Dehydrobromination of the free radical bromide. Dehydrobromination of the free radical bromide, purified as described in the preceeding paragraph, was done by refluxing 6 hr. with anhydrous pyridine. At the end of the heating period the mixture was poured into ice-cold water which had been acidified with hydrochloric acid. The ether extract was washed with water and dried over anhydrous magnesium sulfate. Distillation at atmospheric pressure gave a product with b.p. 133–135°, $n_D^{25.5}$ 1.4560 (lit.[3] for 1-methylcycloheptene: b.p. 136°, n_D^{25} 1.4563).

Isomerization experiment. 3-Methylcycloheptene, prepared as indicated above, was refluxed in a pyridine–pyridine hydrobromide mixture to simulate the dehydrobromination reaction conditions. The reaction mixture was poured into cold, dilute hydrochloric acid, the olefin extracted with several portions of ether, and the ether extracts were combined and dried over anhydrous magnesium sulfate. After the ether was removed under reduced pressure the infrared spectrum of the residual oil was obtained, and this spectrum was found to be identical to the spectrum of an authentic sample of 3-methylcycloheptene.

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Decolorization of Triphenylmethyl Carbonium Ion by Ethyl Ether

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In 1921 Hantzsch noted that the addition of ethyl ether to various solutions containing the triphenylmethyl carbonium ion caused a diminution of the characteristic yellow color of the ion.[1] This he attributed to a reversal of the ion forming reaction with the regeneration of the colorless precursor to the ion. Since solid triphenylmethyl perchlorate is itself highly colored this explanation can hardly hold for the decolorization of solutions of triphenylmethyl perchlorate.

Leffler, in speculating on these observations, proposed the formation of a colorless oxonium salt with the ether as a more likely possibility.[2] If so, then the formation of the complex should follow a regular diminution in color as a function of ether concentration, and one should be able to calculate an equilibrium constant for the complex formation. Such a study has been carried out for triphenylmethyl perchlorate in acetic anhydride and for triphenylmethyl chloride in nitromethane. The results are reported below.

Solutions of triphenylmethyl perchlorate in acetic anhydride were prepared *in situ* by the addition of a stoichiometric excess of perchloric acid to a solution of triphenylcarbinol. The characteristic spectrum of the triphenylmethyl carbonium ion in this solvent is given in Fig. 1A. The solution was stable for thirty to sixty minutes after which the bands due to the carbonium ion slowly decreased in intensity. After twenty-four hours the solution was still deep orange, but the carbonium ion band had entirely disappeared. The addition of ethyl ether lessened the intensity of the carbonium ion bands, Fig. 1C. The data for a series of ether concentrations are given in Table I as are the values of the equilibrium constant calculated for the individual points assuming a one to one complex. The assumption of a two to one complex led to a great variation in the value of K. A plot of carbonium ion concentration *versus* the concentration

