

AN EXAMINATION OF THE MECHANISM OF THE REACTION
OF TRITYL ACETATE WITH PHENYLMAGNESIUM
BROMIDE-PROOF OF RADICAL INTERMEDIATES

By

RUSSELL DWAYNE SHUPE

Bachelor of Science

Oklahoma State University

Stillwater, Oklahoma

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Thesis Approved:

K. D. Berlin

Thesis Adviser

O. D. Dorman

D. D. Durham

Dean of the Graduate College

660279

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INTRODUCTION

In general, free-radical formation at room temperature via the action of Grignard reagents on organic substrates is not well known, except by using various metal halides as catalysts. This study was undertaken to further investigate the phenomenon, previously reported in this Laboratory, of free-radical formation when aryl Grignard reagents were reacted with trityl carboxylic esters. Oxygen-18 labeling experiments were conducted in order to gain evidence concerning the mechanistic pathway leading to the formation of the major product, trityl peroxide. Furthermore, additional evidence, relating to the formation of the various other products in this reaction, was discovered.

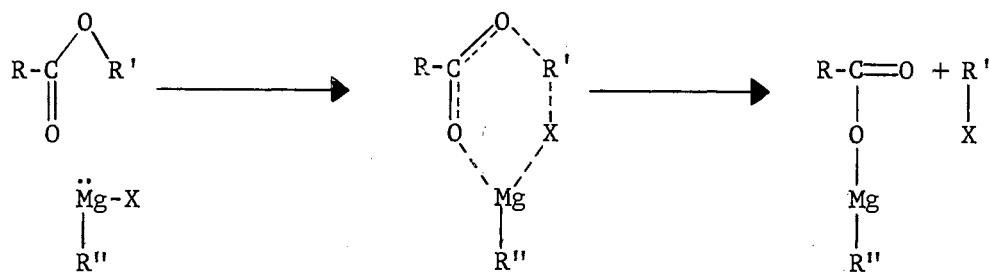
CHAPTER I

HISTORICAL

Reactions of Hindered Esters With Grignard Reagents

Studies involving the reactions of hindered esters with Grignard reagents originated in 1941. Arnold¹ discovered that allyl esters of hindered carboxylic acids were cleaved by phenylmagnesium bromide to yield ultimately, and chiefly, allylbenzene and the carboxylic acid corresponding to the acyl portion of the molecule. The proposed mechanism (which included attack by Grignard reagent on an allyl halide formed in situ) was later disproved by Kharasch,^{32a} although he could not himself suggest a tenable mechanism.

Shortly thereafter, Fuson²¹ reported other unorthodox reactions of Grignard reagents with carboxylic esters. He found that methyl, n-butyl, and benzyl mesitoates react with Grignard reagents to yield mesitoic acid and the halides corresponding to the alkyl groups of the esters. Fuson suggested no mechanism although Kharasch^{32b} later offered the following rationalization:



Fieser¹⁸ was the first to study triphenylmethyl (trityl) carboxylic esters, which with excess alkyl Grignard reagents were found to give 1,1,1-triphenylalkanes in high yields. This observation was explained as due to the special reactivity of the acyloxy group, which resulted in the replacement of the latter by an alkyl moiety. Fuson and Brasure²² arrived at the same conclusion about the unusual reactivity of the acyloxy group in trityl acetate, which with excess t-butyl Grignard reagent gave 1,1,1-triphenyl-2,2-dimethylpropane (20 percent). Some insight concerning this mode of cleavage may be found in two recent papers by Winstein^{50,51} concerning the importance of ion-pair return in reactions of trityl benzoate. Experiments with carbonyl ¹⁸O labeled ester in dry and moist acetone at 75° indicated ¹⁸O equilibration, which was postulated to proceed by way of an ion-pair intermediate. It was also reported that in the presence of lithium azide, the rate of chemical capture was much smaller than the ionization rates. Hence it was concluded that ion-pair return phenomenon could cause an exchange of trityl derivatives since the ionization rate was greater than the rate of ion-pair return. It was also indicated that ion-pair return became less important as water was added to the acetone solvent. This result may well explain the formation of the hydrocarbon, since in the presence of excess Grignard reagents, the medium is somewhat more polar and may promote ion-pair dissociation. Evidence for increased polarity at higher concentrations is given by Evans and Lee,¹⁷ who measured the molar and specific conductivity of 2M, 1M, and 0.5M solutions of phenylmagnesium bromide and ethylmagnesium bromide. In each case, the solution containing the higher concentration of Grignard reagent displayed the higher conductivity. In view of this work, capture of trityl cations by

Grignard reagent may be more facile when excess Grignard reagent is used.

Additional relevant observations are given in many older works,^{23,41} wherein it is recorded that triarylmethyl halides react readily with most Grignard reagents to give good yields of hydrocarbons. This particular type of reaction will receive a more rigorous treatment later in this thesis.

Evidence for Radical Intermediates in Certain

Reactions Involving Grignard Reagents

Maruyama³⁴ has detected free radicals by electron spin resonance techniques during the addition of ethyl, phenyl and *p*-tolyl Grignard reagents to aromatic ketones such as benzophenone, *p*-chlorobenzophenone, *p*-methoxybenzophenone and acetophenone. The carbonyl compounds and the Grignard reagents were mixed at -25° in the absence of air and moisture. The sample was then inserted into a cavity which had previously been cooled with a stream of liquid nitrogen and the ESR spectrum was measured. It was observed that benzophenone and *p*-chlorobenzophenone with phenyl and *p*-tolyl Grignard reagents gave exceptionally well-resolved hyperfine spectra during reaction. That homolytic dissociation of the Grignard reagent in such reactions is not a unimolecular thermal process of the type $\text{RMgX} \rightarrow \text{R}\cdot + \cdot\text{MgX}$ is strongly suggested by at least two considerations. One, analytical studies by Grignard²⁸ and Blaise⁷ indicate that ethereal Grignard reagents, such as methyl or ethylmagnesium iodide, may be heated for considerable periods of time to temperatures as high as 150° without significant decomposition. In contrast, many radical coupling reactions proceed at the boiling point of an

ethereal solution (ca. 40°).^{20,32c} Two, the occurrence of coupling depends, not upon the nature of the Grignard reagent alone, but to a great extent upon the nature of the organic halide also. The coupling process is especially favored in the cases in which the organic portion of the halides are capable of yielding resonance-stabilized free radicals. It thus may be concluded that in such reactions free radicals are generated by the naturally induced homolytic dissociations of the Grignard reagent and the organic halide.



In the case of a condensation involving a Grignard reagent with a ketone, it has been suggested by Blicke and Powers⁸ that the reaction may be initiated by homolytic scission of the Grignard reagent with free radical formation.



They assume that one or more of the following reactions may then take place:

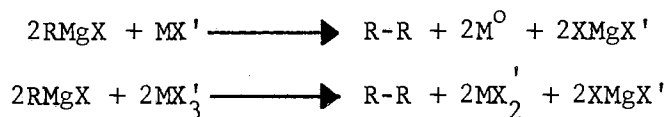
- (1) $RR'\dot{C}(OMgX) + R'' \longrightarrow RR'R''COMgX$
- (2) $RR'\dot{C}(OMgX) + R'' \longrightarrow RR'CHOMgX + R''_{(-H)}$
- (3) $2RR'\dot{C}(OMgX) \longrightarrow [RR'C(OMgX)]_2$
- (4) $2R'' \longrightarrow R''-R''$
- (5) $R'' + (C_2H_5)_2O \longrightarrow R''H + C_2H_5O\dot{C}HCH_3$

One of the first reported occurrences of free radicals involving Grignard reagents and esters was noted by Berlin and Doss.¹⁶ It was found that when aryl Grignard reagents reacted with hindered esters, such as trityl acetate or trityl benzoate, free radicals could be detected in the reaction mixture by ESR measurements. The spectra were obtained by withdrawing a small amount of the reaction mixture, placing

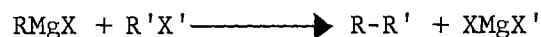
it in a quartz tube and holding the tube at room temperature during the measurements. The reaction could also be initiated in the quartz tube used for the ESR measurements. Typically, a spectrum obtained after a reaction time of 5-10 minutes was quite complex and gave a broad unresolved signal, but after one hour the signal was highly resolved, indicative perhaps of a single free radical. Much similarity can be noted between this signal obtained after one hour and the ESR spectrum of a 10^{-3} molar solution of trityl radicals in toluene at -20° taken by Chestnut and Sloan¹¹ (Plate VIII).

The Role of Grignard Reagents as Reducing
Agents - Radical Mechanism

The literature contains many examples of the use of various metallic halides (notably cobaltous halides) in effecting coupling reactions with Grignard reagents. Such reactions are oxidation-reduction reactions which proceed extremely slowly, or not at all, under ordinary reaction conditions. This generalization may be expressed in formal equations such as the following:



Similarly, the oxidation-reduction aspect of the normal condensation of a Grignard reagent with an organic halide may be emphasized in the formal equation:

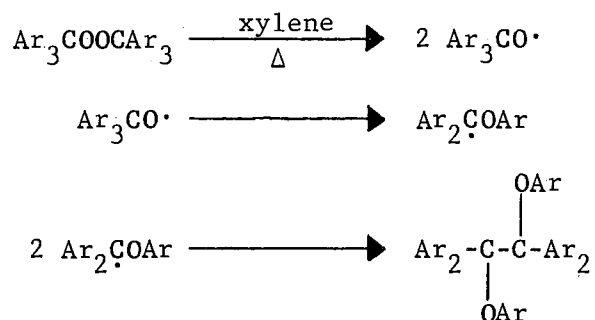


Under certain conditions (depending mainly on the nature of R and R') this reaction may involve radicals. Support for the postulation of radical intermediates is obtained when one considers several older

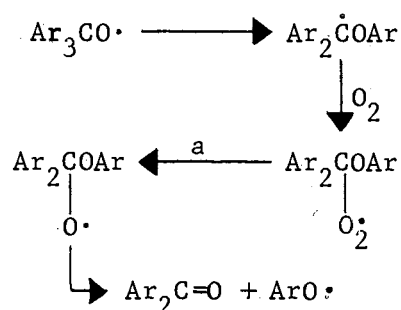
works^{41,23} concerning the reaction of phenylmagnesium bromide and trityl halides. The main product was usually reported as tetraphenylmethane, but invariably products which are extremely difficult to explain by a non-radical mechanism are reported (e.g., trityl peroxide, triphenylmethane, triphenylmethanol, biphenyl and hexaphenylethane). It is quite possible that the trityl cation may be reduced by the Grignard reagent by an electron-transfer process. This would form a trityl radical and a phenyl radical and the products mentioned could then be more easily explained.

Occurrence and Reactions of Trityloxy Radicals

In 1911, Wieland⁴⁸ observed the formation of benzpinacol diphenyl ether, benzophenone, and biphenyl as a result of the thermal decomposition of trityl peroxide. He did not, however, give conclusive physical evidence for the presence of benzpinacol diphenyl ether. The reaction was carried out in boiling xylene (ca. 8 minutes) with benzpinacol diphenyl ether resulting in 70 percent yield. This product was very probably formed through dissociation of the peroxide into trityloxy radicals, followed by free-radical rearrangement and subsequent dimerization.



