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AN INVESTIGATION OF THE REACTION OF BENZHYDRYL CHLORIDE WITH POTASSIUM t-BUTOXIDE IN DMSO

BY

LAWSON GIBSON WIDEMAN -1943-

A

THESIS

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Approved by

Samir B. Hanna (advisor) Donald J. Siehr

D. Vincent Roach K. G. Mayhan

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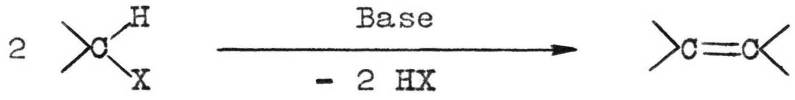
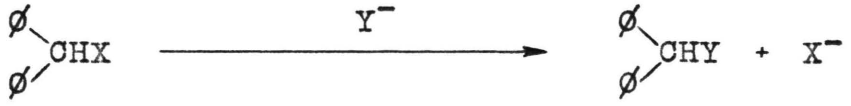
The author wishes to express special acknowledgement to his professor, Dr. Samir B. Hanna, for his guidance and suggestions which made this investigation possible. The author also wishes to thank the Chemistry Department of the University of Missouri at Rolla for providing him with the space, chemicals and necessary equipment. Financial support from U. M. R. in the form of a Special Summer Fellowship (Summer 1966) is gratefully acknowledged.

I. INTRODUCTION

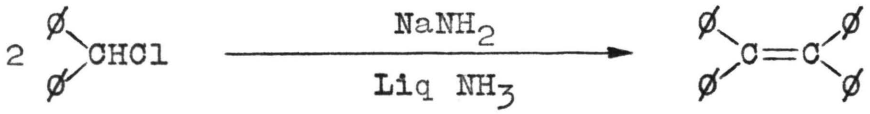
Certain aryl alkyl halides containing a reactive α-hydrogen and no β-hydrogens have been known to be converted by bases to dimeric olefins through eliminative condensations.



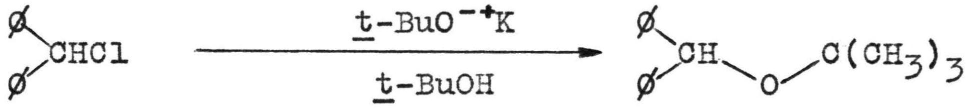
Benzhydryl halides fall into this group. However, benzhydryl halides are also known to react readily with nucleophilic reagents such as HO^-, $C_2H_5O^-$, SCN^-, N_3^- and ϕO^- in homogeneous media to give the corresponding substitution products; thus,



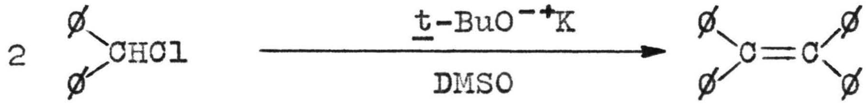
In the presence of the strong base, sodium amide in liquid ammonia, the dimeric olefin, tetraphenylethylene, is formed in quantitative yield from benzhydryl chloride.



With the slightly weaker base, potassium _t_-butoxide in _t_-butyl alcohol, no tetraphenylethylene is formed. Surprisingly, in this case the product is the benzhydryl _t_-butyl ether.



However, with potassium _t_-butoxide in dimethyl sulfoxide, a quantitative yield of tetraphenylethylene is obtained.

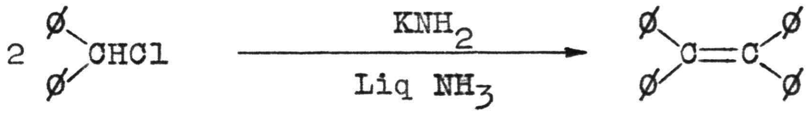


The ultimate aim of this study was to elucidate the mechanism of formation of tetraphenylethylene from benzhydryl chloride and potassium _t_-butoxide in dimethyl sulfoxide. The development of a suitable technique for following the reaction rate and of an analytical method to determine the extent of the reaction became an important object in this project.

II. LITERATURE REVIEW

The kinetics and mechanisms of nucleophilic displacements on benzhydryl chloride have been studied extensively.[1] On the other hand, the reactions of benzhydryl chloride with bases to form dimeric olefins, have only been investigated to a small degree and seem to require many more mechanistic studies before conclusions can be drawn as to the probable reaction paths.

Hauser and co-workers[2] obtained a quantitative yield of tetraphenylethylene from the reaction of benzhydryl chloride with potassium amide in liquid ammonia.



The mechanism for the formation of this dimeric olefin was studied by Hauser and co-workers.[2] They succeeded in isolating the dimeric halide, $\phi_2CH\text{-}CCl\phi_2$, by the addition of sodium amide to a solution of benzhydryl chloride in liquid ammonia at -70°. This intermediate was dehydrohalogenated to tetraphenylethylene on further treatment

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(1) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, 1953, chapter VII.

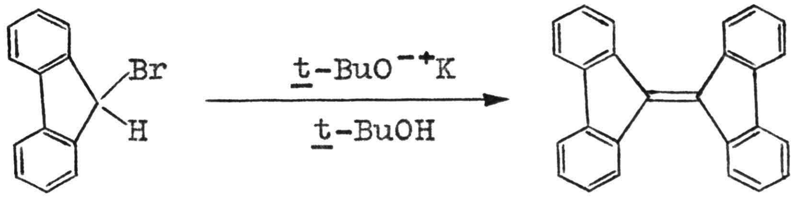
(2) C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor and A. E. Brodhag, J. Am. Chem. Soc., 78, 1653 (1956).

with sodium amide in liquid ammonia. This may be taken as an evidence for an alkylation-dehydrohalogenation mechanism, viz.,

$$2\phi_2CHCl \xrightarrow{\text{Base}} \phi_2CHCCl\phi_2 \xrightarrow{\text{Base}} \phi_2C{=}C\phi_2$$

A similar mechanism was also implied in the formation of stilbene[3] and *9,9*'-bifluorenylidene[2] when benzyl halides and *9*-halofluorenes respectively, were reacted with sodium or potassium amide in liquid ammonia.

Recently, Bethell[4] investigated the kinetics and mechanisms of the reaction of *9*-bromofluorene with potassium *t*-butoxide in *t*-butyl alcohol which gives a quantitative yield of *9,9*'-bifluorenylidene.



The rate expression indicated a reaction of the third order overall, second order in the organic halide, and first order in the base.

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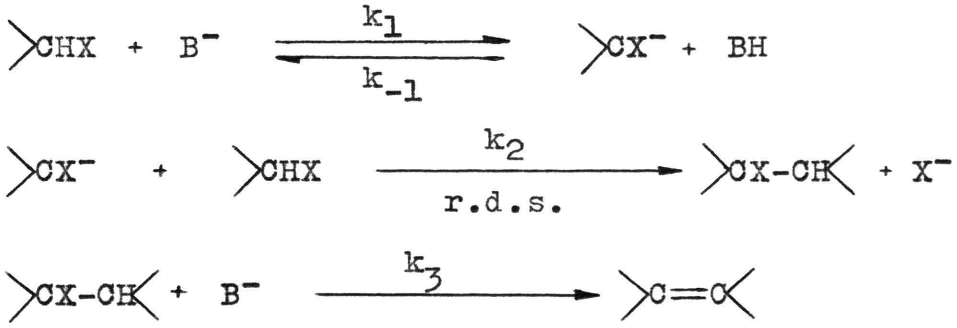
(3) M. S. Kharasch, W. Nudenberg, and E. K. Fields, J. Am. Chem. Soc., 66, 1276 (1944).

$$\text{Rate} = [k_2k_1/k_{-1}]\ [\text{FlHBr}]^2\ [\text{HO}^-]$$

This information together with the observation that the deuterium exchange of the α-H in 9-bromofluorene under the same conditions was fast, prompted Bethell to suggest the following mechanism.



Further proof of this mechanism was published recently.[5] The compound, 9-bromo-9,9'-bifluorenyl, was allowed to react with potassium t-butoxide in t-butyl alcohol and a quantitative yield of 9,9'-bifluorenylidene was obtained. The rate of formation of 9,9'-bifluorenylidene from 9-bromo-9,9'-bifluorenyl was found to be 30 to 50 times faster than the rate of formation of the latter from 9-bromofluorene under identical conditions.

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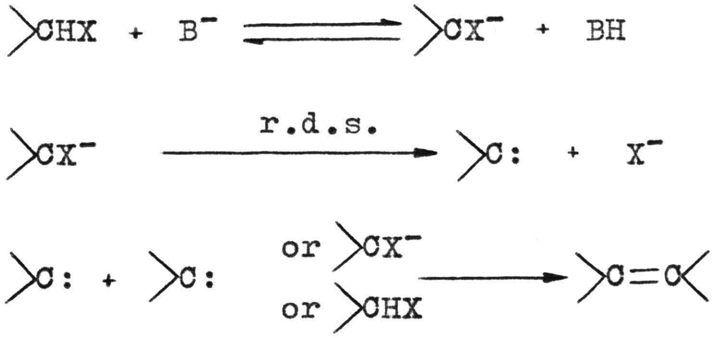
(4) D. Bethell, J. Chem. Soc., 666 (1963).

(5) D. Bethell and A. Cockerill, J. Chem. Soc., B, 917 (1966).

Benzyl chloride was studied in this laboratory under the same conditions, viz., with potassium t-butoxide in t-butyl alcohol.[6] The product was identified as stilbene and the kinetics were second order overall: first order in base, and first order in benzyl chloride. Such kinetics could fit either an alkylation-dehydrohalogenation mechanism similar to Bethell's if the first step were rate-controlling, or an α-elimination mechanism similar to that reported for the p-nitrobenzyl system in 1961.[7]



A kinetic investigation was carried out to determine whether the reaction of p-nitrobenzyl halides with base involves the formation of p-nitrophenyl methylene. The reaction was reported to be first order in base and first

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(6) Der-Rong Chen, M.S. Thesis in Chemical Engineering, UMR, June, 1965.

(7) S. B. Hanna, Y. Iskander and Y. Riad, J. Chem. Soc., 217 (1961).

order in organic halide.[7] This is the kinetic order that would be expected for the methylene mechanism if either the formation of the carbanion or its decomposition to methylene were rate-controlling. The alkylation-dehydrohalogenation mechanism for the formation of dinitrostilbene would also lead to these kinetics if carbanion formation were the rate-controlling step of this reaction. However, this cannot be the case because the unreacted p-nitrobenzyl chloride recovered from treatment with base in dioxane-deuterium oxide contained almost 50% deuterium when the reaction was arrested after about 40% conversion to the stilbene. This shows that the first step of the reaction is fast and reversible. Thus, the alkylation-dehydrohalogenation mechanism may be ruled out here since it would demand greater than first order kinetics in the organic halide.

When _4_-nitrobenzhydryl chloride was allowed to react with potassium _t_-butoxide in _t_-butyl alcohol, _4_,_4_'-dinitrotetraphenylethylene was obtained.[8] The formation of a carbanion was evidenced by the appearence of a deep red color in the reaction mixture and by measuring the rates of proton transfer from the organic halide with a variety of bases.[8]

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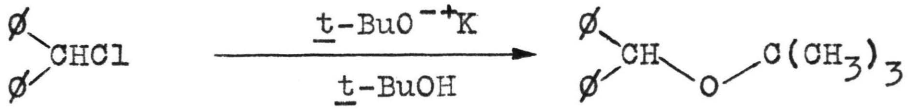
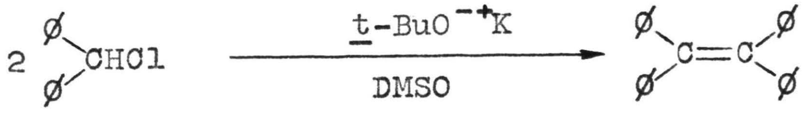
(8) D. Bethell and A. Cockerill, J. Chem. Soc., _B_, 921 (1966).

McElvain,[9] realizing that the benzhydryl halides may form the intermediate methylene in the presence of certain bases by α-elimination, attempted to trap a possible carbene by using dimethylketene dimethylacetal. Using t-butyl alcohol as the solvent, and potassium t-butoxide as the base, no carbene was trapped, but, surprisingly after several hours, an 80% yield of benzhydryl t-butyl ether was obtained.



Thus, the reaction is essentially different from the ones observed with benzyl halides and 9-halofluorenes under identical conditions.

