for the non-acid-catalyzed rate. The slope is in good agreement with the ideal value of unity. This correlation implies that the amount of protonated nitrous acid is small. In contrast, a plot of $-J_0$ *vs.* log k gives a slope between 1.86 and 2.28, which is in disagreement with the ideal value of unity.

Absorption Spectra.—As an incidental outgrowth of this work, a number of absorption spectra of arylmethyl cations were measured. These are presented in detail elsewhere.[19,23]

The two most remarkable facts about the spectra are the close similarity between the spectra of similarly substituted di- and triarylmethyl cations (summarized in Table VI); and the close similarity between the absorption spectrum of the triphenylmethyl cation (Table VI) and that of the 2-phenylbornyl cation, λ_{max} 415 mμ and log e 4.68, although the latter ion contains but a single phenyl ring.

A few additional values of λ_{max} and log e which have not been reported previously appear in Table VII.

TABLE VI

COMPARISON OF SPECTRA FOR DIARYL- AND TRIARYLMETHYL CATIONS IN WHICH ALL RINGS ARE IDENTICALLY SUBSTITUTED

Substituent	λmax, mμ Ar_3C^+	λmax, mμ Ar_2CH^+	log e Ar_3C^+	log e Ar_2CH^+
4-Dimethylamino	590	610	4.95	
4-Methoxy	483	507	5.02[a]	5.04
2-Methyl	454	470	4.46	4.30
4-Methyl	452	472	5.03	4.87
4-*t*-Butyl	458	480	4.92	4.81
Unsubstituted	404	440	4.60	4.64
	431		4.60	
4-Chloro	465	485	5.01	5.14
3-Chloro	412	434	4.47	4.17

[a] H. Lund (THIS JOURNAL, 49, 1346 (1927)) reported a lower value but, as previously suspected,[5] Lund's measurements were made at acid concentrations at which the triarylmethanol was not completely converted to the carbonium ion.

(23) Ph.D. Thesis of J. J. Jaruzelski at the Pennsylvania State University, 1954.

TABLE VII

VALUES OF LOG e AND λ_{max} FOR SEVERAL TRIARYLMETHYL CATIONS

Substituted triphenylmethyl cation	λmax	log e
4,4'-Dimethoxy	500	5.47
4-Methoxy	476	4.75
4-Methyl	450	4.66
4,4',4''-Triisopropyl	456	4.88
4-*t*-Butyl	458	4.67
4,4'-Di-*t*-butyl	458	

Acknowledgment.—We wish to give recognition to the work of two groups of investigators whose investigations have not been discussed directly. Westheimer and Kharasch[24] first used the concept of acidity functions of the type of C_0 in their studies on the mechanism of aromatic nitration. Williams and co-workers[25] defined an acidity function, H_R, similar to C_0 except that no distinction was made between indicator charge types (R^+,R^{++},R^{+++}, etc.). Within the limited region of their investigations, the data indicate that it may not be necessary to distinguish between charge types. However, it is doubtful whether this simplification will hold throughout the water–sulfuric acid system.

(24) F. Westheimer and M. S. Kharasch, THIS JOURNAL, **68**, 1871 (1946).

(25) A. M. Lowen, M. A. Murray and G. Williams, *J. Chem. Soc.*, 3318 (1950).

STATE COLLEGE, PENNA.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, PENNSYLVANIA STATE UNIVERSITY]

Carbonium Ions. II. Linear Free Energy Relationships in Arylcarbonium Ion Equilibria[1]

BY N. C. DENO AND ALAN SCHRIESHEIM

RECEIVED NOVEMBER 11, 1954

The establishment of the C_0 acidity function has provided a basis for determining pK_{R^+} values for the equilibrium $R^+ + H_2O = ROH + H^+$ which are all based on the same standard state. The Hammett σ–ρ treatment is applied to the data and its successes and failures are interpreted. The often suspected parallelism between rates of SN1 reactions and stability of carbonium ions has been demonstrated quantitatively for a series of diarylmethyl cations.

