridine was added 2.0 g. (0.026 mole) of propanethiol and 5.0 g. (0.0155 mole) of trityl bromide. The mixture was stirred at 80°C for 8 hrs. and then poured into 800 ml. of water. Within a few minutes crystals formed and were then washed (H_2O) several times and recrystallized twice (C_2H_5OH). The yield was 2.35 g. (75%), m.p. 97-8°C.

Anal. Calcd for $C_{22}H_{22}S$: C,83.00; H,6.92; S,10.07.

Found: C,82.88; H,7.07; S,10.13.

Preparation of Trityl Benzyl Sulfide (XXII). Benzyl mercaptan, 2.5 g. (0.02 mole) dissolved in 15 ml. of pyridine was added to 5.0 g (0.015 mole) of trityl bromide. The mixture was stirred at room temperature for 6 hrs., then poured into 800 ml. of H_2O. The crystals which settled out were recrystallized three times ($1\text{-}C_3H_7OH$). The yield was 2.5 g. (70%), m.p. 91-2°C, lit. m.p. 91-2°C[20] and 82-3°C.[40]

Anal. Calcd for $C_{26}H_{22}S$: C,85.30; H,6.02; S,8.74.

Found: C,84.92; H,6.20; S,8.88.

Procedure for Obtaining Mass Spectra. Since all trityl compounds are solids, they were placed directly into the ion source by a direct probe. It was found that ion source temperatures above 250°C would cause thermal degradation of some trityl compounds; thus the ion source was not allowed to exceed 220°C during these determinations. It was necessary to experimentally determine the probe temperature required to vaporize the compounds at 10^{-6} mm Hg(never more than 50°C). The trap current was maintained at 65 μamps, the electron multiplier voltage at 1.7 kilovolts, the acceleration voltage at 3.5 kilovolts and the filter at 240 cps. The compounds were subjected to an ionizing voltage of 70 and 20 electron volts. Spectra obtained at 70eV were used for peak measuring and those at 20eV were used for determining positions of metastable peaks. The spectra were obtained on Kodak Direct Print Linagraph Paper by an ultraviolet light recorder.

TABLE V

MASS SPECTRAL DATA FOR TRITYL COMPOUNDS

	Trityl Bromide	Diphenylmethane	9-Phenylfluorene	Triphenylmethane	Triphenylmethane α-^{13}C	1,1,1-Triphenylethane
	I	II	III	IV	V	VI
m/e	% RI	% RI	% RI	% RI	% RI	% RI
38		0.55				
39	1.5	5.5		1.3	2.1	0.7
40		0.55			0.33	
41		1.3			0.21	
50		1.9	0.95	0.5	1.2	0.7
51	1.9	5.4	1.5	1.4	2.9	2.6
52		0.87			0.67	0.4
62	0.6	1.1			0.28	
63	1.9	4.2	1.2	0.96	1.55	0.8
64		1.1			0.7	
65	0.7	7.1		0.73	1.3	0.6
66		0.65			0.33	
69		0.45				
69.5		1.6				
70		1.0				
70.5		0.82				
71		1.8				
74	0.7	1.2	0.46	0.43	0.44	
75	0.84	0.92	0.65	0.52	0.8	
76	0.86	2.4	0.38	0.6	0.9	0.8
77	1.4	2.3	1.1	1.1	1.5	6.1
78	0.8	0.93		0.83	1.2	1.6
79	1.0				0.32	
81	1.0	1.1				
81.5		1.3			0.16	
82		6.2		0.38	0.29	
82.5		5.5			0.51	
83		8.9		0.25	0.44	
83.5		1.5			0.33	
84		2.0				
84.5		0.59				
86	0.45				0.24	
87	0.96	1.0	0.74	0.29	0.52	
88	1.1			0.40	0.63	
89	1.1	5.5		0.89	1.2	0.9
90		2.5			0.71	
91	2.6	18.0		1.1	1.7	1.2
92		1.4			0.51	
93.5	0.85		0.96			

m/e	I	II	III	IV	V	VI
94	0.7				0.43	
94.5	3.0		1.2	0.55	0.72	
95	0.82				1.05	
100	1.1			0.31	0.30	
100.5					0.23	
101			0.66	1.2	1.05	0.8
101.5	0.70				1.2	
102	0.6	1.4		0.38	0.82	0.7
103					0.48	8.8
104						0.9
105	0.50					
105.5	0.42		0.66			
106	0.79		0.47		0.32	
106.5	3.3		1.9	0.79	0.66	
107	1.7		0.69	0.55	1.0	
107.5	4.7		0.67	1.1	1.25	0.7
108	1.7		0.76	0.75	1.5	
108.5	0.35				0.85	
109					0.29	
112	0.65		0.72	0.25	0.27	
113	5.0	0.44	1.9	1.4	1.3	0.8
113.5	1.3		0.67		1.2	
114	2.5	0.44		1.5	1.7	0.6
114.5					1.4	
115	4.0	4.7		3.3	3.6	2.2
116		0.49		0.33	2.1	
117					0.2	
118	0.88		1.2		0.14	
118.5	2.5		2.4	0.59	0.5	
119	3.4		2.4	0.48	0.8	
119.5	9.0		6.6	1.5	1.0	1.2
120	6.2		5.7	0.67	1.8	0.8
120.5	2.0		1.3		1.1	
121	1.8		4.3	0.32	0.4	
121.5	2.7		0.64		0.3	
122	0.67		0.63	0.93	0.83	
122.5					1.0	
126	0.97	0.82		0.47	0.42	0.4
127		1.0		0.4	0.65	0.5
128	0.44	3.0		1.5	1.4	0.6
129		0.49		0.31	1.4	1.0
138					0.35	
139	2.8	2.5	1.5	1.9	1.9	1.2
140		0.57		0.41	1.65	

m/e	I	II	III	IV	V	VI
141	0.64	2.3		0.84	1.0	0.6
142		0.52			0.83	
149					1.0	
150	0.76		0.62	0.25	0.49	0.6
151	0.85	1.9		1.3	1.2	0.7
152	1.7	18.0		10.0	8.3	1.8
153		16.0		2.0	9.4	0.8
154		2.0		0.37	1.95	0.6
155					0.17	
161	0.45		0.43			
162	0.65		0.55			
163	4.4	2.2	3.4	2.3	1.7	1.1
164	4.1	2.2	3.6	3.5	4.1	1.5
165	77.0	23.0	22.0	44.0	33.0	35.0
166	14.0	13.0	2.9	26.0	56.0	9.0
167	5.1	90.0		48.0	56.0	1.2
168	0.61	100.		6.9	48.0	
169		15.0		0.47	5.75	
170		0.75			0.30	
176	1.4			0.44	0.51	1.2
177					0.68	0.98
178	0.67			0.53	0.65	3.2
179					0.47	2.7
180						0.88
181						11.0
182						1.7
187	1.2		1.5		0.28	
188	0.7		0.69		0.37	
189	2.2		1.0	0.79	0.61	0.71
190	0.45				1.0	
191					0.19	
200	1.3		0.83	0.40	0.35	0.58
201	0.83		0.75	0.21	0.54	
202	4.4		1.3	1.5	1.35	1.7
203	1.3		0.4	0.92	2.15	
204					0.67	
211	0.55		1.0			
212	0.50		0.59			
213	2.9		2.7	0.72	0.63	
214	1.1		0.85		0.77	
215	8.5		3.8	2.5	2.0	
216	2.1		0.53	0.8	2.85	
217				0.38	1.15	
218					0.44	
224	0.48		0.37			
225	0.53		0.51			

m/e	I	II	III	IV	V	VI
226	5.3		3.8	1.2	1.1	1.5
227	2.7		1.3	0.87	2.3	0.7
228	13.0			3.3	3.0	3.5
229	2.5			4.0	5.25	1.3
230				0.58	3.9	
231					0.74	
237	3.0		4.8	0.47	0.41	
238	1.8		2.4	0.35	0.6	
239	22.0		25.0	3.2	2.55	3.9
240	8.3		10.0	1.1	3.35	1.1
241	38.0		52.0	2.3	2.5	2.4
242	41.0		100.0	2.0	3.4	1.0
243	100.		8.5	25.0	18.5	100.
244	36.0		2.6	100.	87.0	21.0
245	4.1			21.0	100.	2.1
246				2.2	18.0	
247					1.7	
257						0.25
258						6.5
259						1.6
260						0.2

TABLE VI

MASS SPECTRAL DATA FOR TRITYL COMPOUNDS

	4,4,4-Triphenylbutene VII	1,1,1,2-Tetraphenylethane VIII	2,2-Dimethyl-1,1,1-triphenylpropane IX	3,3-Dimethyl-1,1,1-triphenylbutane X	Cyclohexyltriphenylmethane XI	Tetraphenylmethane XII
m/e	% RI	% RI	% RI	% RI	% RI	% RI
29			1.3	2.2		
39	0.88	0.75	0.82	0.86	0.68	
41	0.87	0.3	2.0	2.4	2.5	
43				1.06		
50			0.35			
51	0.93	0.75	0.53	0.76	0.50	2.8
53					0.44	
54					0.32	
55				0.6	2.2	
56			0.21			
57			1.3	4.0		
63	0.53	0.66	0.32		0.2	0.7
65	0.27	1.7	0.30		0.32	
75		0.17				
76	0.53	0.21	0.22			
77	1.5	0.67	0.65	2.0	0.58	1.8
78	0.65	0.27	0.87	0.7	0.40	0.7
79			0.18			
83					0.35	3.0
85						1.7
88	0.28					
89	0.52	0.37		0.4	0.24	
91	2.1	4.8	1.7	2.0	2.1	1.5
92		0.54				
94.5	0.35			0.36		
101	0.63		0.3			
102	0.54	0.22	0.18	0.5		
103	0.34		0.2	2.2		
105			0.65			
106				0.2		
106.5				0.4		
107.5	0.56					
113	0.49		0.3	0.4	0.27	
114	0.28	0.18			0.14	
115	1.8	2.2	1.4	1.68	1.4	2.6
116	0.38	0.18			0.22	
119	0.56			1.18		
119.5	1.1	0.22	0.3	0.7		
120	0.67		0.31	0.52		
120.5			0.22			
121	0.5					1.0
126	0.39		0.2			
127	0.45		0.28			

m/e	VII	VIII	IX	X	XI	XII
128	0.97	0.33	0.35	0.58	0.62	
129	0.72		0.22		0.29	
139	1.3	0.92	0.66	0.88	0.51	2.4
140	0.24					
141	0.25	0.45	0.25	0.4	0.46	
150		0.38	0.19		0.20	
151	0.39	0.55	0.23	0.72	0.21	
152	1.1	1.1	0.56	1.5	1.2	1.6
153	0.27	0.3	0.15	0.7	0.21	0.8
154	0.52	0.27	0.17	0.54	0.49	1.46
163	0.98	0.88	0.75	0.88	0.49	1.4
164	1.4	1.2	1.0	1.1	0.91	2.0
165	31.0	39.5	27.0	30.0	28.0	48.0
166	5.0	5.4	3.8	6.0	5.0	9.4
167	1.0	1.0	1.6	3.6	2.2	2.0
168				0.66		
176	0.59	0.48	0.35	0.96	0.3	
177	0.35	0.37		0.48		
178	1.2	1.6	0.47	3.4	1.0	
179	0.37	0.52	0.21	3.0	0.5	
180				0.8		
181				0.66		
182				0.48		
187		0.2	0.24			
188		0.2	0.14			
189	0.95	0.59	0.8	0.7	0.61	1.28
190	0.31	0.24	0.22			
191	0.46		0.26		0.45	
200	0.35	0.49	0.25			0.71
201			0.17			0.60
202	2.0	1.9	1.2	1.84	1.2	2.4
203	0.8	0.5	0.47	0.8	0.66	0.76
204	0.33					
205	0.22					
206	0.29					
213	0.58	0.95	0.53	0.6		
214	0.22	0.2	0.29		0.28	
215	2.8	3.2	2.4	3.2	2.0	4.8
216	0.64	0.7	0.4	0.9	0.67	
225		0.31				
226	1.5	2.0	1.4	1.22	1.1	2.6
227	1.1	1.7	1.0	0.86	1.1	1.8
228	4.6	5.0	4.0	3.4	3.5	5.6
229	0.87	0.95	0.7	0.96	0.78	1.4
237	0.52	0.52	0.37	0.25	0.26	1.08
238	0.4	0.42	0.41	0.24	0.24	0.86
239	4.2	4.6	4.0	4.2	2.8	7.0

m/e	VII	VIII	IX	X	XI	XII
240	1.3	2.3	1.4	1.82	1.1	2.2
241	3.2	5.2	4.5	5.6	4.4	7.4
242	2.3	2.5	3.0	4.8	2.2	2.8
243	100.	100.	100.	100.	100.	100.
244	23.0	21.5	23.0	25.8	22.0	20.0
245	2.4	2.3	2.4	2.6	2.3	1.8
246	0.16	0.19	0.13	0.34		
250		0.3				
251		0.23				
252		0.32		0.46	0.27	
253	0.29	0.39		0.44	0.19	
255		0.27		0.48		
256		0.16		0.54		
257				1.28		
258				0.76		
284	0.35					
285		1.1				
314				5.0		
315				1.72		
316				0.26		
300			trace			
319						2.6
320						30.0
321						8.0
322						1.0
326					2.9	
327					0.88	
328					0.1	
333		0.12				
334		0.29				

TABLE VII

MASS SPECTRAL DATA FOR TRITYL COMPOUNDS

	o-Trityltoluene XXIV	1,3,3,3-Tetraphenylpropyne XXV	N-Tritylaniline XXVI	N-Tritylbenzylamine XXVII	N-Tritylethylamine XXVIII	N-Tritylcyclohexylamine XXIX
m/e	% RI	% RI	% RI	% RI	% RI	% RI
29					2.4	0.45
30				0.3	2.9	0.45
31	0.8			0.45		0.35
37			0.22			
38			0.21			
39	1.0	0.85	1.3	1.65	2.0	0.8
41				0.5	1.6	2.1
43						1.85
45					1.6	
50	1.2		0.39	1.6	1.7	0.55
51	2.8	2.45	2.3	3.75	5.5	2.0
52			0.42	1.15	0.8	0.55
53				0.5		
54						0.6
55					2.2	2.25
56						6.0
57						0.45
62				0.55		
63		0.85	0.42	1.25	1.9	0.6
64			0.24			
65		0.5	2.6	4.0	1.0	0.35
66			0.71			
67					0.6	0.3
68					0.9	
70						0.5
74			0.2	0.75		
75			0.19	1.25	1.2	
76			3.1	1.25	1.4	
77	3.2	2.5	5.6	9.4	8.0	3.5
78	1.6	0.75	1.2	3.5	2.9	1.1
79				1.13	0.5	
82						0.35
83					1.9	0.35
87				0.65		0.35
88						0.35
89		0.5	0.3	1.0	1.9	0.7
90				0.95		
91	3.7	1.0	1.0	51.5	2.5	1.1
92			1.0	4.75		
93			2.5			
93.5					0.7	
94.5					1.1	1.2
98						1.1

m/e	XXIV	XXV	XXVI	XXVII	XXVIII	XXIX
99					0.7	1.4
100					0.7	
101				0.55	1.2	0.5
102					1.1	0.4
103				1.15		0.45
104			0.56	7.0	7.9	4.5
105				2.4	3.6	
106				14.7		0.5
106.5					2.9	0.75
107				3.05		0.3
107.5					1.8	0.85
108			0.29	0.75	1.0	0.45
113	1.0		0.32	0.45	0.9	1.25
113.5						0.6
114				0.4	0.8	
115	3.15	1.55	1.6	2.1	3.7	2.45
116	0.8	0.22				
118				0.6		
118.5					0.7	0.45
119		0.48	0.27	0.4	1.2	0.8
119.5	0.75	0.6	0.25	0.6	1.5	1.4
120		0.3		0.45	3.0	0.6
120.5					1.1	0.45
121					1.0	0.55
121.5						0.25
122					0.8	
126	1.25	0.6	0.4	0.6		0.45
127	2.05		0.56	0.8		
128	1.9		0.24	0.65	1.4	0.4
128.5			1.6			
128.5			1,6			
129	0.65		0.31			
131		0.5				
131.5		1.75				
132		0.9				
132.5		1.85				
133		2.15				
133.5	0.5					
134		0.25				
138	0.75					
139	1.4	1.45	0.67	1.6	3.6	1.6
141	0.75		0.37	0.55	1.1	0.65
149			0.18			
150		1.0	0.28			0.6
150.5		0.35				
151	1.3	2.0	0.4	0.65	1.6	0.65
151.5		0.3				
152	3.15	0.9	1.35	4.0	10.0	3.2

m/e	XXIV	XXV	XXVI	XXVII	XXVIII	XXIX
153	1.55		0.63	1.45	2.7	1.35
154	3.35		0.53	2.5	1.6	1.0
155				0.85		
155.5		0.7				
156		0.4				
156.5		1.15				
157		0.6				
157.5		0.45				
158		0.5				
162		0.6				
163	1.25	2.95	0.82	1.25	3.9	1.2
164	2.0	3.0	1.1	2.0	4.8	1.85
165	37.5	15.0	30.5	37.5	66.3	43.5
166	8.5	2.9	5.7	11.0	29.3	12.0
167	6.0	0.85	2.4	11.8	47.5	12.5
167.5			1.1			
168	1.0		0.86	1.67	7.2	1.9
169					0.45	
176	1.75		0.48	0.35	1.0	
177	1.95					
178	11.0	0.65	0.43	0.65	0.8	0.65
179	23.5					
180	7.5		1.8	4.0	1.7	1.25
181	2.0		0.37	0.55	1.0	
182					2.0	8.0
183					1.5	1.1
187		1.1				
188		0.7			0.7	
189	1.35	6.5	0.43	0.85	0.7	1.05
190		1.7			1.1	
191		0.75				
192				0.35		
193				0.35		
194				1.25		
195				0.5		
200	0.7	0.65	0.24		0.8	0.5
201			0.22		0.6	
202	2.5	0.75	1.6	1.95	2.5	1.4
203	1.3		0.54	0.55	1.35	0.7
210					52.5	
211		0.55			11.0	
212					1.4	
213	1.65	0.8	0.57	0.6	1.4	1.05
214			0.2	0.3		0.55
215	4.5	0.75	2.6	3.2	5.0	3.3
216	1.9		0.9	0.7	1.25	1.0
217				0.45	0.7	

m/e	XXIV	XXV	XXVI	XXVII	XXVIII	XXIX
226	3.3	1.4	1.2	1.87	2.9	2.1
227	1.85		1.0	0.9	1.6	1.5
228	4.0		4.9	4.5	6.8	5.25
229	1.85		1.3	2.0	4.4	1.4
230				0.6		
237	1.2	1.25	0.4	0.6	2.1	0.8
238		0.85	0.35	0.35	1.5	0.4
239	8.0	5.0	3.4	5.5	10.5	7.5
240	3.0	1.35	1.2	1.95	3.8	2.7
241	15.0	2.05	3.6	5.5	11.5	11.0
242	8.0	1.65	2.0	3.5	15.0	11.7
243	43.5	0.8	100.	60.0	72.0	100.
244	7.5	1.8	27.0	38.0	100.	45.0
245	1.5	0.4	3.8	6.75	20.0	8.0
246			0.2	0.6	1.8	0.95
250	0.85	1.25				
251		0.8				
252	2.65	9.5				
253	1.9	8.0				
254	1.1	0.5				
255	2.5					
256	1.3		0.8	0.75		
257	100.			0.45		
258	21.5		1.8	40.0	15.0	16.5
259	2.75		0.4	6.75	3.3	4.0
260				0.95		0.45
261		0.75				
262		1.1				
263		8.5				
264		2.2				28.5
265		27.5				6.5
266		9.5				0.7
267		44.4				
268		10.0				
269		1.3				
270				1.25		
271				0.5		
272				100.		
273				25.0		
274				1.95		
276		0.5				
286					0.8	
287					3.4	
288					1.0	
302		1.2				
303		0.7				
313		1.15				

m/e	XXIV	XXV	XXVI	XXVII	XXVIII	XXIX
314		1.1				
315		1.9				
316		0.85				
317		0.45				
318	0.5					
319	15.0					
320	6.75					
321	0.65					
326		2.0				
327		1.3				
328		2.6				
329		3.4				
330		1.2				
333	3.2					
334	95.0		1.15			
335	27.0		4.7			
336	4.1		1.2			
337		0.5				
338		0.4				
339		1.8				
340		1.3				
341		2.5				2.5
342		2.5				0.22
343		11.0				
344		100.				
345		30.0				
346		3.5		0.87		
347		0.35		0.95		
348				0.8		
349				2.5		
350				0.55		