While benzhydryl chloride reacts only slowly with potassium t-butoxide in t-butyl alcohol to give the ether, the change of solvent to dimethyl sulfoxide(DMSO) was reported to give almost instantaneously a quantitative yield of tetraphenylethylene.[10]



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(9) S. M. McElvain and P. L. Weyna, J. Am. Chem. Soc., 81, 2587 (1959).

(10) N. McFarlane, Ph.D. Thesis, Liverpool University, January, 1964, as reported in ref. 11.

Addition of *t*-butyl alcohol diminished the yield of tetraphenylethylene. When the concentration of t-butyl alcohol was 10.5 *M*, no tetraphenylethylene was obtained. Ledwith and Shih-Lin[11] reported that the reaction of benzhydryl chloride with potassium *t*-butoxide in DMSO was too fast to measure and was independent of both the concentration of benzhydryl chloride and potassium *t*-butoxide. From this observation they presumed formation of the carbene intermediate from the carbanion by *α*-elimination. Their attempts to trap a carbene by use of cyclohexene and vinyl ether were in vain.

Enhancement of basic reactivity in dimethyl sulfoxide as a solvent is now well recognized[12] and may be attributed to the formation of the conjugate base of DMSO, namely, the dimsyl ion.[13]

$$\underline{t}\text{-BuO}^{-+}\text{K} + \text{CH}_3\overset{\overset{\text{O}}{\uparrow}}{\text{S}}\text{CH}_3 \rightleftharpoons \text{K}^{+-}\text{CH}_2\overset{\overset{\text{O}}{\uparrow}}{\text{S}}\text{CH}_3 + \underline{t}\text{-BuOH}$$

In support of the existence of this ion is the formation

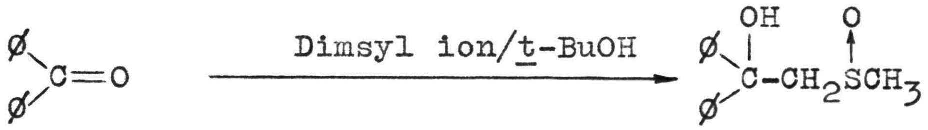
---

(11) A. Ledwith and Y. Shih-Lin, Chem. Ind. (London), 1868 (1964).

(12) C. C. Price and W. H. Snyder, J. Am. Chem. Soc., *83*, 1773 (1961); D. J. Cram, C. A. Kingsbury and B. Rickborn, J. Am. Chem. Soc., *83*, 3688 (1961).

(13) E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc., *84*, 866 (1962).

of the sulfur-containing product obtained when benzophenone is allowed to react with strong base in DMSO;[14] thus,



The dimsyl ion, which is very reactive with oxygen, carbon dioxide, and water,[15] is also prepared by the reaction of DMSO with alkai metal hydrides at elevated temperatures under a nitrogen atmosphere. The metal salts require about 45 minutes to form and are characterized by the formation of a somewhat cloudy, pale yellow-grey solution. When this solution is added to benzhydryl chloride an almost quantitative yield of tetraphenylethylene is obtained.[16]

The kinetics for the formation of tetraphenylethylene in DMSO from benzhydryl chloride and potassium t-butoxide will be investigated in this study to help determine the reaction mechanism.

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(14) H. Nace and J. Monagle, J. Org. Chem., 24, 1792 (1959).

(15) E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc., 87, 1345 (1965).

(16) E. J. Corey and M. Chaykovsky, ibid., 87, 1346 (1965).

III. EXPERIMENTAL

The experimental part of this work will be treated under the following three sections:

A. Preparation and purification of the materials to be studied.

B. Qualitative investigation of the products of the reactions.

C. Kinetic technique and rate measurements, including results and graphical representations.

A. PREPARATION OF MATERIALS

The following materials were either prepared or purchased and purified according to standard procedures.

Benzhydryl chloride. Material of reagent grade was purchased from Aldrich Chemical Company. It was distilled in vacuum (b.p. 139-49° at 4 mm.) using a short-path fractional distillation apparatus. Purity was determined by chloride analysis of the hydrolyzed material, by comparison of the nmr spectrum with the nmr spectrum of benzhydryl chloride in the Varian Catalog, and by comparison of the infrared spectrum with that of a sample prepared by the method of Gilman and Kirby[17] from

---

(17) H. Gilman and J. Kirby, J. Am. Chem. Soc., 48, 1735 (1926).

benzhydrol and thionyl chloride in toluene. Benzhydrol was prepared by the method of Marvel and Hansen[18] by reduction of benzophenone with sodium hydroxide and zinc dust in alcohol. The prepared benzhydryl chloride was distilled twice in vacuum before the infrared analysis was attempted (Figure 1). The infrared spectrum of the purified reagent grade benzhydryl chloride is shown for comparison (Figure 2). The benzhydryl chloride was stored as a solid under a dry nitrogen atmosphere in the refrigerator.

Potassium t-butoxide was sublimed material of reagent grade purchased from Alpha Inorganics. No further purification was needed.

Dimethyl sulfoxide was 99.9% pure Fisher Certified reagent grade which seemed to be contaminated with water, as shown by infrared analysis (Figure 3). The DMSO was distilled in vacuum through a 2-ft. column packed with Linde Type 13X Molecular Sieves to remove water and any mercaptans.[19] The infrared spectrum of the distilled DMSO is shown in Figure 4.

Sodium azide solution was prepared from reagent grade sodium azide purchased from Alpha Inorganics. A stock solution (0.25 M) was prepared by weighing 1.625 g. (0.025

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(18) C. Marvel and N. Hansen, Org. Syn., 8, 24 (1928).

(19) Union Carbide Corp., Linde Division, Chicago, Ill., Adsorption Data Sheet No. P-84-0676.

mole) of NaN_3 into a 100 ml. volumetric flask and making the solution up to the mark with distilled DMSO.

Ferric chloride solution was prepared by adding 16.5 g. (0.10 mole) of $FeCl_3$ to DMSO in a 100 ml. volumetric flask and diluting to the mark with distilled DMSO. The cloudy solution was centrifuged and the clear portion was drawn off for use in colorimetric determinations of ionic azide.

Figure 1 INFRARED SPECTRUM OF BENZHYDRYL CHLORIDE PREPARED AND PURIFIED IN THIS LABORATORY.

Figure 2 INFRARED SPECTRUM OF PURCHASED AND PURIFIED BENZHYDRYL CHLORIDE.

Figure 3 INFRARED SPECTRUM OF COMMERCIAL DMSO.

Figure 4 INFRARED SPECTRUM OF PURIFIED DMSO.

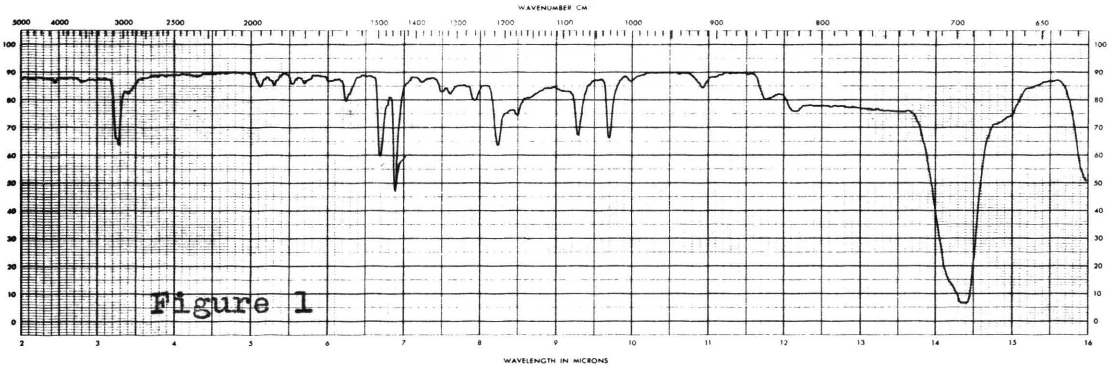

Figure 1

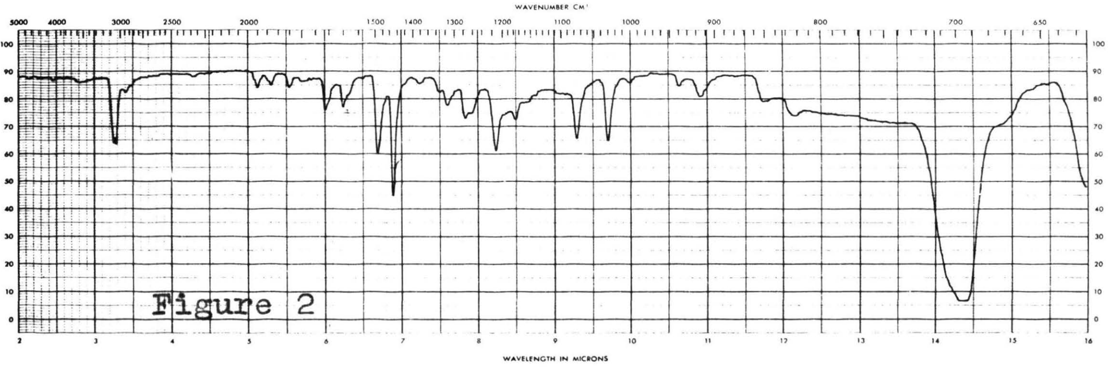

Figure 2

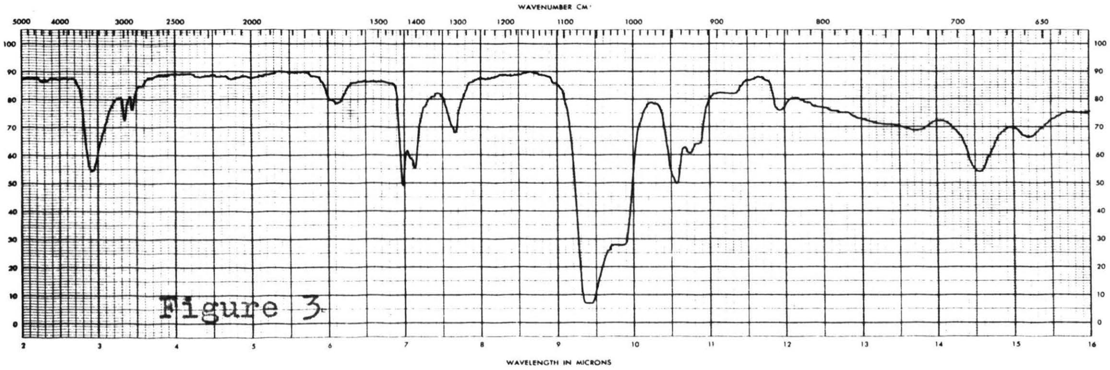

Figure 3

Figure 4

B. QUALITITATIVE INVESTIGATION OF THE PRODUCTS OF REACTIO

<u>Tetraphenylethylene</u>.

Benzhydryl chloride was allowed to react with potassium *t*-butoxide in dimethyl sulfoxide at room temperature for a period of one hour to assure complete reaction.* The initial concentration of benzhydryl chloride was 0.11 *M*, and that of potassium *t*-butoxide was 0.26 *M*. The reaction mixture was then poured into excess water to dissolve the inorganic salts. The light yellow solid that precipitated in aqueous solution was filtered off and washed several times with water to remove any remaining DMSO. The solid was dried and recrystallized twice from ether. The dried material was a light yellow crystalline solid identified as tetraphenylethylene by melting point, 220-21° (lit. 220-21°),[20] by comparison of its infrared spectrum (Figure 5) with that reported in the literature,[21] and by its nmr spectrum which contains only aromatic hydrogens. Although it

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(*) The reaction was reported to be practically instantaneous under such conditions. (cf. ref. 11).

(20) J. Mackenzie, J. Chem. Soc., 1695 (1922); J. Orekhoff, Bull. Soc. Chim., <u>25</u>, 186 (1919).

(21) W. Otting, Chem. Ber., <u>87</u>, 613 (1954).

decolorizes dilute acidic potassium permanganate, it does not form a dibromo derivative.[22]

The infrared spectrum of the combined products from all the kinetics runs was identical to Figure 5.

Product of Reaction of Benzhydryl Chloride with Potassium t-Butoxide in t-Butyl Alcohol.