For the equilibria between alcohols and carbonium ions, eq. 1, an acidity function, C_0, has been evaluated in the water–sulfuric acid system which relates the concentration of acid to the position of equilibrium through eq. 2.[2] By virtue of the definition of C_0, values of pK_{R^+} calculated from eq. 2

$$R^+ + H_2O = ROH + H^+ \quad (1)$$

$$C_0 = pK_{R^+} - \log (c_{R^+}/c_{ROH}) \quad (2)$$

are all based on dilute aqueous solution as the standard state. The subject of this paper will be to compare these pK_{R^+} values with the polar parameters, σ-constants, for the substituent groups to see whether linear free energy relationships exist.

Experimental

Determination of pK_{R^+} Values.—Most of the values of pK_{R^+} have been determined previously.[2] However, the monosubstituted diphenylmethanols and 3,3'-dichlorodiphenylmethanol were so unstable that only a visual estimate of pK_{R^+} could be obtained. This was done by adding a drop of acetic acid solution of the diarylmethanol to a series of sulfuric acids of varying acid concentration. The concentrations were chosen so that the diarylmethanol would

(1) Grateful acknowledgment is made of the partial support of this research by a grant from the National Science Foundation (G468). This report was taken from the Doctoral Dissertation of A. Schriesheim at the Pennsylvania State University, 1954.

(2) N. Deno, J. Jaruzelski and A. Schriesheim, THIS JOURNAL, **77**, 3044 (1955).

have a concentration around 10^{-3} to 10^{-4} M in the acid solution. From experience with more stable arylmethanols, it was found that the color was barely discernible at the acid concentration at which about 10% of the diarylmethanol was ionized to the carbonium ion, and a decrease in color intensity was evident when about 80% was ionized. Values of pK_{R^+} were estimated on this basis and are probably precise to about ± 0.5 pK_{R^+} unit.

Monosubstituted Diphenylmethanols.—The monosubstituted diphenylmethanols were all prepared by reduction of the monosubstituted diphenyl ketones.[3] The monosubstituted diphenyl ketones were prepared by Friedel-Crafts reactions using benzoyl chloride, aluminum chloride and the appropriately substituted benzene derivative.

3,3′-Dinitro- and 4,4′-Dinitrodiphenylmethanol.—These two compounds had been prepared by one of us while working under the direction of Dr. Melvin S. Newman at The Ohio State University. Although only qualitative measurements were made on them, they had been prepared for some time and so their synthesis now is reported.[5]

3,3′-Dinitrodiphenylmethane was prepared from nitrobenzene, formaldehyde and sulfuric acid.[4] This compound, 4.1 g., was oxidized by refluxing with 4 g. of chromium trioxide for 15 hr. in acetic acid. The yield of 3,3′-dinitrodiphenyl ketone was 87%. The m.p., 153.2–154.0°, agreed with that previously reported.[5]

The reduction of the ketone to 3,3′-dinitrodiphenylmethanol was effected with 2-propanol and its aluminum salt similar to the reduction of 4-nitrodiphenyl ketone.[6] The reduction was conducted by slowly distilling 2-propanol through a good column until the distillate was acetone free. This process required about one hr. The undistilled residue was hydrolyzed with cold, dilute hydrochloric acid. The crude product, m.p. 104.0–106.6°, was obtained in 95% yield. Recrystallization from 60% aqueous methanol gave white needles, m.p. 106.8–107.6°, in 75% yield.

Anal. Calcd. for $C_{13}H_{10}O_5N_2$: C, 57.0; H, 3.7; N, 10.2. Found: C, 57.3; H, 3.7; N, 10.2.

4,4′-Dinitrodiphenyl ketone was prepared by nitration of diphenylmethane,[7] and oxidation of the 4,4′-dinitrodiphenylmethane.[8] The ketone was reduced to the alcohol in a manner identical to that used with the 3,3′-dinitrodiphenylmethanol. The crude product, m.p. 158–164°, was obtained in 98% yield. Recrystallization from methanol gave pale yellow flat prisms, m.p. 164–165.5°, in 85% yield.

Anal. Calcd. for $C_{13}H_{10}O_5N_2$: C, 57.0; H, 3.7; N, 10.2. Found: C, 57.0; H, 3.7; N, 10.2.