TABLE VIII

MASS SPECTRAL DATA FOR TRITYL COMPOUNDS

	Triphenylmethanol	Trityl Methyl Ether	Trityl Ethyl Ether	Trityl Allyl Ether	Trityl Cyclohexylmethyl
	XIII	XIV	XV	XVI	XVII
m/e	% RI	% RI	% RI	% RI	% RI
26				1.8	
27				5.5	1.7
28		3.9	4.4	3.6	1.9
29		3.9	5.2	1.9	1.7
30		3.0			
31		1.7	2.9		
32		1.2			
39		1.4	1.8	2.5	3.5
41				3.0	6.5
42					0.6
43			2.6		1.2
50	2.0	1.1	1.6	0.8	0.95
51	14.0	4.6	3.5	3.4	2.9
52	2.5	0.65	1.6		0.6
53					0.8
54					0.9
55				2.6	1.3
56				4.8	1.3
57				0.85	0.95
62		0.75			
63	2.1	2.3	2.9	1.9	1.3
64		1.0			
65		1.5		1.0	0.85
67					2.0
68					3.5
69					0.6
70					1.9
74	1.5	0.55	0.7	0.65	
75	1.0	0.55	0.5	1.1	0.48
76	1.5	1.0	1.0	0.4	0.6
77	56.5	13.4	11.0	6.3	5.5
78	5.0	3.0	3.5	2.5	1.9
79	1.5				1.5
81					1.5
82					1.0
83					6.0
84					0.6
87		1.2		0.5	
88		1.1		1.3	
89		1.6		1.8	1.1
90		0.8			
91	8.7	3.4	2.2	1.4	1.4

m/e	XIII	XIV	XV	XVI	XVII
94					2.1
94.5				1.1	0.7
96					1.3
97					1.3
100			1.5		
101	1.6	2.8	1.0	1.0	0.5
102		1.1	1.0	0.5	0.5
103			0.5		
105	76.0	18.0	25.0	23.5	1.1
106	6.9	2.4	3.2	2.1	1.6
106.5		1.8	1.4	0.7	0.8
107	2.9	1.2	1.5	0.7	1.0
107.5		1.5	2.0	1.6	0.7
108		1.0		1.2	0.45
108.5				0.45	
109			0.5		
112		0.42			1.2
112.5		0.60			
113	1.8	1.9	1.0	1.5	0.75
113.5		0.9	0.8		
114		1.5	1.0	2.0	1.1
114.5		1.1	0.7	0.85	
115	2.2	4.3	4.0	3.4	3.0
118					0.45
118.5		1.5			
119		2.0	0.8	0.7	0.25
119.5	4.5	3.1	4.8	2.8	1.2
120		2.1	2.4	1.7	0.85
120.5			1.1		0.55
121		1.6	0.7	0.8	0.7
121.5			1.3		0.85
122		1.3	1.3	0.55	0.40
126		1.2		0.9	
127		0.5			0.9
128		1.8	2.1	1.2	0.8
137		1.6			
139	2.4	3.5	2.8	2.2	2.1
141		1.4	1.0	0.75	0.7
145				0.7	
150	1.3	0.65	0.9		
151	3.5	2.1	1.4	1.6	0.85
152	6.5	12.8	14.0	11.0	6.0
153	2.9	2.9	3.7	2.6	1.3
154	23.0	0.9	1.0	0.85	2.6
155	21.0				0.95
156	2.2				
162			0.9		

m/e	XIII	XIV	XV	XVI	XVII
163	2.1	2.9	4.9	3.4	1.7
164	2.3	4.3	5.4	4.7	3.6
165	23.5	63.0	69.0	57.5	45.7
166	7.6	29.3	31.0	27.0	16.6
167	8.7	45.2	55.0	46.2	25.6
168		6.5	7.0	7.0	3.3
169		0.65		0.5	
173			0.7		
175			1.0		
176				0.8	
177			0.9		
178					0.75
181	6.6				
182	21.0				
183	100.0		9.8		1.7
184	16.0		1.2		2.6
187		0.7	1.0		
188		0.9		0.5	
189	1.5	2.4	1.0	0.6	0.9
190			1.0		
197		42.3			
198		7.8			
199		0.7			
200	1.2	0.8	0.8	0.9	0.7
201			0.5		
202	1.9	2.7	3.0	2.1	2.6
203		1.0	1.1	1.3	0.8
211			23.6		
212			3.6		0.75
213	1.4	1.8	1.6	1.8	
214	1.3		0.9		
215	2.3	4.4	6.0	3.8	4.0
216	1.6	1.8	2.1	1.8	1.5
217				0.45	
223				8.5	
224				2.0	
225				0.8	
226	1.8	2.6	3.0	2.2	2.1
227	1.4	1.5	2.3	1.4	1.5
228	2.2	4.9	4.9	5.0	4.3
229	1.5	3.8	3.2	4.0	2.9
230			1.3	0.8	0.65
237		1.7	1.7	1.4	0.65
238		1.1		0.8	0.85
239	5.8	9.0	7.4	6.0	7.5
240	1.8	3.1	3.3	3.0	2.3
241	7.0	10.0	13.0	9.0	10.0

m/e	XIII	XIV	XV	XVI	XVII
242	6.2	12.0	11.0	11.5	11.0
243	18.0	62.0	60.0	46.5	100.0
244	20.5	100.0	100.0	100.0	80.0
245	3.7	18.0	19.5	19.0	13.0
246		1.5	2.6	2.1	1.0
258				2.0	
259	2.0			1.0	0.6
260	51.0				0.5
261	13.0				0.3
262	1.8				
273		1.7			
274		32.5			
275		8.1			
276		1.2			
279					8.0
280					1.8
281					0.45
287			1.0		
288			19.0		
289			4.3		
300				3.8	
301				1.0	
302				0.3	
356					11.0
357					3.0
358					0.45

TABLE IX

MASS SPECTRAL DATA FOR TRITYL COMPOUNDS

	Trityl Acetate	Trityl Pivalate	Trityl Benzoate	Trityl Phenyl Sulfide	Trityl Benzyl Sulfide	Trityl *n*-Propyl Sulfide
	XVIII	XIX	XX	XXI	XXII	XXIII
m/e	% RI	% RI	% RI	% RI	% RI	% RI
29		4.4				0.45
38					0.59	
39	1.4	3.0	2.1	1.7	3.5	0.99
40					0.49	
41		8.5			0.64	1.8
42		1.1				0.54
43	10.0	2.0				0.97
44	1.0	3.2				
45	1.1			0.87	6.4	0.84
46						0.36
47						1.3
50	1.1	1.0	3.1	1.2	1.7	0.41
51	4.0	2.5	5.8	2.2	4.7	0.89
52	0.6		2.4		0.76	0.24
55	1.0					
56	1.9					
57	2.9					
58	1.0					
61					0.6	
62					0.8	
63	1.4	1.0	1.2	1.3	0.3	0.38
64					0.67	
65	0.71	0.75	0.6	3.3	0.6	0.3
66				1.4	0.5	
69				1.2		
71		1.2				
73						0.23
74	0.55		1.6	0.67	1.5	0.31
75	0.65		0.9	0.6	1.3	0.26
76	1.1		2.0	1.1	1.5	0.85
77	18.0	7.0	19.0	2.9	5.2	0.5
78	2.7	1.8	17.0	1.3	3.5	0.4
79			1.1		1.6	
83					0.53	
85		4.5				
86					0.57	
87	0.63				0.73	
88	0.75				1.4	
89	0.92			0.65	3.2	0.43
90					0.9	
91	2.2	2.3	2.2	1.1	49.	1.4
92					8.7	
93					0.75	

m/e	XVIII	XIX	XX	XXI	XXII	XXIII
93.5	0.45				0.85	
94	1.6		1.5			
94.5	0.5	1.2		0.61	2.0	0.37
95				0.44	0.79	
98					0.5	
99					0.5	
100	0.58				0.5	
101	1.7	1.4	1.5	0.7	2.0	0.31
102	0.51	0.8		0.46	1.2	0.3
105	19.0	7.0	62.0	0.4	0.51	0.21
106	1.8	0.8	5.6		0.76	
106.5	1.6	1.1	1.4	0.91	2.0	0.3
107	1.1	0.6	1.4	0.35	0.6	
107.5	2.2	1.6	1.8	0.9	2.6	0.28
108	0.88	0.7	0.8	1.4	0.85	0.31
109				7.8		
110				5.4		
111				0.63		
112				0.7		
113	2.4	1.8	2.3	1.1	2.8	0.75
113.5	0.7				0.87	
114	1.2	1.2	1.7	0.6	1.9	0.26
115	3.3	3.4	3.2	1.9	4.3	1.6
116	0.37			0.2		0.21
118	0.36		0.6	0.3		
118.5	1.2	0.6	1.3	0.83	1.5	
119	1.6	0.7	1.2	0.43	1.5	0.27
119.5	3.9	2.8	4.0	1.9	5.0	0.71
120	2.7	1.8	3.0	1.3	3.1	0.54
120.5	0.75	0.6			1.3	
121	0.93	0.95	1.1	0.32	3.8	0.83
121.5	0.43	0.75		0.72	1.1	
122		0.8	1.0	0.35	6.0	0.24
123					9.7	
124					1.8	
125					0.65	
126	0.66				0.94	0.27
127					0.65	
128	0.65				0.52	0.29
139	2.0	2.0	2.5	1.6	2.6	0.87
141	0.62	1.0		0.75	0.83	0.26
149		3.1				
150	0.61				0.6	0.5
151	1.0	1.0	0.9	0.9	1.0	0.32
152	4.4	5.0	4.6	3.9	5.0	1.5
153	1.6	1.6	1.2	1.0	1.5	0.32
154	2.4	1.5	1.3	2.0	1.5	0.57
155	0.69					

m/e	XVIII	XIX	XX	XXI	XXII	XXIII
162					0.58	0.24
163	2.6	2.4	3.2	1.7	3.2	1.3
164	2.9	2.8	3.4	2.4	4.0	1.2
165	59.0	62.0	64.0	43.0	66.0	29.5
166	16.0	19.0	19.0	11.5	19.0	5.9
167	14.0	21.0	18.0	8.3	19.0	3.6
168	2.0	3.1	2.5	1.4	3.5	0.65
176	0.72	0.8		0.35	0.89	0.29
177					0.37	
178	0.5	0.6		0.35	0.73	0.22
179					0.33	
181	5.5	1.5	0.9		0.4	
182	3.3	1.3				
183	9.7	2.6	1.1	0.35	0.27	0.36
184	1.4			1.5		
185				3.5		
186				5.2		
187				1.4	0.81	0.26
188				0.5	0.87	
189	1.4	1.2	1.3	1.2	2.0	0.7
190					0.3	
197						0.35
200	0.66			0.33	1.5	0.28
201	0.5			0.41	0.9	0.25
202	2.9	2.9	3.1	2.3	3.2	1.6
203	1.0	1.1	1.0	0.7	1.2	0.63
204					0.45	0.14
211					0.5	
212					0.25	
213	1.5	1.4	1.6	1.2	2.2	0.78
214	0.65			0.71	23.0	0.37
215	5.4	4.9	6.2	4.2	9.8	2.9
216	1.8	1.5	1.8	0.93	2.6	0.66
217	0.5	0.6			0.55	0.21
218				5.3		
219				0.97		
220				0.5		
224					0.35	
225					0.45	0.2
226	3.3	3.0	3.7	2.5	3.7	1.7
227	1.7	1.5	2.2	1.5	2.4	1.4
228	6.3	5.9	8.2	6.4	8.0	4.2
229	2.1	2.4	3.2	1.9	3.5	1.2
230					0.65	
237	1.4	1.0	1.8	0.97	1.8	0.68
238	0.82	0.8	1.0	0.71	1.2	0.56

m/e	XVIII	XIX	XX	XXI	XXII	XXIII
239	10.0	8.8	13.0	8.5	15.0	5.4
240	3.6	3.2	5.1	3.3	4.8	1.9
241	13.0	10.8	20.0	13.0	26.0	7.5
242	12.0	8.8	21.0	11.0	25.0	5.2
243	85.0	100.	91.0	100.	100.	100.
244	39.0	57.0	50.0	38.0	55.0	28.5
245	6.1	10.0	8.8	4.6	8.4	3.6
246	0.64	0.93	0.8	0.5	1.2	0.21
258	0.48					
259	100.	98.0	100.			
260	60.0	45.0	21.0			
261	9.9	7.5	2.4			
262	1.1	0.75				
302	11.0					
303	2.4					
304	0.26					
318						trace
344		5.4				
345		1.8				
352				0.03		
364			6.6			
365			2.0			
376					trace	

Plate I

TRITYL BROMIDE

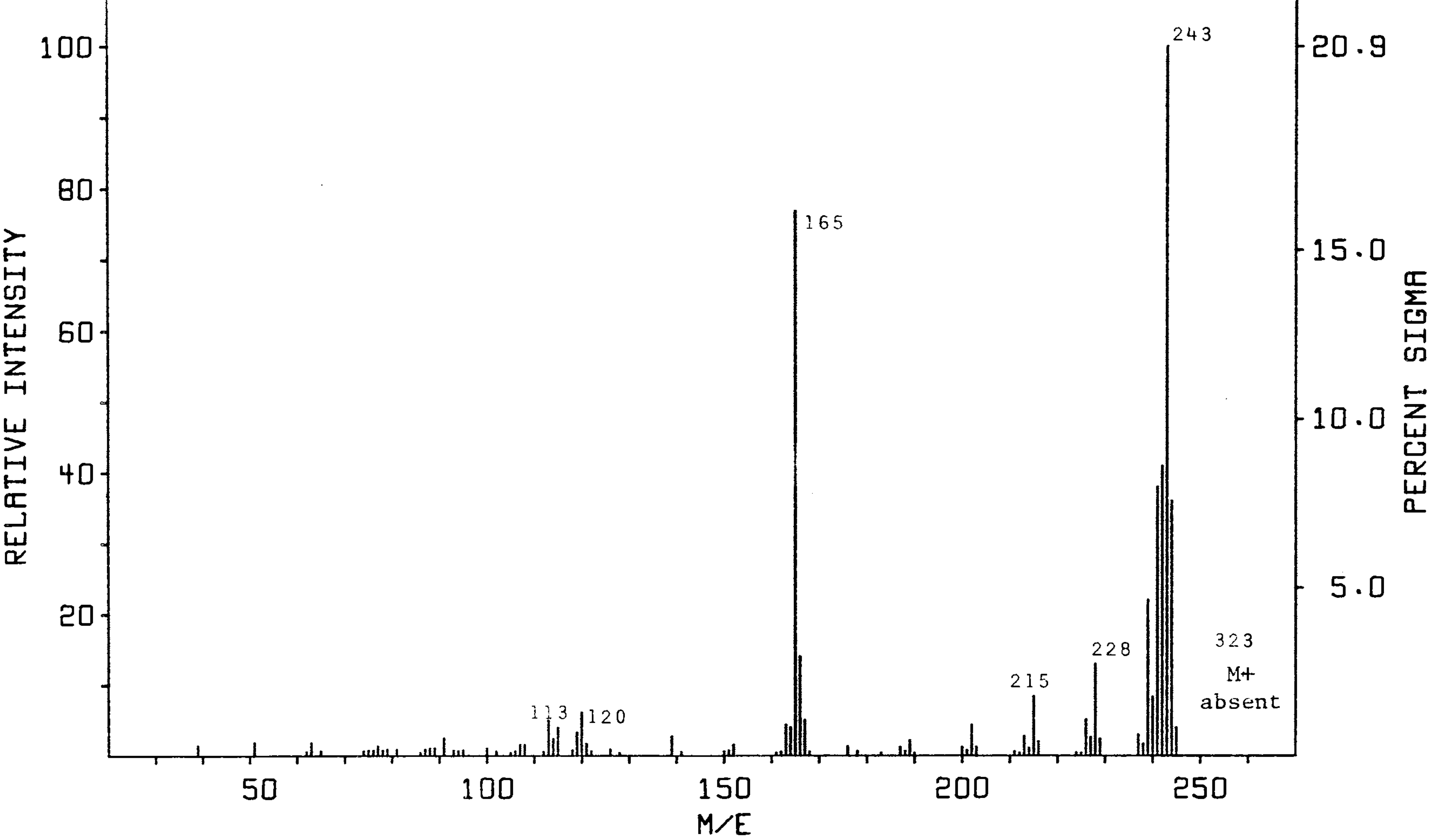


Plate II

TRIPHENYLMETHANE

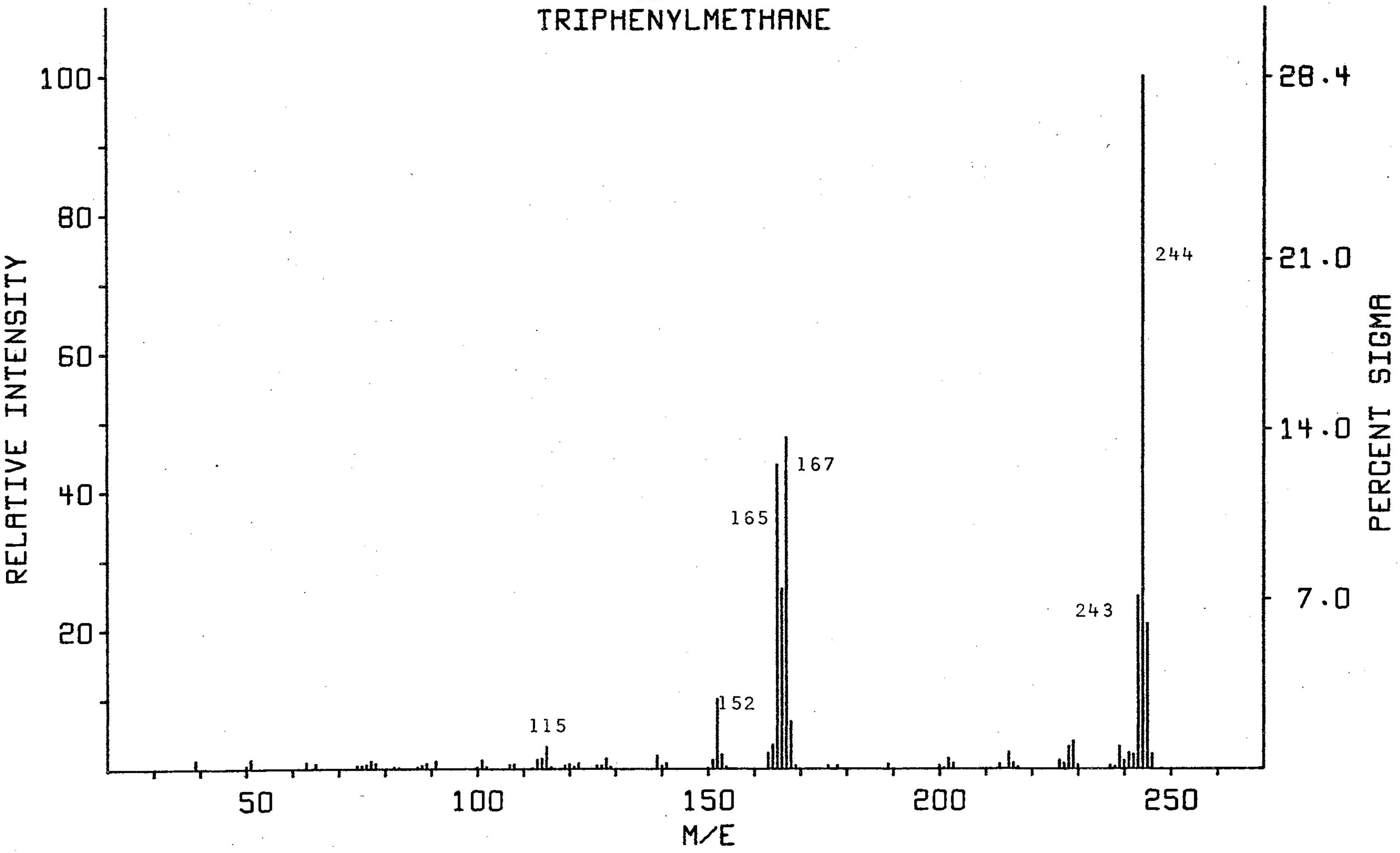


Plate III

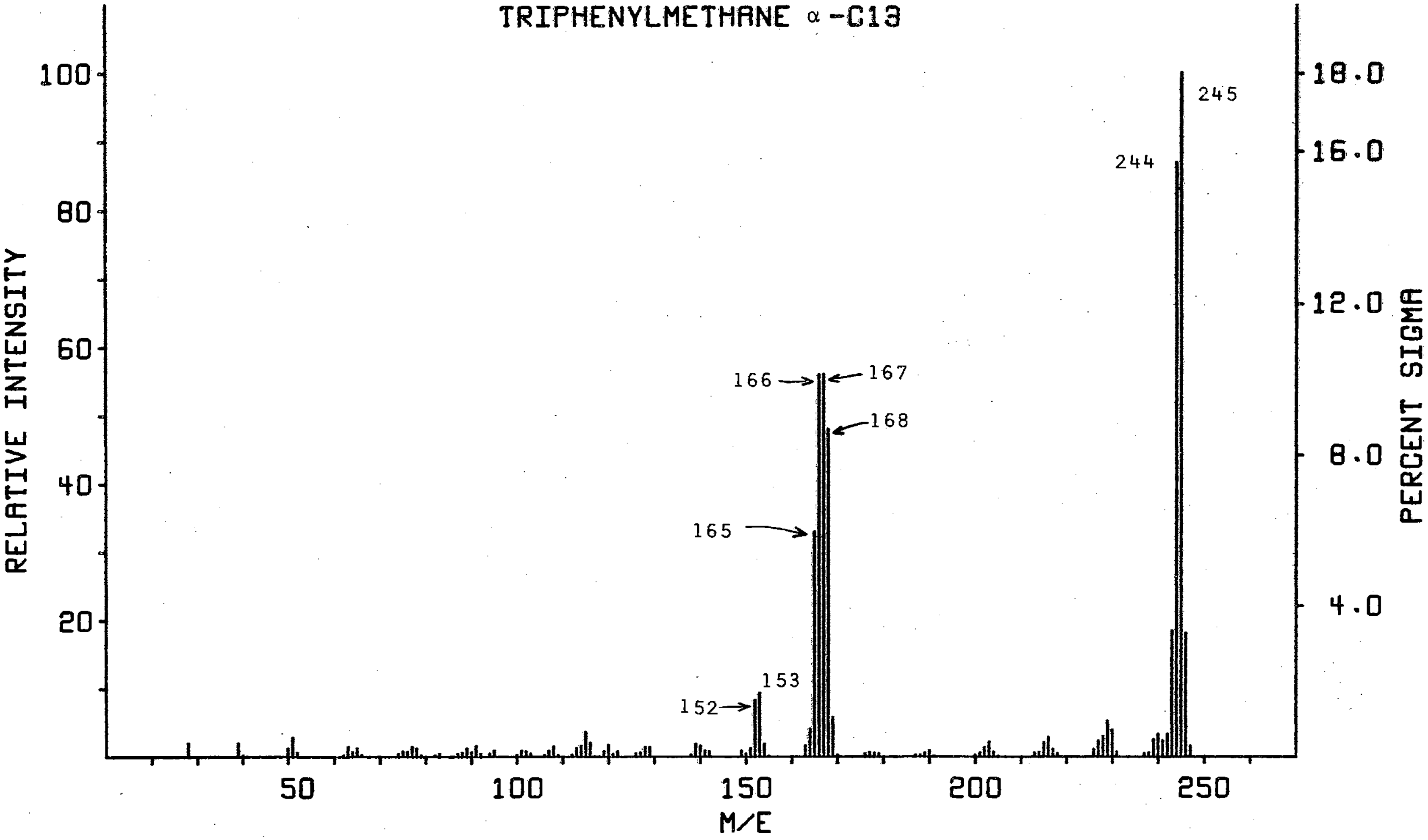

TRIPHENYLMETHANE α-C13
RELATIVE INTENSITY
PERCENT SIGMA
M/E
100
80
60
40
20
50
100
150
200
250
18.0
16.0
12.0
8.0
4.0
245
244
166
167
168
165
153
152

Plate IV

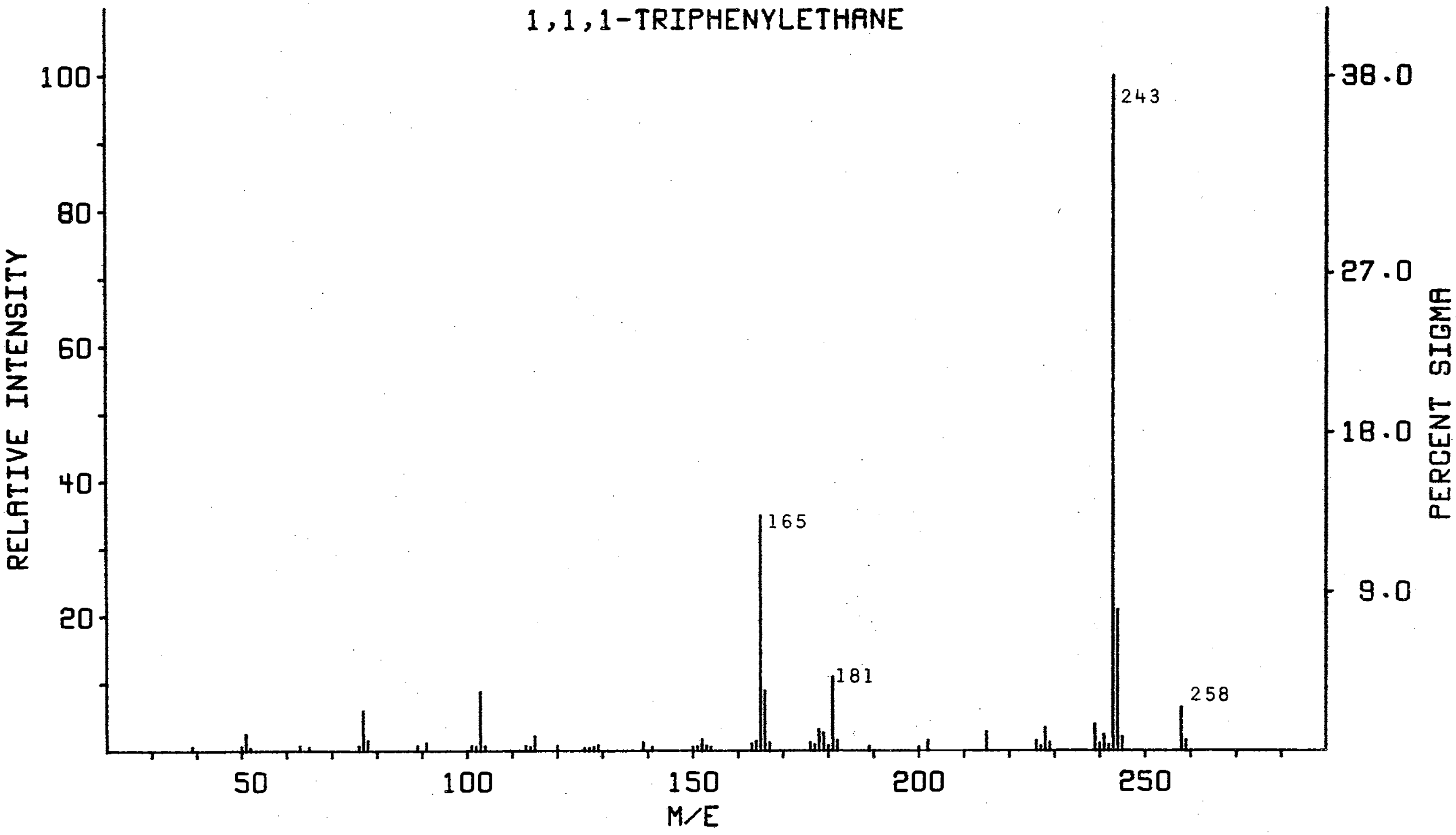

1,1,1-TRIPHENYLETHANE
RELATIVE INTENSITY
100
80
60
40
20
PERCENT SIGMA
38.0
27.0
18.0
9.0
243
165
181
258
50
100
150
200
250
M/E