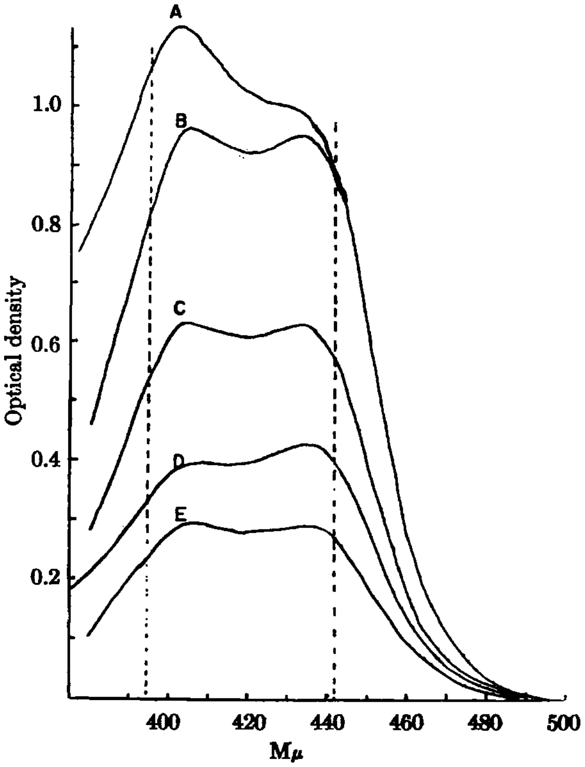

Fig. 1. The spectrum of the triphenylmethyl carbonium ion under various conditions: A, Ph_3CClO_4 ($2.75 \times 10^{-5}M$) in acetic anhydride; B, Ph_3CCl ($0.0804M$) in nitromethane; C, Ph_3CCl ($0.0777M$), Et_2O ($0.192M$) in nitromethane; D, Ph_3CClO_4 ($2.75 \times 10^{-5}M$) and Et_2O ($1.65M$) in acetic anhydride; and E, Ph_3CCl ($0.0791M$) and Et_2O ($0.736M$) in nitromethane

TABLE I

EFFECT OF ETHYL ETHER ON A $2.75 \times 10^{-5}M$ SOLUTION OF TRIPHENYLMETHYL PERCHLORATE IN ACETIC ANHYDRIDE

$(C_2H_5)_2O$	$(Ph_3C^+) \times 10^5$	$[Ph_3C{-}O(C_2H_5)^+_2] \times 10^7$	K
0.0946	2.51	24	0.99
0.1519	2.42	33	0.90
0.3952	2.10	65	0.78
0.4600	1.85	90	0.94
0.8340	1.59	116	0.88
1.650	1.06	169	0.97
2.240	0.84	191	1.02
			$K_{av} = 0.93$

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[1] A. Hantzsch, *Ber.*, 54, 2573 (1921).

[2] J. E. Leffler, *The Reactive Intermediates of Organic Chemistry*, p. 97, Interscience Publishers, New York, 1956.

of complex divided by the ether concentration was linear. Assuming a one to one complex, one may write:

$$Ph_3C^+ + (C_2H_5)_2O = [Ph_3C{-}O(C_2H_5)_2{}^+]$$

$$K = \frac{[Ph_3C{-}O(C_2H_5)_2{}^+]}{(Ph_3C^+)[(C_2H_5)_2O]}$$

The value of K taken from the slope of the plot was 0.93 which agrees with the average value of K taken from the data for the individual points.

Solutions of triphenylmethyl chloride in nitromethane have varying degrees of stability depending on the history of the solvent. Leffler and Smith[3] found that the color of the carbonium ion rapidly decreased in carefully purified commercial nitromethane. On the other hand, Evans has reported that such solutions are stable for days.[4] Pocker reported stability for twenty-four hours; the implication being that the color of the ion decreased after this time.[5] Vapor phase chromatography of a sample of a popular brand of spectroscopic grade nitromethane, purified by the method of Evans, produced four bands other than that due to the solvent itself. Thus, it seems likely that the results reported earlier by Leffler and Smith reflect impurities in their nitromethane. In order to overcome the difficulties of purifying commercial nitromethane we synthesized our own by the usual procedure.[6] This material gave only one band on vapor phase chromatography. Solutions of triphenylmethyl chloride in this material were stable for at least one hour. Three determinations of the ionization constant gave an average value of 3.48 × 10^{-4} with a maximum error of 3%. This value agrees well with those reported by Evans[7] and Pocker.[5]

The data for a series of solutions of triphenylmethyl chloride and ethyl ester in nitromethane are given in Table II. The values of K were determined on the assumption that the following equilibria existed. The pertinent equations for calculation are also given (where the superscripts *o* and *f* mean original and final concentrations, respectively).

$$Ph_3CCl \overset{K_i}{=} Ph_3C^+Cl^- \quad K_i = \frac{(Ph_3C^+)}{(Ph_3CCl)} = 3.48 \times 10^{-4}$$