Discussion

Triarylmethanols.—A plot of pK_{R^+} against Hammett σ-values is linear for triarylmethanols with identically substituted rings providing the plot is restricted to the two *meta* substituents, the unsubstituted triphenylmethanol and the 4-nitro substituent. These groups would not be expected to share the positive charge of the carbonium ion. Equation 3 was obtained by treating the data for these four triarylmethanols by the method of least squares. For trisubstituted triarylmethanols n is 3 corresponding to the presence of three substituents, one on each of the rings. The value of ρ is 3.98 considering all three substituents to be effective.

$$pK_{R^+} = -3.98n\sigma - 6.84 \qquad (3)$$

It may appear that four points is an insufficient basis for eq. 3, but subsequently it will be shown that several correlations result from this treatment.

(3) E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 954 (1940).

(4) M. Schopff, *Ber.*, **27**, 2321 (1894).

(5) A. Baeyer, *Ann.*, **354**, 192 (1907); E. D. Barnett and M. A. Matthews, *J. Chem. Soc.*, **125**, 767 (1924).

(6) H. Lund, *C. A.*, **31**, 6612 (1937).

(7) W. W. Hartmann and R. Phillips, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 232.

(8) A. Nastjakow, *Chem. Zentr.*, **80, I**, 535 (1909).

We have chosen to express the deviation of the data from eq. 3 in terms of $\Delta\sigma$ in Table I. This $\Delta\sigma$ is the difference between σ computed from eq. 3 and the normal σ-value taken from the tables of Jaffe.[9]

TABLE I

CORRELATION OF VALUES OF pK_{R^+} AND σ THROUGH EQUATION 3

Substituted triphenylmethanol	pK_{R^+}	σ[a]	$\Delta\sigma$[b]	σ_R[c]
3,3′,3″-Trimethyl	− 6.35	−0.069	+0.028	
Unsubstituted	− 6.63	.00	− .018	
3,3′,3″-Trichloro	−11.03	+ .373	− .023	
4,4′,4″-Trinitro	−16.27	+ .778	+ .012	
4,4′,4″-Tris-dimethylamino	+ 9.36[d]	−0.600	+0.76	−1.36
4,4′,4″-Triamino	+ 7.57[d]	− .660	+ .55	−1.21
4,4′,4″-Trimethoxy	+ 0.82	− .268	+ .37	−0.64
4,4′,4″-Trimethyl	− 3.56	− .170	+ .10	− .27
4,4′,4″-Trichloro	− 7.74	+ .227	+ .15	+ .08

[a] Copied from the tables in ref. 9. [b] This is the difference between the value of σ calculated from eq. 3 and the normal value listed in the preceding column. [c] This is the value of σ calculated from eq. 3. The subscript "R" signifies resonance interaction and σ_R has the same significance as σ^* in ref. 9. We have preferred not to use the symbol σ^* since it has been used for another type of σ function in a series of papers by R. W. Taft, Jr. [d] R. J. Goldacre and J. H. Phillips, *J. Chem. Soc.*, 1724 (1949).

For the substituents that would be expected to share the positive charge of the carbonium ion, the data deviate markedly from eq. 3, as evidenced by the magnitude of $\Delta\sigma$ in Table I. This deviation is in the expected direction and also qualitatively parallels the increase in λ_{max} and log e of each absorption spectrum as compared with that of the triphenylmethyl cation.

When the triphenylmethyl cation is substituted successively by 4-methoxy, 4-methyl or 4-nitro groups, the change in pK_{R^+} per added substituent is of the same order of magnitude. The data in Table II demonstrate this relation. The data for the 4-amino, 4-dimethylamino, and 4-*t*-butyl substituents do not even qualitatively follow this principle and hence have not been included in Table II.

TABLE II

COMPARISON OF CHANGES IN pK_{R^+} ON SUCCESSIVE SUBSTITUTION IN TRIPHENYLMETHYL CATIONS

Substituted triphenylmethanol	pK_{R^+}	ΔpK_{R^+}
Unsubstituted	−6.63	
		> 3.23
4-Methoxy	−3.40	
		> 2.16
4,4′-Dimethoxy	−1.24	
		> 2.06
4,4′,4″-Trimethoxy	+0.82	
Unsubstituted	−6.63	
		> 1.39
4-Methyl	−5.24	
		> 1.68/2 = 0.84
4,4′,4″-Trimethyl	−3.56	
Unsubstituted	−6.63	
		> 2.52
4-Nitro	−9.15	
		> 3.75
4,4′-Dinitro	−12.90	
		> 3.37
4,4′,4″-Trinitro	−16.27	

The data for 4,4′,4″-triisopropyl and 4,4′,4″-tri-*t*-butyltriphenylmethanols fail to fit eq. 3. The sug-

(9) H. H. Jaffe, *Chem. Revs.*, **53**, 222 (1953).

gestion made previously[10] appears to still be the best interpretation, even though the absolute and even relative values of pK_{R^+} have been revised.

