Solvolysis of Diarylcarbinyl Chlorides

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In connection with studies on naphthalene reactivity, we were following the solvolysis of naphthylphenylcarbinyl chlorides at the time of publication of the important work of Brown and Okamoto[1,2] on σ^+ values. It then seemed logical to expand our solvolytic studies to obtain σ^+ figures for comparison with those of Brown and Okamoto. Deno and Evans[3] have recently compared independently determined values for these parameters and the limited data available to them on arylphenylcarbinyl chloride ethanolysis are extended by the results now reported.

Hughes, Ingold, and Taher[4] followed the ethanolysis of certain phenyl-*p*-alkylphenylcarbinyl chlorides at 25°. Norris and co-workers[5,6] also reported rate data for a number of compounds, but they included only two *meta* substituents, and to obtain an accurate ρ value without resorting to Brown's σ^+ values, more *meta*-substituted compounds were required for study.

TABLE I

SOLVOLYSIS OF $ArCH(C_6H_5)Cl$

R	$k \times 10^5$ (sec.$^{-1}$) 5°	10°	15°	25°	35°	45°	55°	65°	75°
1-Naphthyl	4.06	7.83	15.2	49.6					
I	4.10	8.11	15.2	47.6					
	4.01	8.17		48.8					
				49.1					
2-Naphthyl	3.24	6.12	12.2	40.6					
II	3.21	6.04	11.6	40.4					
		6.06	11.6	41.4					
		6.15	10.8						
m-Tolyl				13.7					
III				13.7					
Phenyl			1.49	5.45[a]	17.4	51.8			
IV			1.54	5.38	17.8	53.1			
				5.34	18.1	49.4			
						51.3			
m-Bromophenyl				0.131		1.58		14.0	
V								13.9	
m-Chlorophenyl				0.121		1.55		13.1	
VI								12.5	
m-Nitrophenyl				0.0103[b]		0.123	0.366	1.10	2.86
VII						0.118		1.03	2.78

[a] *Cf.* k = 5.30,[4] 4.43.[5] [b] Obtained by extrapolating the Arrhenius plot.

EXPERIMENTAL

Of the carbinyl chlorides listed in Table I, compounds I, II, III, and IV were prepared by the action of dry hydrogen chloride on the parent carbinols. In preparing the less reactive carbinyl chlorides V, VI, and VII, thionyl chloride replaced hydrogen chloride. All the parent carbinols were prepared by one of two standard methods depending on the commercial availability of the appropriately substituted benzaldehyde or benzoic acid. Carbinols prepared by the action of phenylmagnesium bromide on an aldehyde were obtained in 40–50% yield. Carbinols prepared from the relevant acid *via* a substituted benzophenone were obtained in overall yields of 55–65%. Reduction of phenyl *m*-nitrobenzophenone was effected by a Meerwein-Poundorf-Verley reduction, as compared with the zinc/alkali method adopted in other cases. Data on the carbinyl chlorides, together with analyses where appropriate, are as follows:

I, m.p. 58°.

II, m.p. 74.8°.

III, b.p. 119°/1 mm.; n_D^{20} 1.5958.

Anal. Calcd. for $C_{14}H_{13}Cl$: C, 77.59; H, 6.05; Cl, 16.36. Found: C, 77.78; H, 6.00; Cl, 16.37.

IV, b.p. 134°/4 mm.

V, b.p. 133°/1 mm.; n_D^{20} 1.6180.

Anal. Calcd. for $C_{13}H_{10}BrCl$: C, 55.45; H, 3.58; Br, 28.38; Cl, 12.59. Found: C, 55.70; H, 3.50; Br, 27.95; Cl, 12.39.

VI, b.p. 126°/1 mm.

VII, b.p. 152°/1 mm.; n_D^{20} 1.6112.

Anal. Calcd. for $C_{13}H_{10}O_2NCl$: C, 63.04; H, 4.07; N, 5.66; Cl, 14.32. Found: C, 63.14; H, 3.94; N, 5.50; Cl, 14.27. Phenyl *m*-nitrophenylcarbinol melted at 65.5°.

Anal. Calcd. for $C_{13}H_{11}O_3N$: C, 68.11; H, 4.84; N, 6.11. Found: C, 68.34; H, 4.62; N, 6.20.

The titration method of the earlier workers was adopted in following the solvolyses in ethanol.

Results. First-order rate constants and derived Arrhenius data are given in Tables I and II. Unimolecular solvolysis was checked by ethoxide additions, which were accompanied by unchanged reaction rates except with higher concentrations approaching that of the carbinyl chloride (*ca.* 0.01*M*).

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(1) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1913 (1957).

(2) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

(3) N. C. Deno and W. L. Evans, *J. Am. Chem. Soc.*, **79**, 5804 (1957).

(4) E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 949 (1940).

(5) J. F. Norris and C. Banta, *J. Am. Chem. Soc.*, **50**, 1804 (1928).

(6) J. F. Norris and J. T. Blake, *J. Am. Chem. Soc.*, **50**, 1808 (1928).