The formation of benzophenone can be explained via beta-cleavage, which gives rise to a phenyl radical and thus also accounts for the formation of biphenyl. Such a mechanism has been questioned by Starnes,⁴³ however. An alternative mechanism not requiring a beta-scission step has been suggested by Spielman⁴² and Kharasch.³¹ Starnes⁴³ has suggested:



(Step a in this sequence could occur in a number of reasonable ways, which are described in the literature.²⁷) This mechanism may be a more feasible explanation for the formation of benzophenone especially in reactions which occur at moderate temperatures. If this mechanism is operative, however, one would expect to observe the formation of phenol instead of the biphenyl Wieland had previously reported.

Recent Advances Concerning the Structure of Grignard Reagents

The nature of Grignard reagents have been the subject of continuous investigation and speculation^{12,14,15} since their discovery over sixty years ago. Grignard compounds in diethyl ether solution have been assumed for many years to consist of the dimeric species $\text{R}_2\text{Mg}\cdot\text{MgX}_2$. Stucky and Rundle⁴⁴ have examined by X-rays the structure of phenylmagnesium bromide and have found that the empirical formula of the concentrated reagent is $\text{C}_6\text{H}_5\text{MgBr}\cdot 2(\text{C}_4\text{H}_{10}\text{O})$. The composition of the crystals does not depend upon concentration so long as the ratio of ether to phenylmagnesium bromide is greater than two. At higher

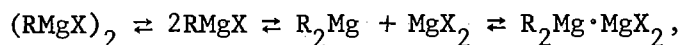
concentrations the reagent forms an amorphous polymer, and the entire reagent polymerizes if all the ether is removed. It is questionable, however, that a single solid-state structure can be equated to species in solution. Ashby^{3,4} has shown that RMgX is indeed the initial species formed when RX and Mg react and he also has given proof for the existence of RMgX species in ether solution. Ebullioscopic molecular weight measurements are reported⁴ which indicate that many Grignard solutions in diethyl ether contain essentially monomeric species at low concentrations (0.05 M) and essentially dimeric species at higher concentrations (0.5-1.0 M). Of the compounds studied, the alkyl and aryl-magnesium bromides and iodides follow this pattern, whereas the alkyl-magnesium chlorides are essentially dimeric, even at low concentrations. For a closer examination of the phenylmagnesium bromide reagent see Chart I.

Chart I

Association Factors for Phenylmagnesium Bromide in Diethyl Ether

Moles RMgX per l. soln.	Mol. wt./formula wt.
0.042	1.07
0.111	1.17
0.179	1.31
0.241	1.50
0.326	1.71

The evidence presented supports the conclusion that, in general, the composition of Grignard compounds in diethyl ether is best presented by equilibria involving both monomeric and dimeric species:



with the positions of the equilibria being a function of the nature of the R group, the halogen and the solvent as well as the concentration.

CHAPTER II

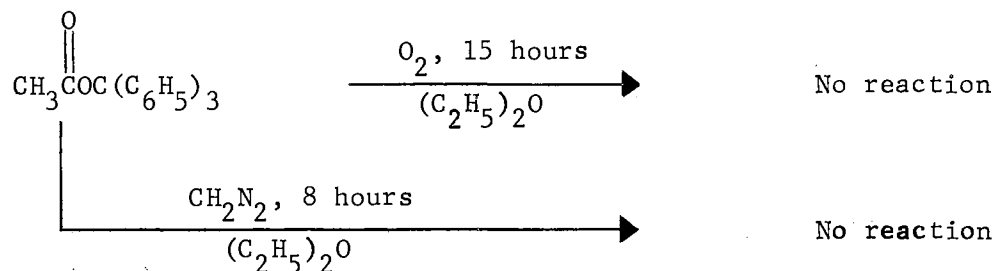
DISCUSSION OF RESULTS AND CONCLUSIONS

It is already well known that many alkyl Grignard reagents, when allowed to react with triarylmethyl carboxylic esters, give 1,1,1-triaryllkanes in good yields.^{18,22}

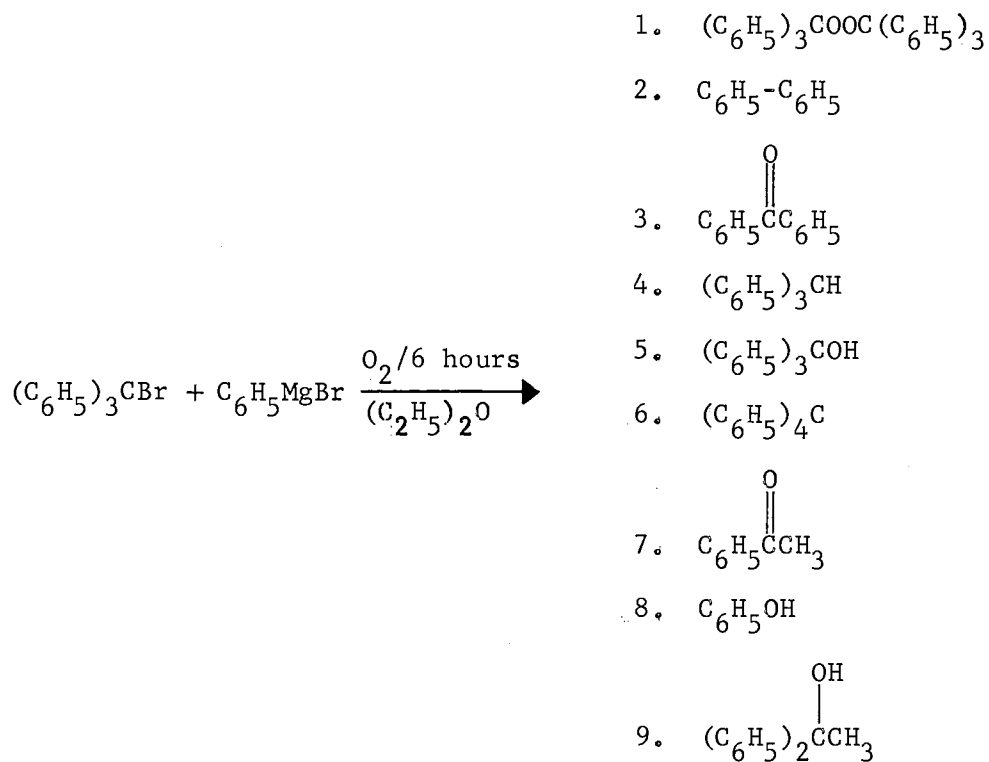
It was the objective of this study to make a thorough mechanistic examination of the reactions involving triphenylmethyl acetate with phenyl Grignard reagent.

We examined the products obtained by reacting trityl acetate (I) with phenylmagnesium bromide (Table I) and found that the formation of some of them was more easily explained by a free-radical mechanism than by an ionic mechanism. Since free-radicals have already been proved to be present during this reaction by Doss¹⁶ with her ESR studies, it was decided to attempt to trap these radicals with a radical scavenger. The presence of trityl radicals was suspected because the ESR spectrum of the reaction mixture after one or more hours was very similar to the ESR spectrum of 10^{-3} M trityl radical presented by Chestnut and Sloan¹¹ (Plate VIII). An ethereal solution of trityl acetate with diazomethane would probably give 1,1,1,3,3,3-hexaphenylpropane if trityl radicals were present.⁴⁰ An ethereal solution of trityl acetate with dry oxygen would give trityl peroxide if trityl radicals were present.^{37,47} In both cases, GLC analysis of the reaction mixture showed only the products: benzophenone, triphenylmethane and triphenylmethanol. These

products are the same as detected when an ethereal solution of I is analyzed by GLC (suggests thermal decomposition of I). We thus conclude the following:



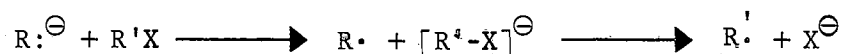
Many older references^{19,23,25,26,41} report the formation of trityl peroxide as a by-product of the reaction of trityl halides with aryl Grignard reagents. Since this reaction may proceed via a radical mechanism, it was rechecked in this Laboratory. The following products were observed:



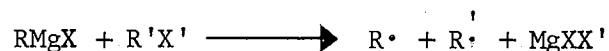
On the basis of work by Gilman and Jones²³ it seems likely that a prominent, unidentified GLC peak may be biphenyldiphenylmethane (biphenyl =

4-phenylphenyl). It was reported in 47 percent yield as a result of the reaction of trityl bromide with phenyl Grignard reagent.

The formation of the other products observed in this reaction may be explained rather easily if it is assumed that the first step in the mechanism is an electron-transfer reduction of the trityl cation by the Grignard reagent to yield a trityl radical and a phenyl radical. Some indication that the trityl cation is the ultimate source of trityl radical is presented by Doss,¹⁶ who was able to react trityl acetate and phenylmagnesium bromide in the presence of bromine and recover some trityl bromide (11 percent) from the reaction mixture (see also reference 46; trityl cation reacts with many nucleophiles). Support for the electron-transfer reduction of the trityl cation to the trityl radical is given by James and Plesch,³⁰ who observed that trityl cations, in either methylene dichloride or concentrated sulfuric acid, are easily reduced at the negative electrode of a polarographic cell to yield trityl radicals. Substances which undergo facile electrolytic reduction may also react with carbanions by what appear to be electron-transfer processes.³⁹ Alkyl and some aryl halides react with a number of organometallic reagents by an electron-transfer process:

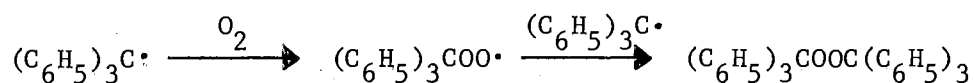


Examples of this type of process are recognized where the donor $R:\ominus$ is a radical-anion,^{35,53} a dianion,^{9,35} an alkyllithium,¹⁰ or a Grignard reagent.^{32d,33} It has been suggested by Kharasch^{32d} that a direct homolytic reaction can occur, which does not require the use of a metal halide catalyst.



Trityl radicals formed in this manner can react with oxygen to give

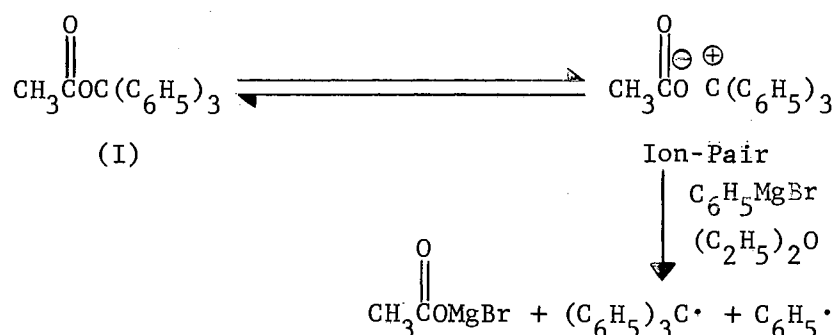
trityl peroxide.