Diarylmethanols.—For the disubstituted diphenylmethanols a plot of the values of pK_{R^+} against σ_R (σ in the case of the 3-chloro substituent) gave a linear curve represented by eq. 4.

$$pK_{R^+} = -5.63n\sigma - 13.2 \qquad (4)$$

We have chosen again to express the deviations from this eq. in terms of $\Delta\sigma$ and these values appear in Table III.

TABLE III

CORRELATION OF VALUES OF pK_{R^+} AND σ THROUGH EQUATION 4

Substituted diphenylmethanol	pK_{R^+}	σ_R[a]	$\Delta\sigma$[b]
4,4'-Dimethoxy	− 5.71	−0.64	−0.03
4,4'-Dimethyl	−10.4	− .27	+ .02
Unsubstituted	−13.3	.00	+ .01
4,4'-Dichloro	−13.96	+ .08	+ .01
3,3'-Dichloro[c]	−17.3	+ .373[c]	− .01

[a] These are the σ_R values listed in Table I except for the last entry. These values of σ_R were evaluated from data of triarylmethanols. [b] This is σ calculated from eq. 4 minus σ_R. [c] In this case the value of pK_{R^+} was estimated visually and is correspondingly less accurate. The normal value of σ was used since the 3-chloro substituent does not share the positive charge of the carbonium ion.

The fit of the data in Table III is remarkable because rarely do σ_R values from one series apply so well to another series. Generally the amount of resonance stabilization for a particular substituent varies so much from series to series that σ_R values are not constant as already noted by Jaffe[9] for electron donating substituents. An example of this variance is a comparison of the σ_R values obtained above with those obtained by Kochi and Hammond[11] from the kinetics of solvolysis of benzyl tosylates. They reported −2.5 and −0.63 for 4-methoxy and 4-methyl, respectively.

We suspect that σ_R values will prove to have little general applicability for either electron-donating or electron-withdrawing substituents and any reported values, such as those in Table I, should be used cautiously.

Several monosubstituted diphenylmethanols were investigated briefly but they proved to be too unstable to be worth attempting careful measurements. Visually estimated pK_{R^+} values are listed in Table IV. The carbonium ions were much more stable in 97% sulfuric acid so that it was possible to measure the absorption spectra of the ions. The values of λ_{max} and log e appear in Table IV.

TABLE IV

VALUES OF pK_{R^+}, λ_{max}, AND LOG e FOR MONOSUBSTITUTED DIPHENYLMETHYL CATIONS

Substituent	pK_{R^+}	λ_{max}	log e
4-Methoxy	− 7.9	466	4.52
4-Methyl	−11.6	456	4.43
4-Ethyl	−11.6	460	4.33
4-Isopropyl	−11.6	460	4.18
4-*t*-Butyl	−11.8	434	4.43
4-Chloro	−13.7		

The 3,3'- and 4,4'-dinitrodiphenylmethanols did not appear to be converted appreciably to carbonium ion in 97% sulfuric acid so that their pK_{R^+} values are less than −19.

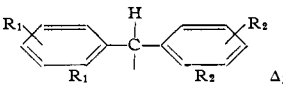
Relation of Equilibria to Solvolysis Kinetics.—The rates of solvolysis of many diarylchloromethanes in methanol, ethanol and 2-propanol have been studied by several groups of investigators.[12] A linear curve was obtained by plotting the log of the relative rates against the difference between pK_{R^+} for each compound and pK_{R^+} for diphenylmethanol. This latter difference is equivalent to the log of the relative equilibrium constants for eq. 1.