Benzhydryl chloride and potassium *t*-butoxide were stirred mechanically for 21 hours in *t*-butyl alcohol at room temperature. The initial concentration after mixing of the organic halide was 0.25 *M* and that of the base was 0.50 *M*. A white precipitate appeared when the reaction mixture was poured into water to dissolve the inorganic salts. The white solid was washed with water and dried. Recrystallization of the solid from cold ether gave white crystals identified as benzhydryl *t*-butyl ether by melting point, 58-59°(lit. 54-55°),[23] by its infrared spectrum (Figure 8), and by ether cleavage using excess hydroiodic acid in aqueous solution. The product from ether cleavage was isolated from ethyl ether as a crystalline solid with a melting point of 110°. The infrared spectrum

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(22) R. Shriner, R. Fuson and D. Curtin, "The Systematic Identification of Organic Compounds", 5th edition, John Wiley and Sons, Inc., New York, p 150.

(23) S. M. McElvain and P. L. Weyna, J. Am. Chem Soc., **81**, 2587 (1959).

(Figure 9) indicates that the cleavage of benzhydryl _t_-butyl ether in aqueous hydroiodic acid affords benzhydryl ether.

The infrared spectrum of the product compares point by point to that of benzhydryl ether given in the literature.[24]

Product from Aged Solutions of Benzhydryl Chloride in Aqueous DMSO.

When benzhydryl chloride was allowed to sit in an excess of 50% aqueous DMSO for several weeks, a large quantity of clear plates formed in the flask. The clear plates were identified as benzhydryl ether by melting point, 108-10° (lit. 110°),[25] and by comparison of its infrared spectrum (Figure 9) with that of benzhydryl ether reported in the literature.[24] The benzhydryl ether was found not to undergo cleavage in aqueous HI at refluxing temperatures for 24 hours. A possible interpretation of the mechanism of the reaction is in the Discussion.

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(24) T. Sato, A. Takatsu and K. Hata, Bull. Chem. Soc. Japan 37 (6), 902 (1964).

(25) "Handbook of Chemistry and Physics", The Chemical Rubber Publishing Company, Cleveland, Ohio, 1964, 45th edition, p C-317.

Product of Reaction of Benzhydryl Chloride with Sodium Methoxide in DMSO.

The product of reacting benzhydryl chloride (0.5 M) and sodium methoxide (1.0 M) in DMSO was definitely not tetraphenylethylene, but a yellow highly viscous oil which seemed insoluble when the reaction mixture was poured into excess water to remove the inorganic salts. The yellow liquid was dissolved in ether, dried over calcium chloride and clarified with Norit. The only attempts made to analyze the liquid were by infrared analysis, which indicated the presence of an ether such such as benzhydryl methyl ether, and by the product of cleavage with aqueous hydroiodic acid.

Product of Reaction of Benzhydrol in Aqueous Hydroiodic Acid.

When benzhydrol (ca. 5 g.) was subjected to the conditions for ether cleavage, i.e., refluxed for 24 hours in excess aqueous HI, a solid product, m.p. 108-110°, was obtained. This product was shown by infrared spectral analysis and by the undepressed melting point when mixed with an authentic sample of benzhydryl ether, to be benzhydryl ether.

Product from Attempts to Trap a Possible Carbene.

A solution of tetramethylethylene (0.05 M) and benzhydryl chloride (0.50 M) in DMSO was reacted with an equal volume of potassium *t*-butoxide (1.0 M) in DMSO; a deep red color formed immediately which turned much darker upon standing for 1 hour. When the reaction mixture was poured into water, a light yellow precipitate was formed along with a brown oil which was less dense than water. The precipitate was identified as tetraphenylethylene by methods already described, and the brown oil was shown by infrared analysis to possess absolutely no aromatic character. No further attempts to identify the oil were made.

Figure 5 INFRARED SPECTRUM OF TETRAPHENYLETHYLENE PREPARED IN THIS LABORATORY.

Figure 6 INFRARED SPECTRUM OF REAGENT GRADE BENZOPHENONE.

Figure 7 INFRARED SPECTRUM OF REAGENT GRADE BENZHYDROL.

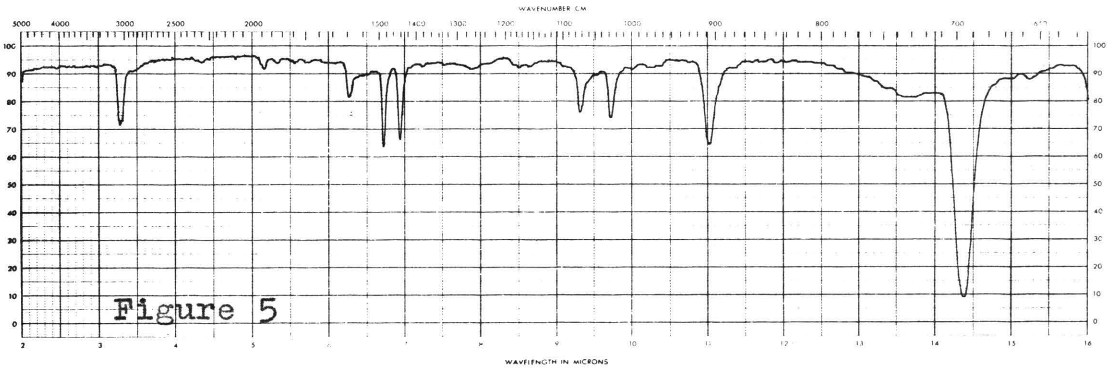

Figure 5

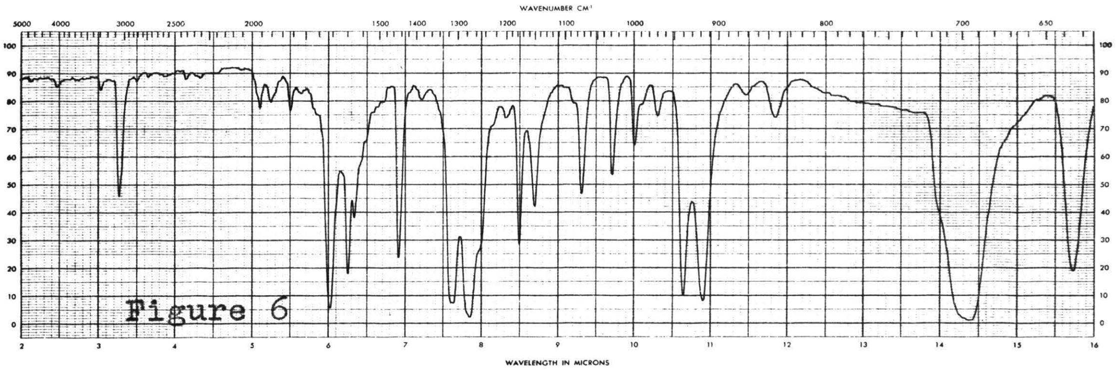

Figure 6

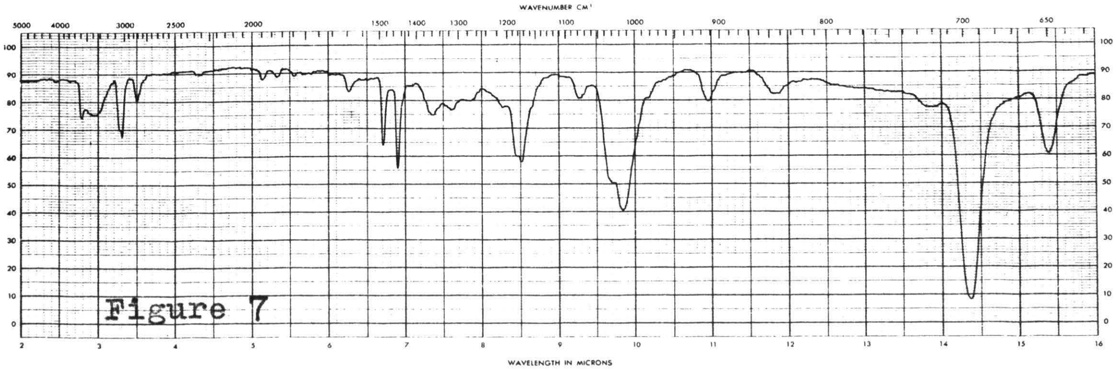

Figure 7

Figure 8 INFRARED SPECTRUM OF BENZHYDRYL *t*-BUTYL ETHER PREPARED IN THIS LABORATORY.

Figure 9 INFRARED SPECTRUM OF BENZHYDRYL ETHER PREPARED IN THIS LABORATORY.

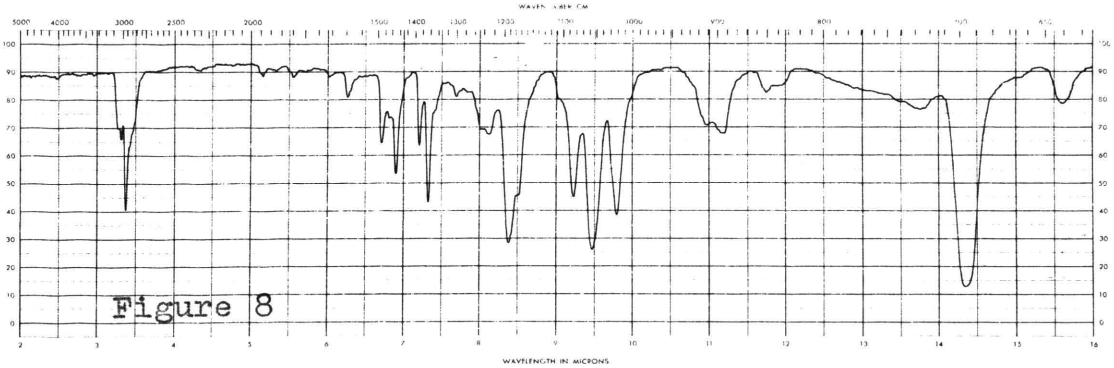

Figure 8

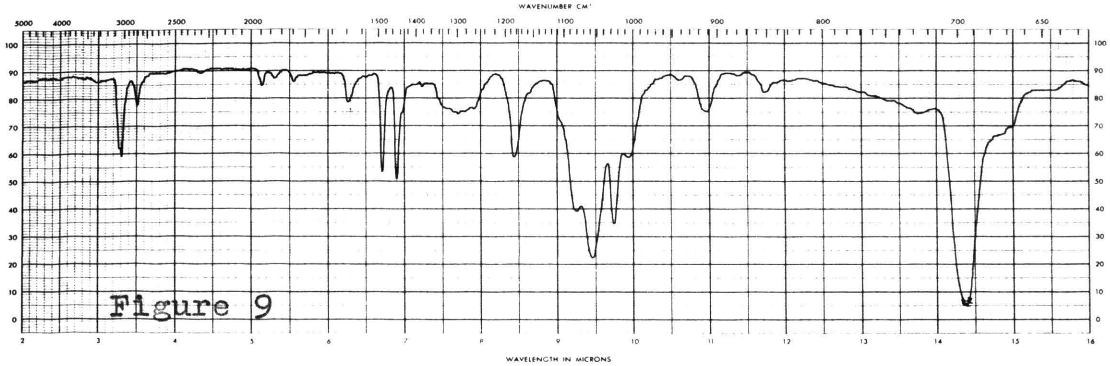

Figure 9

C. KINETIC TECHNIQUE AND RATE MEASUREMENTS

Method of Analysis.

In earlier studies in this laboratory the rates of reactions of organic halides with bases were followed by withdrawing samples of the reaction mixture and quenching in aqueous acid. It was known that the hydrolysis of the organic halides under investigation was very slow in aqueous-neutral or -acidic media. The samples could then be titrated electrometrically for their ionic halide content. The titration set-up[26] consisted of a cell containing a platinum-quinhydrone-hydrogen ion electrode and a silver-silver chloride electrode joined by a potassium nitrate-agar salt bridge. The electrodes were connected to a zero-point galvanometer which showed a deflection when ionic chloride was present in the titration cell. Silver nitrate was used to titrate the ionic chloride. When the pH of the buffer in the quinhydrone electrode is 3.2, the cell has a zero EMF at the end point of titration, i.e., when all the chloride ion in the titration vessel has been precipitated as silver chloride.

Attempts to quench the reaction, of benzhydryl chloride

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(26) Der-Rong Chen, M. S. Thesis in Chemical Engineering, UMR, June, 1965, p 18.

and potassium t-butoxide in DMSO, in aqueous acid and to titrate for the ionic chloride were futile. The half-life for the hydrolysis of benzhydryl chloride in 90% aqueous-acetone is about 2 hours at 50°.[27] Such a half-life in a quenching procedure would have been ideal for our case since the reaction of benzhydryl chloride with base in DMSO appeared to be relatively fast. However, benzhydryl chloride seemed to hydrolyze quite fast in DMSO-H_2O mixtures and the idea of quenching our reaction in aqueous acid medium was abandoned.