II

The other products observed upon reacting trityl acetate with phenylmagnesium bromide will be given more attention later in this discussion.

Winstein^{50,51} has shown that a significant amount of ion-pair formation may occur in acetone solutions of trityl benzoate. This is explicable on the grounds that the oxygen-trityl group bond in trityl esters is weakened by steric factors (X-ray work has shown that a similar molecule, trityl bromide,^{45a} has a C-Br bond length of 1.99 Å compared to a C-Br bond length in methyl bromide^{45b} of 1.91 Å; furthermore, bond dissociation energies of trityl compounds are known to be exceptionally low,⁵ and it is not unreasonable that facile cleavage of such a bond could occur in solution). In addition, the trityl cation is well known to be a very stable ion. Winstein also showed that less ion-pair return occurred when the polarity of the solution was increased. It is not unreasonable then to assume that ion-pair formation from trityl acetate in highly polar Grignard solutions is possible. Just as in the case of trityl bromide, the Grignard reagent may act as an electron-transfer agent and cause the formation of trityl radical and phenyl radical.

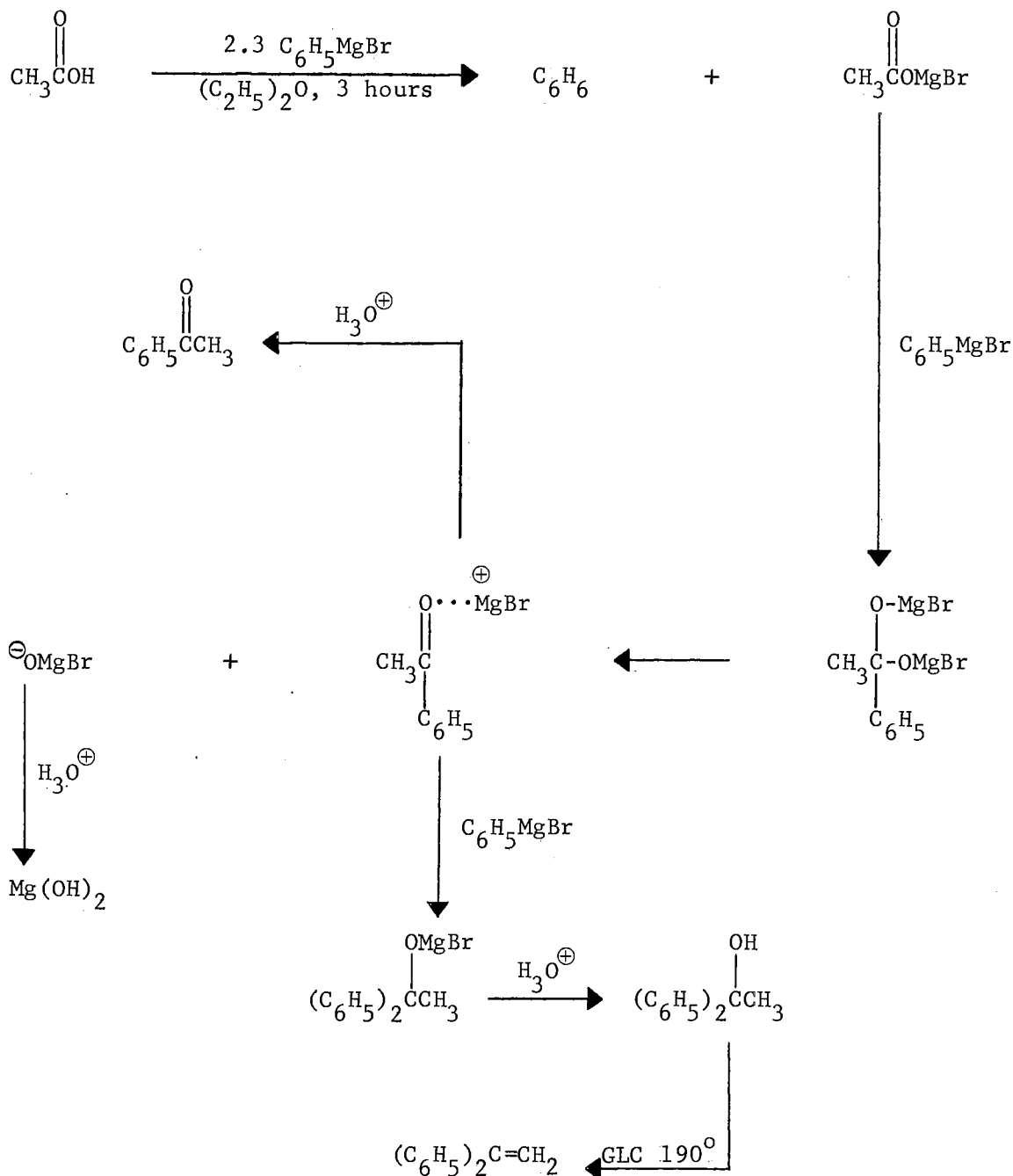


The trityl radical can, as in the case of the reaction of trityl bromide with phenyl Grignard reagent, react with oxygen to give trityl peroxide (II).

If trityl peroxide was indeed formed by the oxidation of trityl radical, it might be possible to limit or drastically decrease the yield of trityl peroxide by excluding oxygen from the reaction system. Such a tedious experiment gave rise to a yellow reaction mixture which after approximately one hour became blood-red, but with no visible formation of the yellow trityl peroxide. After hydrolysis, the reaction mixture still contained no solid, but upon exposing it to air the yellow trityl peroxide immediately began to precipitate. The yield of trityl peroxide was low (15 percent), and a relatively poor material balance was obtained. Nevertheless, it was indicated that trityl radical has a substantial lifetime under these reaction conditions. However, an equilibrium between trityl radical and hexaphenylethane is not excluded.

If trityl radical is being formed from the trityl cation as a result of reduction by the Grignard reagent, the remaining portion of the molecule will be the bromomagnesium salt of acetic acid. Upon hydrolysis of the reaction mixture, acetic acid would be an expected product (from hydrolysis of the bromomagnesium salt or hydrolysis of I). The percent yield of acetic acid (80.4 percent based on I) was determined by a NMR study of the aqueous layer of the reaction mixture. Since acetophenone is known to be a product in the reaction of trityl acetate with phenylmagnesium bromide, the logical question which arises is: can acetic acid with excess phenylmagnesium bromide give rise to acetophenone? Acetic acid was allowed to react with phenylmagnesium bromide (molar ratio 1:2.3). The first mole of Grignard reagent was

destroyed by the labile proton on the acetic acid. This reaction formed the assumed desired species, that is, bromomagnesium acetate. This salt did indeed react with the Grignard reagent to give acetophenone, 1,1-diphenylethanol and the dehydration product of the latter, 1,1-diphenylethene. The reaction is heterogeneous and the mechanism postulated below is better attributed to a solution phenomenon. The



combined yield of the three products was about 55 percent based on acetic acid. The Grignard reagent, however, may have been the limiting factor since one mole was destroyed initially and two moles were needed for the formation of the tertiary alcohol.

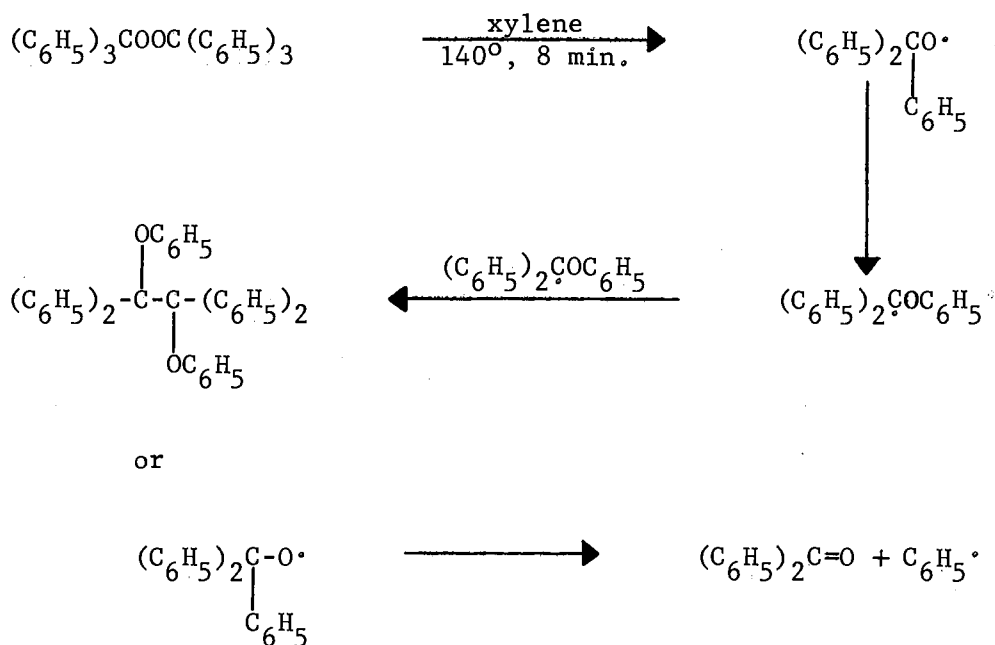
An experiment with oxygen-18 labeled trityl acetate and phenylmagnesium bromide was performed to explain the overall mechanism and to determine the mode of formation of trityl peroxide. Trityloxy radicals could form by homolytic acyl-oxygen bond cleavage of trityl acetate under the influence of an aryl Grignard reagent. Coupling of trityloxy radicals could lead to trityl peroxide.⁵² The labeled trityl acetate (47 percent ¹⁸O) gave trityl peroxide which was not noticeably enriched with ¹⁸O as determined by mass spectral analysis. The peroxide obtained from the reaction probably came from reaction of trityl radical with oxygen dissolved in the reaction medium. The remaining oxygen containing products (except acetic acid) in the reaction mixture were analyzed by mass spectrometry with the LKB-9000 GLC-mass spectrometer. The column used was CA-1. The acetophenone produced was found to be enriched (13-16 percent) in ¹⁸O, this being considerably less than expected (42 percent). This suggests that some oxygen exchange may occur during the hydrolysis step with aqueous hydrochloric acid. The triphenylmethanol produced was slightly enriched (3-5 percent), the enrichment probably resulting from hydrolysis of unreacted trityl acetate, while much of the triphenylmethanol was formed via hydrogen abstraction by the trityloxy radical. The trityloxy radical probably resulted by decay of the tritylperoxy radical²⁷ since it did not contain excess ¹⁸O. The benzophenone produced was not enriched with ¹⁸O, thus indicating that it formed by rearrangement of the trityloxy radical^{13,36,48,49}

(see references 29, 31 and 42, however), in which case one would not expect any excess ^{18}O to be present. The other oxygen-containing product, acetic acid, was not found to be enriched with ^{18}O although it is quite possible that the ^{18}O originally present in the acetic acid exchanged with ^{16}O from water in the aqueous layer. If this were true, one would expect the water layer to be slightly enriched with ^{18}O . No such enrichment in the water layer was detectable, probably because of a high dilution factor since the amount of H_2^{18}O expected should be less than 0.20 percent of the water layer.