Plate V

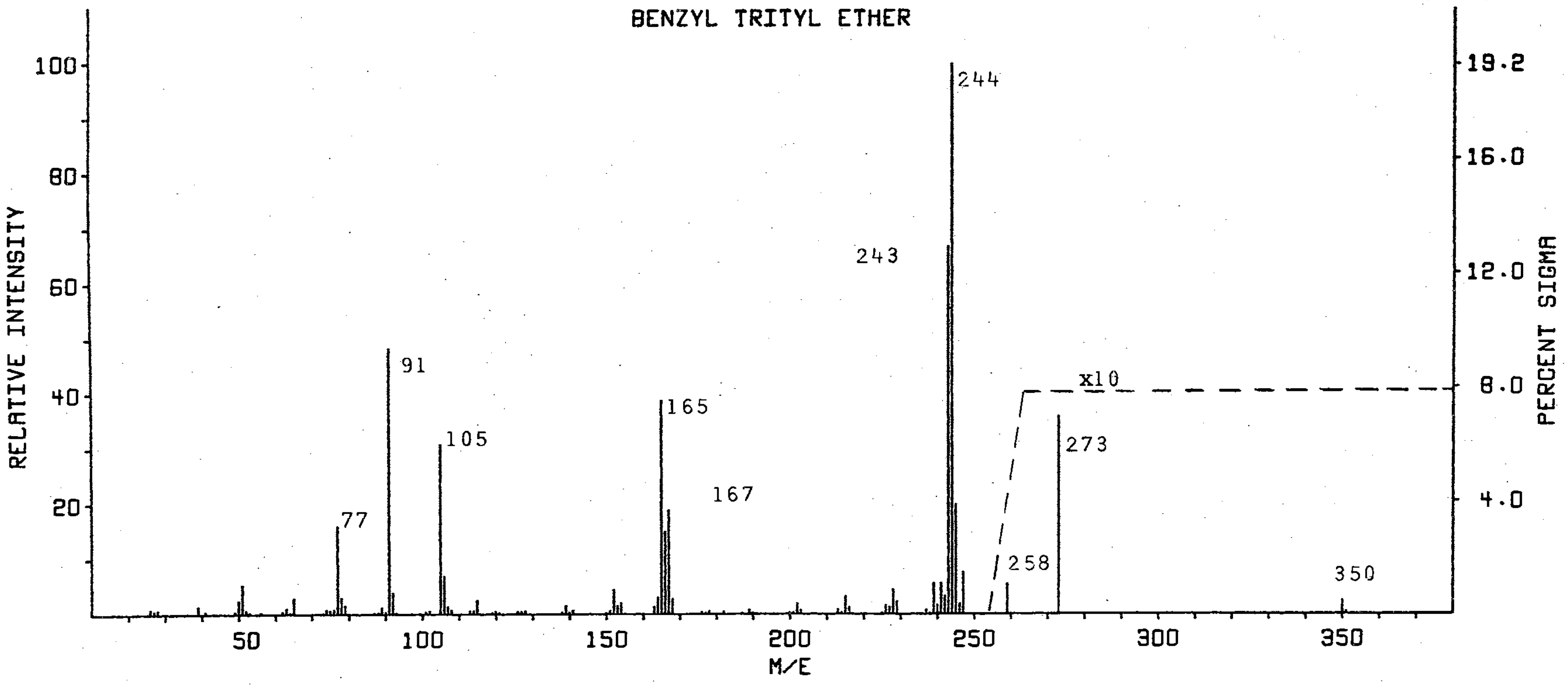

BENZYL TRITYL ETHER
RELATIVE INTENSITY
100
80
60
40
20
PERCENT SIGMA
19.2
16.0
12.0
8.0
4.0
x10
77
91
105
165
167
243
244
258
273
350
50
100
150
200
250
300
350
M/E

Plate VI

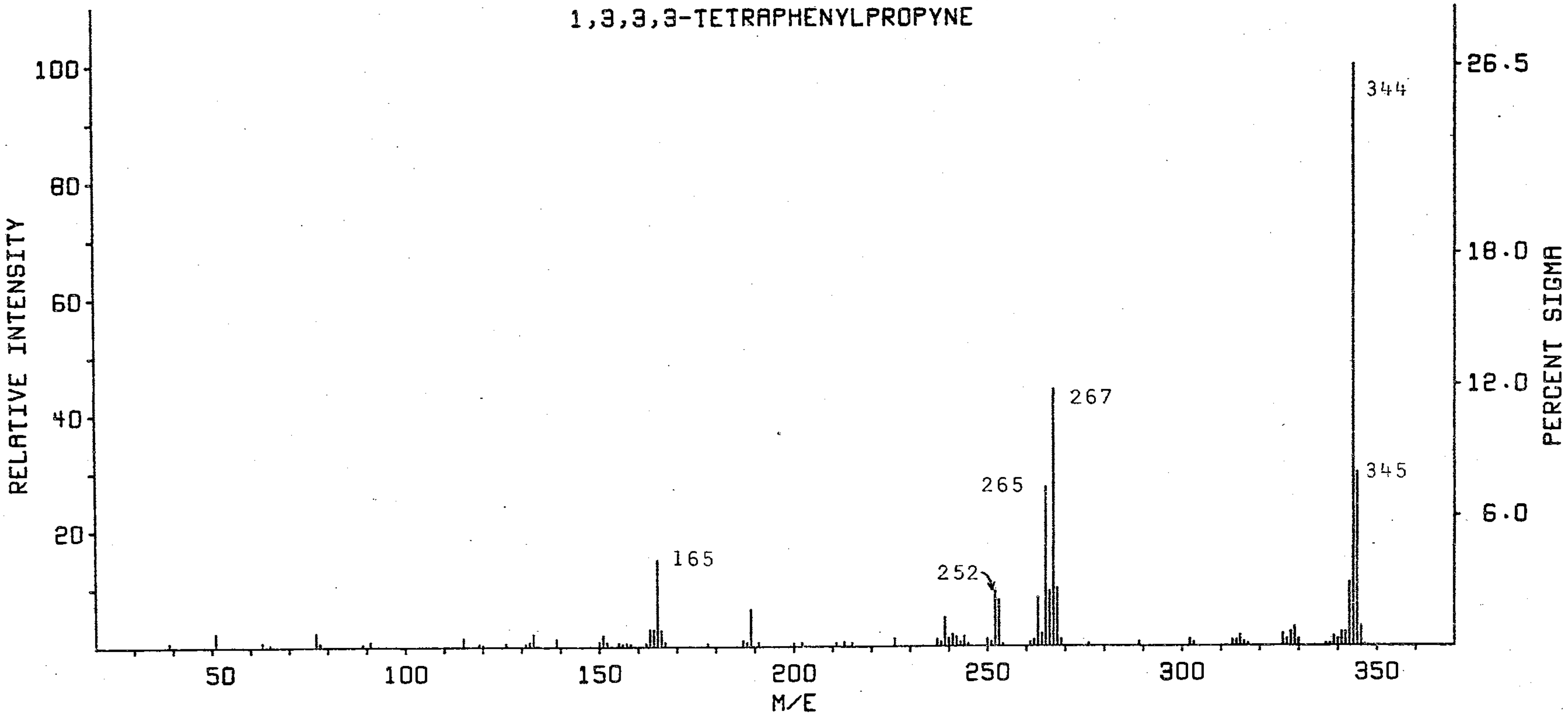
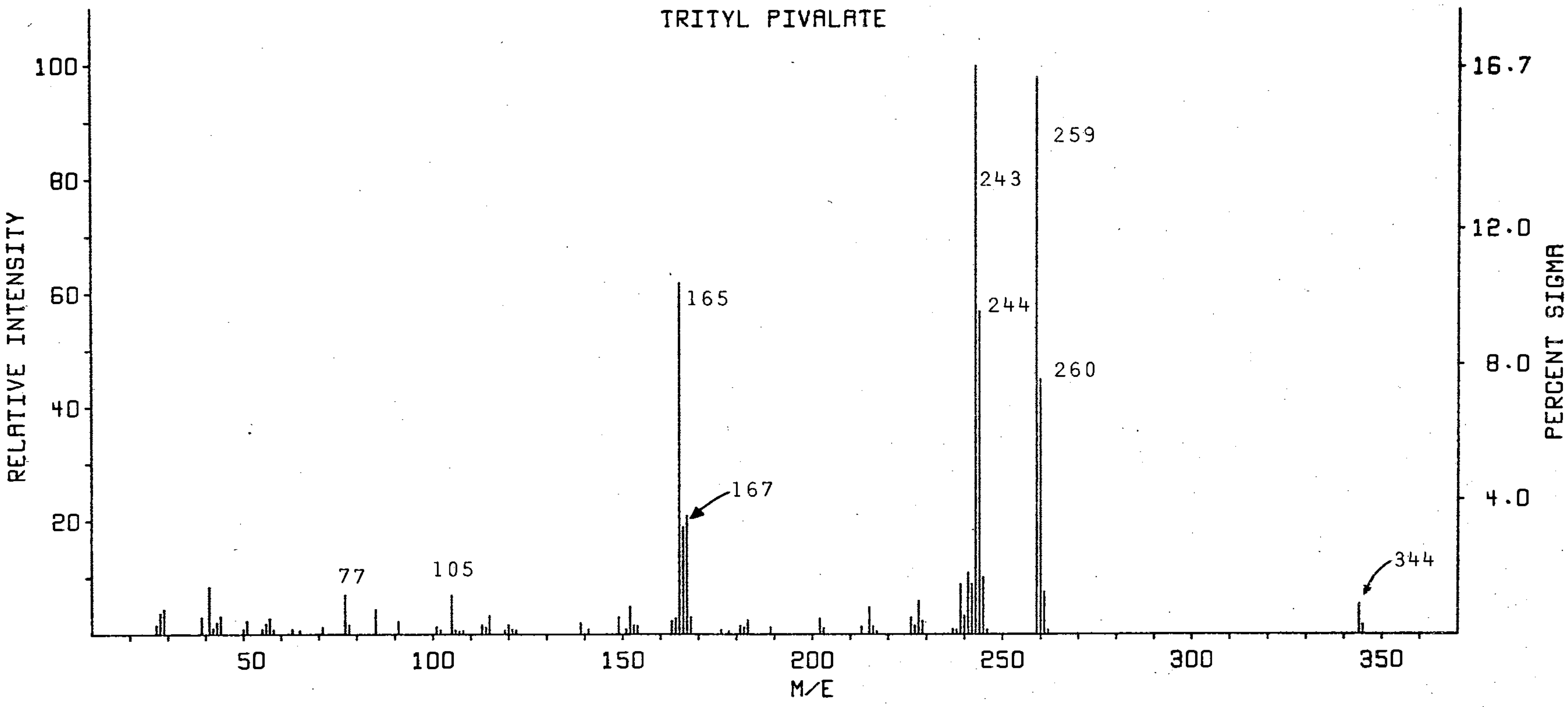

1,3,3,3-TETRAPHENYLPROPYNE
RELATIVE INTENSITY
100
80
60
40
20
PERCENT SIGMA
26.5
18.0
12.0
6.0
M/E
50
100
150
200
250
300
350
344
345
267
265
252
165

Plate VII



TRITYL PIVALATE
RELATIVE INTENSITY
100
80
60
40
20
PERCENT SIGMA
16.7
12.0
8.0
4.0
M/E
50
100
150
200
250
300
350
77
105
165
167
243
244
259
260
344

Plate VIII

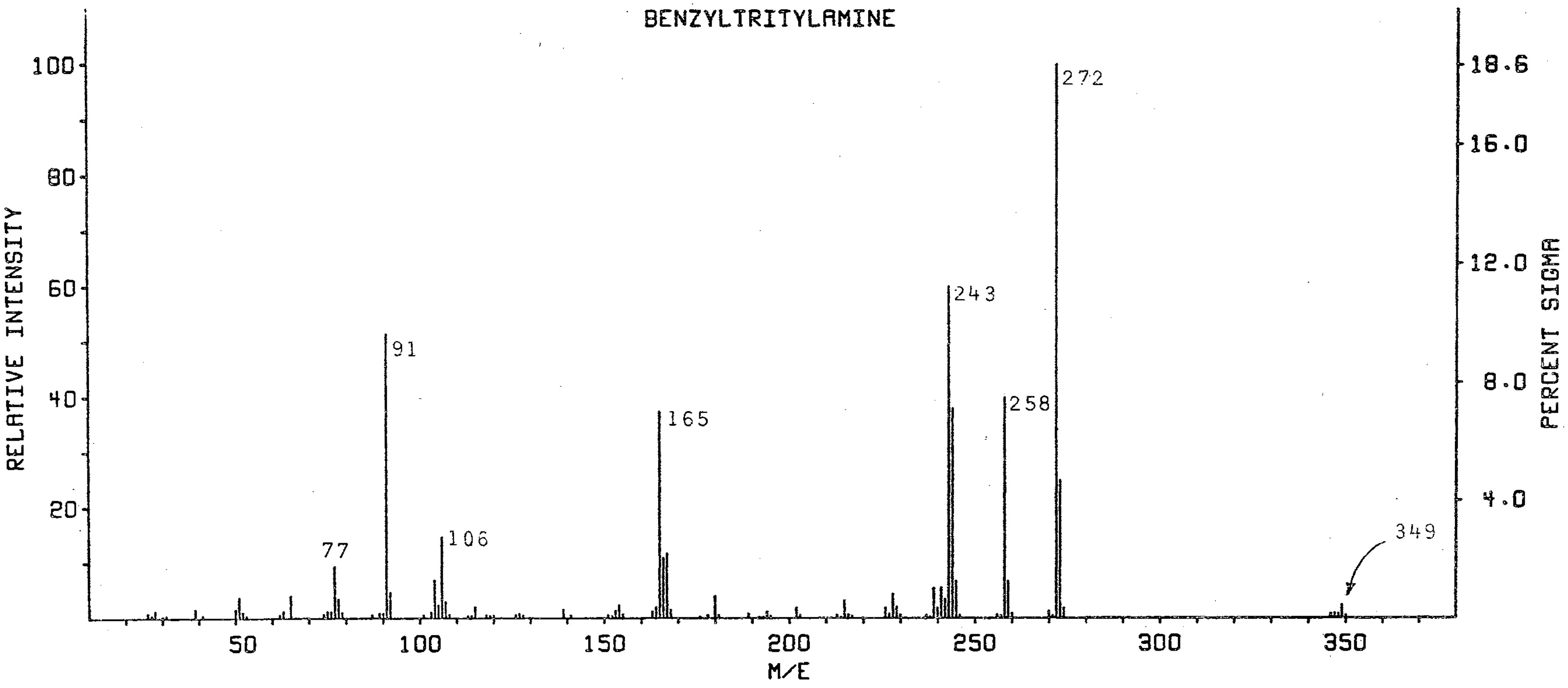
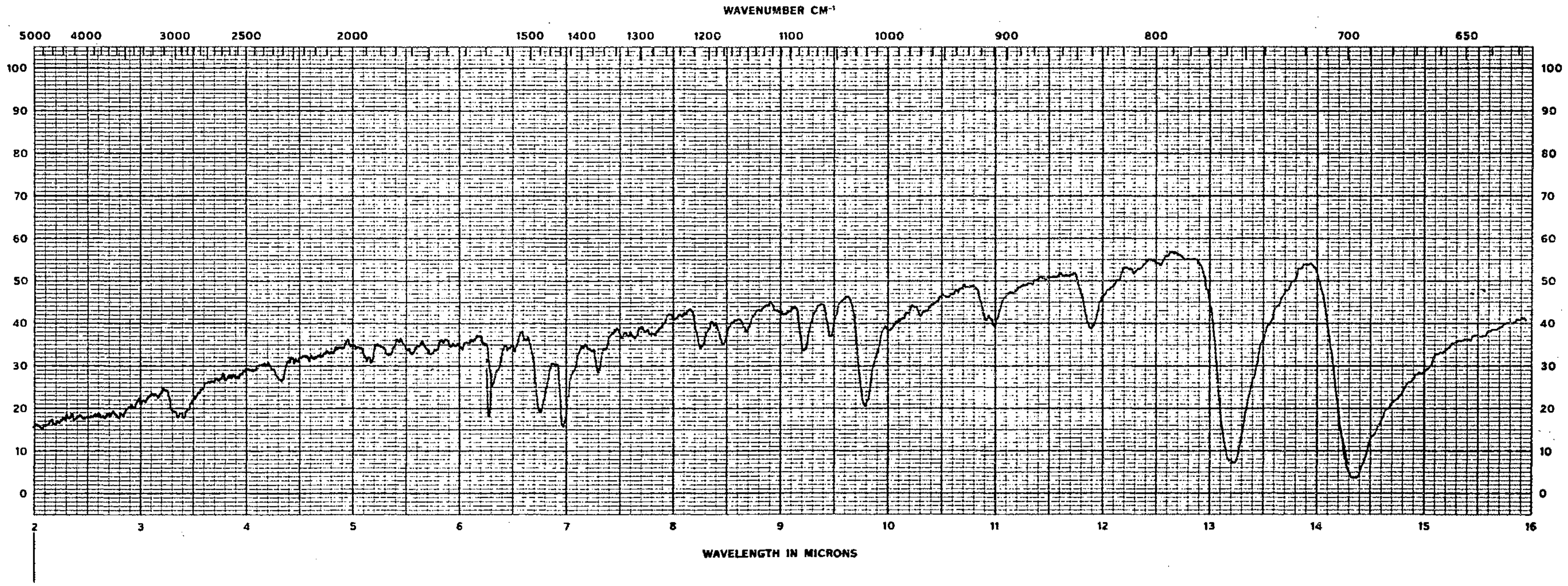
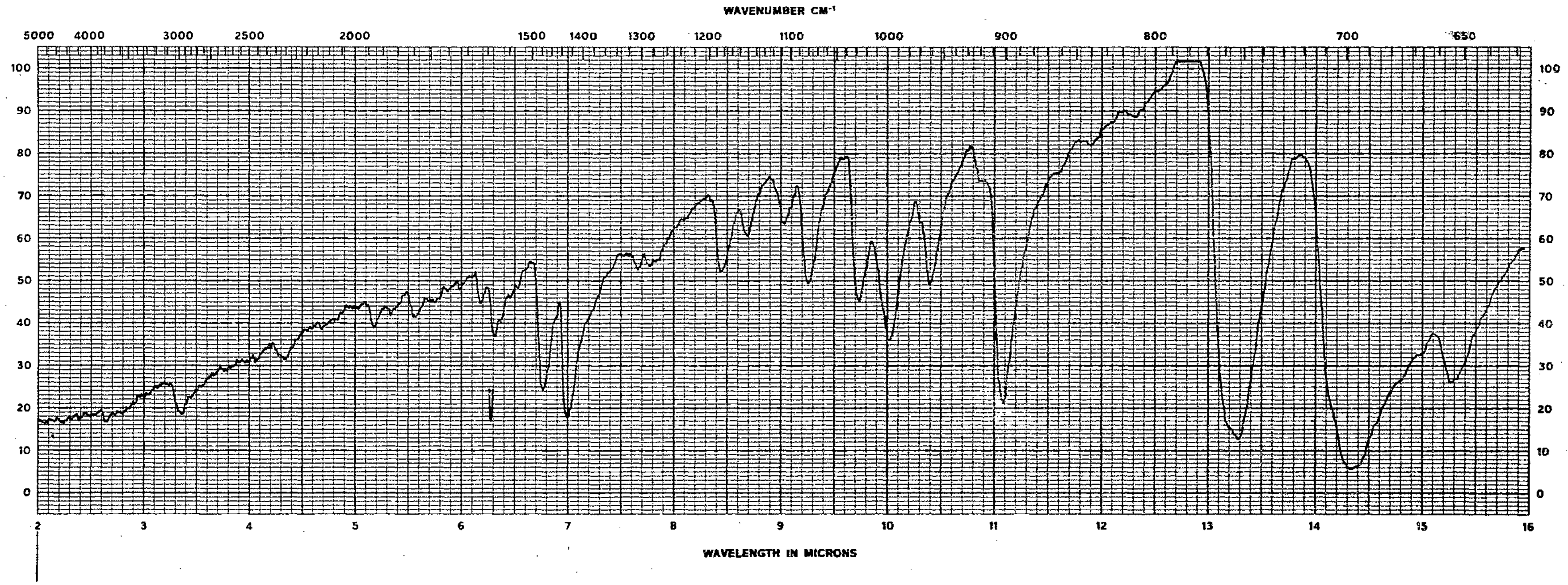

BENZYLTRITYLAMINE
RELATIVE INTENSITY
100
80
60
40
20
PERCENT SIGMA
18.6
16.0
12.0
8.0
4.0
M/E
50
100
150
200
250
300
350
77
91
106
165
243
258
272
349