Attempts to quench the reaction using a nonaqueous acid were tried. Benzoic acid was dissolved in DMSO in concentrations equivalent to that of the original base concentration. The Ag/AgCl electrodes were stored in DMSO and silver nitrate was dissolved in DMSO for titration of the chloride. The titrations were extremely erratic and accompanied by a brown precipitate which appeared to be Ag_2O instead of AgCl; the results were not reproducible.

The azide ion is known to react with benzhydryl chloride to give benzhydryl azide which is stable in basic media.[28]

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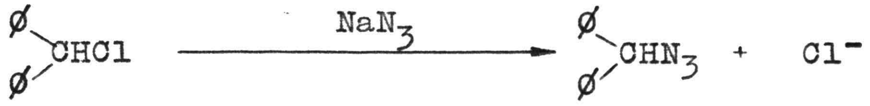
(27) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, 1953, p 355.

(28) C. G. Swain, C. B. Scott and K. H. Lohmann, J. Am. Chem. Soc., 75, 140 (1953); M. G. Church, E. D. Hughes and C. K. Ingold, J. Chem. Soc., 966 (1940).



We thought that this reaction may be suitable for quenching if it were faster than the benzhydryl chloride-base reaction in DMSO. On addition of the reaction mixture to a solution of a known excess of an ionic azide salt in DMSO, the unreacted benzhydryl chloride would react with the azide ion. The excess azide would then be complexed with a ferric salt. Ferric ions are known to react with ionic azides to give a deep violet color complex.[29] The color complex was formed when ferric and azide ions were brought together in DMSO. By using a rapid stopped-flow set-up (Figure 11), solutions in DMSO (both of equal concentration) of sodium azide in one vessel and benzhydryl chloride in the other were forced together by a pressure of 5 p.s.i. of dry nitrogen gas into a mixing chamber and quenched in excess ferric chloride in DMSO.* No violet color

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(29) C. Roberson and C. Austin, Anal. Chem., <u>29</u>, 854 (1957); A. Anton and J. Dodd, Anal. Chem., <u>32</u>, 1209 (1960).

(*) Dividing the volume of the reaction tube (0.2 ml.) by the flow-rate (0.76 ml. DMSO/sec.) gives the time spent by the mixed reactants in the reaction tube. The flow-rate was calculated from 3 independent runs for times to collect 25 ml. of the reaction mixture: 32.5, 32.7 and 32.7 seconds.

appeared , showing complete reaction of benzhydryl chloride with azide ions within the flow system. The time spent by the reactants together in the flow system was calculated to be under 0.3 seconds. The mixing efficiency was found to be very good from the loss of color observed when a 0.1 M NaOH solution containing phenolphthalein was mixed with hydrochloric acid about 1% more concentrated. The time required for this complete mixing was found to be less than 0.05 sec. (i.e., within 2 cm. of the mixing chamber).

The use of the colorimetric method to follow the reaction rate depends on the validity of Beer's Law under the circumstances of our measurements. To check this point the wavelength of maximum absorbance for the ferric azide complex in DMSO in the visible region was first determined in a Beckman DK-2A recording spectrophotometer. This was found to be 580 mμ, which is about 100 mμ higher than the value found in aqueous solution.[29] This shift could be attributed to the DMSO solvent system. The change of absorbance with concentration of the complex was measured in a Bausch and Lomb Spectronic 20 colorimeter. The results are recorded in Table I, and are also depicted in Figure 10 which shows that Beer's Law is obeyed in the concentration region of azide used to quench the reaction.

As the reaction progresses there will be less and less benzhydryl chloride present. On quenching in sodium azide solution whose concentration is equal to the initial concentration of benzhydryl chloride there will be more and more sodium azide left unreacted, which in turn will form a stronger color complex with the ferric ion solution. By reading the absorbance of the complex corresponding to a certain reaction time, the concentration of excess azide could be calculated by comparison to the absorbance corresponding to infinity time. Subtracting the concentration of the excess azide from the initial concentration gives the concentration of benzhydryl chloride at that time since reactant halide and azide are in equal initial concentrations.

$$(\text{Initial conc. of azide})(A_t/A_\infty) = (\text{Conc. of azide at } t)$$

where

A_t = Absorbance of ferric azide at a certain reaction time, t.

A_∞ = Absorbance of ferric azide at infinity time, ∞.

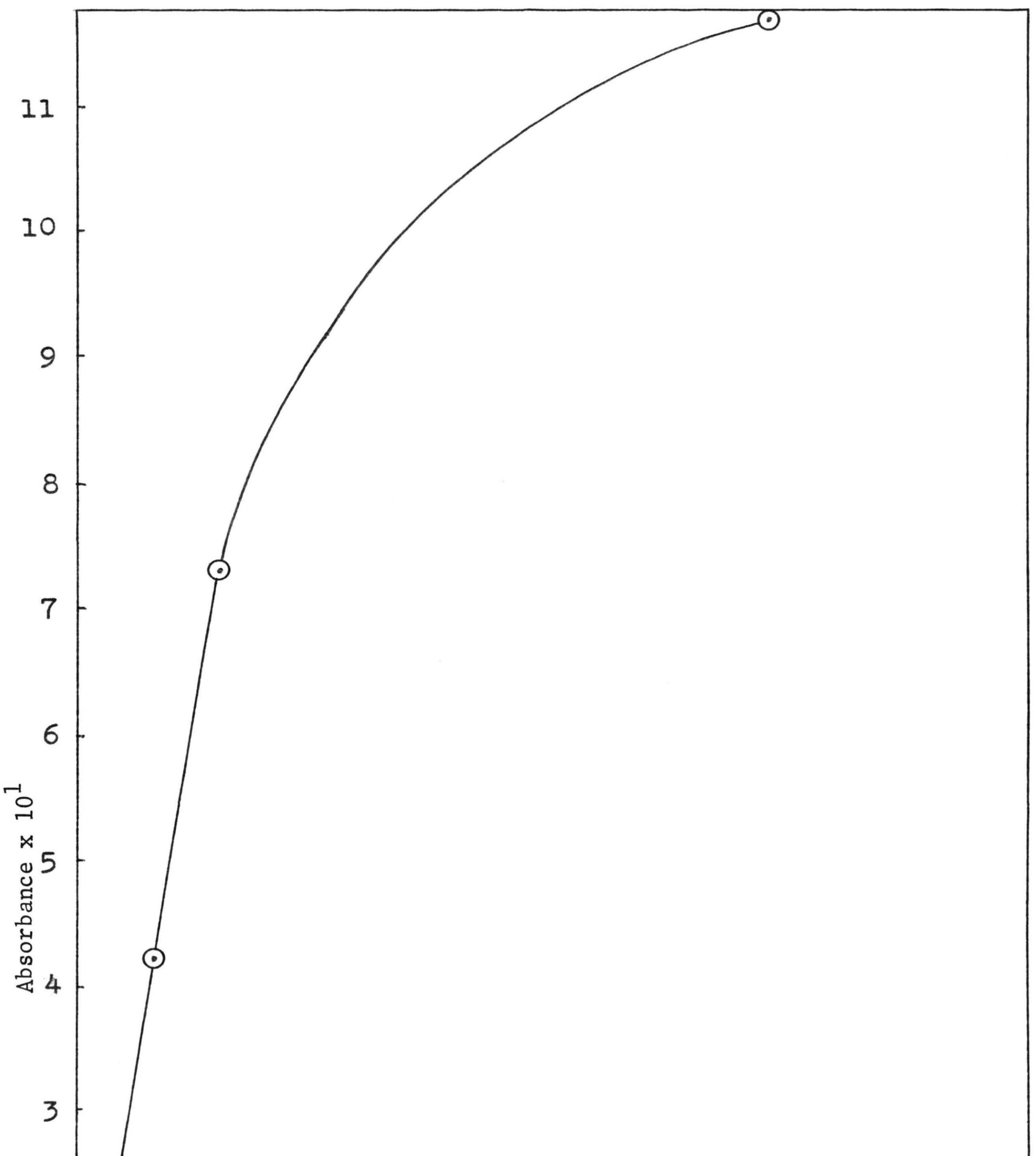
TABLE I

THE CHANGE OF ABSORBANCE WITH CONCENTRATION OF THE FERRIC AZIDE COLOR COMPLEX.*

Concentration of azide (M)	A (580 mμ)
0.02500	1.250
0.00500	0.730
0.00250	0.420
0.00050	0.155
0.00025	0.082

* Figure 10 is a graphical plot of these results.

Figure 10 PLOT OF ABSORBANCE VS. CONCENTRATION FOR THE FERRIC AZIDE COLOR COMPLEX. (BEER'S LAW)


Absorbance x 10^1
11
10
9
8
7
6
5
4
3
2
1
50
100
150
200
250
300
C x 10^4

Conventional Kinetic Technique.

The reaction we intended to study was reported in the literature to be instantaneous.[11] This prompted us to construct and employ a rapid stopped-flow apparatus, modeled after Wahl's,[30] as shown in Figure 11. When the analytical method to follow the reaction with time was developed, an approximate half-life of ½ hour at 25° was found. The method for fast reactions was then abandoned and conventional means were employed.

A kinetic run in detail was as follows: Benzhydryl chloride (0.404 g.) was weighed directly into a 100 ml. volumetric flask and the solution made up to the mark with distilled DMSO. Potassium *t*-butoxide (0.224 g.) was also weighed directly into a 100 ml. volumetric flask and the solution made to the mark with distilled DMSO. Both volumetric flasks were thermostated in a Lauda constant temperature bath set at 25° ± 0.02°. A third empty flask was kept in the water bath. After about 20 minutes, 50 ml. of each of the organic halide and of the base solutions were added by pipet to the third flask which was immediately and vigorously shaken to ensure good mixing, and the electric timer started. An immediate red-orange color developed in the reaction flask. Five milliliter samples were withdrawn

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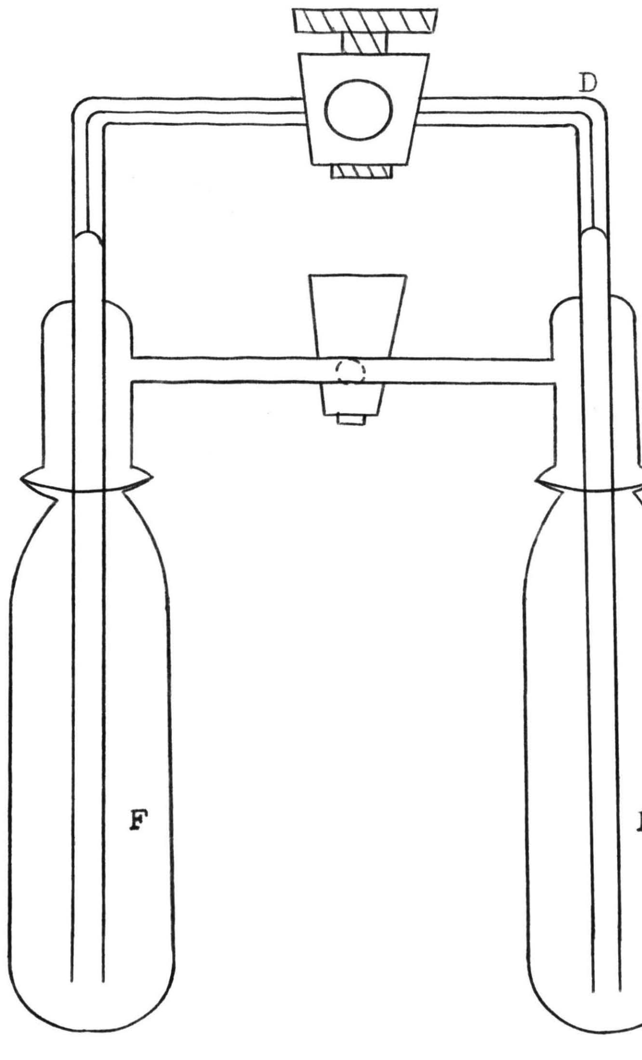
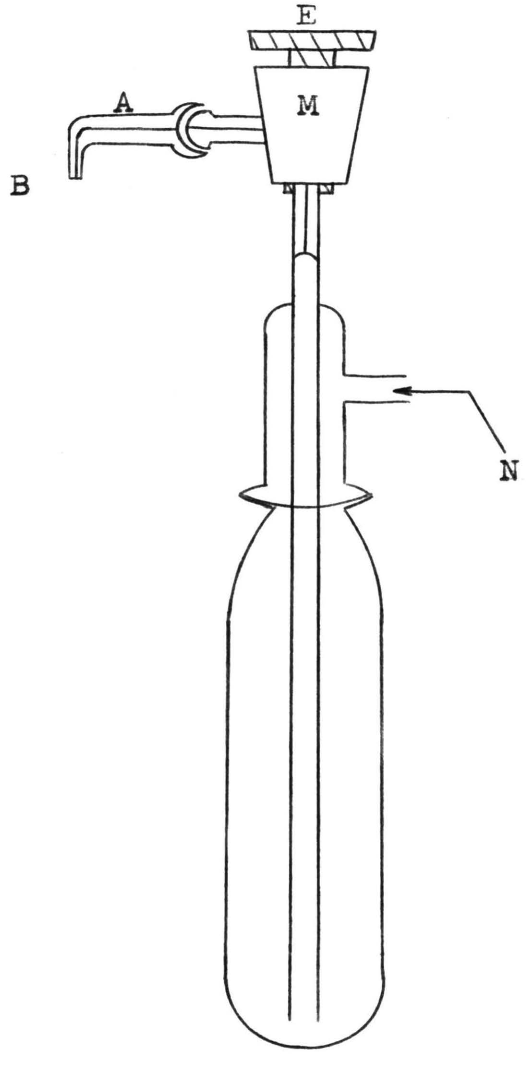
(30) A. C. Wahl and B. M. Gordon, J. Am. Chem. Soc., 80, 273 (1958).