Another isotopic labeling experiment was carried out in a separate attempt to establish the presence of trityl radical. The approach taken was to hydrolyze the reaction mixture with deuterium oxide in order to form deuterotriphenylmethane. However, the mass spectrum did not indicate the presence of deuterotriphenylmethane. No triphenylmethanol-d was found either. This reaction should be repeated later.

In summation, the overall reaction mechanism which most easily explains the formation of the products is as follows (see Reaction Scheme I). The formation of benzophenone can be explained by two routes: (1) a beta-cleavage of trityloxy radicals to give benzophenone and phenyl radicals (see Reaction Scheme II). This type of cleavage would help explain a high yield of biphenyl, but it is thought to be a high-energy step and has been questioned by Starnes.⁴³ Wieland⁴⁸ reported the formation of benzophenone along with biphenyl and benzpinacol diphenyl ether upon solution pyrolysis of trityl peroxide (ca. 140°). Apparently in such a pyrolysis the necessary energy for beta-cleavage is furnished. It has not been substantiated that such a cleavage can occur at, or slightly above, room temperature. (2) The other pathway from trityloxy

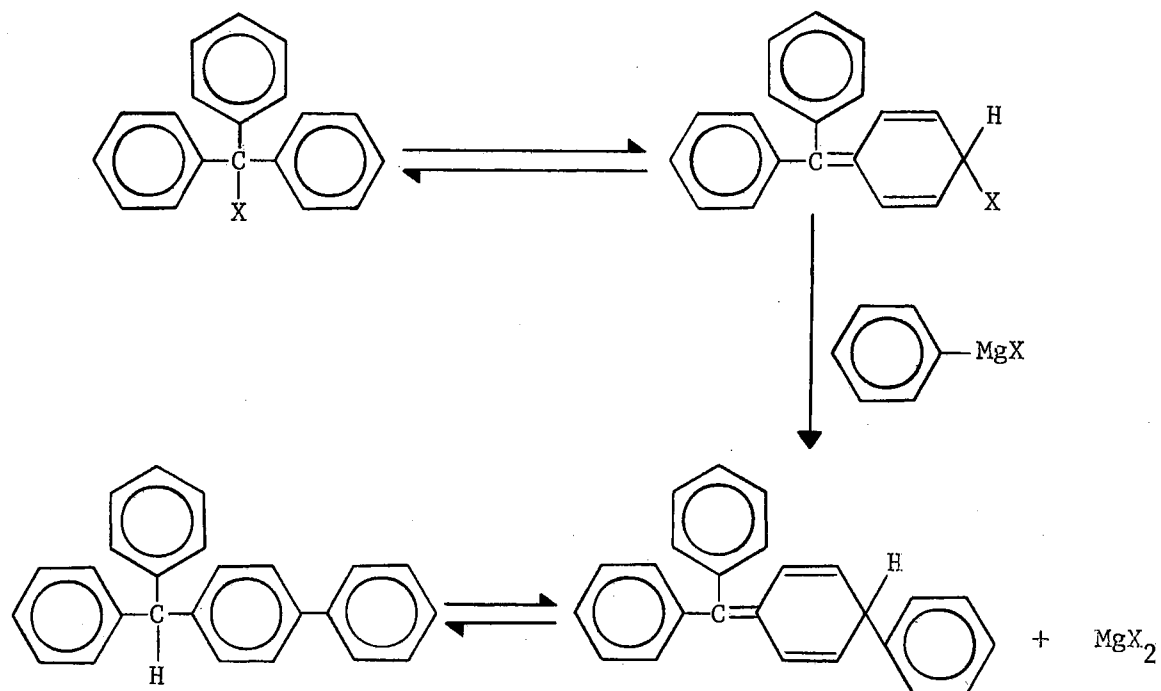
REACTION SCHEME II



radicals to benzophenone, not involving a beta-cleavage step, is given by Starnes⁴³ (see Historical). No matter which mechanism is operating, one would not expect the benzophenone to be enriched with ¹⁸O in the ¹⁸O-labeling experiment. It is important to note, however, that phenol would be a by-product in the mechanism⁴³ listed on page 7. Phenol was not detected in the reaction mixture of trityl acetate and phenylmagnesium bromide.

The formation of tetraphenylmethane, in low amounts, is not surprising when one considers several older works^{19,23,25,26,41} reporting the formation of tetraphenylmethane from trityl halides and phenyl Grignard reagent. It is believed that the Grignard reagent may attack the trityl cation which is presumed to be present in the reaction mixture. It has previously been mentioned that Gilman and Jones²³ found biphenyldiphenylmethane to be the major product (47 percent) of the reaction of trityl halides with phenyl Grignard reagent. Schoepfle and Trepp⁴¹ have attempted to explain this product via a quinonoid modification of

the trityl halide:



Other high molecular weight products, reported in low yields by Schoepfle during this reaction, may help explain the unidentified peaks in the GLC tracings of the reaction mixture of trityl acetate and phenyl Grignard reagent (Plate IV). He reports low yields of dibiphenylphenylmethane, biphenyltriphenylmethane and traces of triphenylmethane.

CHAPTER III

EXPERIMENTAL^{a-g}

Preparation of Trityl Bromide. The method used was similar to that presented by Dr. Rathore.³⁸ The reagents used were triphenylmethanol (120 g., 0.46 mole), anhydrous benzene (100 ml.) and acetyl bromide (66 g., 0.54 mole). This procedure gave 85.0 g. (0.264 mole) of trityl bromide (57%), m.p. 151-153° (lit. m.p. 152-154°).³⁸ Thorough washing with anhydrous Skelly Solvent F followed by drying in the vacuum oven at 75° raised the m.p. to 153-153.5°.

^aAll melting points are corrected. Skelly Solvent F boiled at 30-60°.

^bColumn CA-1 is: 6' x 1/8", 6% SE-30 on Chromosorb G, 60/80 mesh.

^cThe proton magnetic resonance spectra were made by Mr. L. G. Williams using a Varian Model A-60 high resolution spectrometer with a field-sensing stabilizer ("Super-Stabilizer").

^dThe computer program for printing the mass spectrographs was supplied by Mr. Hsiao Yuan Li.

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

^fThe infrared spectra were determined on a Beckman IR-5A spectrometer as potassium bromide pellets.

^gGas chromatographic analyses were performed using a Varian-Aerograph Hy-Fi Model 1520 with a hydrogen flame ionization detector.

Preparation of Phenylmagnesium Bromide. A 2000-ml., round-bottom, three-necked flask was oven-dried and then flushed with nitrogen for one hour. Magnesium (24.0 g., 1.00 mole) was added along with about 50 ml. of anhydrous ether. The mixture was mechanically stirred. Anhydrous bromobenzene (157 g., 1.00 mole) was added dropwise through an addition funnel along with portions of ether (800 ml. total). The remaining procedure followed was that often reported. The yield calculated from the usual titration method²⁴ was 98%. When employing this Grignard reagent at later times, it was usually retitrated prior to use.

Preparation of Silver Acetate. The procedure was essentially that followed by Berlin.⁶ Potassium hydroxide (5.60 g., 0.10 mole), dissolved in 25 ml. of water, was placed in a 100-ml., one-necked, round-bottom flask. Acetic acid (6.00 g., 0.10 mole) was added slowly through an addition funnel. Excess aqueous silver nitrate was then added in complete darkness. The precipitated silver acetate was washed thoroughly with water, then with anhydrous methanol. The salt was dried under vacuum for several days before using.

Small-Scale Preparation of Trityl Acetate (I). The procedure was slightly modified from that originally developed in this Laboratory.⁶ A 50-ml., two-necked, round-bottom flask was equipped with a condenser, a nitrogen inlet tube, a drying tube (CaCl_2) and a magnetic stirring bar. All glassware was carefully dried for several hours in a drying oven at above 105° . Nitrogen, dried by passing through four 3A molecular sieve drying towers, was passed through the system for 2 hours before any reagents were added. To the reaction vessel was added 1.60 g. (0.0049 mole) of trityl bromide, then 40 ml. of reagent grade benzene dried over 3A molecular sieve. The solution was then brought to reflux

and 0.50 g. (0.0061 mole) of anhydrous sodium acetate was added all at once. The resulting heterogeneous reaction mixture was stirred at near reflux for 8 hours, after which time the sodium bromide and any unreacted sodium acetate was filtered from the hot benzene solution. Again, all glassware used in the filtration process was carefully oven-dried. The benzene was immediately stripped from the dissolved trityl acetate by using a flash evaporator. A very viscous oil remained. This oil was allowed to stand under nitrogen for one hour, then 5-10 ml. of cold, anhydrous petroleum ether was added. White crystals of trityl acetate formed in about two hours. The crystals were powdered with a mortar and pestle and then placed under high vacuum for about one hour. No recrystallization was necessary. Trityl acetate (0.95 g., 0.0031 mole) was obtained in 64% yield, m.p. 82.5-83°C.

Reaction of Trityl Acetate (I) With Phenylmagnesium Bromide

(1:1.3). A three-necked, 100-ml., round-bottom flask was oven-dried, then fitted with a nitrogen inlet tube, an addition funnel and a drying tube (CaCl_2). The system was flushed with nitrogen which had passed through 3A molecular sieve for two hours. Anhydrous ether (50 ml.) and 8.60 ml. (0.0133 mole) of 1.55 M phenylmagnesium bromide were added to the reaction vessel.

Trityl acetate (3.09 g., 0.0102 mole) dissolved in ether was added dropwise to the stirred Grignard solution over a period of one hour. The reaction mixture was then allowed to stir at room temperature for 12 hours while ether was added as necessary to keep the volume near 50 ml. The mixture was cooled in an ice bath and 50 ml. of ice-cold 6N hydrochloric acid was added very slowly to destroy any excess Grignard reagent. The organic layer was washed successively with 15 ml. of water,

15 ml. of 10 percent sodium bicarbonate solution and 15 ml. of water. A pale yellow solid, trityl peroxide (II), was filtered from the organic layer, after which the organic layer was dried with $MgSO_4$. The organic layer was analyzed by GLC, using Column CA-1 (Plate IV). The products were identified by mixed injections of known compounds. Percent yields of the products were calculated by using standard solutions of the reaction products and comparing peak areas with the aid of the disc integrater on the Aerograph 1520 unit (Table IV). One of the products, acetic acid, was present in both the aqueous and organic layers. The identification and determination of yield of acetic acid was accomplished by a NMR study of the aqueous layer. The methyl protons of acetic acid were identified by examination of the NMR spectrum of the aqueous layer of the reaction mixture; a small amount of acetic acid added caused the peak to increase in height. After determination of the partition coefficient of acetic acid between 6N hydrochloric acid and ether (equal volumes) under the conditions of the reaction as described above, the percent yield of acetic acid could be determined as follows: a known amount of dimethyl sulfoxide was added to the aqueous layer and then the area under the NMR peaks due to the methyl protons in dimethyl sulfoxide was compared with that due to the methyl protons in acetic acid. Then the percent yield of acetic acid based on trityl acetate (I) was calculated by using the partition coefficient so determined. For this particular determination the organic layer was not washed with water and sodium bicarbonate solution, as described above; instead, the aqueous layer was analyzed directly for acetic acid.