Plate IX



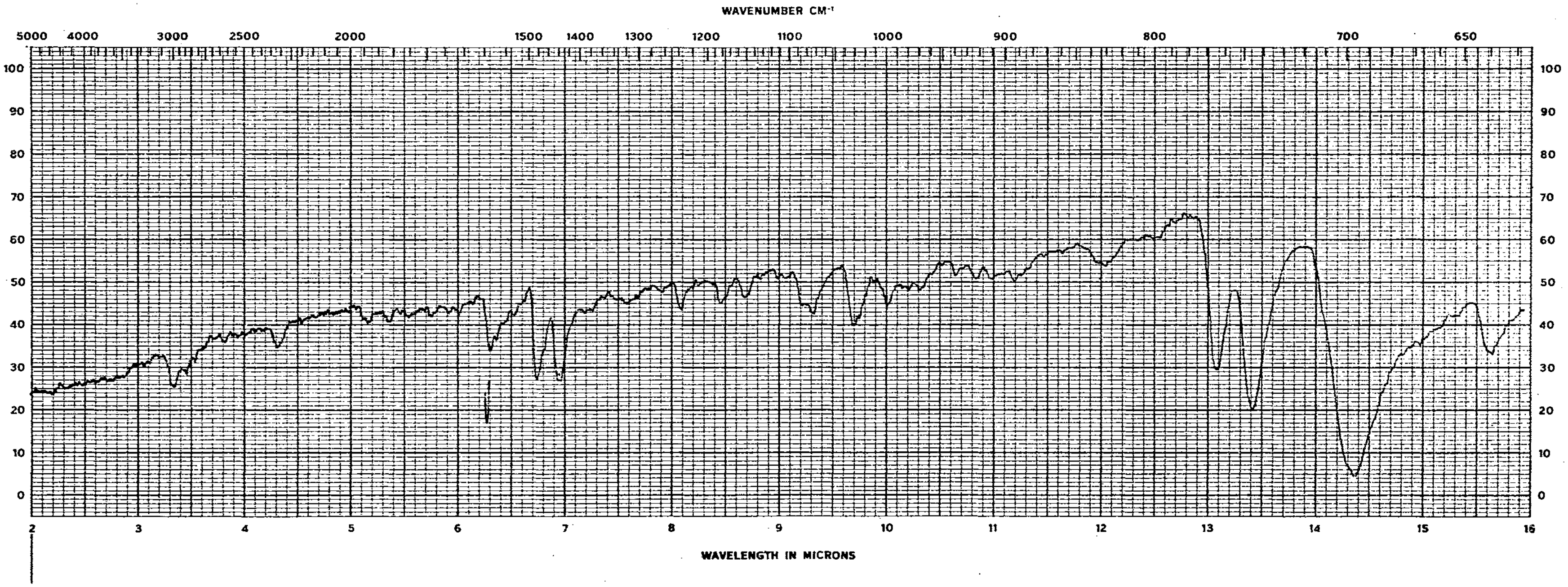
1,1,1-Triphenylethane (VI)

Plate X



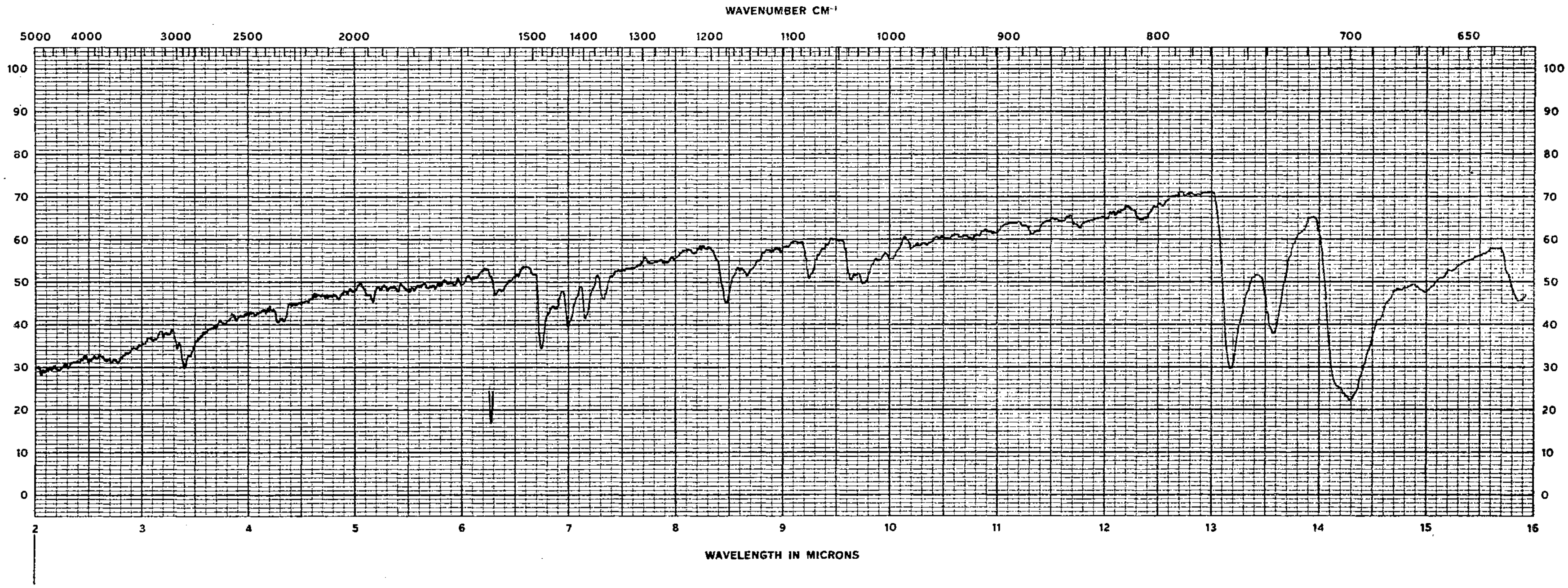
4,4,4-Triphenylbutene (VII)

Plate XI



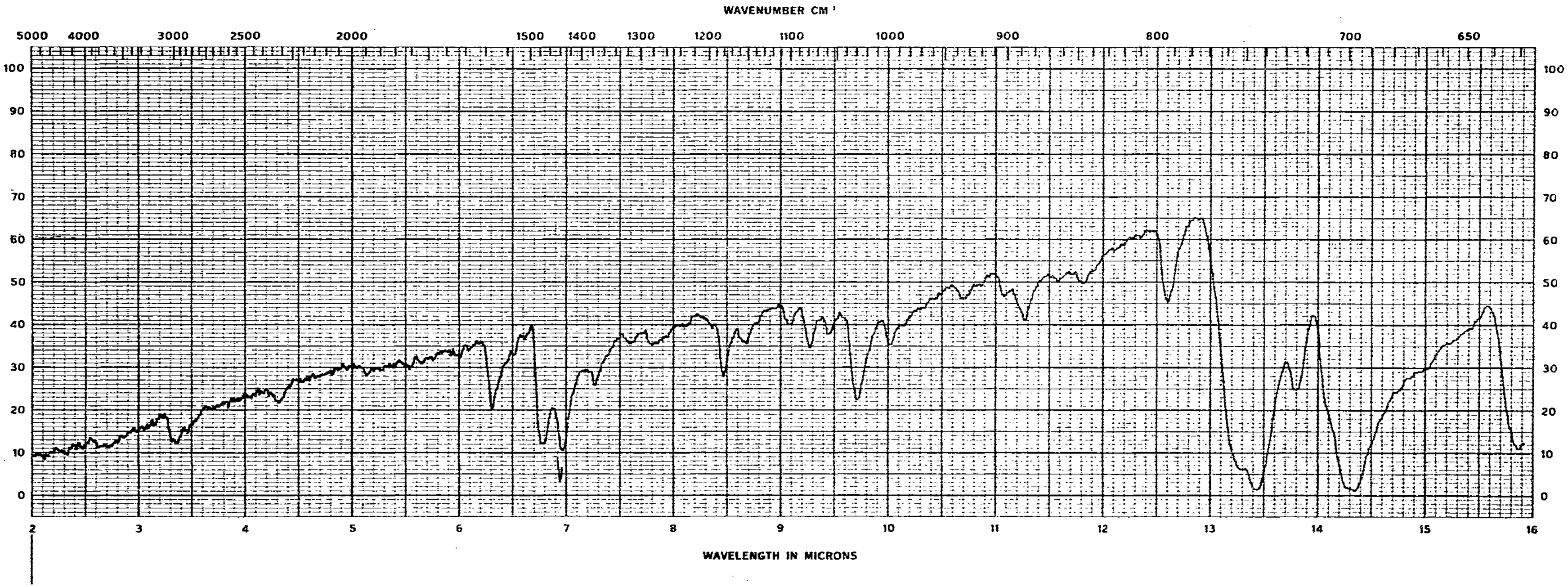
1,1,1,2-Tetraphenylethane (VIII)

Plate XII



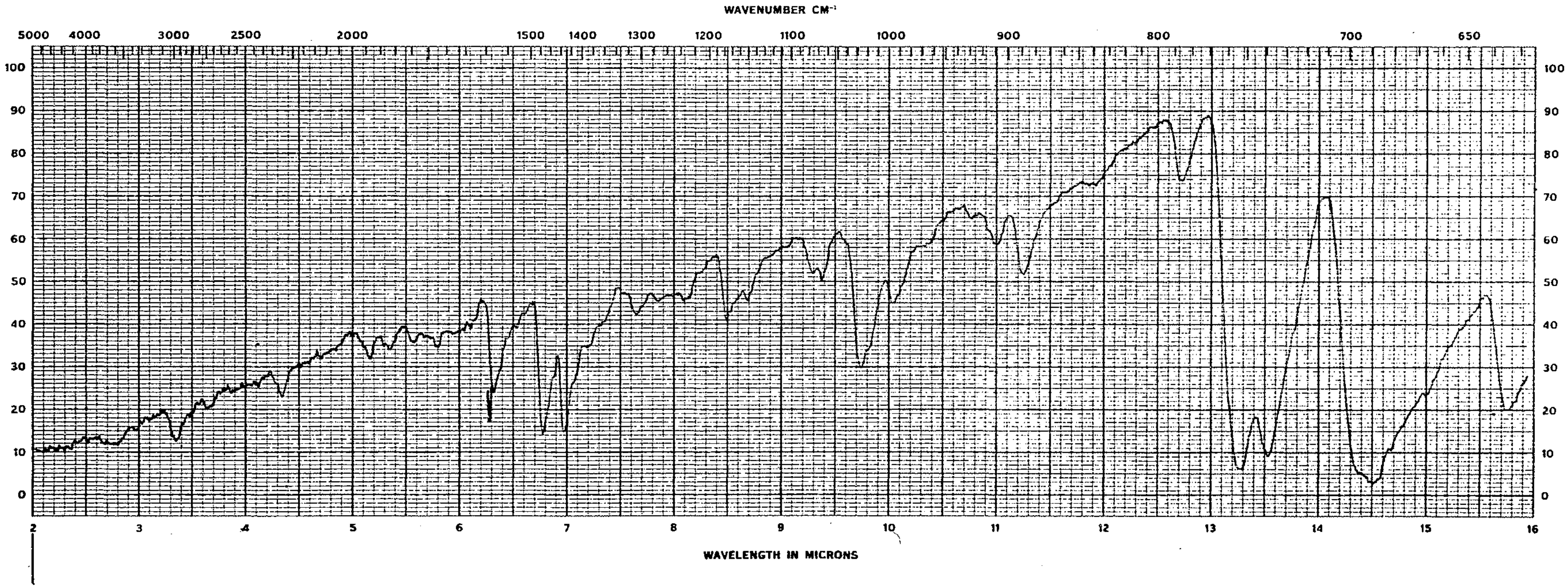
2,2-Dimethyl-1,1,1-triphenylpropane (IX)

Plate XIII



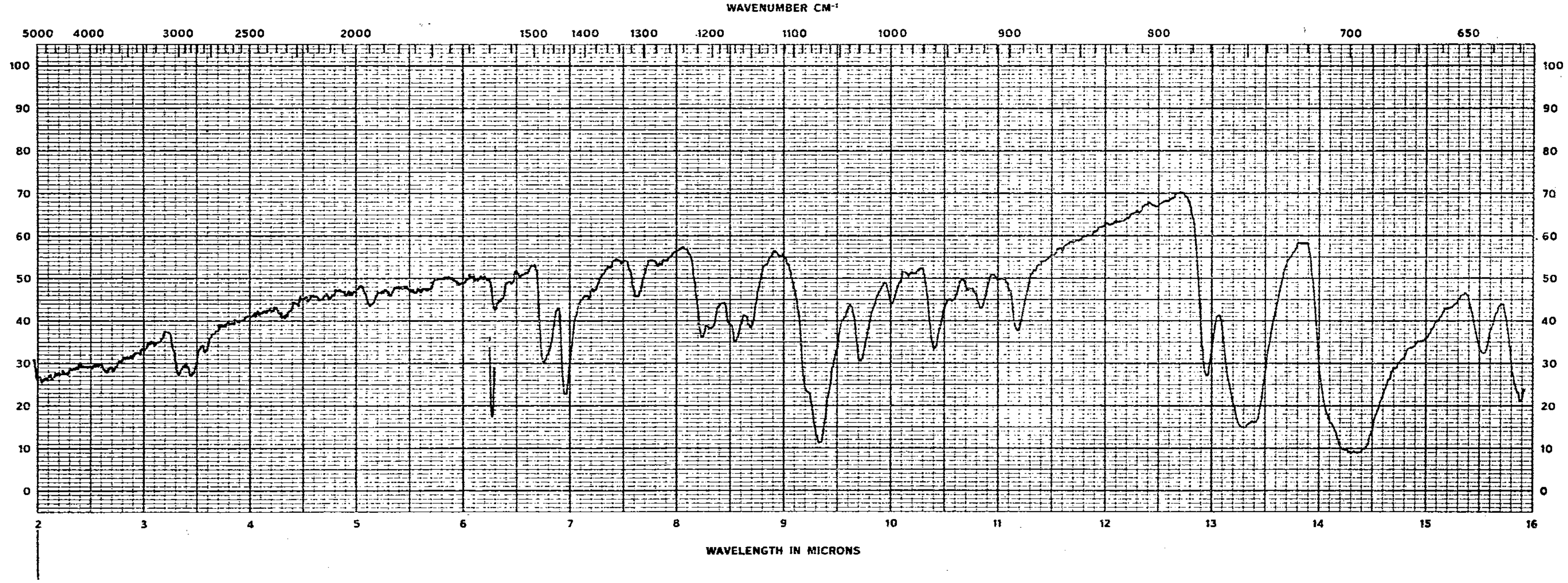
o-Trityltoluene (XXIV)

Plate XIV



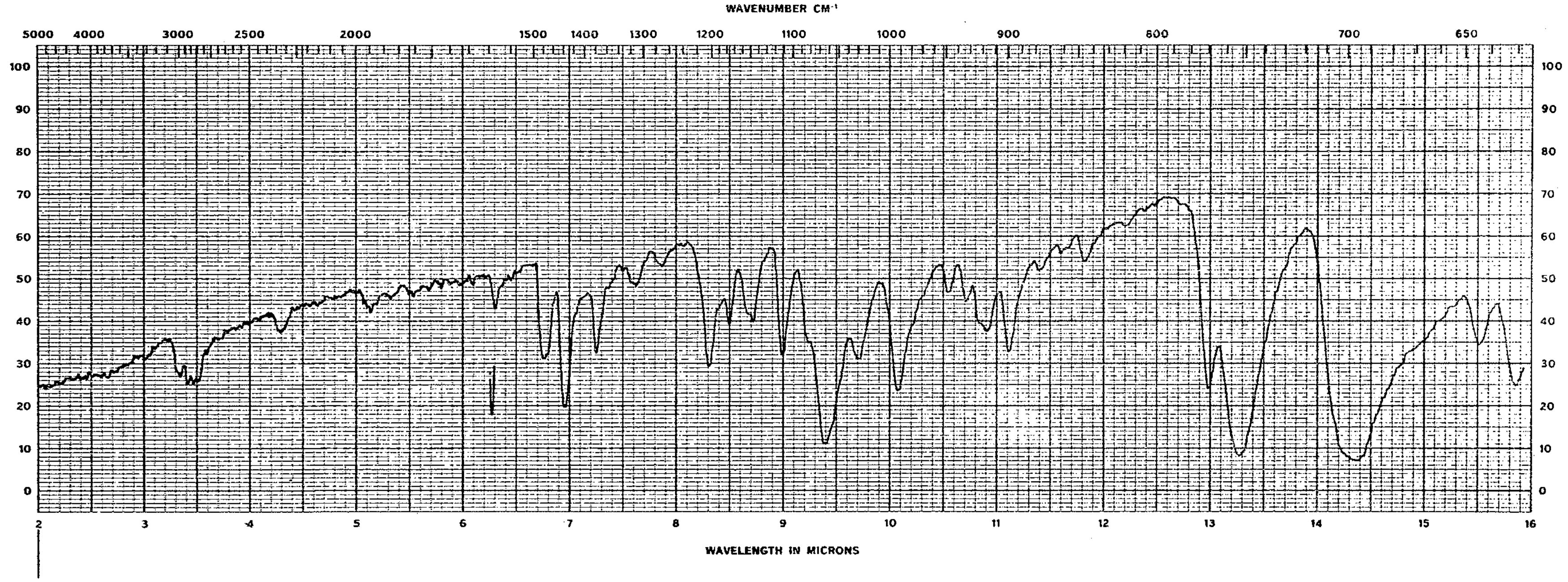
1,3,3,3-Tetraphenylpropyne (XXV)

Plate XV



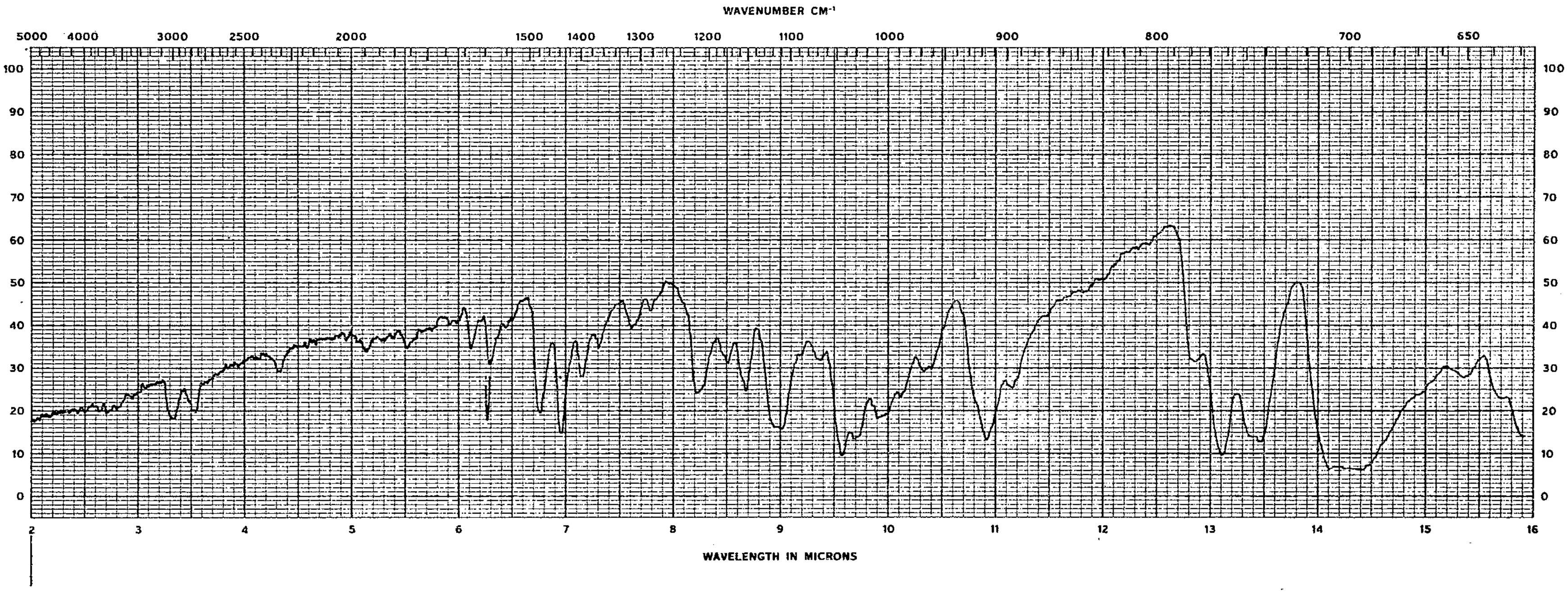
Trityl Methyl Ether (XIV)

Plate XVI



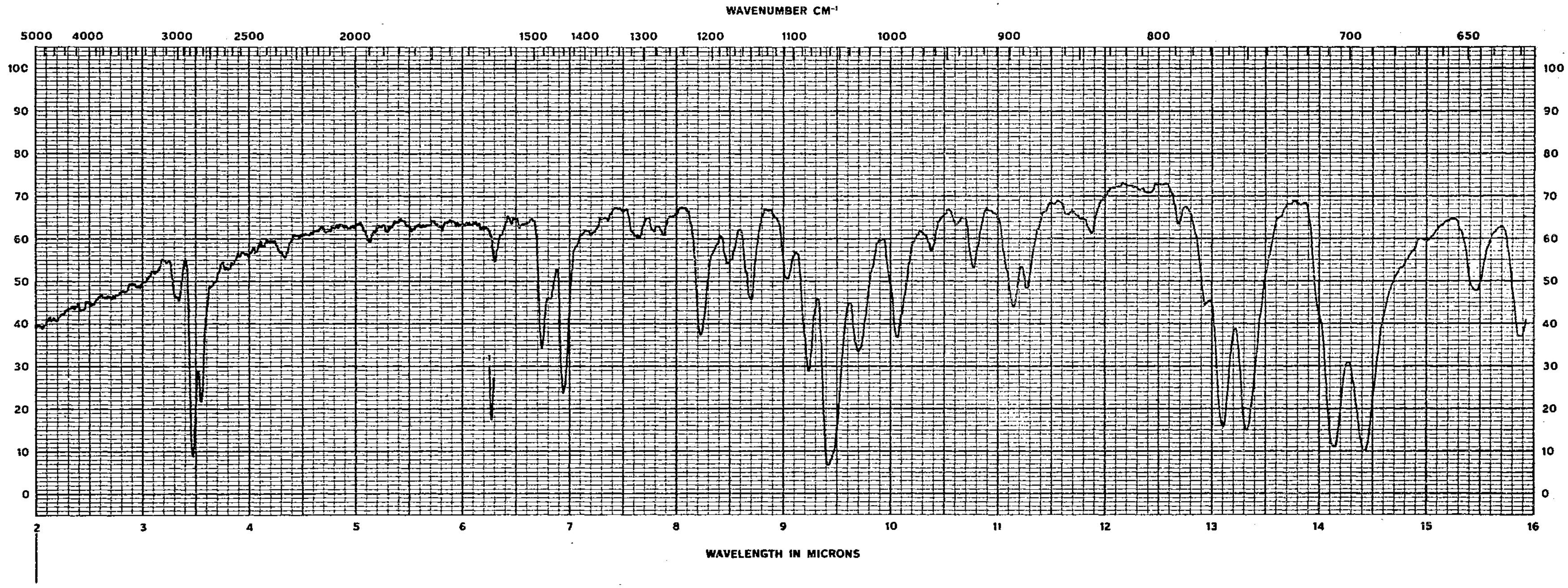
Trityl Ethyl Ether (XV)