from the reaction flask at certain recorded intervals of time and immediately quenched in 5 ml. of sodium azide in DMSO. The concentration of the sodium azide was set equal to the initial concentration of the organic halide in the reaction mixture. An equal amount of excess ferric chloride was added to each of the quenched reaction samples, and the absorbance of the violet color complex was immediately measured and recorded.

Figure 11 RAPID STOPPED-FLOW APPARATUS.

A - Reaction tube
B - Rate-controlling tip
D - Capillary tubing
E - Teflon plug
M - Mixing chamber
N - Compressed nitrogen gas inlet
F and F' - Reservoirs


D
F
F'


E
A
M
B
N

Kinetic Data.

Run 15A

At 25.0°.

Concentration of Benzhydryl Chloride = 0.010 mole/l

Concentration of Potassium t-Butoxide = 0.010 mole/l

Time in min.	0.42	4.10	8.05	11.5	15.2	21.8	29.3
Absorbance	0.05	0.07	0.09	0.10	0.12	0.14	0.16

Infinity absorbance = 0.32 $t_{\frac{1}{2}} = 37$ min.

Run 17A

At 25.0°.

Concentration of Benzhydryl Chloride = 0.010 mole/l

Concentration of Potassium t-Butoxide = 0.010 mole/l

Time in min.	11.5	16.0	20.6	26.7	33.9	42.6	49.1
Absorbance	0.20	0.27	0.33	0.42	0.46	0.47	0.51

Infinity absorbance = 0.90 $t_{\frac{1}{2}} = 35$ min.

Run 1E

At 25.0°.

Concentration of Benzhydryl Chloride = 0.010 mole/l

Concentration of Potassium t-Butoxide = 0.010 mole/l

Time in min.	0.90	4.20	7.70	11.3	15.6	18.7	22.5
Absorbance	0.18	0.20	0.23	0.29	0.31	0.34	0.36

Infinity absorbance = 1.10 $t_{\frac{1}{2}} = 38$ min.

Run 9A

At 25.0°.

Concentration of Benzhydryl Chloride = 0.010 mole/l

Concentration of Potassium t-Butoxide = 0.020 mole/l

Time in min.	0.66	3.80	7.00	11.5	14.5	19.1	22.6
Absorbance	0.29	0.32	0.43	0.45	0.52	0.72	0.77

Infinity absorbance = 1.40 $t_{\frac{1}{2}}$ = 19 min.

Run 2E

At 25.0°.

Concentration of Benzhydryl Chloride = 0.010 mole/l

Concentration of Potassium t-Butoxide = 0.020 mole/l

Time in min.	0.90	3.80	6.60	9.20	12.5	15.4	17.9
Absorbance	0.27	0.35	0.40	0.42	0.48	0.50	0.52

Infinity absorbance = 1.00 $t_{\frac{1}{2}}$ = 16 min.

Run 7A

At 25.0°.

Concentration of Benzhydryl Chloride = 0.020 mole/l

Concentration of Potassium t-Butoxide = 0.020 mole/l

Time in min.	3.60	5.30	7.10	9.10	11.2	13.1	19.3
Absorbance	0.09	0.13	0.21	0.33	0.35	0.40	0.47

Infinity absorbance = 0.49 $t_{\frac{1}{2}}$ = 8 min.

Run 18A

At 25.0°.

Concentration of Benzhydryl Chloride = 0.020 mole/l

Concentration of Potassium *t*-Butoxide = 0.020 mole/l

Time in min.	0.55	6.50	10.8	14.9	20.2	28.5	33.0
Absorbance	0.17	0.20	0.23	0.29	0.41	0.45	0.52

Infinity absorbance = 0.52 $t_{\frac{1}{2}}$ = 12 min.

Run 3E

At 25.0°.

Concentration of Benzhydryl Chloride = 0.020 mole/l

Concentration of Potassium *t*-Butoxide = 0.020 mole/l

Time in min.	1.00	3.90	7.20	10.7	14.8	19.1	22.1
Absorbance	0.40	0.44	0.46	0.49	0.52	0.64	0.66

Infinity absorbance = 0.95 $t_{\frac{1}{2}}$ = 9 min.

Run 1F

At 20.0°.

Concentration of Benzhydryl Chloride = 0.010 mole/l

Concentration of Potassium t-Butoxide = 0.010 mole/l

Time in min.	1.10	4.70	7.80	11.5	15.9	20.6	24.8
Absorbance	0.15	0.17	0.21	0.23	0.29	0.33	0.35

Infinity absorbance = 0.89 $k = 5.05 \times 10^{-2}$ l/mole-sec.

Run 17A

At 25.0°.

Concentration of Benzhydryl Chloride = 0.010 mole/l

Concentration of Potassium t-Butoxide = 0.010 mole/l

Time in min.	11.5	16.0	20.6	26.7	33.9	42.6	49.1
Absorbance	0.20	0.27	0.33	0.42	0.46	0.47	0.51

Infinity absorbance = 0.90 $k = 4.80 \times 10^{-2}$ l/mole-sec.

Run 2F

At 30.0°.

Concentration of Benzhydryl Chloride = 0.010 mole/l

Concentration of Potassium t-Butoxide = 0.010 mole/l

Time in min.	1.20	3.70	6.80	10.7	14.4	19.0	22.6
Absorbance	0.21	0.23	0.26	0.29	0.31	0.31	0.34

Infinity absorbance = 0.71 $k = 6.95 \times 10^{-2}$ l/mole-sec.

Run 3F

At 35.0°.

Concentration of Benzhydryl Chloride = 0.010 mole/l

Concentration of Potassium t-Butoxide = 0.010 mole/l

Time in min.	1.20	4.50	9.40	12.3	20.0
Absorbance	0.60	0.73	0.75	0.80	0.89

Infinity absorbance = 1.60 $k = 13.90 \times 10^{-2}$ l/mole-sec.

Run 4F

At 40.0°.

Concentration of Benzhydryl Chloride = 0.010 mole/l

Concentration of Potassium t-Butoxide = 0.010 mole/l

Time in min.	1.40	5.40	9.40	13.2	16.3	19.6	23.1
Absorbance	0.25	0.29	0.32	0.35	0.40	0.44	0.52

Infinity absorbance = 0.68 $k = 16.70 \times 10^{-2}$ l/mole-sec

TABLE II

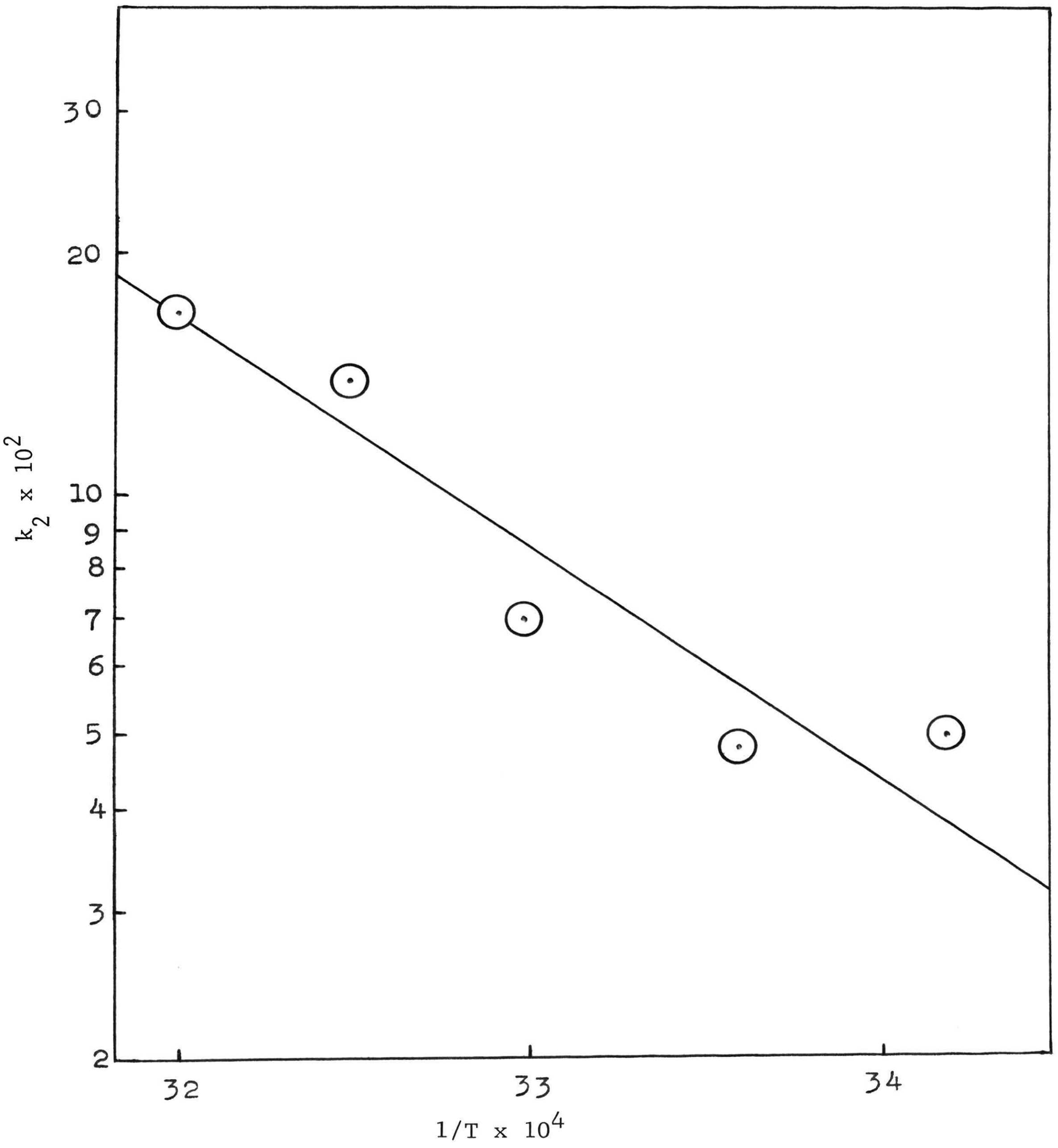
DATA FOR ACTIVATION ENERGY CALCULATION.*

k, 1/mole-sec.	t°C.	T°K.	$1/T \times 10^4$
5.05×10^{-2}	20.0	293	34.2
4.80×10^{-2}	25.0	298	33.6
6.95×10^{-2}	30.0	303	33.0
13.90×10^{-2}	35.0	308	32.5
16.70×10^{-2}	40.0	313	32.0

* Figure 12 is a graphical plot of these results.