The equation for this linear curve, eq. 5, was obtained by the method of least squares using all the data available except those for 4-methoxydiphenylchloromethane. The rate of solvolysis for this compound was so fast that an accurate rate was not obtainable.[12] In several cases, the rates of solvolysis were measured in more than one alcohol. The relative rates were nearly the same so that an average value was employed in obtaining eq. 5. The deviations from eq. 5 are given in Table V.

$$\log K/K_0 = (pK_{R^+})_0 - (pK_{R^+}) = -1.10 (\log k/k_0) - 0.20 \qquad (5)$$

TABLE V

RELATION OF RATES OF SOVOLYSIS TO FREE ENERGIES OF IONIZATION FOR DIPHENYLMETHYL DERIVATIVES



		ΔpK_{R^+}[a]	log k/k_0[b]	Deviation[c]
4-Methoxy	4-H	−5.4	3.7	−1.1[d]
4-Methyl	4-Me	−2.9	2.68	+0.3
4-Methyl	4-H	−1.7	1.37	0.0
4-Ethyl	4-H	−1.7	1.35	0.0
4-*i*-Propyl	4-H	−1.7	1.30	− .1
4-*t*-Butyl	4-H	−1.5	1.27	+ .1
4-H	4-H	0.0	0.00	+ .2
4-Chloro	4-H	+ .4	− .38	− .1
4-Chloro	4-Cl	+ .7	− .82	0.0

[a] pK_{R^+} for diphenylmethanol minus pK_{R^+} for substituent listed. [b] The k is the first-order rate constant for the solvolysis of the substituted diaryl chloromethane in methanol, ethanol or 2-propanol; k_0 is the same rate constant for diphenylchloromethane. [c] This is the difference between ΔpK_{R^+} (experimental) and ΔpK_{R^+} calculated from eq. 5. These deviations are generally less than the estimated errors in pK_{R^+} and thus the agreement must be considered as partly fortuitous. [d] The rate of solvolysis in this case was so rapid that an accurate rate constant was not available. For this reason this value was not used in determining eq. 5.

The significance of the above correlation is that the free energy of activation for the solvolysis of the chloromethane in alcohols is proportional to the free energy of ionization for correspondingly substituted diarylmethanols. One possible explanation for this correlation is that if in the solvolysis of the chloromethanes, the transition state corresponded to a nearly complete separation of ions, the free energy of activation might then approxi-

(10) N. Deno, J. Jaruzelski and A. Schriesheim, *J. Org. Chem.*, **19**, 155 (1954).

(11) J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3445 (1953).

(12) S. Altscher, R. Baltzly and S. W. Blackman, *ibid.*, **74**, 3649 (1952); J. F. Norris and C. Banta, *ibid.*, **50**, 1804 (1928); J. F. Norris and J. T. Blake, *ibid.*, **50**, 1808 (1928); E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 949 (1940).

mate the free energy of ionization of the chloromethanes. It would still be necessary that a proportionality exist between the free energies of ionization of the chloromethanes in alcohols and the diarylmethanols in aqueous sulfuric acid.

Resonance Energy of Diaryl- and Triarylmethyl Cations.—Three lines of evidence give an indication that the resonance energy of diaryl- and triarylmethyl cations may be similar. First is the difference between pK_{R^+} for Ar_3C^+ and pK_{R^+} for Ar_2CH^+ where Ar represents a particular substituted phenyl ring. For a limited series it had been noticed that this difference was nearly constant independent of the substituent on the phenyl ring.[10] This series has been extended and revised using the values of pK_{R^+} based on the C_0 scale and the results are summarized in Table VI. This constant difference had been interpreted in terms of a constant difference in the energy term arising from release of steric strain on ionization for the triaryl series as compared with the diaryl series.[10] This interpretation requires that the size of groups around the central carbon be identical throughout the diaryl series and throughout the triaryl series. It thus was expected that the above correlation would not be valid for *ortho* substituents,[10] and this is demonstrated by the data on the 2-methyl derivatives. The data for the 4-dimethylamino derivatives also fail to follow the above relation.