Plate XVII



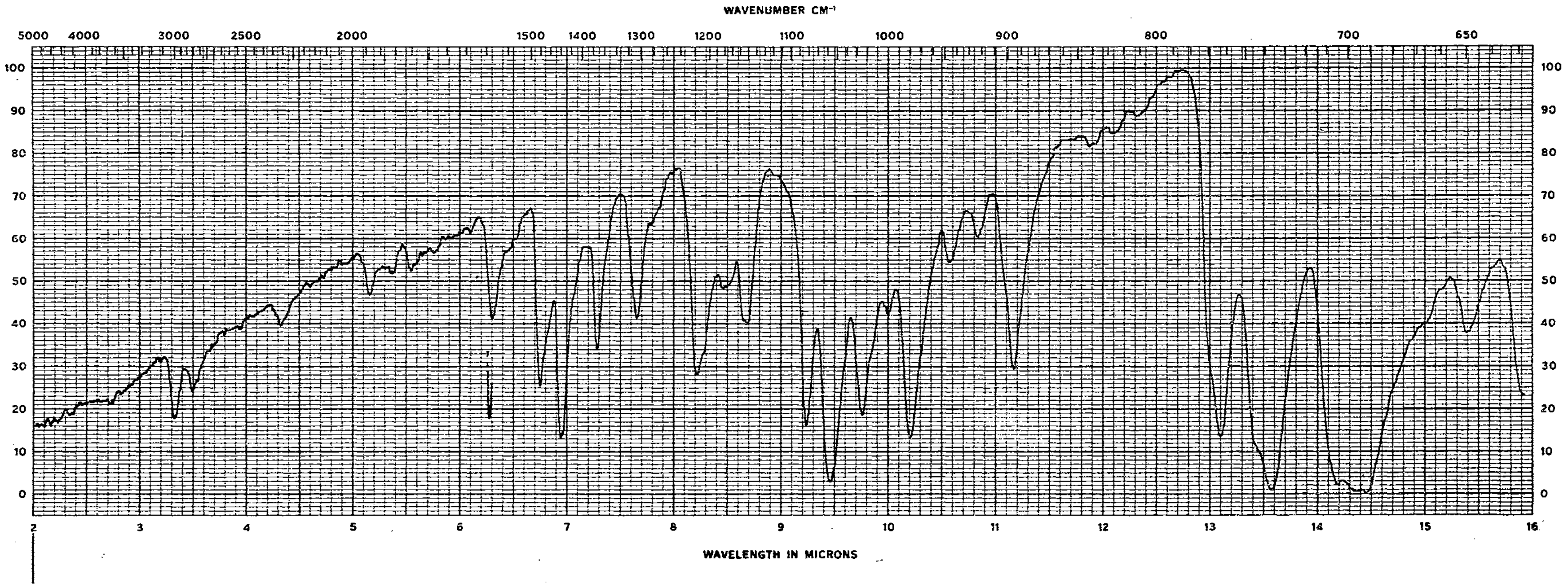
Trityl Allyl Ether (XVI)

Plate XVIII



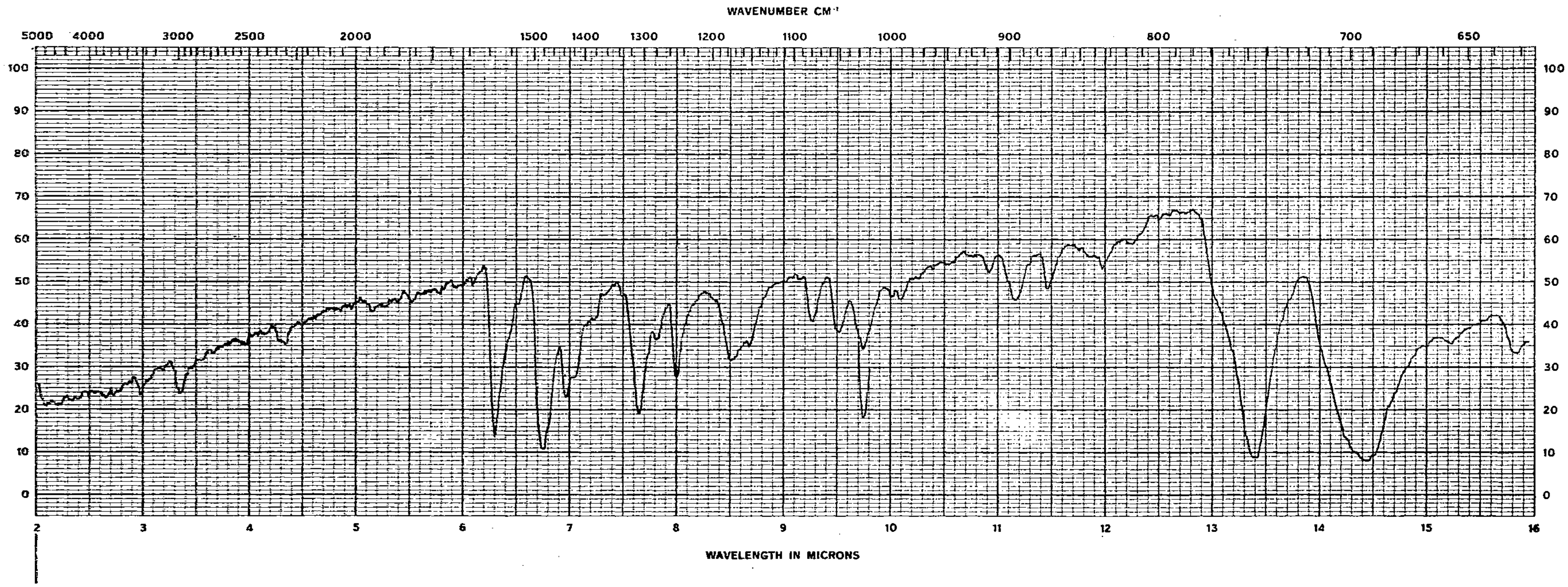
Trityl Cyclohexylmethyl Ether (XVII)

Plate XIX



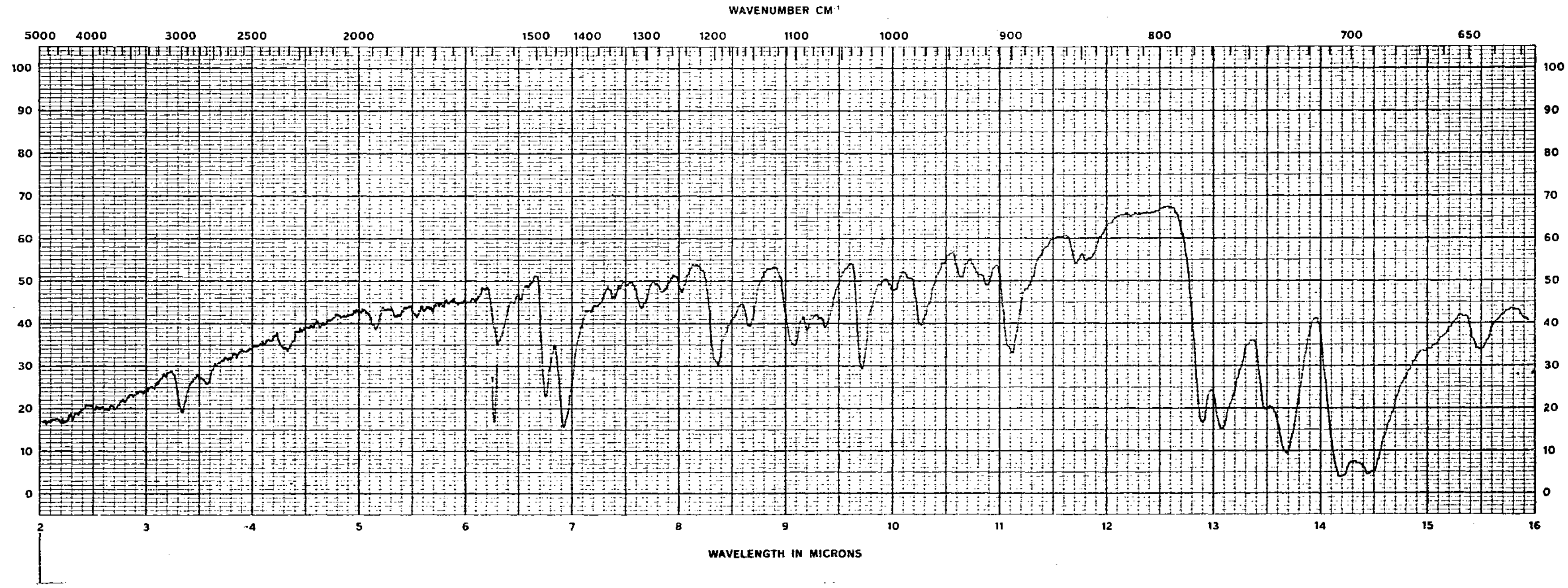
Trityl Benzyl Ether (XXX)

Plate XX



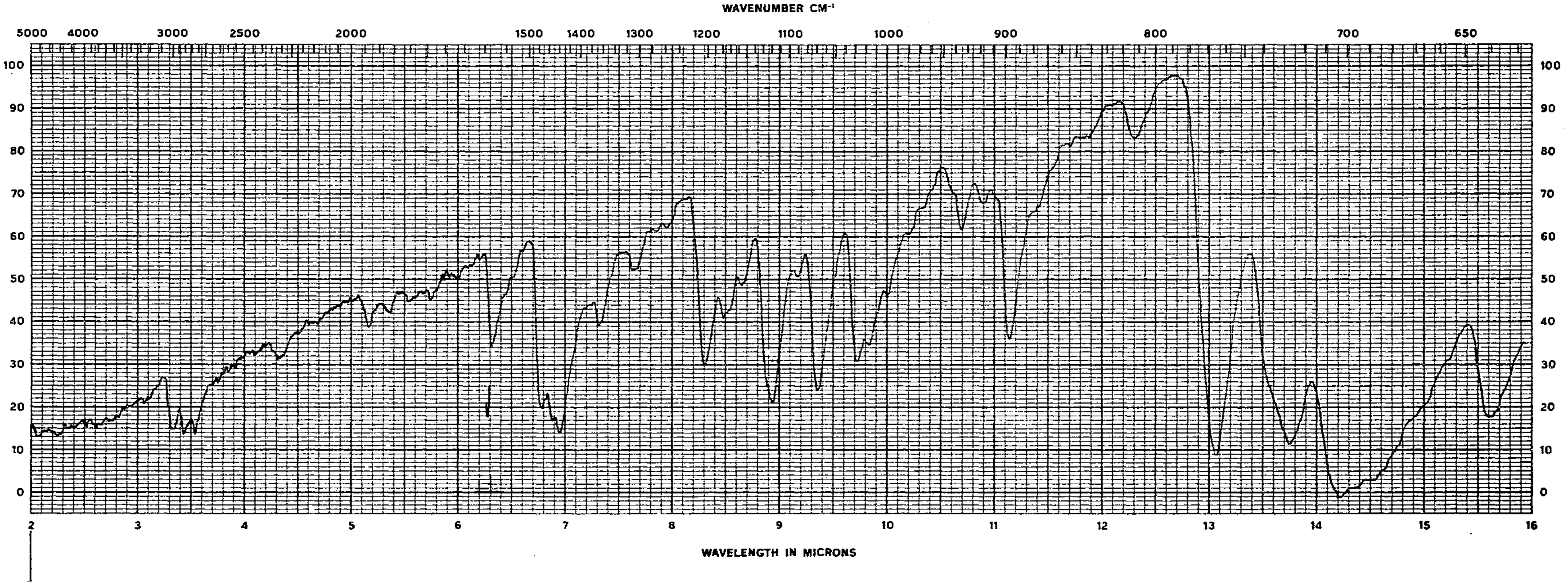
N-Tritylaniline (XXVI)

Plate XXI



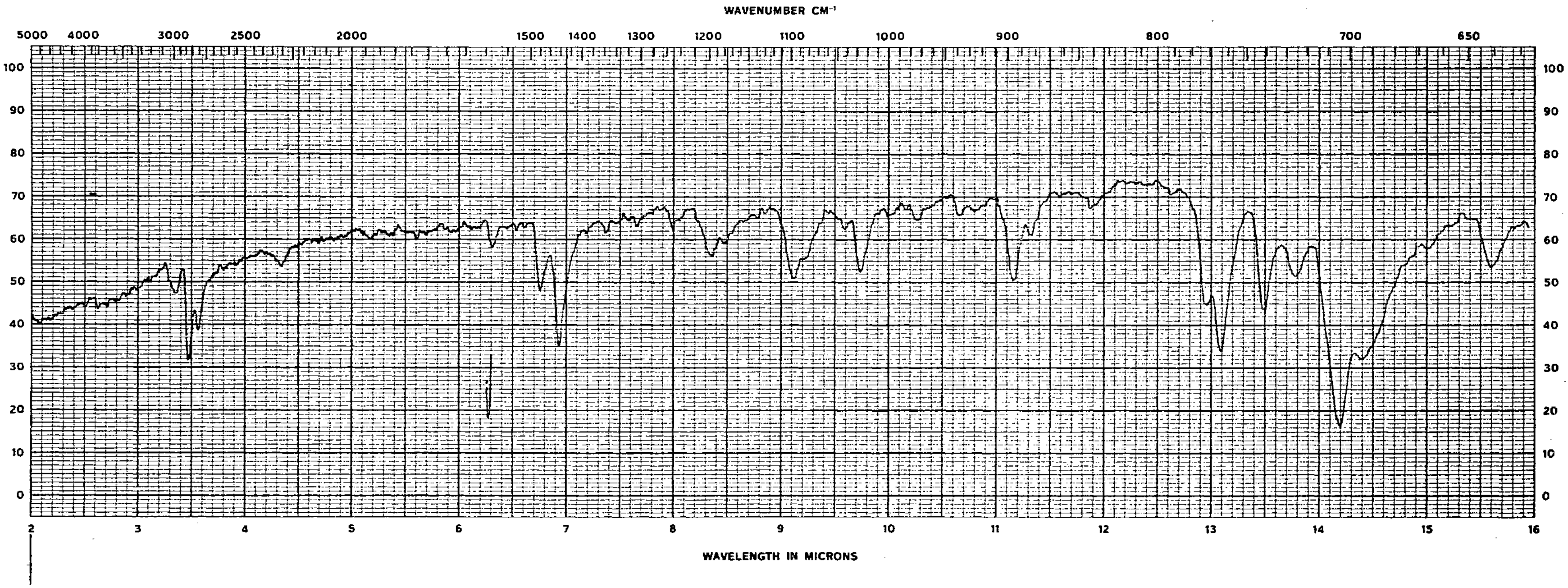
N-Tritylbenzylamine (XXVII)

Plate XXII



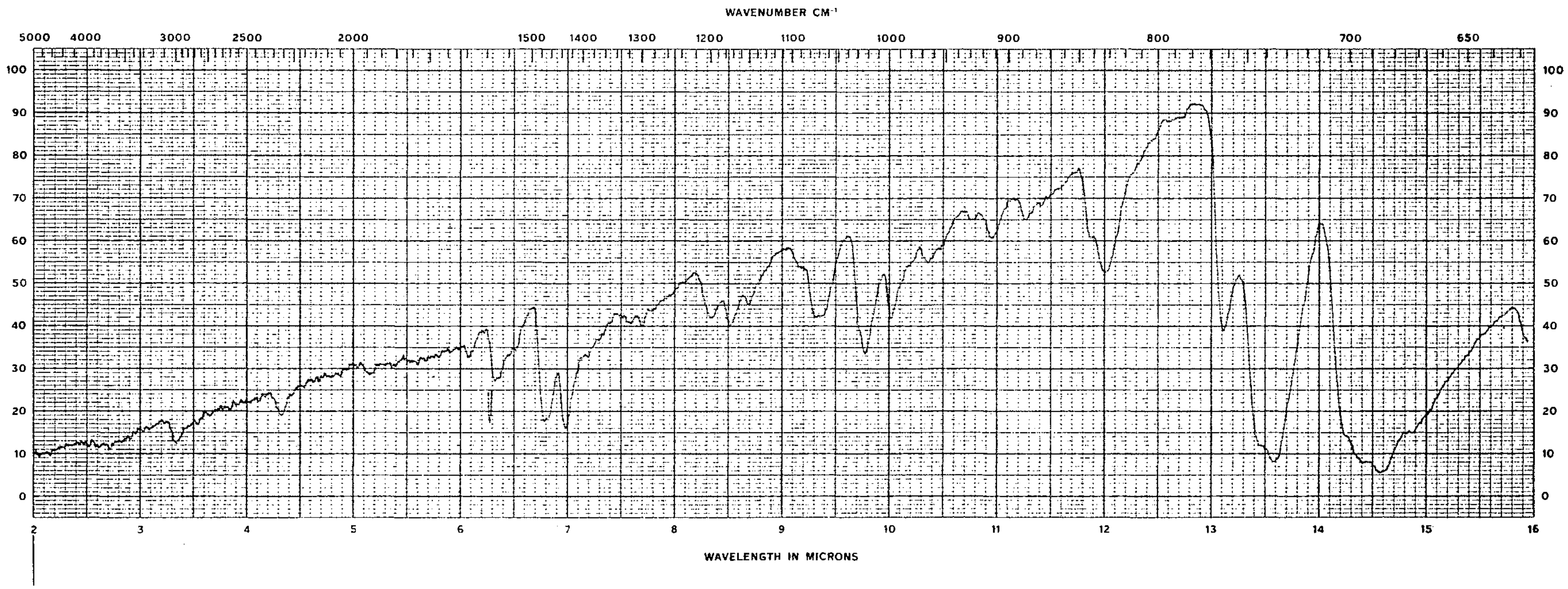
N-Tritylethylamine (XXVIII)

Plate XXIII



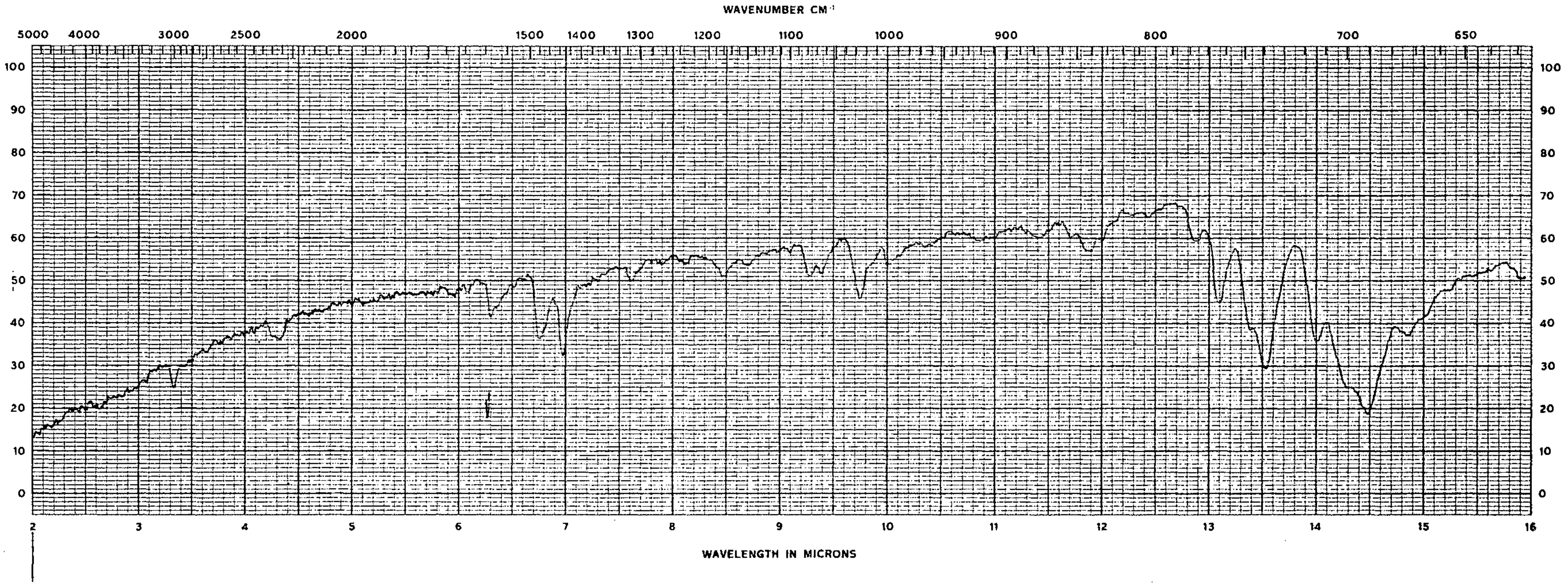
N-Tritylcyclohexylamine (XXIX)

Plate XXIV



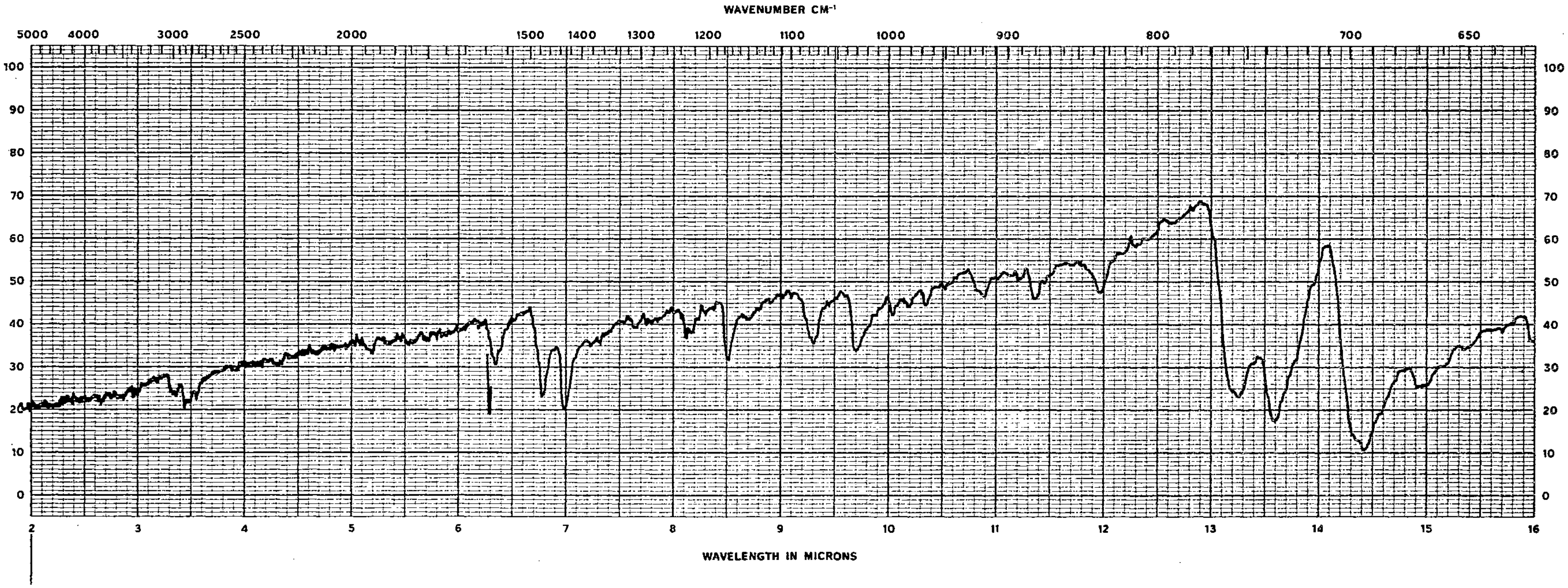
Trityl Phenyl Sulfide (XXI)