$E_a = \text{Slope} \times 2.303 \times 1.987 = 13{,}200$ calories

Figure 12 PLOT OF SECOND-ORDER RATE CONSTANTS ON A LOG SCALE *VS*. 1/T FOR DETERMINATION OF ARRHENIUS ACTIVATION ENERGY, E_a.



30
20
10
9
8
7
6
5
4
3
2
$k_2 \times 10^2$
32
33
34
$1/T \times 10^4$

IV. DISCUSSION

THE PRODUCT OF THE REACTION

The product of the reaction between benzhydryl chloride and potassium t-butoxide in DMSO is tetraphenylethylene. This compound was formed in a quantitative yield and was shown by infrared analysis, nmr spectrum and its melting point to be not contaminated with other possible products. Earlier work[31] has shown that benzhydryl chloride gives benzophenone in 44% yield by heating in DMSO for 2 hours at 100°. Hydrolysis by adventitious moisture would convert benzhydryl chloride to benzhydrol. Neither of these 2 compounds were formed under the reaction conditions and with the precautions we employed. The infrared spectra of reagent grade benzophenone (Figure 6) and reagent grade benzhydrol (Figure 7) are given for comparison with the infrared spectrum of the tetraphenylethylene prepared in this laboratory (Figure 5).

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(31) H. Nace and J. Monagle, J. Org. Chem., 24, 1792 (1959).

THE ORDER OF THE REACTION

Reactions carried out with various concentrations of benzhydryl chloride and _t_-butoxide ion seem to indicate that the over-all reaction order is two, first order in each of the reactants.

The results of Table III suggest the following rate law,

$$\text{Rate} = dx/dt = k_2 [\text{Benzhydryl chloride}] [\underline{t}\text{-Butoxide}] .$$

In the case of equal concentrations of reactants,

$$dx/dt = k_2 \; [C]^2$$

and,

$$dx/[C]^2 = k_2 \; dt$$

This may be readily integrated to

$$k_2 = 1/t_{\frac{1}{2}} \; [C_o]$$

where C_o = initial concentration of reactants

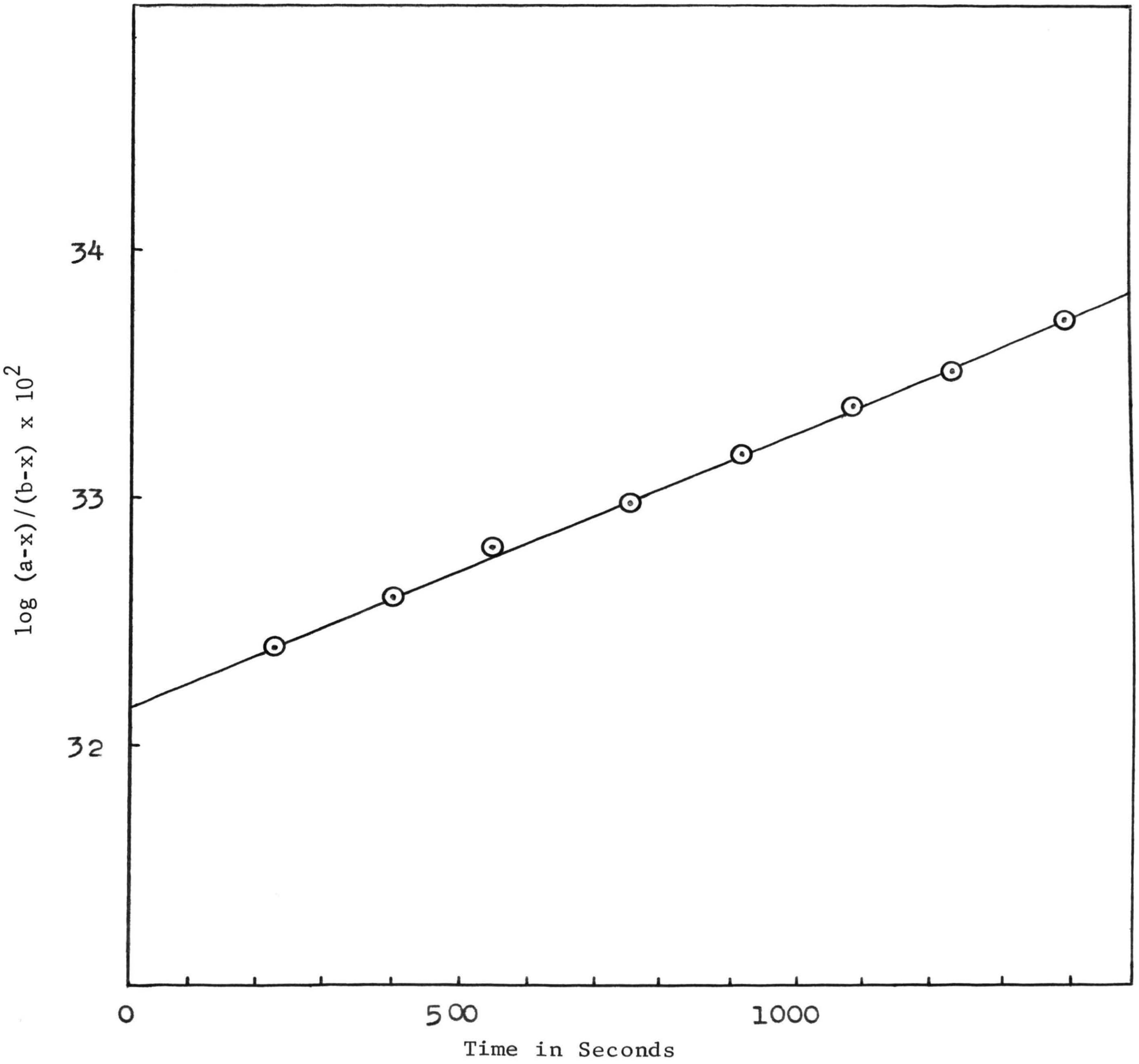
TABLE III

SECOND ORDER RATE CONSTANTS FOR REACTION OF BENZHYDRYL CHLORIDE WITH POTASSIUM t-BUTOXIDE IN DMSO AT 25.0°.*

Run No.	$t_{\frac{1}{2}}$ (min.)	Conc. of Halide, M	Conc. of t-Butoxide, M	$k_2 \times 10^2$ M^{-1} sec^{-1}
15A	37	0.010	0.010	4.50
17A	35	0.010	0.010	4.76
1E	38	0.010	0.010	4.38
			Average	4.55
9A	19	0.010	0.020	14.90
2E	16	0.010	0.020	9.45
			Average	12.17
7A	8	0.020	0.020	10.40
18A	12	0.020	0.020	6.94
3E	9	0.020	0.020	9.26
			Average	8.86

* For equal concentration of reactants the rate constants were calculated by $k_2 = 1/t_{\frac{1}{2}} [C_o]$. Values of k_2 for runs with unequal concentrations of reactants are taken from the second order plot of their graphs. The plot of Run 2E is shown in Figure 13.

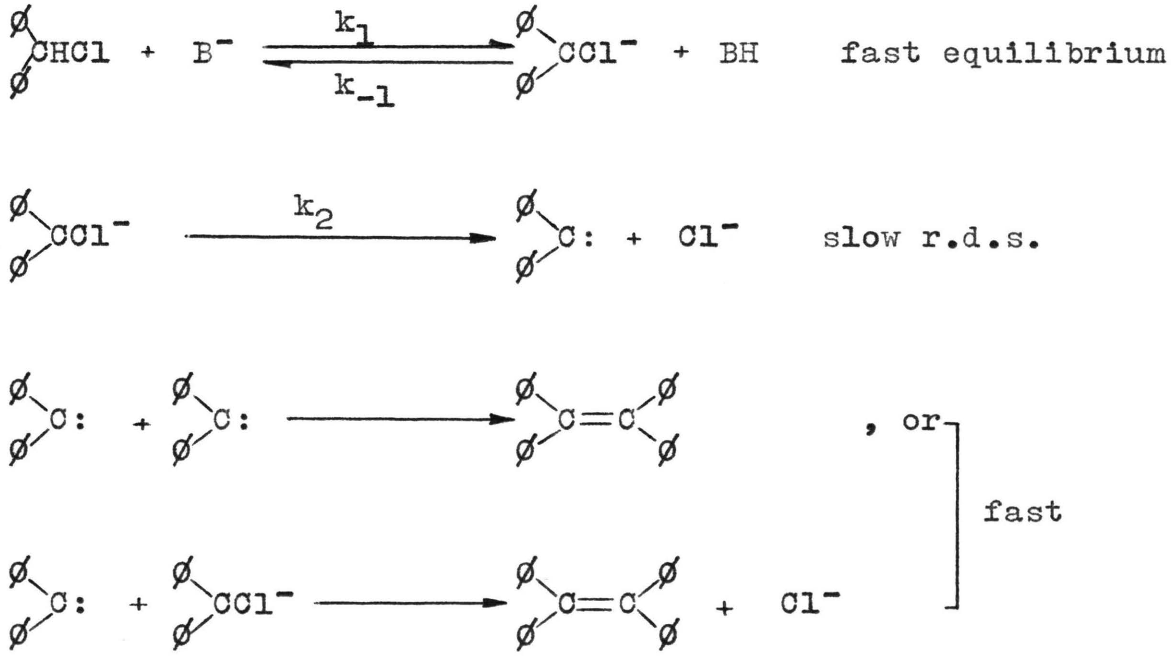
Figure 13 THE SECOND-ORDER PLOT FOR THE REACTION BETWEEN BENZHYDRYL CHLORIDE AND POTASSIUM <u>t</u>-BUTOXIDE IN DMSO AT 25.0°.


34
33
32
log (a-x)/(b-x) x 10^2
0
500
1000
Time in Seconds

MECHANISM OF THE REACTION STUDIED

The formation of tetraphenylethylene from benzhydryl chloride and strong base can be accounted for by at least two distinct mechanisms.

(A) THE α-ELIMINATION MECHANISM:



The operation of this mechanism in the p-nitrobenzyl series has recently been proved by using kinetic methods in conjunction with deuterium exchange experiments.[7,32]

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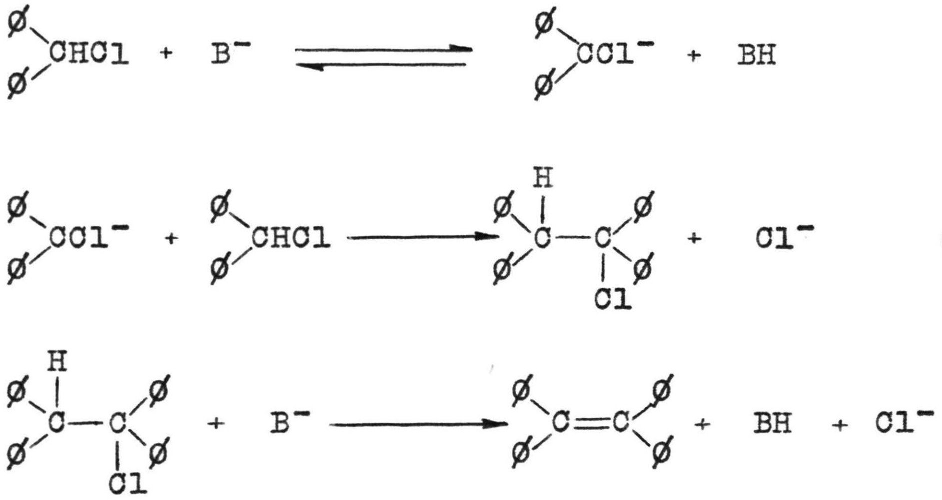
(32) C. G. Swain and E. R. Thornton, J. Am. Chem. Soc., 83, 4033 (1961).

(B) THE BIMOLECULAR ALKYLATION-DEHYDROHALOGENATION:



(I)

Isolation of the intermediate "dimeric halide" (I) at low temperatures was taken as evidence for the occurrence of this mechanism in the benzyl and the benzhydryl series.[2]

Mechanisms (A) and (B) are distinguishable kinetically, provided that the proton transfer in the first step in each mechanism is faster than the succeeding steps. Mechanism (A) would demand first-order kinetics in the benzhydryl halide, while mechanism (B) is satisfied by second-order kinetics in the organic halide.