TABLE VI

COMPARISON OF pK_{R^+} FOR Ar_3C^+ AND Ar_2CH^+ WITH IDENTICALLY SUBSTITUTED PHENYL RINGS

Substituent	pK_{R^+} Ar_3C^+	pK_{R^+} Ar_2CH^+	Difference in pK_{R^+}
4-Methoxy	+ 0.82	− 5.71	6.53
4-Methyl	− 3.56	−10.4	6.8
4-*t*-Butyl	− 6.5	−13.2	6.7
Unsubstituted	− 6.63	−13.3	6.7
4-Chloro	− 7.74	−13.96	6.22
3-Chloro	−11.03	−17.3	6.3
4-Dimethylamino	+ 9.36	+ 5.61	3.75
2-Methyl	− 3.38	−12.5	9.1

The second indication is based on a comparison of the value of ρ for the diaryl and triaryl series, −5.63 and −3.98, respectively. A substituent is thus more effective in changing pK_{R^+} in the diaryl series and interestingly, 2ρ for the diaryl series (−11.26) is nearly equal to 3ρ for the triaryl series (−11.94). Thus the total substituent effect is nearly equal in both series.

The final indication is the similarity in absorption spectra between correspondingly substituted diaryl- and triarylmethyl cations. This has been noted previously.[2]

STATE COLLEGE, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

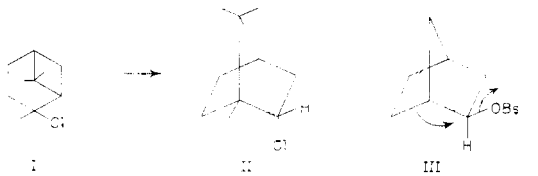
Neighboring Carbon and Hydrogen. XVIII. Solvolysis of the Nopinyl *p*-Bromobenzenesulfonates

BY S. WINSTEIN AND N. J. HOLNESS[1]

RECEIVED OCTOBER 26, 1954

The nopinyl system, a simpler analog of that in pinene hydrochloride, is interesting in connection with carbonium ion behavior. In the present study, the diastereomeric α- and β-nopinols have been prepared and characterized, and the solvolysis of the *p*-bromobenzenesulfonates has been examined. Besides traces of apocyclene, the solvolysis product from the nopinyl *p*-bromobenzenesulfonates in aqueous acetone consisted of 72 ± 4% of highly optically active apoisoborneol, 26 ± 5% of racemic β-fenchoisocamphorol, together with several per cent. of *exo*-camphenilol. No appreciable amounts of norterpineol or *endo* bicyclic alcohols were observed. The rates and products of solvolysis suggest the following description of the solvolysis. Anchimeric acceleration of ionization is at most small. Migration of the migrating group proceeds to completion, a rearranged carbonium ion being formed. This unbridged rearranged carbonium ion immediately is converted to the more stable bridged structure. From the latter arises active apoisoborneol and *exo*-camphenilol. Hydrogen shift of the 1,3-variety (2,6-in bicyclic structures) within the bridged carbonium ion gives rise to new bridged carbonium ions. One of the latter accounts for formation of optically inactive β-fenchoisocamphorol. Another accounts for formation of some enantiomorphic apoisoborneol.

The solvolysis of the nopinyl *p*-bromobenzenesulfonates VI and VII is of some interest, especially in connection with questions regarding anchimeric[2] assistance to ionization and the nature and behavior of carbonium ion intermediates. The nopinyl system is a simpler analog of that in pinene hydrochloride I, whose rearrangement to bornyl chloride II is a classical example of the Wagner–Meerwein rearrangement,[3] and whose high reactivity in solvolysis has been reported by Hughes[4] to appear to provide an example of anchimeric acceleration. Further, the nopinyl system, with its unique geometry, provides an interesting comparison with systems containing the [2,2,1]bicycloheptyl skeleton such as *exo*-norbornyl *p*-bromobenzenesulfonate (III).[5,6] The preparation of the α- and β-nopinols



I II III

(1) Hercules Powder Co. Fellow, 1953–1954.

(2) S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, THIS JOURNAL, **75**, 147 (1953).

(3) H. Meerwein and K. van Emster, *Ber.*, **55**, 2500 (1922).

(4) E. D. Hughes, *Quart. Revs.*, **5**, 245 (1951); *Bull. soc. chim.*, **18**, 39 (1951).

(5) (a) S. Winstein and D. S. Trifan, THIS JOURNAL, **71**, 2953 (1949); (b) S. Winstein, *et al.*, *ibid.*, **74**, 1127 (1952); (c) S. Winstein and D. S. Trifan, *ibid.*, **74**, 1154 (1952).

(6) J. D. Roberts and C. C. Lee, *ibid.*, **73**, 5009 (1951).