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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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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[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).

[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.

Our data for the acid-catalyzed equilibration of the $\Delta^{1,9}$- and $\Delta^{9,10}$- octalin mixture suggests that the apparent enrichment in the latter is more likely the result of removal of the former by polymerization side-reactions. Thus, while the ratio of $\Delta^{9,10}$-isomer to $\Delta^{1,9}$-isomer increases with time of exposure to phosphoric acid, the undistillable residue shows a corresponding increase (see Experimental).

This explanation is supported by the composition of the equilibrated system when a carbanion catalyst[3] is used. In contrast to strong protic acid catalysts, such carbanion catalysts cannot effect polymerization. A mixture composed of 72% $\Delta^{9,10}$-octalin, 26% $\Delta^{1,9}$-octalin and 2% *trans*-decalin after 42, 48, and 65 hours at reflux over a "benzylsodium" catalyst[3] had the constant composition 70% $\Delta^{9,10}$-, 20% $\Delta^{1,9}$-, 4% *trans*-$\Delta^{1,2}$-, 4% *trans*-$\Delta^{2,3}$-, and 2% *trans*-decalin. Thus the equilibrium ratio of $\Delta^{9,10}$- to $\Delta^{1,9}$-octalin is considerably smaller (7/2) than can be realized by the acid catalyzed "isomerization". The latter is really an enrichment of the unpolymerized octalin mixture by a preferential polymerization of the $\Delta^{1,9}$-isomer.

Our experience with the lithium-ethylamine reduction of tetralin or naphthalene by Benkeser's procedure[4] has been essentially that reported by Dauben.[1]

EXPERIMENTAL

Dehydration of 2-decalol. A mixture of 2-decalol isomers obtained from the hydrogenation of 2-naphthol over nickel-kieselguhr was added to three times its weight of 100% phosphoric acid with stirring and the system was rapidly raised to 150°. A slight vacuum was applied to the system and water was added dropwise while maintaining the temperature at 150°. After all of the steam-volatile product had distilled, considerable (*ca.* 20%) of the reaction product remained as nonvolatile residue. The volatile product was analyzed by vapor partition chromatography through a 1000 plate tri-*m*-cresyl phosphate-on-fire-brick column and was found to consist of 80% $\Delta^{9,10}$-octalin, 20% $\Delta^{1,9}$-octalin, yield 75–80%.

$\Delta^{9,10}$-*Octalin nitroso chloride.* Equimolar amounts of isoamyl nitrite and iced hydrochloric acid were mixed at −10° with 0.5 mole of the octalin mixture. After 1.5 hr. the blue precipitate was filtered and washed with ice cold ethanol; yield, 75%. Recrystallization from acetone-ether gave 55–65% of blue prisms, m.p. 91–92°.[5]

Regeneration of $\Delta^{9,10}$-*octalin.* The blue nitroso chloride, 19.0 g. (0.094 mole), and 30 ml. of *N,N*-dimethylaniline in a 100 ml. flask with a reflux condenser were slowly warmed to 70° when gas evolution began. (Caution! If the temperature is raised too rapidly to this point, gas evolution becomes violent.) The temperature was gradually raised to 85° and maintained there for 2.5 hr. at which time gas evolution was complete. Dilution with water, extraction with pentane, and washing of the pentane extracts with dilute hydrochloric acid served to isolate the product. This distilled at 77.5° at 14 mm., n_D^{20} 1.4990: yield 11–12 g. (85–95%). This product exhibited a single peak when analyzed on the tri-*m*-cresyl phosphate column.

Isomerization studies. A. *Over phosphorus pentoxide.* A 22.0-g. sample having the composition 53% $\Delta^{9,10}$-octalin, 9% $\Delta^{1,9}$-octalin and 38% *trans*-decalin was heated on the steam bath for 2 hr. over 10 g. of phosphorus pentoxide. It was then extracted with ether and distilled. The undistillable residue amounts to 5 g. The volatile product had the composition 47% of $\Delta^{9,10}$-, 7% $\Delta^{1,9}$-, and 46% *trans*-decalin. A second 2-hr. treatment of the mixture left 5.2 g. of polymeric residue. The volatile material had the composition 32% $\Delta^{9,10}$-, 4% $\Delta^{1,9}$-, and 64% *trans*-decalin.

B. Over "benzylsodium" catalyst.[3] A sample of mixed octalins having the composition 72% $\Delta^{9,10}$-, 26% $\Delta^{1,9}$, and 2% *trans*-decalin was refluxed with "benzylsodium" catalyst.[3] A sample was removed periodically for analysis on the 1000 plate tri-*m*-cresyl phosphate column. After 42 hr., the composition was constant at 70% $\Delta^{9,10}$-, 20% $\Delta^{1,9}$-, 4% *trans*-$\Delta^{1,2}$-, 4% *trans*-$\Delta^{2,3}$-, and 2% *trans*-decalin. Additional samples removed at 48 hr. and at 65 hr. had the same composition.

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Are Organic Group Influences Additive in All Reactions of Aromatic Compounds?

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The consensus of opinion is that group influences are additive. Jaffé states in summary that the effect of multiple substitution in the reactivity of a functional group can be expressed in the Hammett equation by the sum of the substituent constants[3]: $\log K/K_0 = \rho\Sigma\sigma$. Since the publication of this work, Benkeser and co-workers[4] have shown that the sigma constants of 3,5-dialkyl groups, including the bulky *tert*-butyl group, are additive in the loss of a trimethylsilane group from an aromatic ring. The predicted dissociation constant of 3,5-di-*tert*-butylbenzoic acid, calculated in this laboratory from published data,[5] does not substantiate Benkeser's conclusions. As the data of Ref. 5 are less extensive and our calculation dependent on two different sources of information,

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[2] To whom correspondence should be sent.

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[4] R. A. Benkeser, R. A. Hickner, D. I. Hoke, and O. H. Thomas, *J. Am. Chem. Soc.*, **80**, 5289 (1958).

[5] Data from E. E. Betts and L. R. C. Barclay, *Can. J. Chem.*, **33**, 1768 (1955). Assuming that rho, the slope, is 1.24 in 50% aqueous methanol,[6] we calculate the dissociation constant of 3,5-di-*tert*-butylbenzoic acid to be 3×10^{-6}. Betts and Barclay report 1.66×10^{-6}. Thus, the *meta-tert*-butyl groups appear to be too strong as electron donors in this reaction.

[6] E. Grunwald and B. J. Berkowitz, *J. Am. Chem. Soc.*, **73**, 4939 (1951).