Peak integration gave the DMSO:acetic acid ratio as 1.25:1. Since 0.248 g. (0.00318 mole) DMSO had been added, and since DMSO has six

protons to every three for acetic acid, the number of moles of acetic acid present in the aqueous layer was given by: $\left[\frac{0.00318}{1.25} \right] \times 2$, or 0.00508 mole. But since the partition coefficient, aqueous:organic, is 0.62, there remained $(0.38/0.62) (0.00508) = 0.00312$ mole of acetic acid in the ether layer. Thus the total yield of acetic acid was 0.00820 mole (80.4%).

Reaction of Trityl Acetate With Diazomethane. Trityl acetate (1.80 g., 0.006 mole) was dissolved in 50 ml. of anhydrous ether in a one-necked, round-bottom flask. A considerable excess of diazomethane, prepared from EXR-101 (N,N'-dinitroso-N,N'-dimethylterephthalamide), was distilled into the ethereal solution of trityl acetate and the solution stirred at room temperature for 8 hours. After the excess diazomethane had been destroyed by warming the solution, the reaction mixture was analyzed by GLC on column CA-1. The products identified were benzophenone, triphenylmethane and triphenylmethanol, which are the products one observes by GLC analysis of pure trityl acetate. Since neither 1,1,1,3,3,3-hexaphenylpropane nor methyl acetate was observed to be present in the reaction mixture, and since diazomethane is an excellent radical scavenger for trityl radical,⁴⁰ it is assumed that radical-pair formation does not occur to an appreciable extent in solutions of trityl acetate at room temperature.

Reaction of Trityl Acetate (I) With Oxygen. Dry oxygen was bubbled through an ethereal solution of trityl acetate (I) (1.0 g., 0.0033 mole) for 15 hours. GLC analysis of the reaction mixture on column CA-1 showed that the products were the same as those expected if trityl acetate itself were passed through the gas chromatograph: benzophenone, triphenylmethanol and triphenylmethane. Thus, since no trityl

peroxide was formed, it is again indicated that radical-pair formation of the ester in solution is not appreciable.

Preparation of ^{18}O -Labeled Trityl Acetate. The procedure was essentially that described previously. The reagents used were 1.00 g. (0.0031 mole) of trityl bromide, 0.30 g. (0.0018 mole) of regular silver acetate and 0.40 g. (0.0024 mole) of 82% ^{18}O -labeled silver acetate purchased from: Isotopes, Inc., Westwood, N. J. The yield was 0.51 g. (0.00169 mole, 55%) of ^{18}O -labeled trityl acetate.

Reaction of ^{18}O -Labeled Trityl Acetate (I) With Phenylmagnesium Bromide (1:1.3). The procedure was the same as described earlier. Trityl acetate (I) (0.45 g., 0.00147 mole) was added to 0.00191 mole of phenylmagnesium bromide in 50 ml. of anhydrous ether. After hydrolysis of the reaction mixture the trityl peroxide (II) was filtered out and subjected to mass spectral analysis. No ^{18}O was found to be present in the trityl peroxide (Plate VII).

Reaction of Trityl Bromide With Phenylmagnesium Bromide and Oxygen. A three-necked, 100-ml., round-bottom flask was fitted with an addition funnel, oxygen inlet tube and a drying tube (CaCl_2). Phenylmagnesium bromide (0.0121 mole) was added to the reaction vessel along with 50 ml. of anhydrous ether. Then 3.0 g. (0.0093 mole) of trityl bromide dissolved in anhydrous ether was added dropwise through the addition funnel. After one hour, the reaction mixture was a dark orange-red color but no solid material had formed. At this time oxygen was passed through the reaction mixture. After 6 hours the reaction mixture had turned to a pale yellow color and trityl peroxide was readily visible. The reaction mixture was cooled in an ice bath and then hydrolyzed with 40 ml. of ice cold 6N hydrochloric acid. The yield of trityl peroxide

was 47% (1.10 g., 0.00212 mole). Other products, observed by GLC analysis on Column CA-1, were: benzene, bromobenzene, phenol, acetophenone, biphenyl, benzophenone, triphenylmethane, triphenylmethanol and tetraphenylmethane. It is assumed that the Grignard reagent was acting as a reducing agent for the trityl cation and producing a trityl radical and a phenyl radical. No explanation is offered for the formation of acetophenone, although it was found to be present in small amounts by mixed injections using GLC.

Reaction of Trityl Acetate (I) With Phenylmagnesium Bromide With Oxygen Excluded From the System. Deoxygenated nitrogen² was passed through a stainless steel, helium leak-tested dry box for three days. The necessary materials were put into the dry box and then deoxygenated nitrogen passed through for one more day. Trityl acetate (I) (1.22 g., 0.004 mole) was added dropwise through an addition funnel to 0.0052 mole of phenylmagnesium bromide in 50 ml. anhydrous ether. The ether used as solvent was degassed with deoxygenated nitrogen via a gas dispersion tube for two hours. With the first small addition of trityl acetate the reaction mixture became bright yellow, indicative of trityl radicals. After one hour the reaction mixture turned a wine red color. After stirring for 11.5 hours with continuous deoxygenation of the reaction mixture, 40 ml. of 6N, deoxygenated, hydrochloric acid was added to hydrolyze the excess Grignard reagent. After hydrolysis the ether layer was still a wine red and no solid material could be seen in the reaction vessel. When the reaction mixture was removed from the dry box and exposed to the atmosphere the ether layer instantly turned yellow as the pale yellow trityl peroxide began to settle out. The yield of trityl peroxide (II) was 15% (0.15 g., 0.0003 mole), all of

which formed after taking the reaction mixture out of the dry box. This experiment indicates that trityl radicals actually have a considerable lifetime under the conditions of this reaction.

Reaction of Acetic Acid With Phenylmagnesium Bromide (1:2.3).

Acetic acid (1.0 g., 0.0167 mole) was slowly added to 0.035 mole of phenylmagnesium bromide in 50 ml. of anhydrous ether. The reaction mixture was stirred for 3 hours and then cooled and hydrolyzed with cold 6N hydrochloric acid. Analysis of the organic layer was accomplished by GLC on Column CA-1. The following products were found: benzene, bromobenzene, phenol, acetophenone, biphenyl, 1,1-diphenylethanol and 1,1-diphenylethene. The olefin is formed by dehydration of part of the tertiary alcohol. Acetophenone was found to be present in 15 percent yield (based on the acid) and the combined amounts of the tertiary alcohol and its corresponding dehydration product amount to about 40 percent yield (based on the acid). These yields are not unreasonably low when one considers that one mole of the Grignard reagent was destroyed by the acidic proton on acetic acid. This experiment proves that the bromomagnesium salt of acetic acid can yield acetophenone when attacked by phenylmagnesium bromide.

Determination of the Partition Coefficient of Acetic Acid Between Ether and 6N Hydrochloric Acid. The general procedure was to make up equal-volume solutions of 6N hydrochloric acid and ether, each pre-saturated with the other component, and then add to these immiscible liquids the materials that would be present after hydrolysis of a reaction mixture of trityl acetate and phenylmagnesium bromide. For example, in one experiment, based on 0.0066 mole of trityl acetate as starting material, the mixture contained 60 ml. of 6N hydrochloric acid

and 60 ml. of ether. To these liquids were added acetophenone, biphenyl, benzophenone, triphenylmethane, triphenylmethanol and magnesium bromide hexahydrate in amounts corresponding to their percent yields given in Table I. To this mixture was added 1.00 g. (0.0167 mole) of acetic acid and 0.508 g. (0.0065 mole) of dimethyl sulfoxide. NMR peak area integration gave an average DMSO:acetic acid ratio of 23:18. Thus, only 62.4 percent of the acetic acid remained in the aqueous layer. An average of three different determinations, each of slightly different volumes of the two liquids, resulted in an average partition coefficient (ether/acid) of $(0.376/0.624) = 0.603$, which indicates that acetic acid preferentially remains in the aqueous layer by a factor of $(0.624/0.376) = 1.66$.

Hydrolysis of the Reaction Mixture of Trityl Acetate (I) and Phenylmagnesium Bromide With Deuterium Oxide and Subsequent Mass Spectral Analysis of the Products. After trityl acetate (I) and phenylmagnesium bromide had been caused to react for 10 hours in the usual manner, the reaction mixture was hydrolyzed with 50 ml. of deuterium oxide (99.6%). The mass spectrograms of two of the products, triphenylmethane and triphenylmethanol, were obtained. Neither of these two products was found to contain an increased amount of deuterium over the natural abundance.

Mass Spectral Analysis of ¹⁸O-Labeled Trityl Acetate. The solid trityl acetate was introduced directly into the ion source of the magnetic sector instrument with the aid of a direct probe. The percent relative intensities of m/e in the range 302-308 are given below:

<u>m/e</u>	<u>% RI</u>
302	100
303	25

<u>m/e</u>	<u>% RI</u>
304	40
305	10
306	86
307	20
308	2

The odd numbered m/e peaks may be disregarded except for extremely precise work. The total peak height of the even numbered peaks is 226.

$$\text{Thus: } \% \text{ } ^{18}\text{O} = (0.0/226) + \frac{1}{2}(40/226) + (86/226)$$

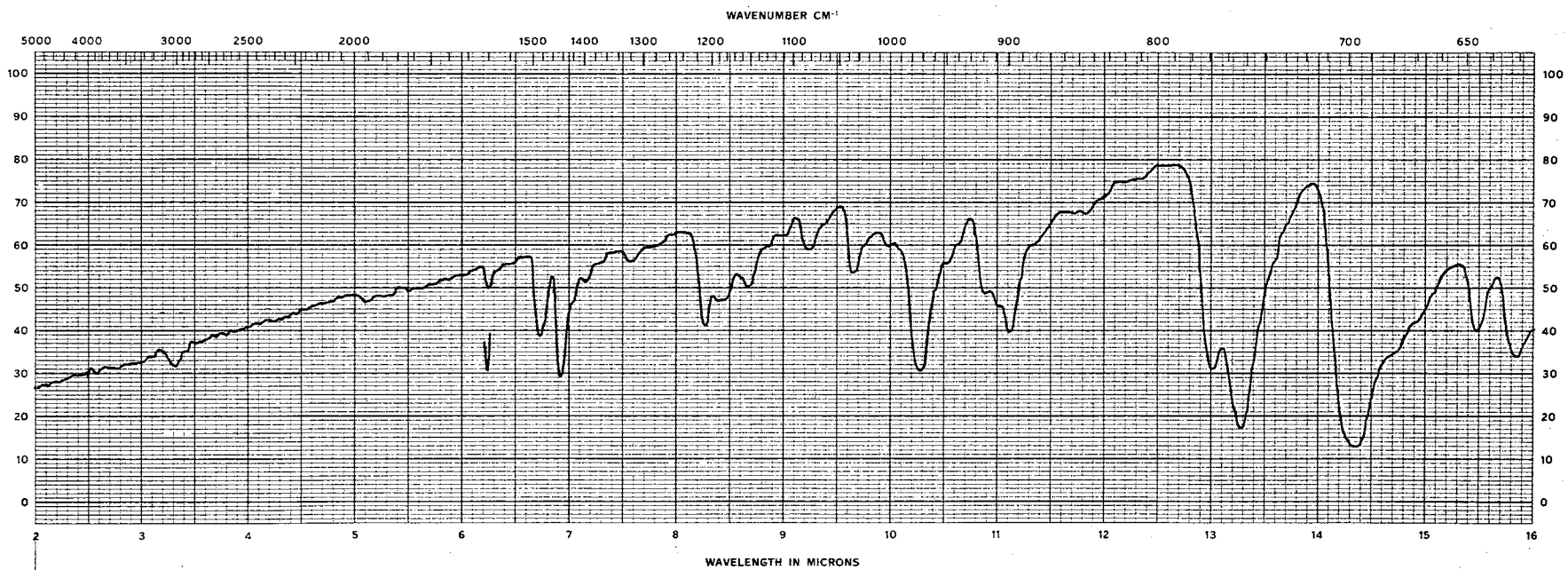
$$\% \text{ } ^{18}\text{O} = 0 + 0.09 + 0.38 = 0.47$$

This means that the probability of any oxygen atom in the trityl acetate having an oxygen with mass 18 is 0.47. This percentage (47%) has been verified by comparison with the other oxygen-containing peaks in the spectrum (Plate VI).