Plate XXV



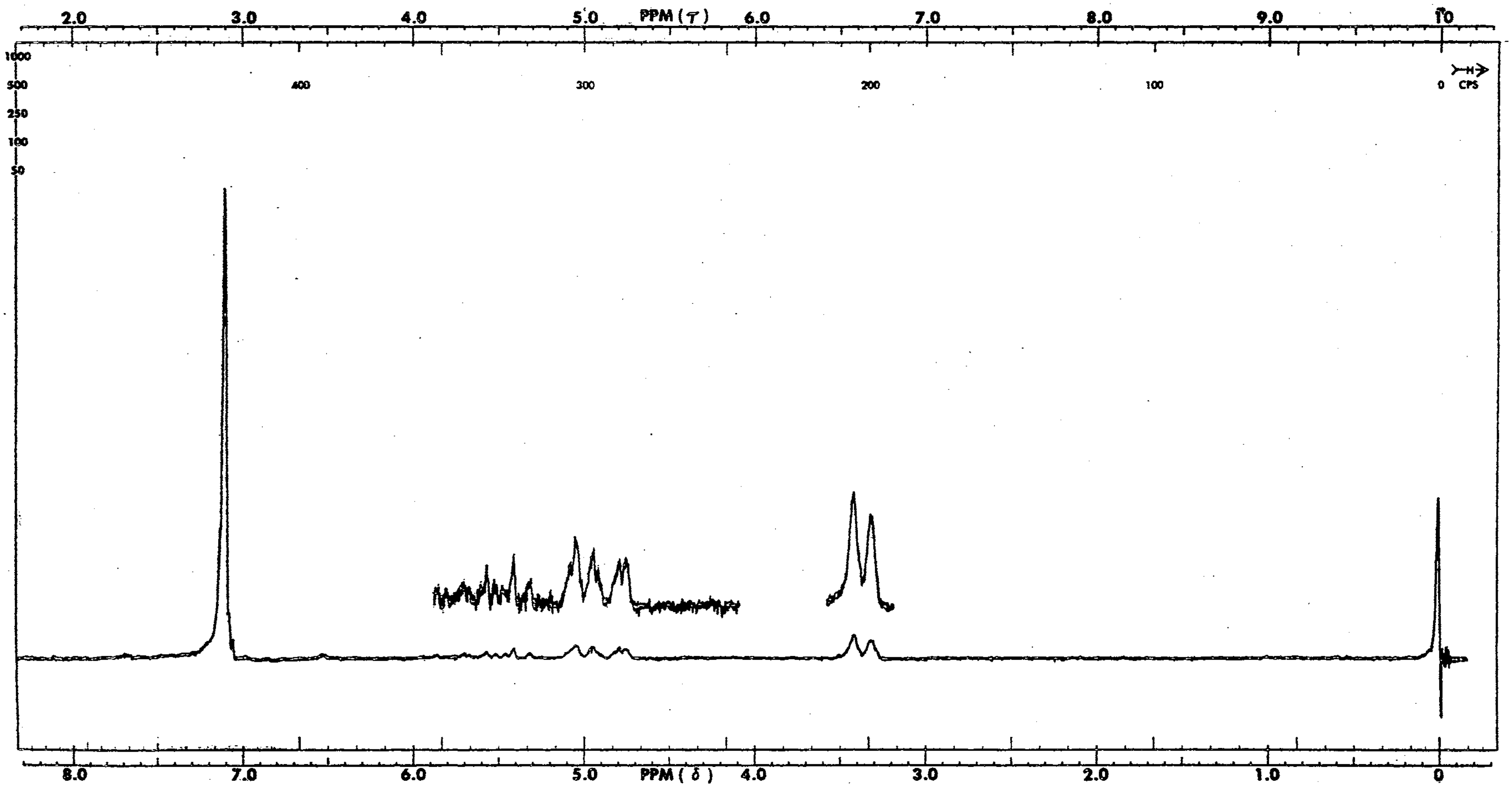
Trityl Benzyl Sulfide (XXII)

Plate XXVI



Trityl n-Propyl Sulfide (XXIII)

Plate XXVII

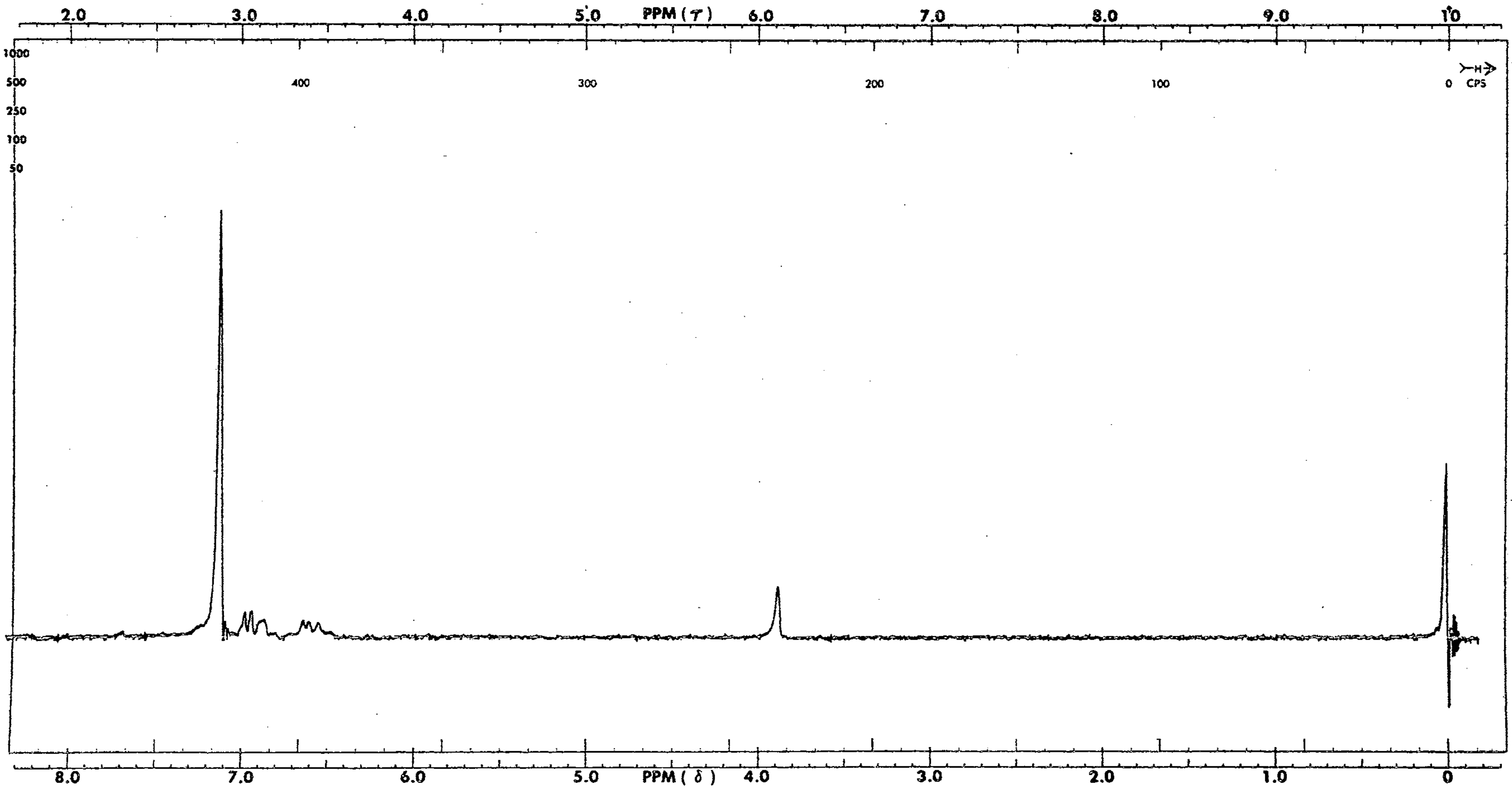


4,4,4-Triphenyl-1-butene (VII)

Solvent .... CCl_4 R. F. Field .... 0.05 mG S. W. .... 500 cps S. A. 2.5

F. B. .... 4.0 cps S. T. .... 250 sec S. O. .... 020 cps I. A. 16

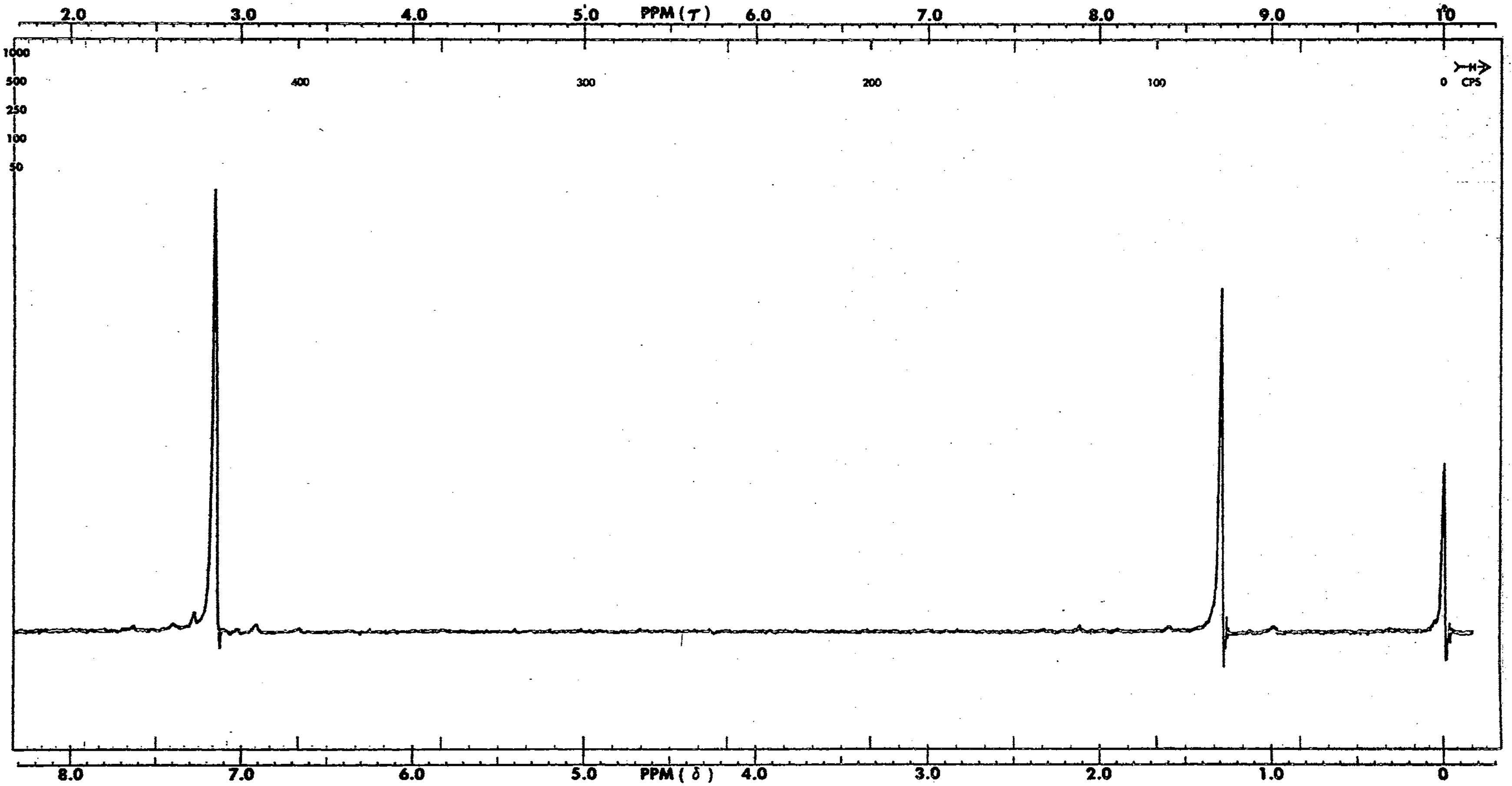
Plate XXVIII



<u>1,1,1,2-Tetraphenylethane (VIII)</u>

Solvent	CCl_4	R. F. Field	0.04 mG	S. W.	500 cps	S. A.	2.5
F. B.	4.0 cps	S. T.	250 sec	S. O.	020 cps	I. A.	63

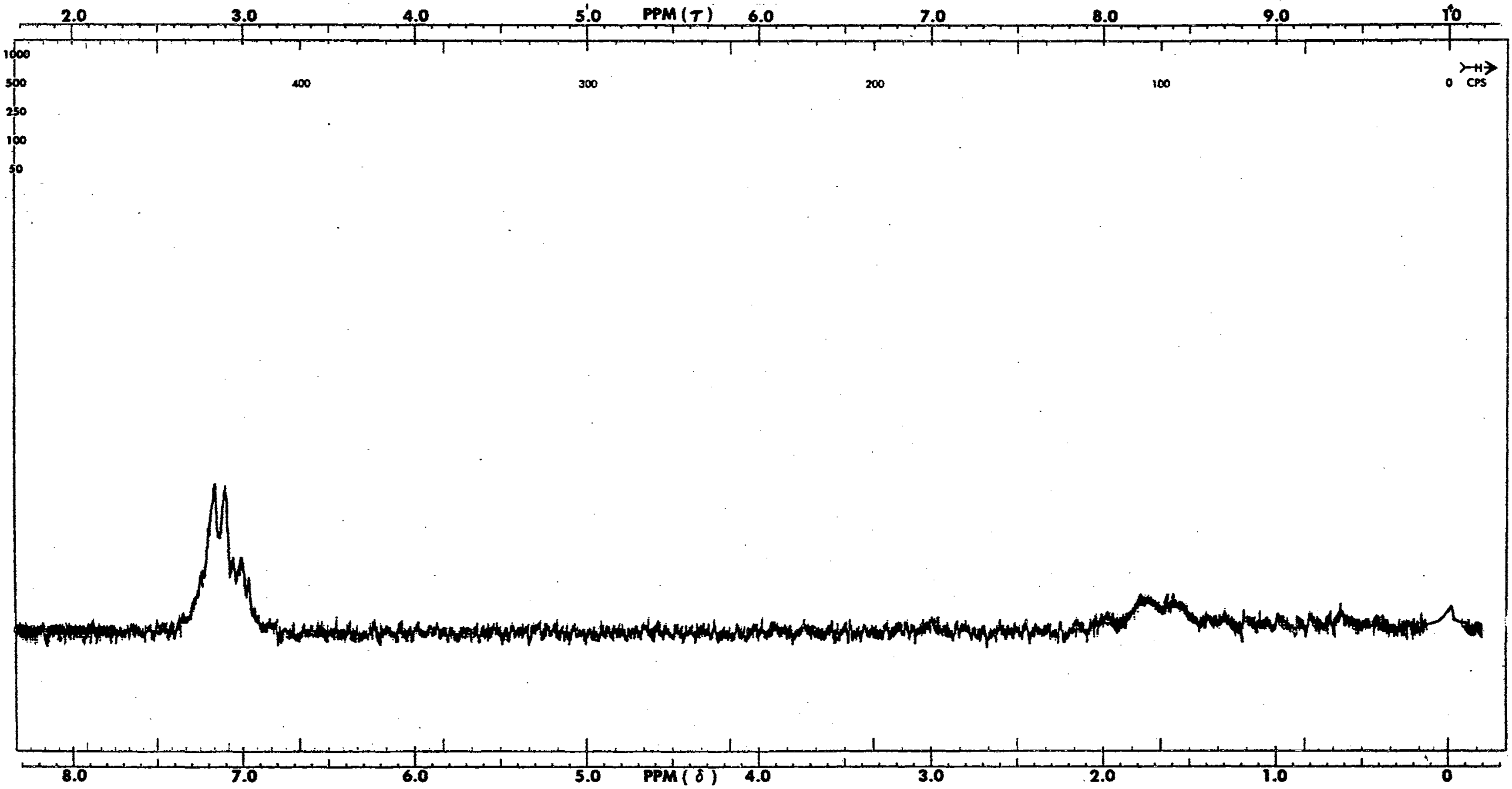
Plate XXIX



2,2-Dimethyl-1,1,1-triphenylpropane (IX)

Solvent	$CDCl_3$	R. F. Field	0.05 mG	S. W.	500 cps	S. A.	4.0
F. B.	2.0 cps	S. T.	250 sec	S. O.	020 cps	I. A.	40

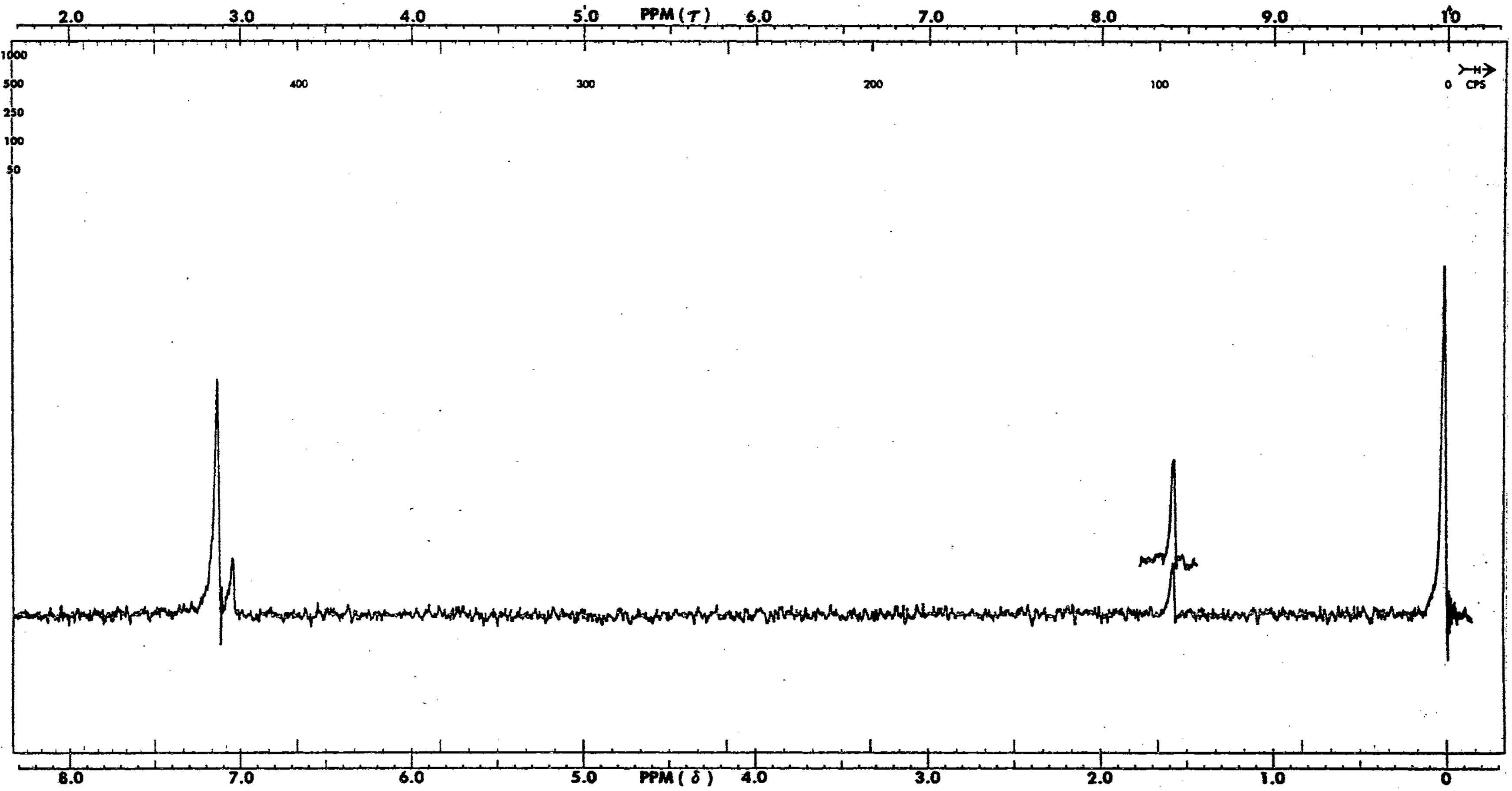
Plate XXX



Cyclohexyltriphenylmethane (XI)

Solvent	CCl_4	R. F. Field	0.05 mG	S. W.	500 cps	S. A.	16
F. B.	2.0 cps	S. T.	250 sec	S. O.	010 cps	I. A.	off

Plate XXXI

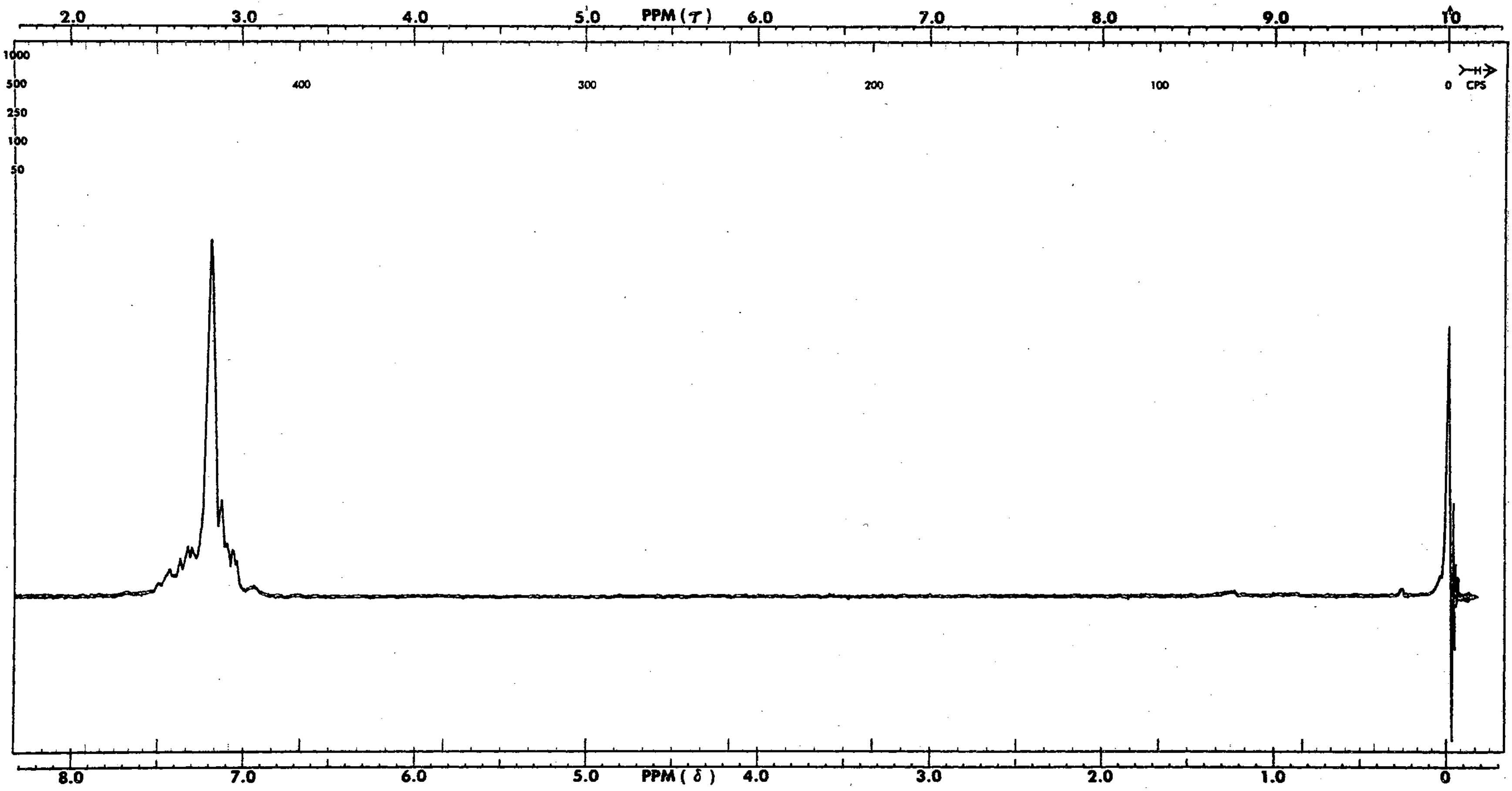


o-Trityltoluene (XXIV)