On account of the relative acidity[33] of benzhydryl chloride, i.e., 10^2-10^3 times greater than DMSO, the react-

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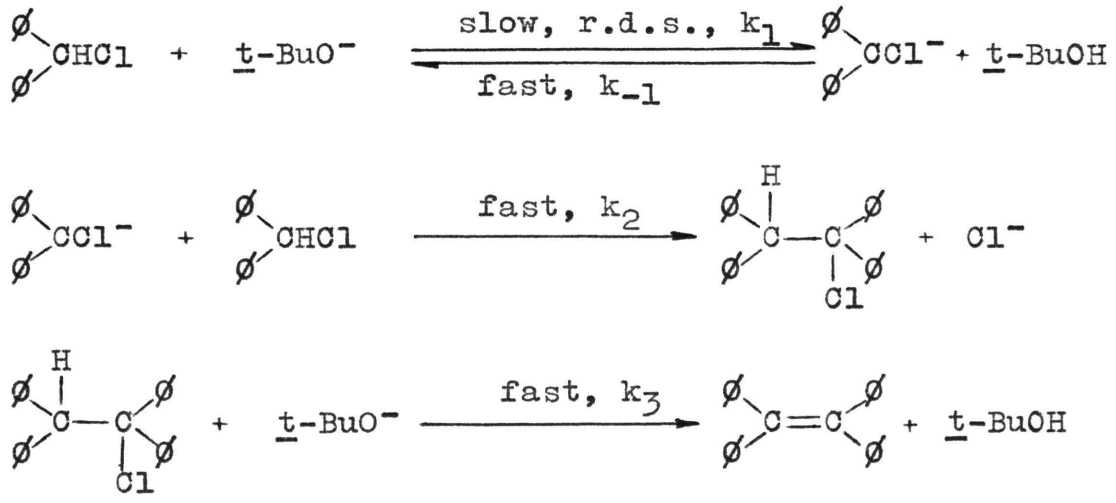
(33) E. C. Steiner and J. M. Gilbert, J. Am. Chem. Soc., 85, 3054 (1963); A. Ledwith and N. McFarlane, Proc. Chem. Soc., 108 (1964).

ion studied would strongly favor carbanion formation in DMSO, and this was supported by the immediate formation of a red color.

The failure to trap a benzhydryl carbene intermediate does not disprove its existence in this reaction system, only that if it is present in the reaction mixture, it must possess a very much greater reactivity for itself or for the benzhydryl carbanion than the electron rich double bond of the trapping agent.

At a first glance, our results seem to favor the $\underline{\alpha}$-elimination mechanism. However, an alternative mechanism (C) is possible.

(C)



Mechanisms (A) and (C), but not (B), lead to second-order overall kinetics as is evidenced from the following:

(A)'

$$d[Cl^-]/dt = k_2[\phi_2CCl^-]$$

But

$$[\phi_2CCl^-] = K_e[\phi_2CHCl][B]$$

where K_e = equilibrium constant = k_1/k_{-1}

Therefore,

$$d[Cl^-]/dt = k_1k_2/k_{-1}\ [\phi_2CHCl][B]$$

$$= k_2'[\phi_2CHCl][B]$$

where $k_2' = k_1k_2/k_{-1}$

(C)'

$$-d[\phi_2CHCl]/dt = k_1[\phi_2CHCl][\underline{t}\text{-BuO}^-]$$

where k_1 is second-order rate constant

A distinction between mechanisms (A) and (C) may be accomplished by deuterium exchange experiments.

We believe that the isolation of the "dimeric halide" by Hauser and co-workers[2] at low temperatures does not necessarily indicate that mechanism (B) is operative in liquid ammonia. Only kinetic measurements coupled with tracer techniques on the parent compound as well as on this "dimeric halide" would help in establishing the true mechanism.

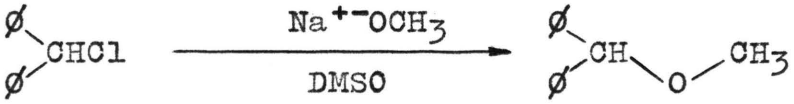
POTASSIUM t-BUTOXIDE SOLUTIONS IN DMSO

A stock solution of potassium t-butoxide would turn a deep orange-yellow color on standing if it were simply stored in a glass stoppered bottle. Addition of this deep colored base to benzhydryl chloride produced no apparent reaction, only a slight dilution of the color of the base was observed. Not much is known about the equilibrium between t-butoxide and DMSO and the rate at which it is attained.

$$t\text{-BuO}^- + \text{DMSO} \rightleftharpoons t\text{-BuOH} + \text{DMSO}^-$$

There is evidence, however, for the existence of the dimsyl ion, DMSO$^-$,[13] but virtually nothing has been reported about it even in a semi-quantitative manner. We wondered whether our observation was due to a slow attainment of equilibrium between t-BuO$^-$ and DMSO coupled with an inhibited activity for the dimsyl ion generated, of necessity, in the vicinity of a t-BuOH molecule. Infrared spectral scans of the 3500 cm^{-1} region at 10-min. intervals for a period of 40 minutes showed a continuous growth of an OH absorption peak from nil shortly after mixing t-BuO$^-$ and DMSO to quite an evident peak, possibly representing an equilibrium, at about 40 minutes from mixing (Figure 14 a - e). We would have liked to hang firmly on this reproducible observation to explain the behavior of aged solutions of t-BuO$^-$ in DMSO and also to account for some of the erratic behavior encountered in some of our rate measurements. However, the straw could not stay afloat for long. We constructed another experiment to further test our postulate. In this experiment we handled all materials under a blanket of dry nitrogen. Potassium t-butoxide solution in DMSO was prepared and stored under a nitrogen atmosphere for 4 days. It was then reacted with a freshly prepared benzhydryl chloride solution in DMSO to give a quantitative yield of the ethylene. This shows that a quantitative yield of tetraphenylethylene is obtained if the solution is freshly prepared or if allowed to stand for a length of time (92 hours) in the absence of air. From this observation it was concluded that the partially exposed base (not sealed under N_2) in DMSO had found the dimsyl ion reactive with air as reported in the literature.[15]

In order to find if other bases similar to the t-butoxide ion, i.e., alkoxide ions, would attain a similar equilibrium with DMSO, the methoxide ion was employed. Sodium methoxide was allowed to react with benzhydryl chloride in DMSO. As shown in the Experimental Section the product was definitely not tetraphenylethylene but probably benzhydryl methyl ether.



This seems to support the non-existence of an equilibrium between this alkoxide ion and DMSO. As would be expected, we find that methyl alcohol is a stronger acid than t-butyl alcohol,[34] i.e., the t-butoxide ion being the stronger base, would have a much greater affinity for a DMSO proton.

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(34) R. T. Morrison and R. N. Boyd, "Organic Chemistry", Allyn and Bacon, Inc., Boston, 1962, p 344.

BENZHYDRYL CHLORIDE SOLUTIONS IN DMSO

In the early stages of this investigation we prepared stock solutions of benzhydryl chloride in DMSO which could be diluted appropriately for rate measurements. We observed that the reaction rates were both fast and erratic, and we wondered whether a solution of benzhydryl chloride in DMSO had undergone some transformation on standing. The nmr spectra, one taken immediately after preparing a stock solution (Figure 15) and another one week later (Figure 15), seemed to indicate the possible existence of a benzhydryl carbonium ion, presumably as the carbonium chloride ion-pair, in aged solutions. With more ageing, the signal for the proton we assigned to the carbonium ion seemed to grow in intensity at the expense of a decrease in the peak height of the proton of benzhydryl chloride (Figure 16). Our assignment of the benzhydryl carbonium ion peak was well backed by work reported by Olah[35] on the nmr spectra of benzhydryl carbonium ions produced by other means, e.g., the decarbonylation of the crystalline diphenylacetyl fluoride-antimony pentafluoride complex.

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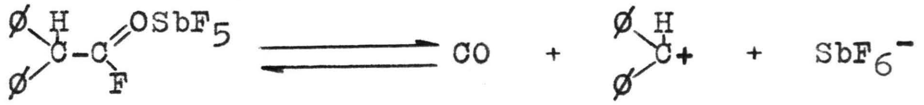
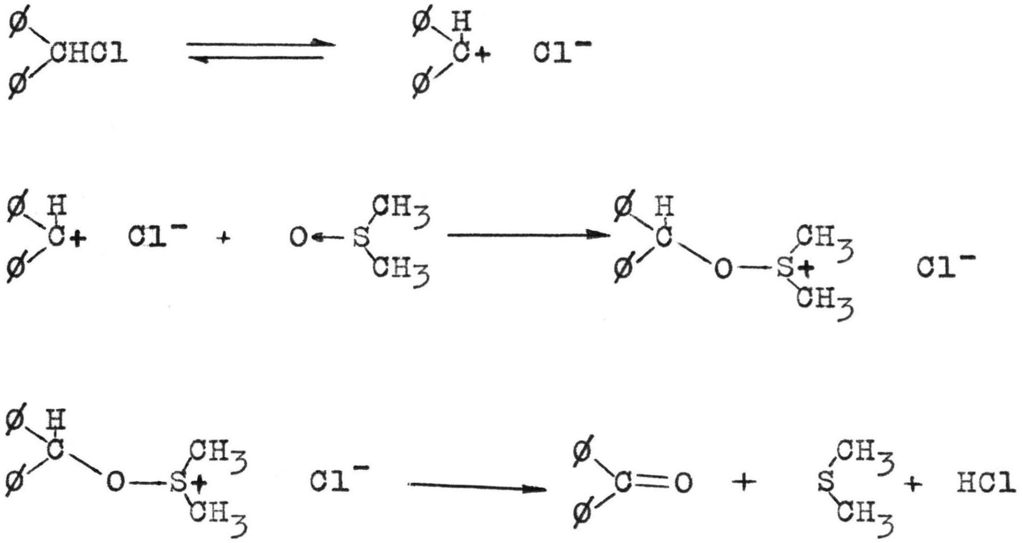
(35) G. A. Olah, J. Am. Chem. Soc., <u>86</u>, 933 (1964).

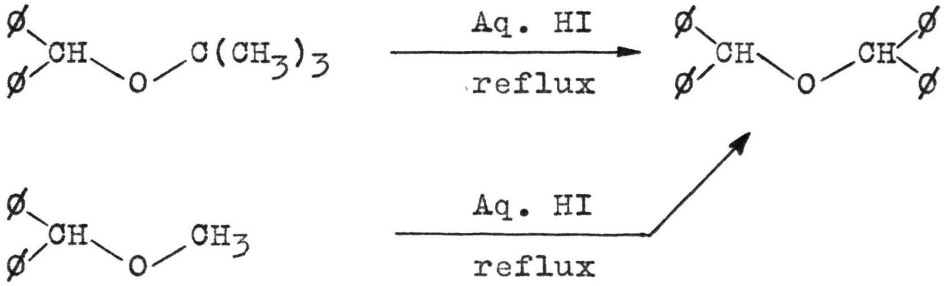


The transformation of benzhydryl chloride to benzophenone in DMSO by heating for a couple of hours[31] may be explained in terms of a carbonium chloride ion-pair.



MECHANISM FOR THE FORMATION OF BENZHYDRYL ETHER.

The cleavage of benzhydryl t-butyl ether and of benzhydryl methyl ether in aqueous hydroiodic acid is suggestive of a benzhydrol intermediate.



Thus, when benzhydrol was refluxed in aqueous hydroiodic acid under identical conditions the product was found to be benzhydryl ether.

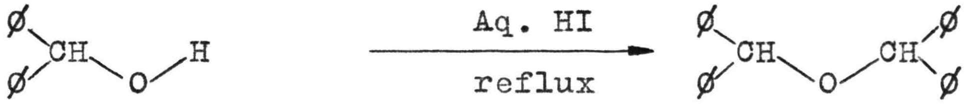


Figure 14 CHANGE IN THE INFRARED ABSORPTION SPECTRA OF POTASSIUM t-BUTOXIDE IN DMSO WITH TIME.