Mass Spectral Analysis of the Products Resulting From the Reaction of Labeled Trityl Acetate and Phenylmagnesium Bromide. The oxygen-containing products resulting from the reaction of ^{18}O -labeled trityl acetate (47%) and phenylmagnesium bromide were analyzed with a mass spectrograph. Solid trityl peroxide (II) was introduced into the ionization chamber with the aid of a direct probe. It was found to be void of ^{18}O above and beyond the natural abundance. The other oxygen-containing products present in the ether layer were analyzed with the aid of the gas chromatography unit, which is an added feature of the LKB-9000 instrument. The percent ^{18}O in excess of the natural abundance was found to be as follows: acetophenone 13-16%, benzophenone 0%, and triphenylmethanol 3-5%. The water layer was analyzed by vaporizing the mixture directly into the ionization chamber of a time-of-flight instrument.

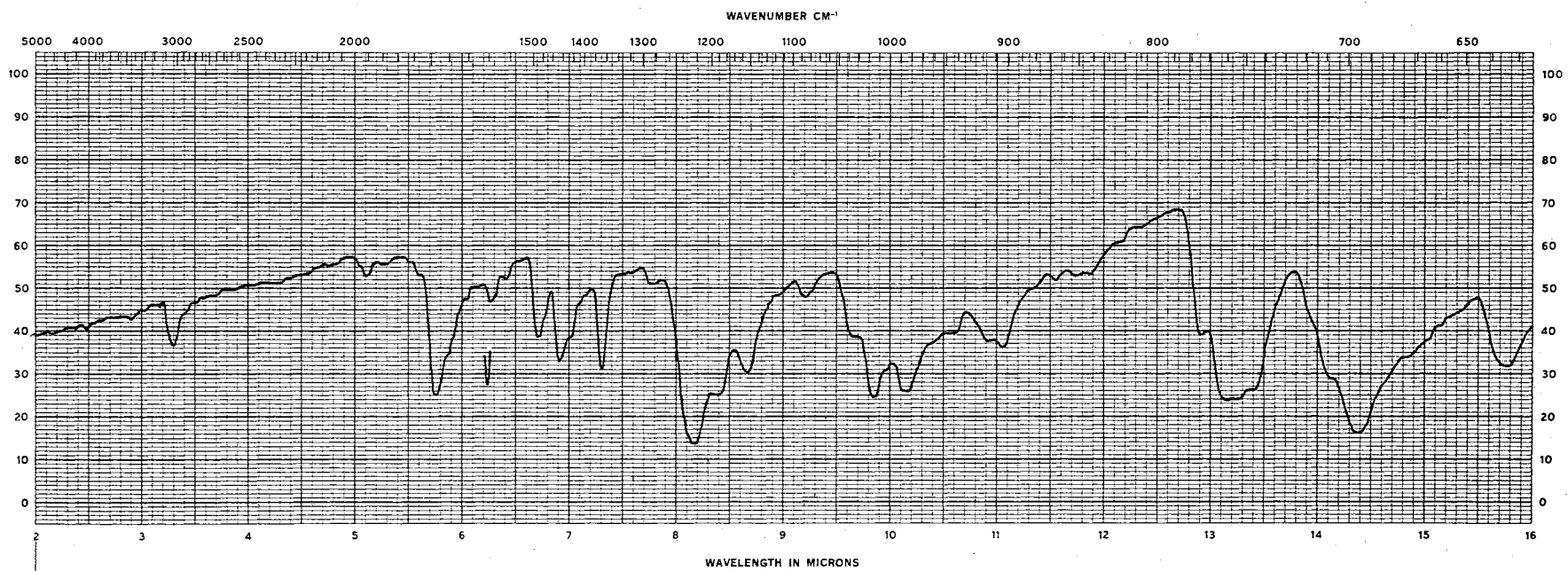
The acetic acid present in the water layer was not noticeably enriched with ^{18}O . It is assumed that oxygen from the water exchanged with oxygen in the acetic acid. Although no enrichment of ^{18}O in the water itself was evident, it is believed that it was present but was too dilute to be detected. Since we started with 0.00147 mole of trityl acetate only 0.00118 mole of acetic acid would have formed, based on typical yields. Since there are 2 oxygen atoms in each molecule of acetic acid compared to one for water, we would expect 0.00236 mole of ^{18}O -labeled water if the acetic acid was fully labeled and the exchange was quantitative. The ester used as starting material was 47% labeled with ^{18}O , so we expect 0.00111 mole of H_2^{18}O . This corresponds to 0.02 g. of H_2^{18}O which is about 0.17% of the 12 ml. aqueous layer.

Plate I



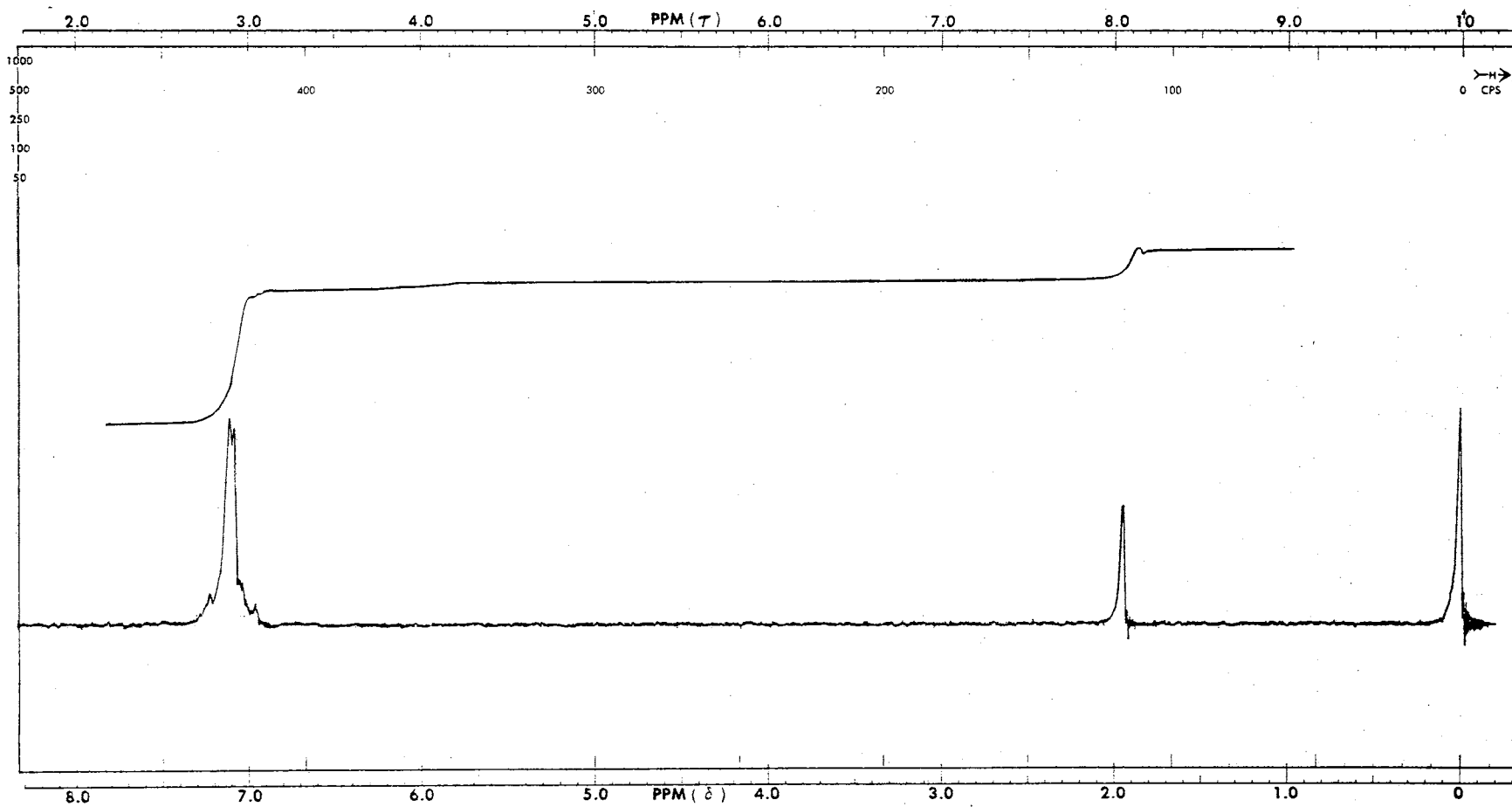
Trityl Peroxide (II), KBr Pellet

Plate II



Trityl Acetate (I), KBr Pellet

Plate III



Trityl Acetate (I)

Solvent.....CCl ₄	R. F. Field.....0.04 mG	S.W.....500 cps	S.A.....3.2
F.B.....2.0 cps	S.T.....250 sec	S.O.....000 cps	I.A.....63