Rate increases in the latter instances were probably the result of appreciable increases in ionizing power of the solvent, to which the S_N1 reaction is very sensitive.

TABLE II

ARRHENIUS PARAMETERS AND DERIVED DATA

Compound	E_a kcal. mole^{-1} (± 0.20)	$\log_{10}$ A (± 0.1)	$\Delta\Delta H^+$ kcal. mole^{-1}	$T\Delta\Delta S^{+}_{25^\circ}$ kcal. mole^{-1}
I	20.45	11.67	−1.01	0.30
II	21.04	12.01	−0.43	0.76
IV	21.47	11.45	(0.00)	(0.00)
V	23.38	11.24	1.91	−0.29
VI	23.32	11.17	1.85	−0.38
VII	23.20	10.00	1.73	−1.97

In calculating ρ for the reaction, only *meta* substituent data were used and the linear plot of $\log_{10} k_{25^\circ}$ *versus* σ was fully satisfactory. Relevant information on the plot is given by the figures: $\rho = -4.030$; $r = 0.996$; $s = 0.14$; $n = 5$, where the symbols have their standard significance.[7]

Where comparison is possible, the rate constants of Hughes, Ingold, and Taher are consistently higher than those of Norris by a reasonably constant difference which has been commented upon by the first-named group. The value now reported for diphenylcarbinyl chloride agrees closely with that of Hughes *et al.* and a "correction" factor has been applied to the results of Norris to make them comparable with the data of Hughes and of the present work. Results then lead to the figures in Table III.

TABLE III

σ^+ PARAMETERS

Substituent	$k_{25^\circ} \times 10^5$ (sec.$^{-1}$)	σ^+ (Present Work)	σ^+ (Okamoto & Brown)
m-NO_2	0.0103^a		
m-Cl	0.124^a		
m-Br	0.132^a		
m-CH_3	13.7^a		
H	5.41^a		
3:4-C_6H_4	40.3^a	−0.207	−0.132
p-CH_3	123.0^b	−0.327	−0.306
p-C_2H_5	120.0^b	−0.324	−0.291
p-iso-C_3H_7	106.0^b	−0.311	−0.276
p-tert-C_4H_9	98.7^b	−0.303	−0.250
p-Cl	1.48^c	−0.158	−0.112
p-Br	1.23^c	−0.179	−0.148
p-OC_6H_5	1170.0^c	−0.555	-0.63^d
p-C_6H_5	50.2^c	−0.218	-0.12^d

[a] Present work. [b] Ref. 4. [c] Refs. 5 and 6. [d] See ref. 3.

Agreement between the last two columns is seen to be good. The effect of the 3:4 C_6H_5 substituent in a number of reactions is currently being reviewed by us and comment on this substituent is at present withheld.

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(7) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

Reactions of Some Organochlorosilanes in Acetone

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The author wishes to report on the conversion of some organochlorosilanes to siloxanes in acetone. When solutions of organochlorosilanes in acetone are allowed to stand at room temperature for extended periods, conversion to organopolysiloxanes occurs, all of the silicon-chlorine bonds being replaced by silicon-oxygen bonds.

EXPERIMENTAL

Reagents and general procedure. Silicon tetrachloride (hereafter called STC), methyltrichlorosilane (MTS), dimethyldichlorosilane (DDS), diphenyldichlorosilane (DPDS) provided in purified grades by the Shin-etsu Chemical Industrial Company were used. Acetone was purified according to the ordinary method; titration with Karl Fischer reagent showed 0.2% (mean) water content. Each solution of the chlorosilane in acetone was enclosed in a Pyrex glass tube of 2 cm. in diameter and 15 cm. in length and allowed to stand at room temperature. After several days, the solution developed a yellowish color which became dark gradually. Ultimately it turned dark red, nearly black, and at the same time the corresponding polysiloxane was formed. The time required for these changes, and the character of polysiloxane finally formed, varied with the concentration and with the chemical identity of the chlorosilane used, but much more with the water content of acetone used. For example, the addition of a small amount of water (or methanol) to the initial mixture promoted the coloration and the formation of polysiloxanes remarkably.

The reactions of individual silanes in acetone thus observed are described below.

STC, MTS. Each of them shows an entirely similar reaction in acetone; solutions in acetone finally form dark red gels. Especially when the solution consists of 1 mole of silane and 3–5 moles of acetone, the whole mixture solidifies, transforming into a dark red, brittle gel. The reaction takes a period of 3 or 4 weeks. In a previous publication,[1] this red gel was described as an addition compound of STC and acetone, but no information about its structure or composition was given.

The author now concludes that these red gels are polysiloxane $(SiO_2)_n$ and methylpolysiloxane $(CH_3SiO_{1.5})_n$, respectively. For evidence, the gel was decolorized gradually on being extracted with fresh acetone, ultimately turned to white and translucent, while acetone acquired a deep red color and emitted a characteristic terpene-like odor. The X-ray powder pattern for white gels showed broad halos

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(1) W. R. Trost, *Nature*, **169**, 289 (1952).