$$Ph_3C^+ + (C_2H_5)_2O \overset{K}{=} Ph_3C{-}O(C_2H_5{}^+)_2{}^+$$

$$K = \frac{(Ph_3C{-}O(C_2H_5)_2)}{(Ph_3C^+)[(C_2H_5)_2O]^f} \qquad (1)$$

$$(Ph_3CCl)^f = \frac{(Ph_3C^+)}{K_i} \qquad (2)$$

$$[Ph_3C{-}O(C_2H_5)_2{}^+] = (Ph_3CCl)^o - (Ph_3CCl)^f \qquad (3)$$

$$[(C_2H_5)_2O]^f = [(C_2H_5)_2O]^o - [Ph_3C{-}O(C_2H_5)_2] \qquad (4)$$

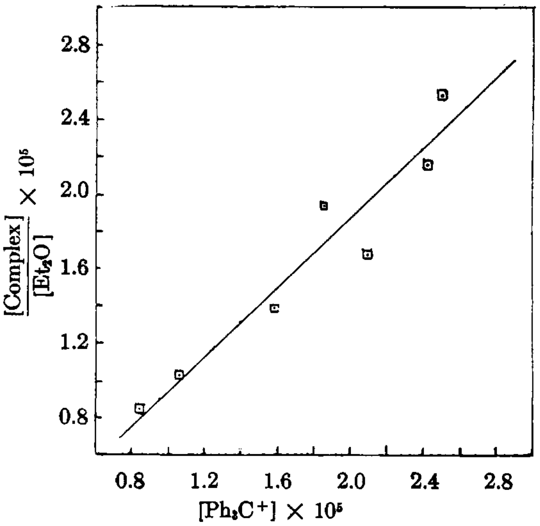

Fig. 2. A plot of the data obtained for the system triphenylmethyl perchlorate and diethyl ether in acetic anhydride

The values of K in nitromethane are not as self-consistent as those in acetic anhydride. This may be due to one or more of several reasons. The Equation 2 above may be an oversimplification. Pocker[5] has shown that solutions of triphenylmethyl chloride in nitromethane are more complex than simple ionization to an ion pair as stated by Evans.[7] For our purposes all that is required is that species other than the complex be controlled by the value of K_i and be nonabsorping in this region. In view of the constancy of K_i over a wide range of concentrations of the chloride this assumption would seem to be reasonable. Any possible variations in K_i over the concentration range of ether used in this study were ignored since no systematic variation in the values of K were noted.

Because we prepared our own nitromethane, smaller amounts were used in making up each sample than in the anhydride solvent. Thus, the variation may reflect the inaccuracies in preparing exact dilutions of ether in a small solvent sample.

Finally, solutions of triphenylmethyl chloride and ether in nitromethane were not so stable as those without the ether. The color of the carbonium ion started to decay within ten minutes after the solutions were prepared. An attempt was made to carry out a similar study with triphenylmethyl perchlorate in nitromethane. In the absence of ether the carbonium ion was stable for over a day. On the addition of ether the color decreased rapidly, and the characteristic spectrum of the carbonium ion was gone at the end of an hour.

The above data strongly support Leffler's suggestion of a covalent complex formed between the triphenylmethyl carbonium ion and ethyl ether. The great difference in equilibrium constants for complex formation in these two solvents is of in-

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[3] Bill B. Smith and J. E. Leffler, *J. Am. Chem. Soc.*, **77** 1700 (1955).

[4] I. W. Bayles, A. G. Evans, and I. R. Jones, *J. Chem. Soc.*, 1020 (1957).

[5] Y. Pocker, *J. Chem. Soc.*, 240 (1958).

[6] W. J. Hickinbottom, *Reactions of Organic Compounds*, p. 237, Longmans, Green and Co., London, 1948.

[7] A. Bentley, A. G. Evans, and J. Halpern, *Trans. Faraday Soc.*, **47**, 711 (1951).

TABLE II

Effect of Ethyl Ether on Various Solutions of Triphenylmethyl Chloride in Nitromethane

$(Ph_3CCl)^o$	$[(C_2H_5)_2O]^o$	$(Ph_3C^+) \times 10^o$	$[Ph_3C{-}O(C_2H_5)_2^+]$	$K \times 10^{-4}$
0.0792	0.077	2.23	0.0151	1.09
0.0764	0.084	2.37	0.0083	0.46
0.0777	0.192	1.87	0.0239	0.76
0.0779	0.261	1.77	0.0270	0.65
0.0764	0.484	1.22	0.0412	0.76
0.0772	0.585	1.32	0.0393	0.55
0.0756	0.668	1.17	0.0420	0.57
0.0791	0.736	0.86	0.0544	0.93
0.0768	0.936	0.56	0.0607	1.24
0.0816	1.172	0.49	0.0675	1.25
				$K_{av} = 0.83$

terest. Gillespie and coworkers[8] have shown that acetic anhydride is a much stronger base than nitromethane in concentrated sulfuric acid. On this basis it would be expected that the anhydride would be more able to solvate the ion and would compete with the ether more avidly than nitromethane. The altered spectrum of the carbonium ion in acetic anhydride as opposed to the spectrum of the ion in nitromethane or sulfuric acid may reflect this solvation effect.