TABLE I

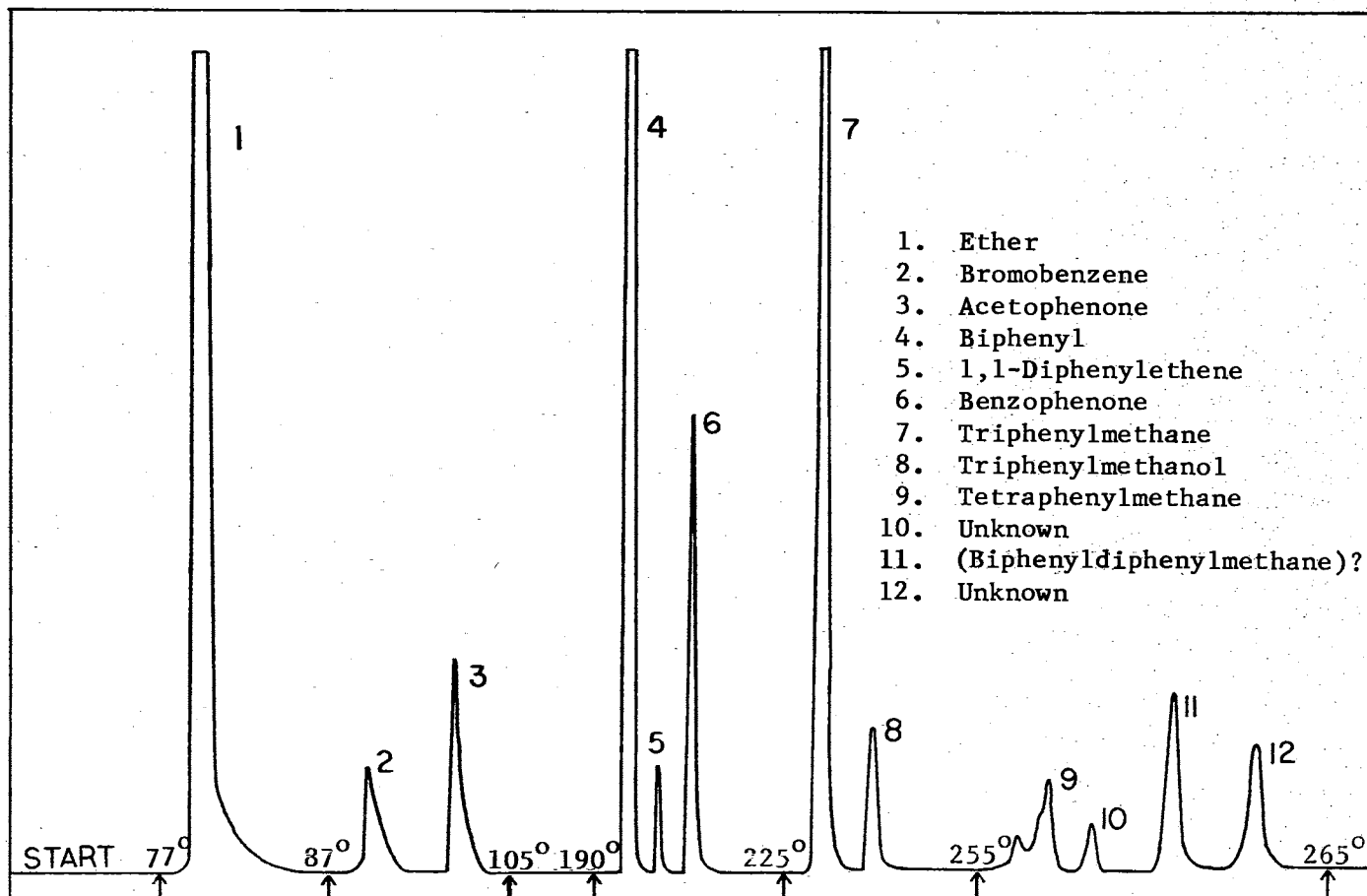
QUANTITATIVE GAS CHROMATOGRAPHIC ANALYSIS OF REACTION MIXTURE
RESULTING FROM REACTION OF TRITYL ACETATE (I) WITH
PHENYLMAGNESIUM BROMIDE-(1:1.3)

Column: CA-1, Flow Rate = 55 ml./min.

Temperature: Manually Controlled

<u>Product</u>	<u>Typical Yield</u>
1. Bromobenzene	Not determined
2. Acetophenone	14%
3. Biphenyl	Not determined
4. 1,1-Diphenylethanol	< 2%
5. Benzophenone	12%
6. Triphenylmethane	22.5%
7. Triphenylmethanol	< 5%
8. Tetraphenylmethane	1.5%
9. Acetic Acid	80.4%
10. Trityl Peroxide	60%

Plate IV



Reaction Mixture of Trityl Acetate (I) and Phenylmagnesium Bromide

Column.....CA-1
 He Flow.....55 ml/min.

Column Temperature.....Manually Adjusted
 Detector.....Thermal Conductivity

Plate V

TRITYL ACETATE

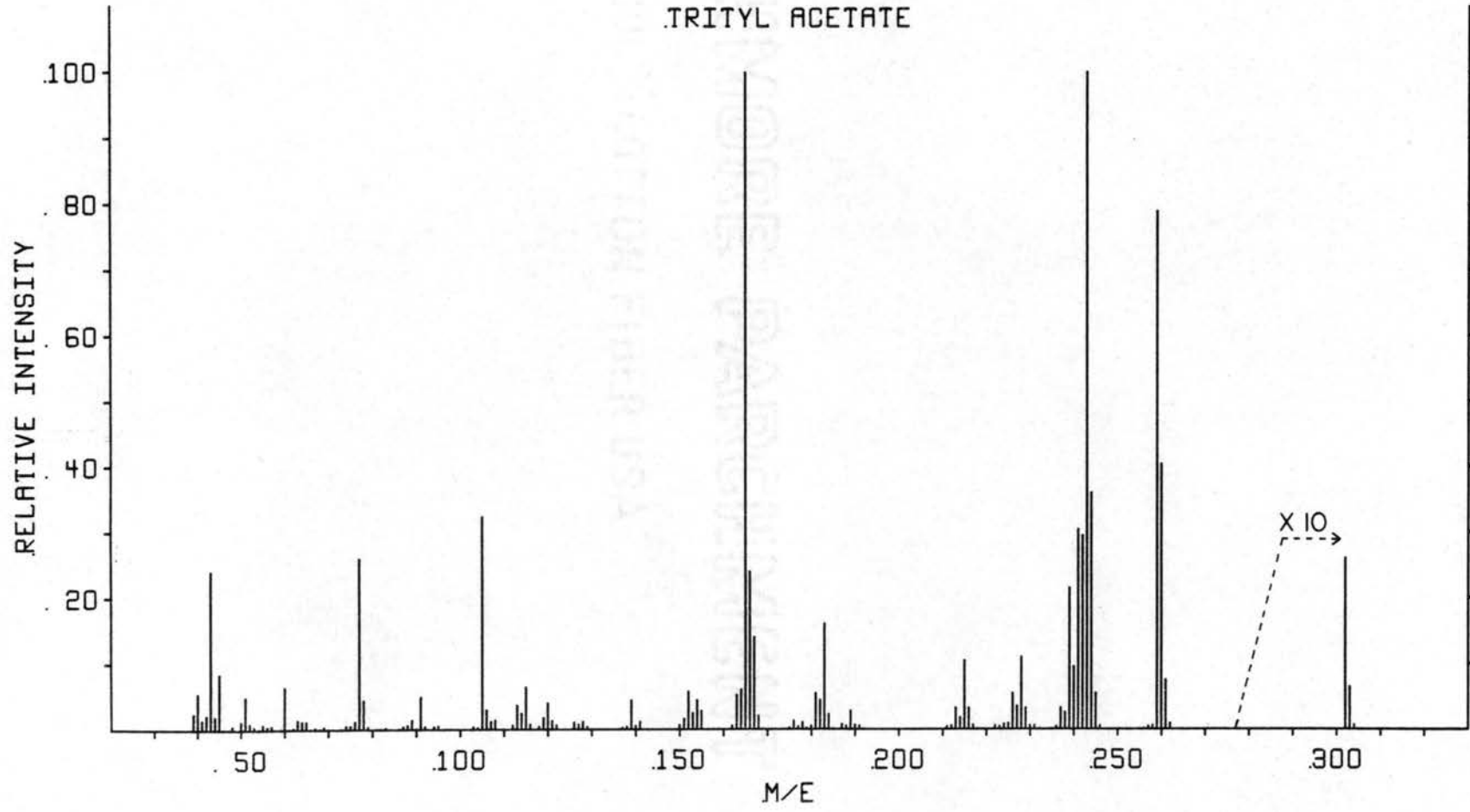


TABLE II

MASS SPECTRAL DATA OF TRITYL ACETATE (#189-1)

Inlet	Direct Probe
Ionizing (Trap) Current	38 μ Amps
Ionization Voltage	70 eV
Electron Multiplier Voltage	1.7 KV
Acceleration Voltage	3.5 KV
Filter	20 cps
Source Temperature	270 $^{\circ}$ C
Probe Temperature	30 $^{\circ}$ C

Intense Ions of Spectrum

<u>m/e</u>	<u>% RI</u>		<u>m/e</u>	<u>% RI</u>
243	100		105	32.5
165	100		241	30.5
259	79		242	29.5
260	40.5		77	26
244	36		43	24

Metastable Ions

<u>Apparent Mass</u>	<u>% RI</u>	<u>Transition Denoted</u>	<u>Probable Neutral Product</u>
241.0	1.0	(243 $^{+}$) ——— (242 $^{+}$) + 1	H
222.1	0.65	(302 $^{+}$) ——— (259 $^{+}$) + 43	CH ₃ CO
112.05	0.77	(243 $^{+}$) ——— (165 $^{+}$) + 78	C ₆ H ₆
112.5	0.83	(242 $^{+}$) ——— (165 $^{+}$) + 77	C ₆ H ₅