Solvent .... CCl_4 R. F. Field .... 0.02 mG S. W. .... 500 cps S. A. 10

F. B. .... 2.0 cps S. T. .... 250 sec S. O. .... 000 cps I. A. .... off

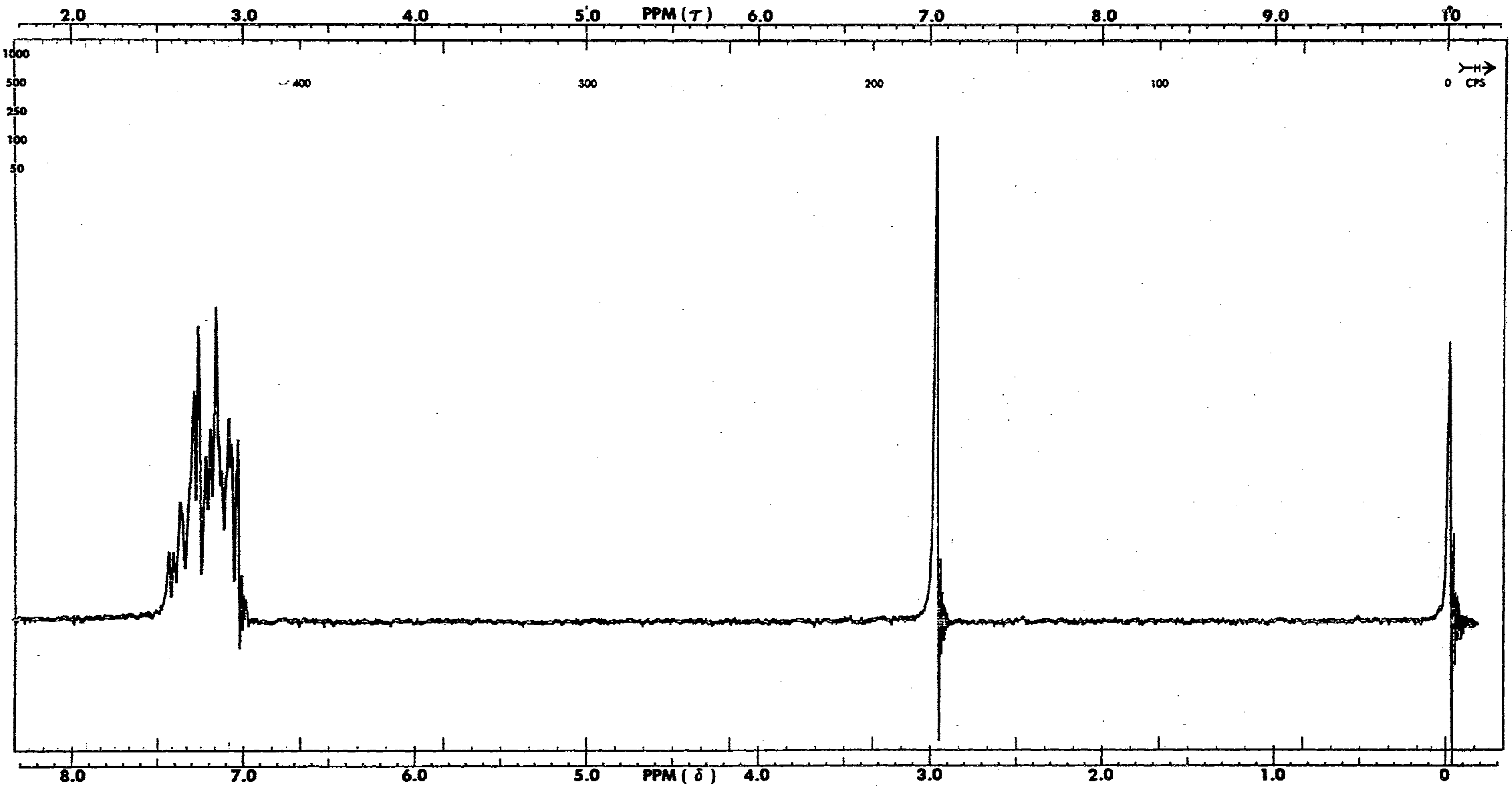
Plate XXXII



1,3,3,3-Tetraphenylpropyne (XXV)

Solvent .... CCl_4	R. F. Field .... 0.05 mG	S. W. .... 500 cps	S. A. 2.5
F. B. .... 4.0 cps	S. T. .... 250 sec	S. O. .... 013 cps	I. A. .... off

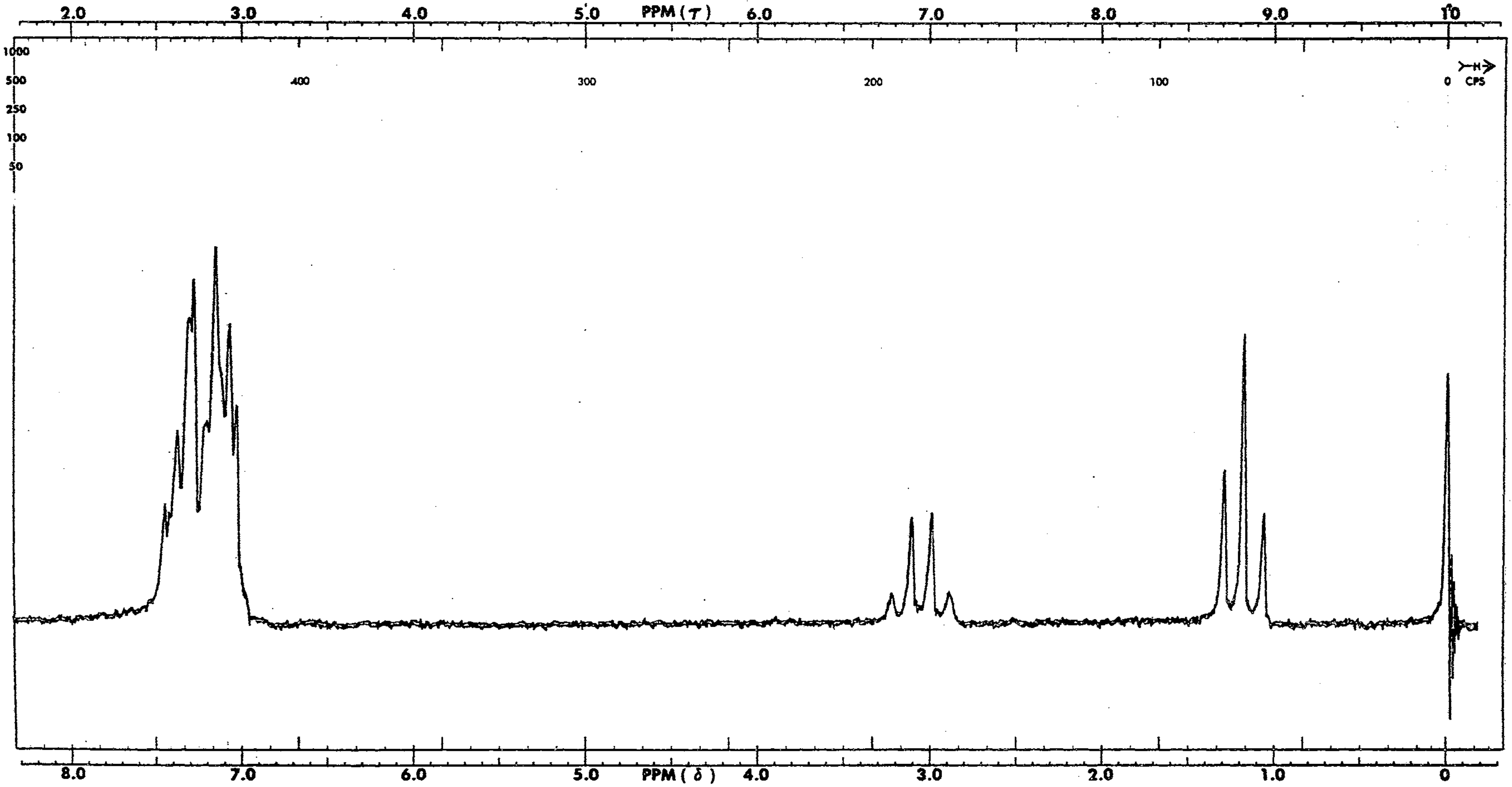
Plate XXXIII



Trityl Methyl Ether (XIV)

Solvent	CCl_4	R. F. Field	0.05 mG	S. W.	500 cps	S. A.	6.3
F. B.	2.0 cps	S. T.	250 sec	S. O.	050 cps	I. A.	off

Plate XXXIV

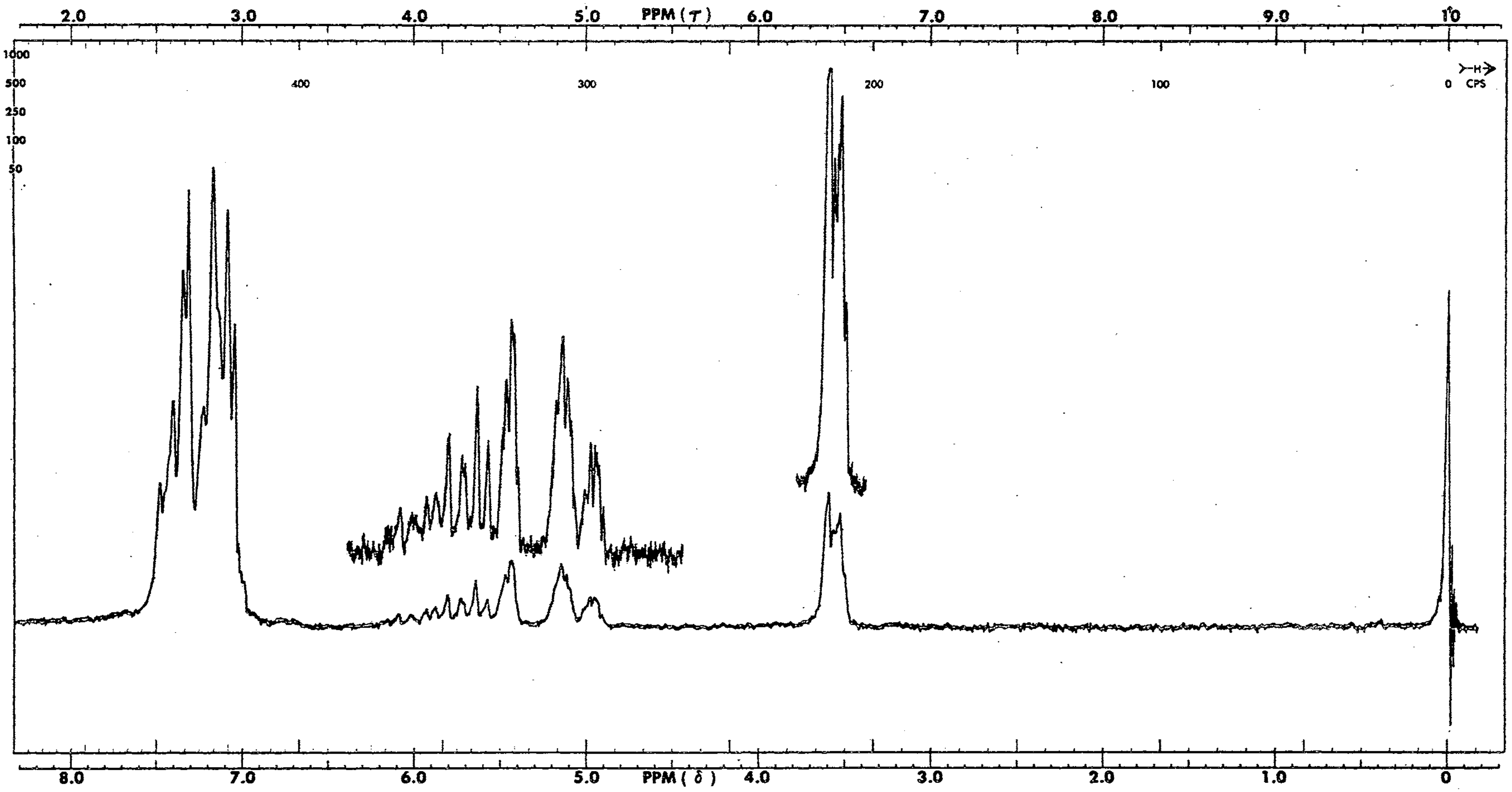


Trityl Ethyl Ether (XV)

Solvent .... CCl_4 R. F. Field .... 0.05 mG S. W. .... 500 S. A. 8.0

F. B. .... 2.0 cps S. T. .... 250 sec S. O. .... 050 I. A. 20

Plate XXXV

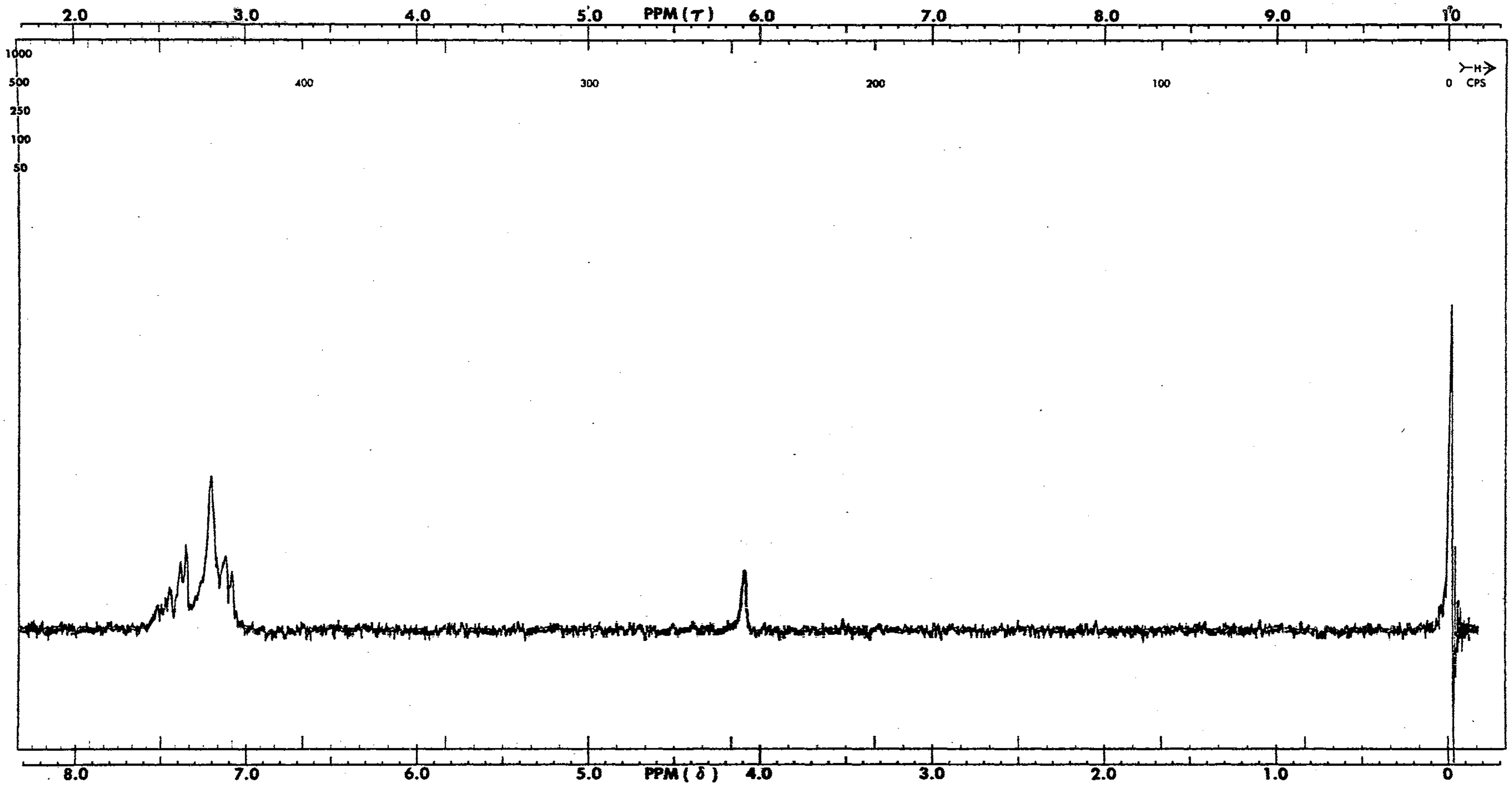


Trityl Allyl Ether (XVI)

Solvent .... CCl_4 R. F. Field .... 0.05 mG S. W. .... 500 cps S. A. 6.3

F. B. .... 2.0 cps S. T. .... 250 sec S. O. .... 050 cps I. A. 25

Plate XXXVI

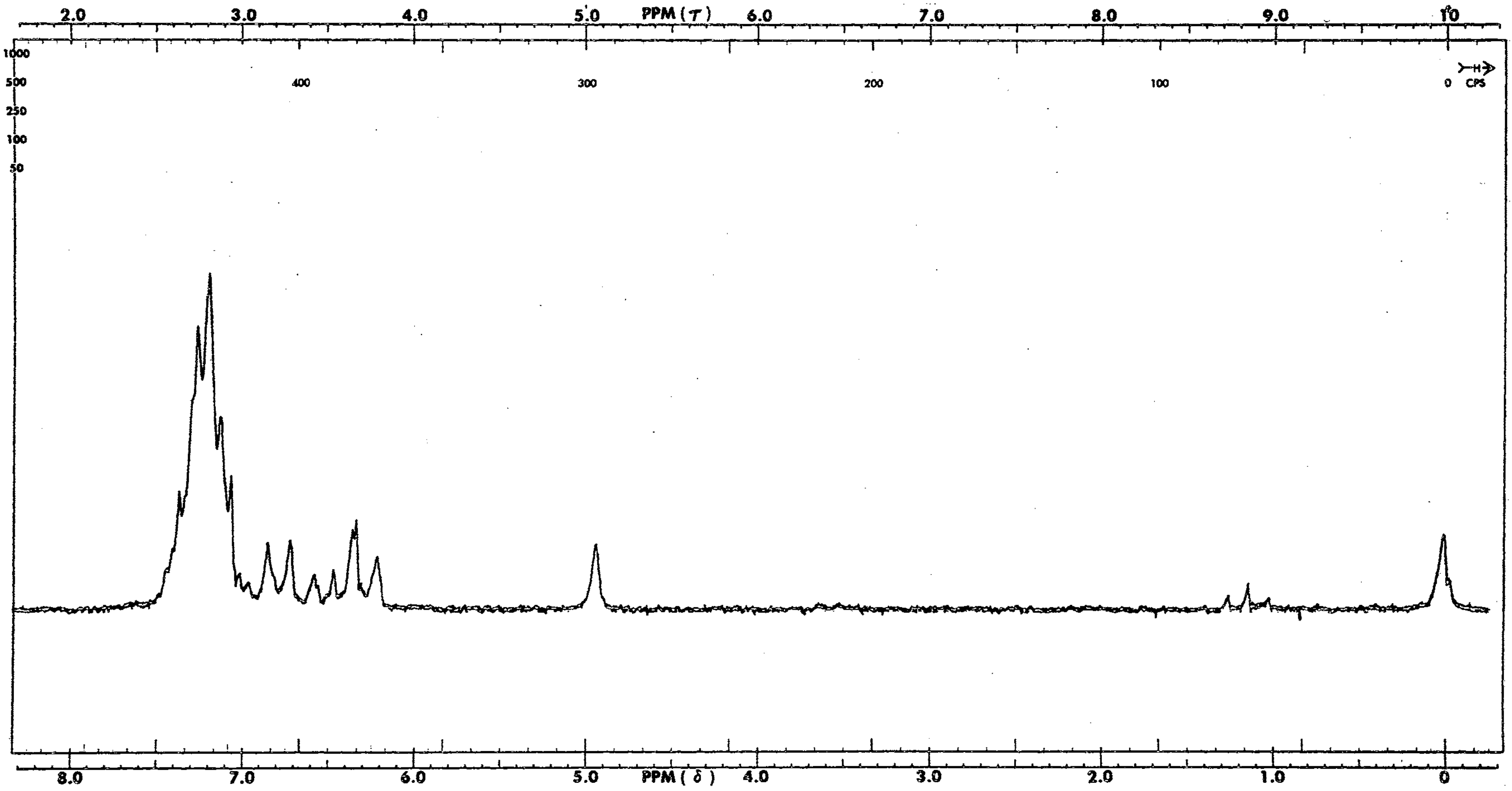


Trityl Benzyl Ether (XXX)

Solvent .... CCl_4 R. F. Field .... 0.05 mG S. W. .... 500 cps S. A. 12

F. B. .... 2.0 cps S. T. .... 250 sec S. O. .... 050 cps I. A. .... off

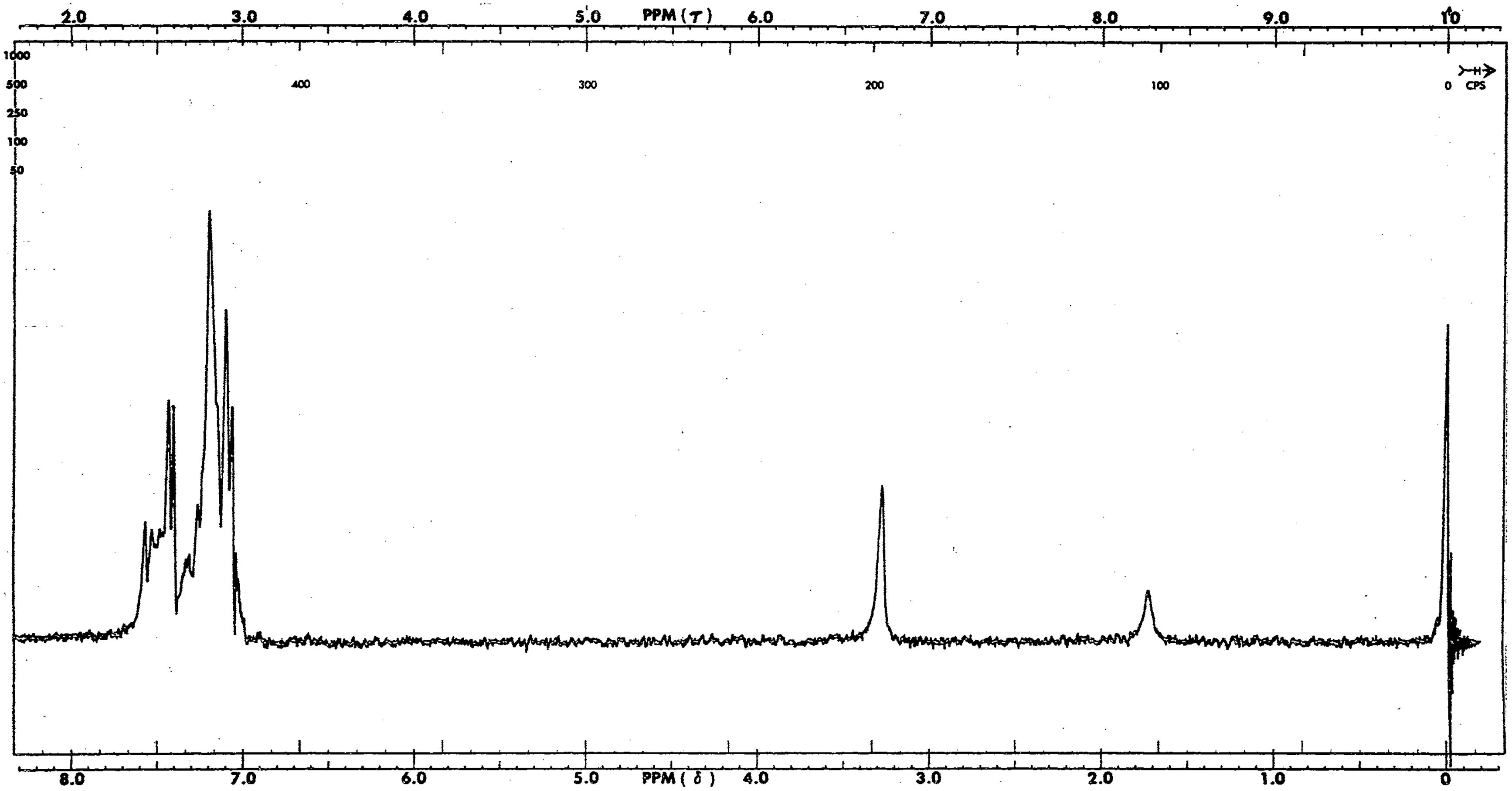
Plate XXXVII



N-Tritylaniline (XXVI)