EXPERIMENTAL

Triphenylmethyl chloride was prepared in the usual fashion from triphenylmethylcarbinol,[9] m.p. 112–113°. Nitromethane was prepared from chloroacetic acid,[6] dried over phosphorous pentoxide and distilled, b.p. 99–100°. Acetic anhydride and ethyl ether were Mallinckrodt Analytical Reagent grade chemicals taken from freshly opened containers in each case.

Determinations of the carbonium ion concentrations were made with a Cary model 14 Spectrophotometer. All work was done at room temperature, 24–26°.

Triphenylmethyl perchlorate in acetic anhydride. A stock solution of triphenylmethylcarbinol ($5.50 \times 10^{-5}M$) in acetic anhydride was prepared. Aliquots (5.0 ml.) of this stock solution were taken, and the appropriate amount of ether was weighed in. The samples were then diluted to a final volume of 10 ml. with additional acetic anhydride. A silica cell (1 cm. thick) was filled with the sample, and 1 drop of 70% perchloric acid was added. The addition of 2 or 3 drops of acid did not alter the intensity of the carbonium ion absorption. The spectrum was then run immediately after the acid addition.

In view of the variance in the shape of the carbonium ion absorption curve at different concentrations, the area under the curves was taken between the limits of 395 mμ and 442 mμ. A standard sample of the carbonium ion in acetic anhydride was used to determine the relationship between area under the curve and the concentration of the carbonium ion. This method represents a compromise between the usual method of determining the concentration at one wave length and the more desirable practice of using oscillator strengths.

The various concentrations of ether used and the K's calculated therefrom are given in Table I.

Triphenylmethyl chloride in nitromethane. The desired amount of triphenylmethyl chloride was weighed into a 5 ml. volumetric flask, and a small amount of nitromethane was added. The ethyl ether was weighed into this flask, and the volume was brought up to 5.0 ml. with additional nitromethane. The flask was shaken to ensure solution. Determination of the carbonium ion concentration was as described above. The data are given in Table II. The method of calculation is given in the text. The determination of the initial concentration of carbonium ion in nitromethane alone was carried out in the same fashion as that used by Evans[7] and Pocker.[5] It was assumed that the extinction coefficient for the carbonium was the same as that of the ion in sulfuric acid; a value of 35,500 at 404 mμ was used.[3]

Several experiments were carried out with triphenylmethyl perchlorate in nitromethane. The perchlorate was generated *in situ* as previously described. These solutions were stable for over 24 hr., and the usual spectrum for the carbonium ion was observed. However, the addition of ethyl ether to these solutions caused an immediate diminution of the carbonium ion color, the resultant solutions were not stable. The color of the ion was completely discharged within 30–60 min.

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[8] (a) R. Flower, R. J. Gillespie, and S. Wasif, *J. Chem. Soc.*, 607 (1956). (b) R. J. Gillespie and C. Solomons, *J. Chem. Soc.*, 1796 (1957).

[9] W. E. Bachmann, *Org. Syntheses*, **23**, 100 (1943).

The Equilibrium Composition of the Octahydronaphthalenes

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The preparation of pure $\Delta^{9,10}$-octalin by way of the dehydration of 2-decalol, separation of the nitroso chloride derivative of the $\Delta^{9,10}$-isomer, and the regeneration of the olefin has been recently described.[1,2] Our procedure is essentially that described by Dauben and coworkers[1] except that the regeneration of the olefin from its purified nitroso chloride derivative by warming with *N*,*N*-dimethylaniline furnishes the pure olefin in 85–95% yield.

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[1] W. G. Dauben, *et al.*, *J. Org. Chem.*, **23**, 1205 (1958).

[2] A. S. Hussey, J.-F. Sauvage and R. H. Baker, Abstracts, 134th Meeting, American Chemical Society, Chicago, Ill., September 7–12, 1958, p. 80P.