Plate VI

TRITYL ACETATE 0-18

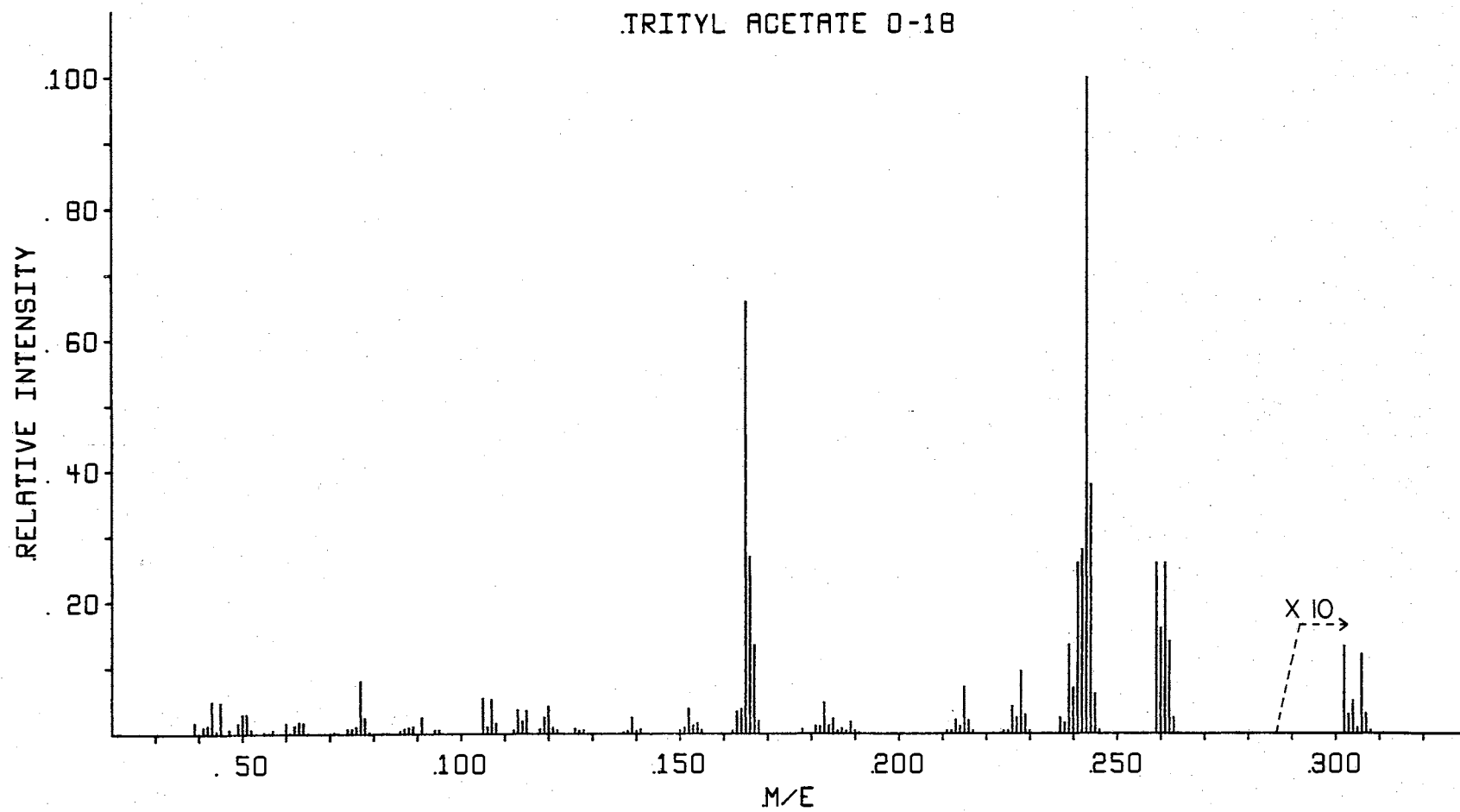


TABLE III

MASS SPECTRAL DATA OF TRITYL ACETATE LABELED WITH O-18 (#275-2)

Inlet	Direct Probe
Ionizing (Trap) Current	38 μ Amps
Ionization Voltage	70 eV
Electron Multiplier Voltage	1.7 KV
Acceleration Voltage	3.5 KV
Filter	20 cps
Source Temperature	250 $^{\circ}$ C
Probe Temperature	30 $^{\circ}$ C

Intense Ions of Spectrum

<u>m/e</u>	<u>% RI</u>	<u>m/e</u>	<u>% RI</u>
243	100	241	26
165	66	259	26
244	38	261	26
242	28	239	13.5
166	27	167	13.5

Metastable Ions

<u>Apparent Mass</u>	<u>% RI</u>	<u>Transition Denoted</u>	<u>Probable Neutral Product</u>
241.0	0.5	(243 $^+$) ——— (242 $^+$) + 1	H
222.1	0.2	(302 $^+$) ——— (259 $^+$) + 43	CH ₃ CO
112.05	0.1	(243 $^+$) ——— (165 $^+$) + 78	C ₆ H ₆
112.5	0.1	(242 $^+$) ——— (165 $^+$) + 77	C ₆ H ₅

Plate VII

TRITYL PEROXIDE

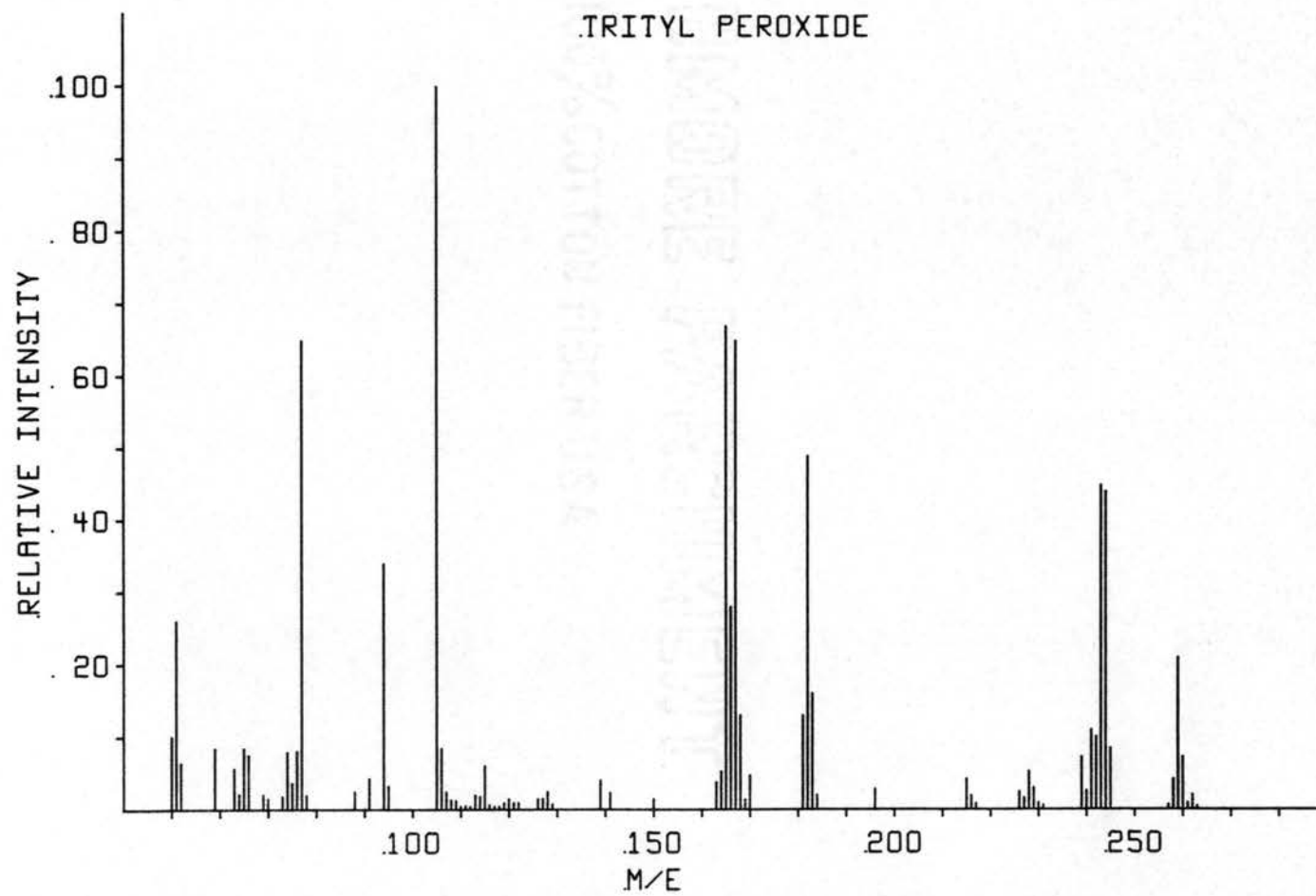


TABLE IV

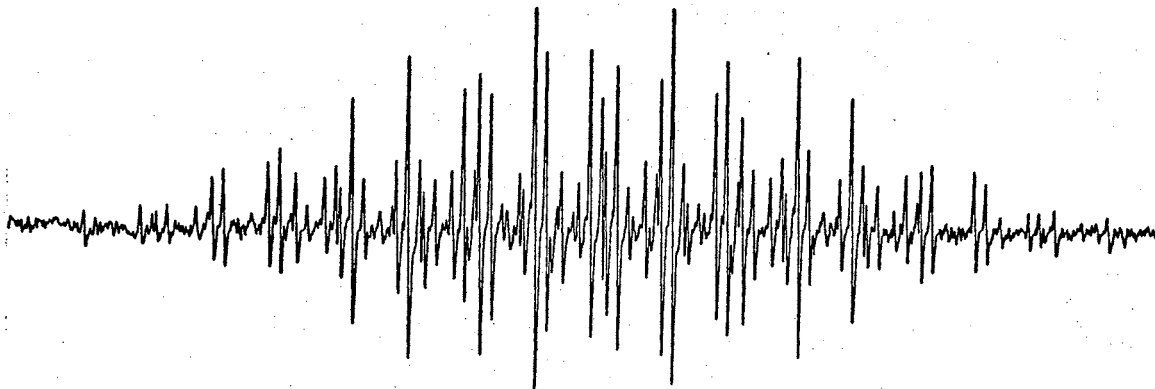
MASS SPECTRAL DATA OF TRITYL PEROXIDE RESULTING FROM REACTION OF
TRITYL ACETATE WITH O-18 AND PHENYLMAGNESIUM
BROMIDE (#277-3)

Inlet	Direct Probe
Ionizing (Trap) Current	38 μ Amps
Ionization Voltage	70 eV
Electron Multiplier Voltage	2.1 KV
Acceleration Voltage	3.5 KV
Filter	20 cps
Source Temperature	290 $^{\circ}$ C
Probe Temperature	130 $^{\circ}$ C

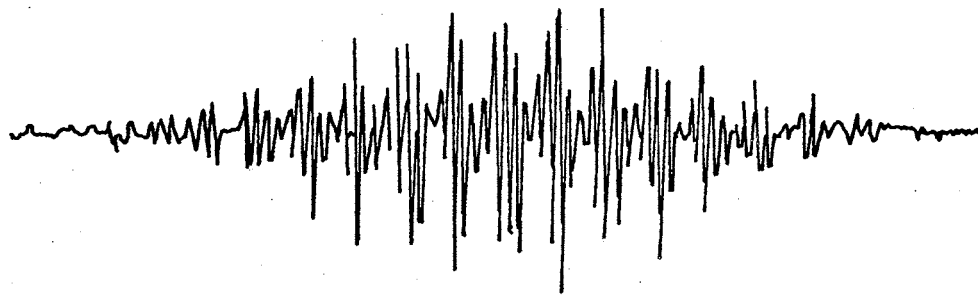
Intense Ions of Spectrum

<u>m/e</u>	<u>% RI</u>	<u>m/e</u>	<u>% RI</u>
105	100	243	45
165	67	244	44
167	65	94	34
77	65	166	28
182	49	51	26
		259	21

PLATE VIII



E.S.R. Spectrum of a 10^{-3} molar solution of trityl radical in toluene at -20°C . (Chestnut and Sloan, J. Chem. Phys. 33, 637 (1960)).



Strong, resolved signal of reaction mixture of trityl acetate and phenyl magnesium bromide (1:1.3) at room temperature, in diethyl ether after 0.5 hours.

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VITA

Russell Dwayne Shupe

Candidate for the Degree of

Master of Science

Thesis: AN EXAMINATION OF THE MECHANISM OF THE REACTION OF TRITYL ACETATE WITH PHENYLMAGNESIUM BROMIDE-PROOF OF RADICAL INTERMEDIATES

Major Field: Organic 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 completed the requirements for the Master of Science degree in July, 1967.

Professional Experience: The author was a recipient of a National Aeronautics and Space Administration Fellowship during the period September, 1965 to July, 1967.

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