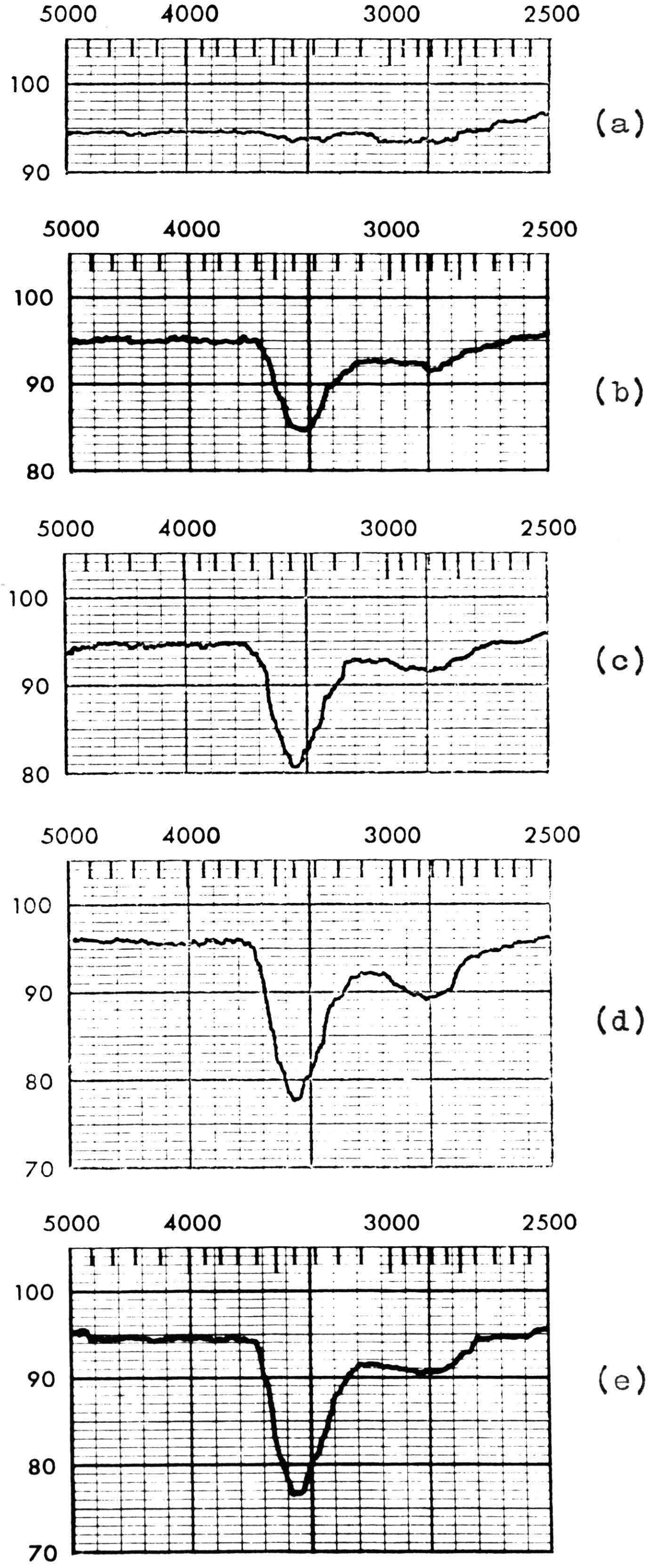

5000
4000
3000
2500
100
90
(a)
5000
4000
3000
2500
100
90
80
(b)
5000
4000
3000
2500
100
90
80
(c)
5000
4000
3000
2500
100
90
80
70
(d)
5000
4000
3000
2500
100
90
80
70
(e)

Figure 14

Figure 15 NMR SPECTRA OF AGED BENZHYDRYL CHLORIDE IN DMSO. A DECREASE IN THE BENZHYDRYL METHYL PROTON SIGNAL.

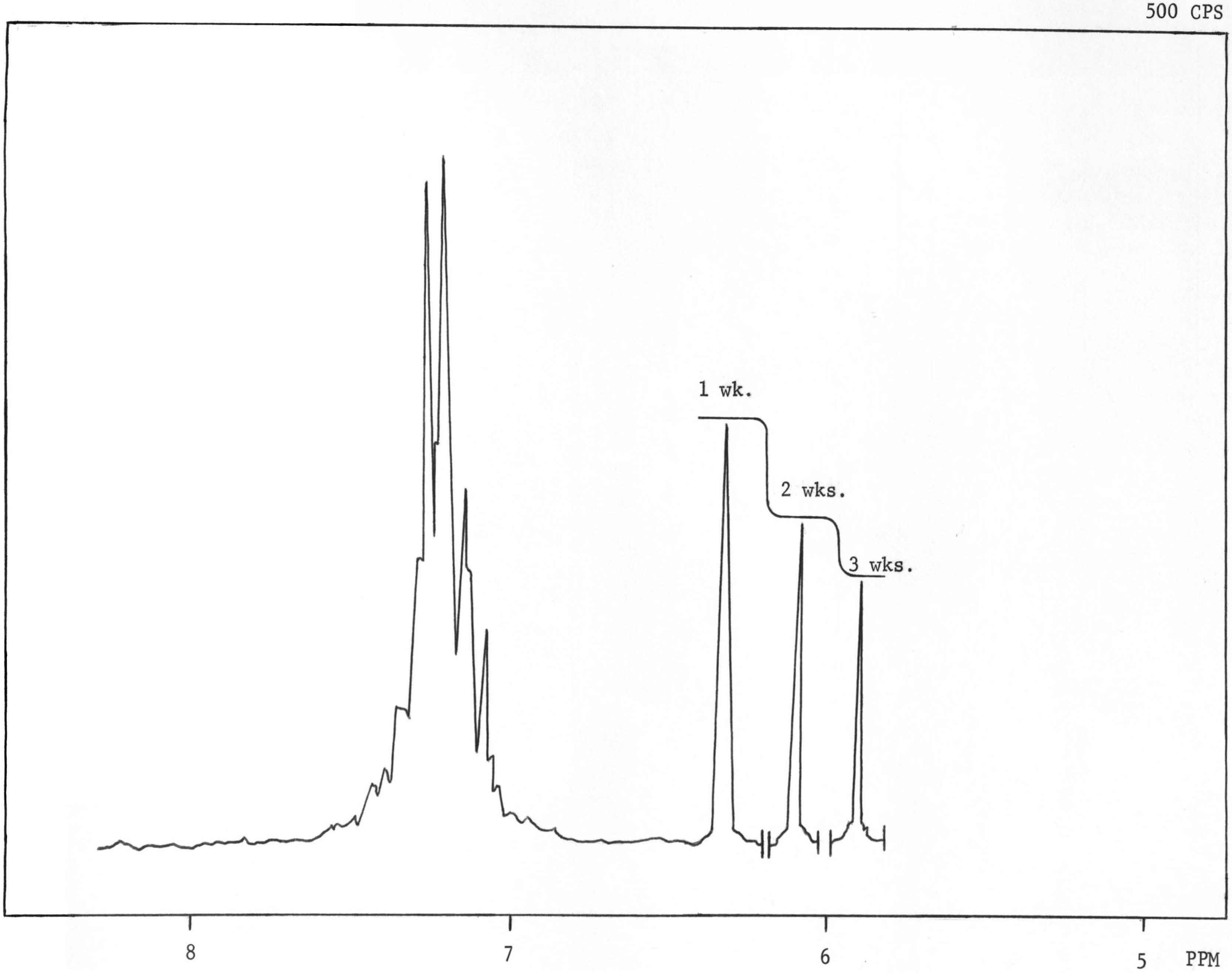
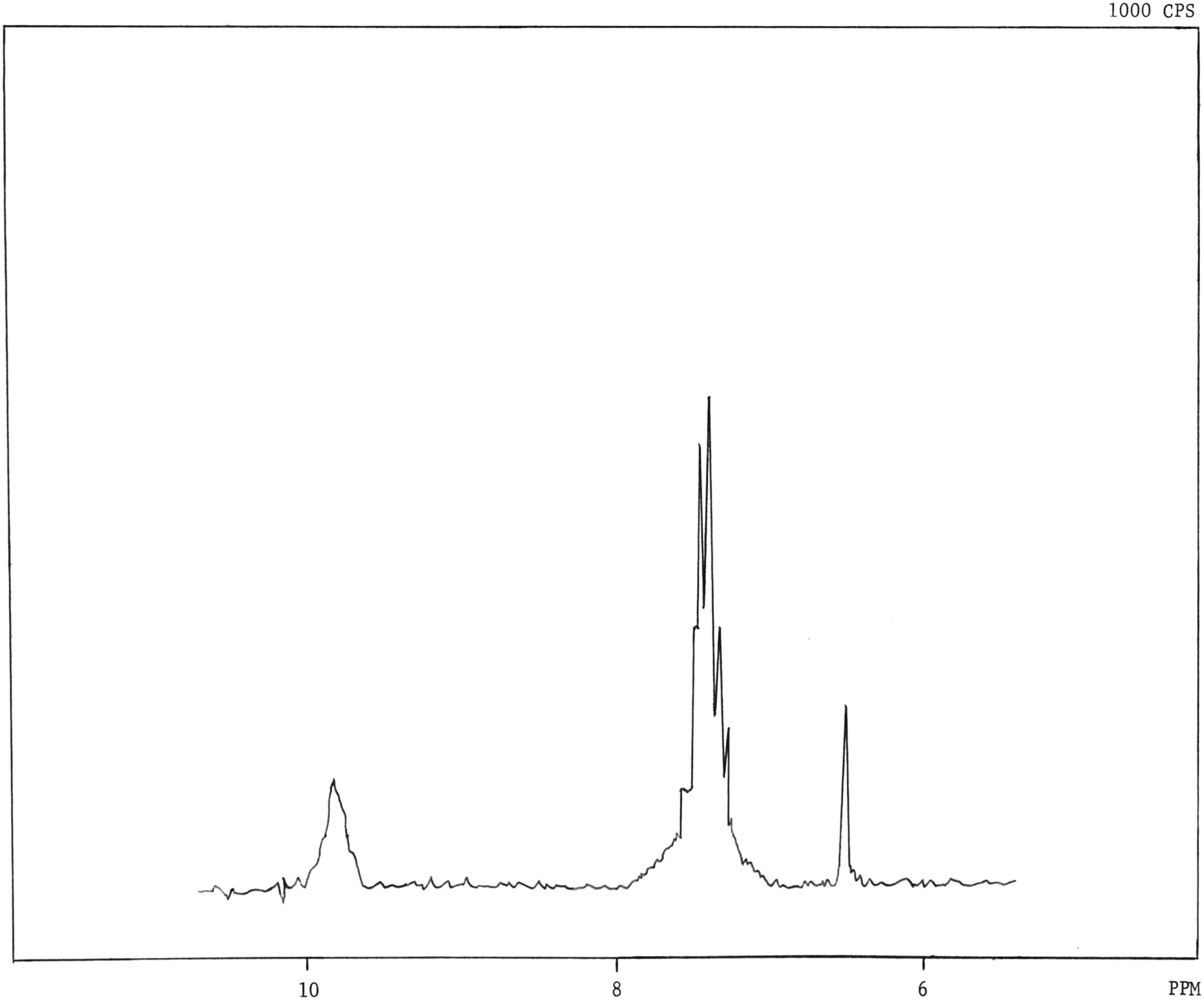

500 CPS
1 wk.
2 wks.
3 wks.
8
7
6
5
PPM

Figure 16 NMR SPECTRUM OF AGED BENZHYDRYL CHLORIDE IN DMSO. THE BENZHYDRYL CARBONIUM ION SIGNAL.


1000 CPS
10
8
6
PPM

V. CONCLUSIONS

Benzhydryl chloride is transformed quantitatively to tetraphenylethylene by the action of potassium *t*-butoxide in DMSO. The reaction, contrary to reports in the literature, has a measurable rate, and seems to be second order overall. In the absence of information concerning the relative rate of deuterium exchange in benzhydryl chloride under the reaction conditions described in this thesis, we believe that a clear cut distinction between *α*-elimination and the alkylation-dehydrohalogenation mechanism is not possible at this stage.

VI. RECOMMENDATIONS

(1) Exchange experiments on benzhydryl chloride under normal reaction conditions would definitely elucidate whether or not the first step of the reaction is fast and reversible. Hence it is recommended that the reaction between benzhydryl chloride and potassium t-butoxide be carried out in DMSO-D_6 and the deuterium content be analyzed after arresting the reaction at partial conversion to the product.

(2) A quantitative study of the DMSO-potassium t-butoxide equilibrium is very much needed to better understand the system under investigation.

(3) Other methods for following the reaction rate should should be attempted.

A. Spectrophotometrically

B. Use of ion exchange resin to quench and separate ionic from covalent chloride.

(4) Studies of the chlorine kinetic isotope effects, $k_{Cl^{35}}/k_{Cl^{37}}$, to determine the extent of bond breaking in the transition state should be carried out and compared with typical β-elimination and with α-elimination reactions.

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