Solvent .... $CDCl_3$	R. F. Field .... 0.05 mG	S. W. .... 500 cps	S. A. 6.3
F. B. .... 2.0 cps	S. T. .... 250 sec	S. O. .... 053 cps	I. A. 63

Plate XXXVIII

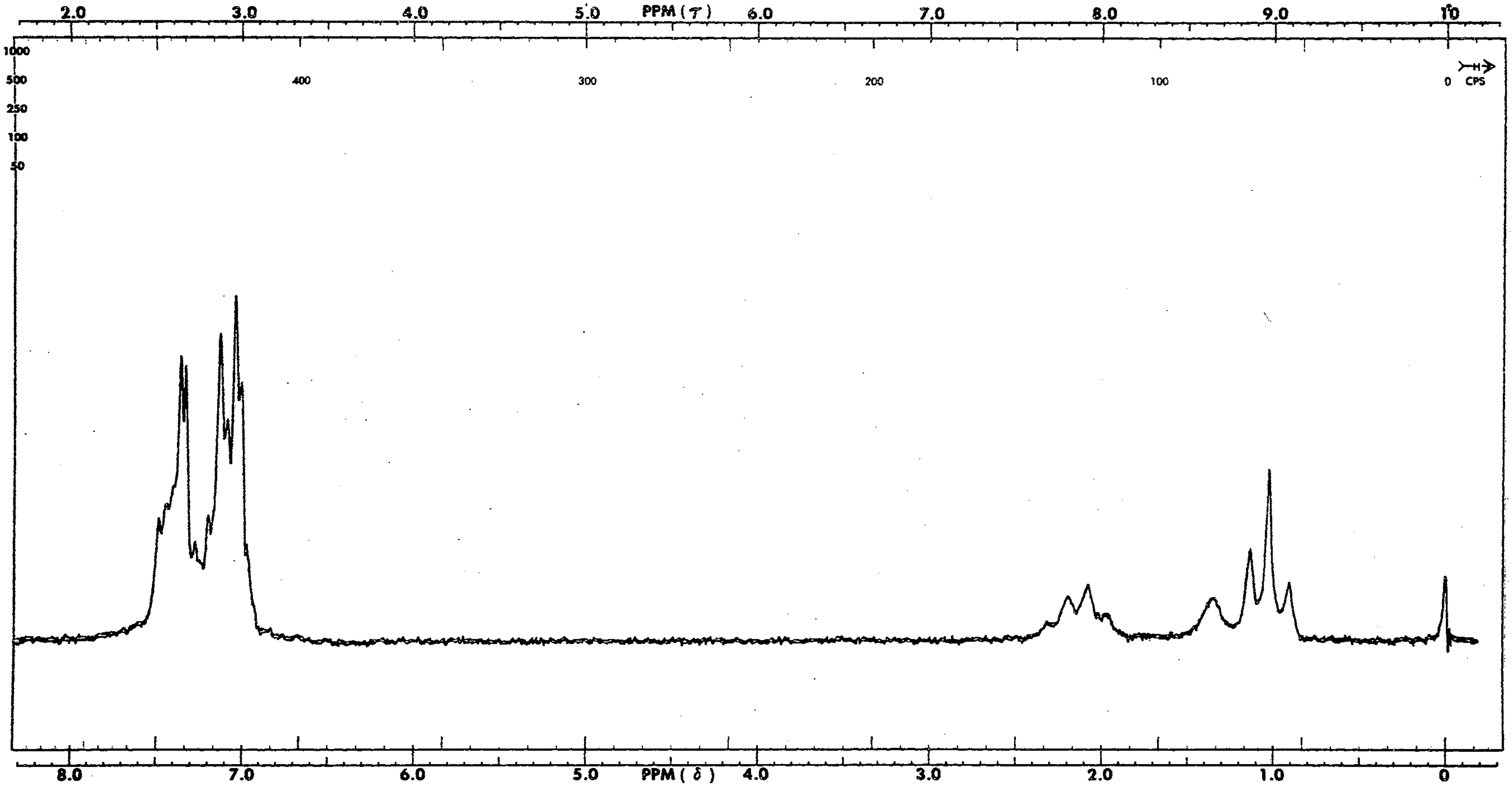


N-Tritylbenzylamine (XXVII)

Solvent .... CCl_4 R. F. Field .... 0.05 mG S. W. .... 500 cps S. A. 8.0

F. B. .... 2.0 cps S. T. .... 250 sec S. O. .... 045 cps I. A. 40

Plate XXXIX

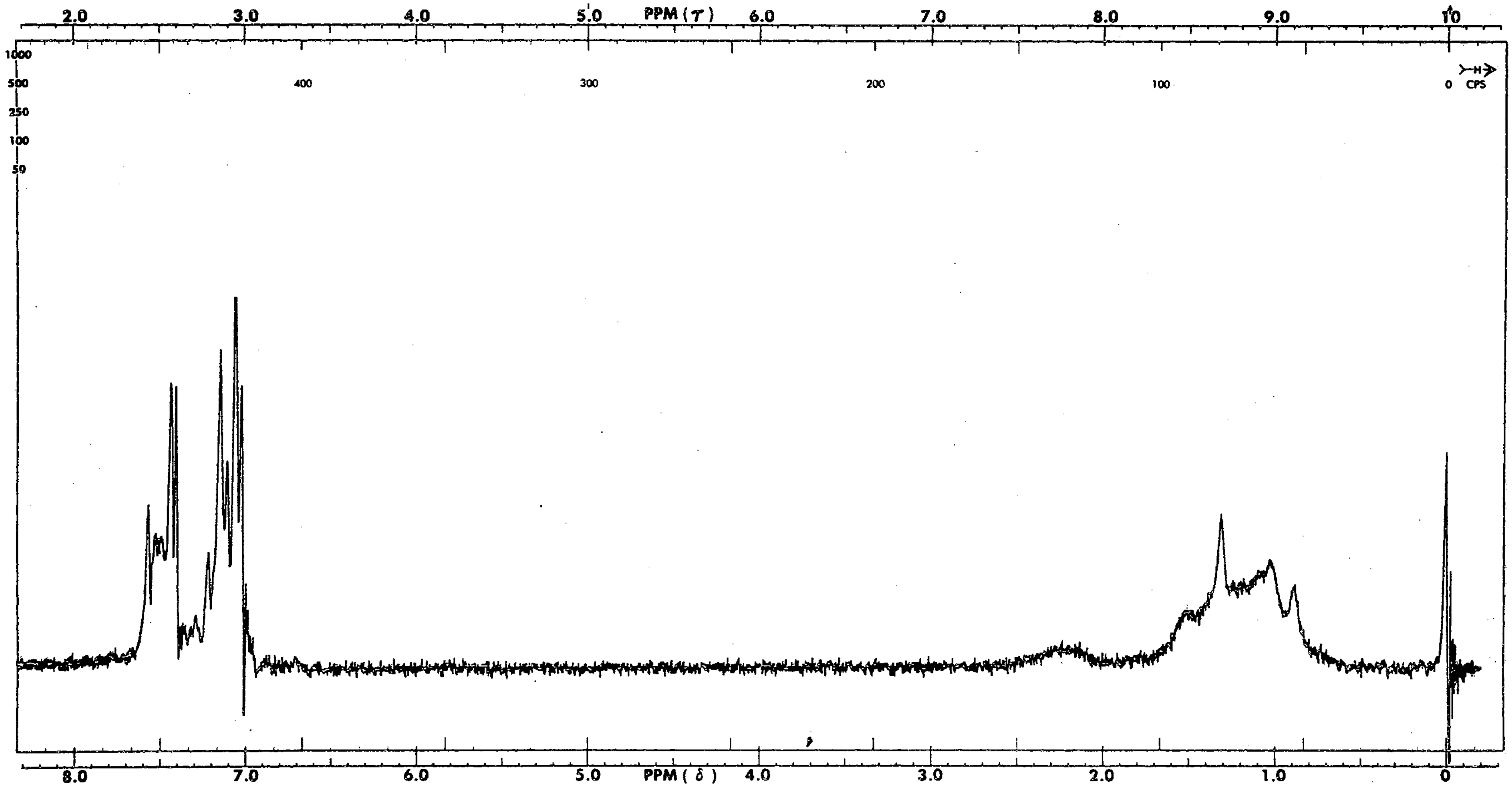


N-Tritylethylamine (XXVIII)

Solvent .... CCl_4 R. F. Field .... 0.05 mG S. W. .... 500 cps S. A. 6.3

F. B. .... 2.0 cps S. T. .... 250 sec S. O. .... 053 cps I. A. 40

Plate XL

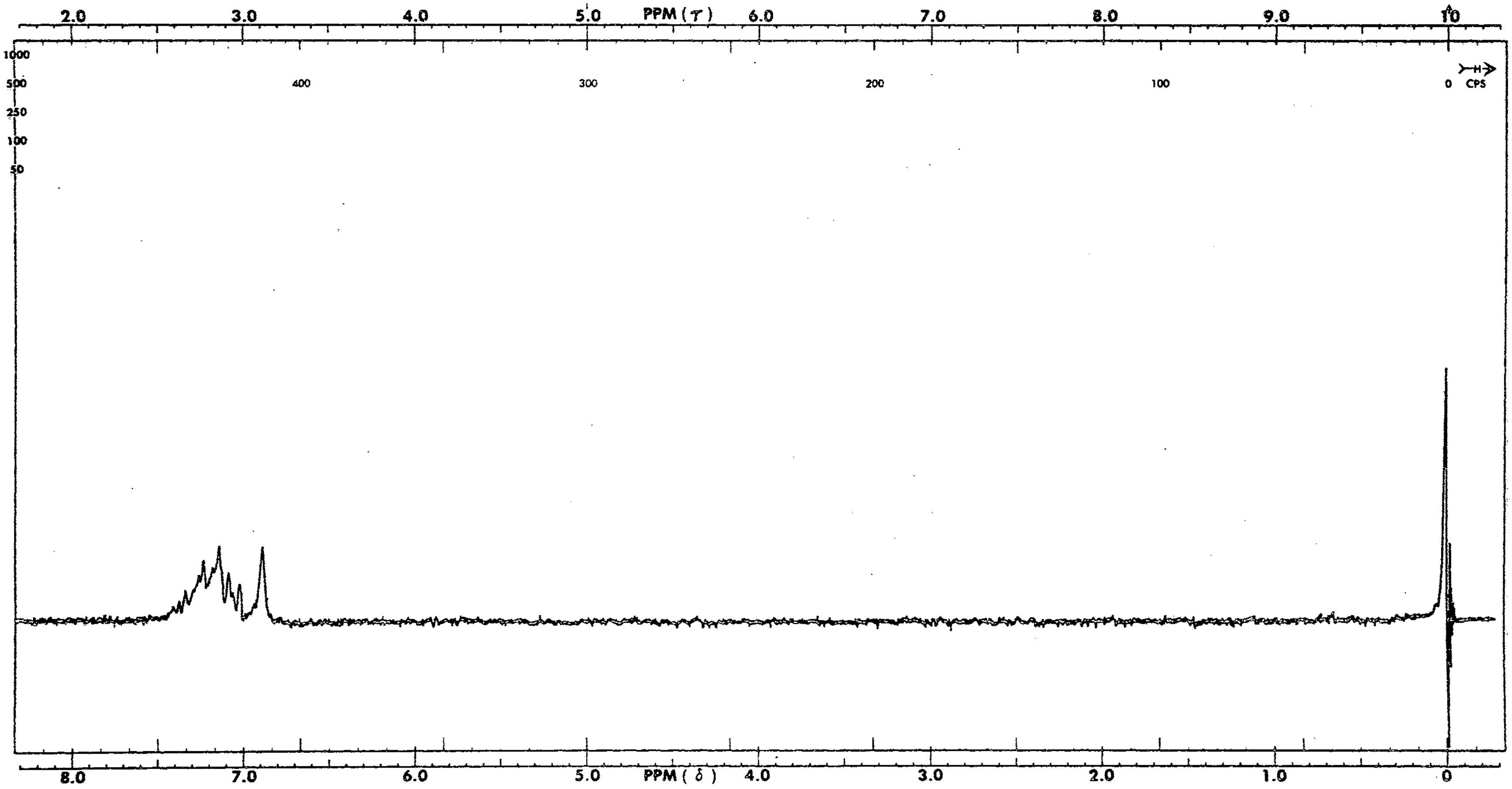


N-Tritylcyclohexylamine (XXIX)

Solvent .... CCl_4 R. F. Field .... 0.05 mG   S. W. .... 500 cps   S. A. 8.0

F. B. .... 4.0 cps   S. T. .... 250 sec   S. O. .... 045 cps   I. A. 25

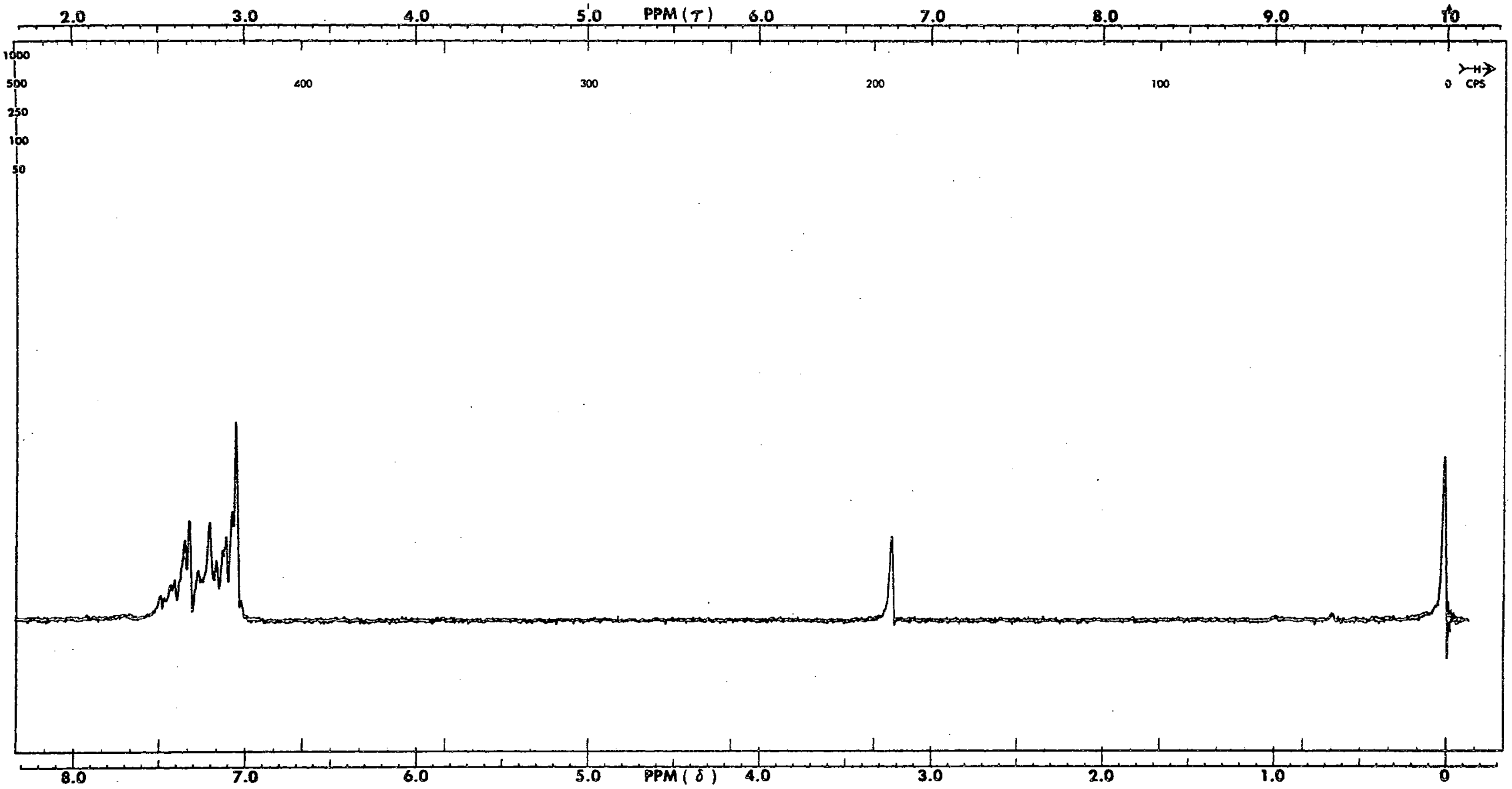
Plate XLI



Trityl Phenyl Sulfide (XXI)

Solvent .... CCl_4	R. F. Field .... 0.05 mG	S. W. .... 500 cps	S. A. 8.0
F. B. .... 2.0 cps	S. T. .... 250 sec	S. O. .... 000 cps	I. A. .... off

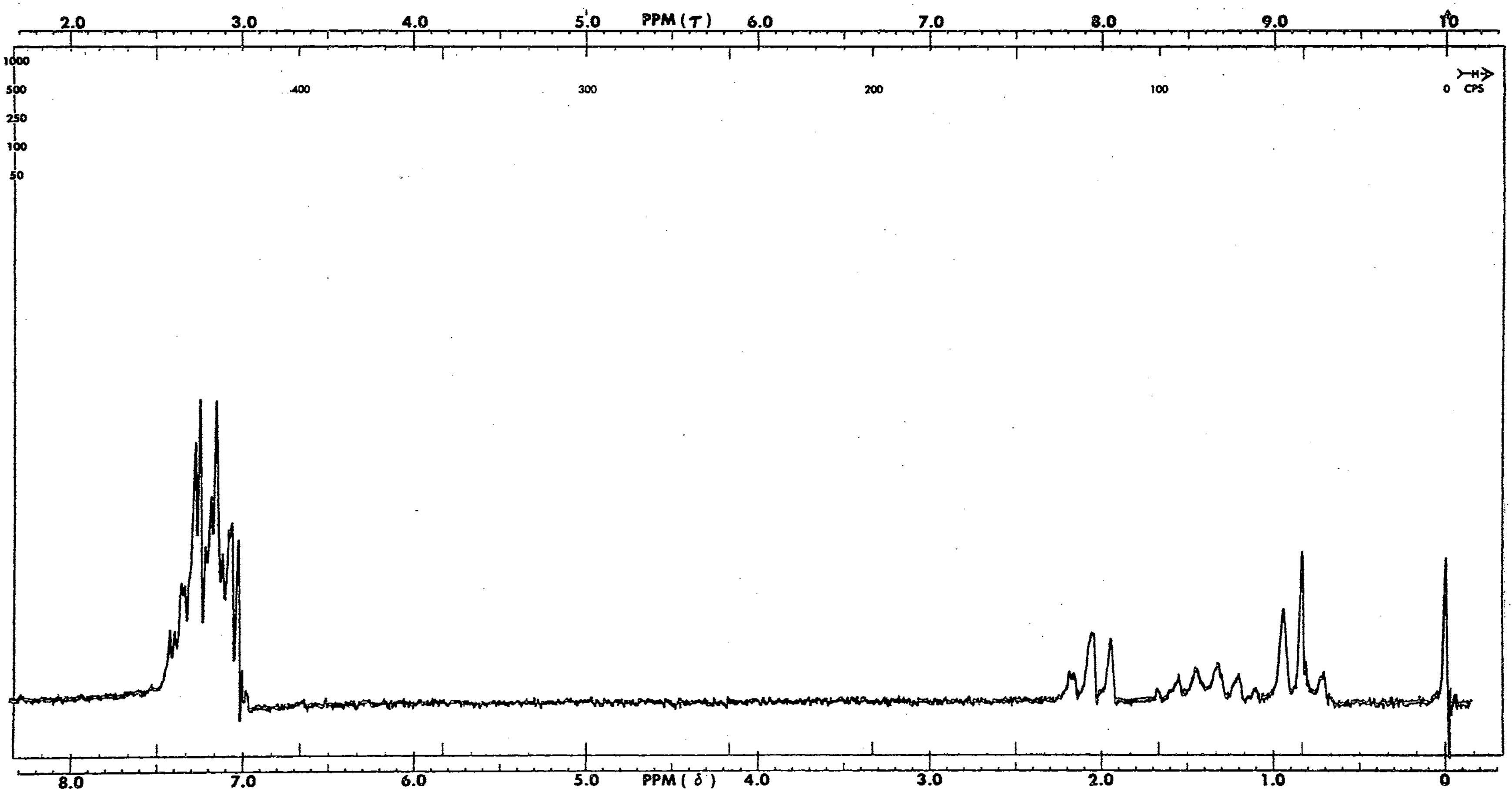
Plate XLII



Trityl Benzyl Sulfide (XXII)

Solvent	CCl_4	R. F. Field	0.05 mG	S. W.	500 cps	S. A.	4.0
F. B.	4.0 cps	S. T.	250 sec	S. O.	000 cps	I. A.	63

Plate XLIII



Trityl n-Propyl Sulfide (XXIII)

Solvent .... CCl_4 R. F. Field .... 0.05 mG S. W. .... 250 cps S. A. 8.0

F. B. .... 2.0 cps S. T. .... 250 sec S. O. .... 000 cps I. A. 50

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VITA

3

Russell Dwayne Shupe

Candidate for the Degree of

Doctor of Philosophy

Thesis: I. ALKYL-OXYGEN FISSION IN THE REACTION OF TRITYL ACETATE-^{18}O WITH PHENYLMAGNESIUM BROMIDE

II. MASS SPECTRA OF TRITYL-SUBSTITUTED COMPOUNDS--LOSS OF ^{12}C FROM $(C_6H_5)_3{}^{13}CH$ VIA ELECTRON BOMBARDMENT

Major Field: Chemistry

Biographical:

Personal Data: The author was born in Arkansas City, Kansas, on January 14, 1943, the son of Helen Marie and Ralph Owen Shupe.

Education: The author graduated from Newkirk High School in Newkirk, Oklahoma, in 1961. In September, 1961, he entered Oklahoma State University, Stillwater, Oklahoma, where he received a Bachelor of Science degree in Chemistry in August, 1965. In September, 1965, he was admitted to the Graduate School of Oklahoma State University, Stillwater, Oklahoma, where he obtained the Master of Science degree in July, 1967. In May, 1969, he completed the requirements for the Doctor of Philosophy degree.

Professional Experience: The author was a recipient of a National Aeronautics and Space Administration Traineeship during the period September, 1965 to July, 1968.

Membership in Professional Societies: The author is a member of Phi Lambda Upsilon.