Table I. Reduction Potentials of Carbonium Ions in 10.2 M H_2SO_4, 25.0°

Cation	$-\epsilon_2$[a]	$-\epsilon_4$[a]	Obsd[b] $\Delta\epsilon_2$	Lit. $\Delta\epsilon_2$[b]	$\delta_R F_{R^+}$[c]	$\delta_R F_{R\cdot}$[d]	$\delta_R F_{R^-}$[e]	m[f]	X[g]
Triphenylmethyl (1)	0.58	1.11			0.0	13.4	39.0	0.0	1.26
9-Phenylfluorenyl[h] (2)	0.01	0.57			5.8	6.0	19.1	0.141	1.11
5-Phenyldibenzo[*a*,*d*]cycloheptenyl (3)	0.71	1.20			−1.4	15.0	42.7	−0.128	1.53
Triphenylcyclopropenyl[i] (4)	1.83		1.25	1.04[j]	−13.4	28.8		−0.504	1.66
9-Phenylxanthyl (5)	0.81	1.28	0.23	0.20[k]	−10.6	8.1	37.6		
9-Phenylthioxanthyl (6)	0.84	1.26			−10.8	8.5	37.6		
Tris-*p*-anisylmethyl (7)	1.09	1.21	0.51	0.49[l]	−10.1	15.0	42.9		

[a] Reduction peak potential (volts) *vs.* Hg|Hg_2SO_4–17 M H_2SO_4; ±0.01 V; scan rate 200 V/sec. [b] Potential difference between ion and triphenylmethyl cation. [c] In kcal/mol, from eq 1. [d] In kcal/mol, $\delta_R F_{R\cdot} = \delta_R F_{R^+} - \mathfrak{F}\epsilon_2$. [e] In kcal/mole, $\delta_R F_{R^-} = \delta_R F_{R^+} - \mathfrak{F}(\epsilon_2 + \epsilon_4)$. [f] Lowest unfilled Hückel MO, $\alpha + m\beta$. [g] Energy difference between radical and cation, units of β; $\omega = 1.4$ (see ref 19). [h] Extrapolated from measurements in 14–17 M H_2SO_4 ±0.02 V. [i] Extrapolated from measurements in 0.9–6 M H_2SO_4. Complete reversibility is not achieved at 200 V/sec ± 0.04 V. [j] Cyclic voltammetry in CH_3CN.[14] [k] Standard cell potentiometry; glacial acetic acid.[11] [l] Direct current polarography in CH_3CN: L. D. McKeever, Ph.D. Thesis, University of California, Irvine, 1966.

The reduction peak potentials[17] at a scan rate of 200 V/sec for several cations in 10 M H_2SO_4 are listed in Table I. The results agree fairly well with previous work, where such information is available. The reduction potentials (ϵ_2) for the four hydrocarbon cations give a fair correlation with the energy (m in Table I) of the lowest unfilled molecular orbital (Hückel approximation) with $\beta = 2.7$ eV,[18] but the correlation is not improved by ω-technique calculations (χ in Table I).[19]

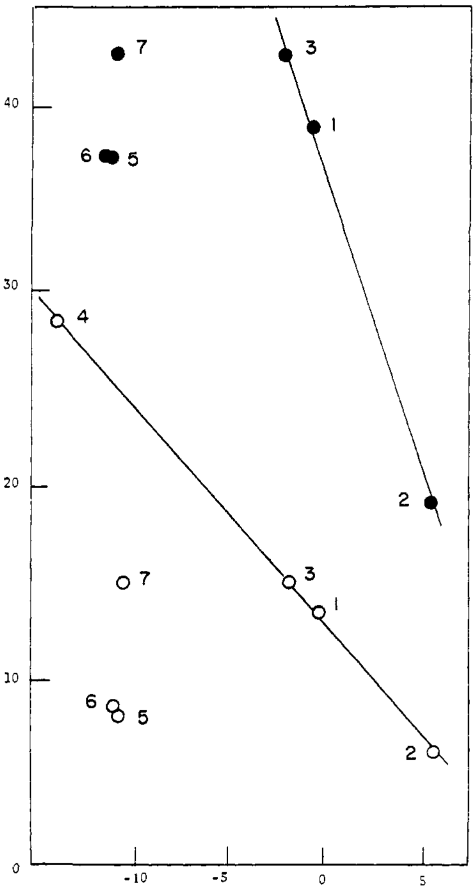

Figure 1. Relative stabilities of trivalent carbon species in 10.2 M H_2SO_4. Abscissa: $\delta_R F_{R^+}$; ordinate: $\delta_R F_{R\cdot}$ (open circles) and $\delta_R F_{R^-}$ (closed circles). Numbers correspond to those used in Table I.

The relative free energies (20) of the various species listed in Table I, derived from the above equations, are compared in Figure I. The linear relationships shown for the hydrocarbon systems indicate that *the stabilization of an aromatic species is proportional to the destabilization of the corresponding antiaromatic*[8] *species.* This novel result has not been previously noted, nor has a theoretical basis, such as the Hush–Pople theorem[21] for odd-alternant hydrocarbon species, been proposed.

The further usefulness of the type of analysis shown here in studying stabilities of trivalent carbon species, especially as applied to electron-transfer reactions,[22] will be presented soon.

Acknowledgments. We thank Professor R. W. Taft and Dr. L. McKeever for providing us with their results, Professor S. W. Staley for MO calculations, and Professor M. A. Battiste, W. T. Bowie, and N. Thame for compounds.

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[17] The peak potentials (ϵ_2) do not represent equilibrium potentials (which are measured at 85% of the peak current), but the peaks are more precisely determined. Since the small error is approximately the same for each cation, the relative values of $\delta_R F_{R\cdot}$ are not substantially affected.

[18] For the direct current polarographic reduction of benzenoid hydrocarbons in aqueous dioxane, $\beta = -2.37$ eV: G. J. Hoijtink, *Rec. Trav. Chim.*, **74**, 1525 (1955).

[19] A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, **82**, 4123 (1960).

[20] The free energies include constant terms for solvation energies (assumed equal) and the reference electrode potential. The assumption that ϵ_4 may be used instead of ϵ_3 to determine $\delta_R F_{R^-}$ is based on the observation that polarographic reduction potentials of aromatic hydrocarbons in dimethylformamide ($R + e \rightleftarrows R\cdot^-$) are linearly related to the potentials in protic solvents ($R + e + H^+ \rightarrow RH\cdot$): A. Streitwieser, Jr., and I. Schwager, *J. Phys. Chem.*, **66**, 2316 (1962). We anticipate future work on the radical–carbanion couple in aprotic solvents to test this assumption directly.

[21] N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

[22] W. T. Bowie, unpublished results.

[23] NASA Predoctoral Trainee, 1965–1968; American Chemical Society Division of Analytical Chemistry Summer Fellow, 1968.

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Received April 7, 1969

Silylation of Acid Chlorides. A New Method of Forming the Carbon–Silicon Bond

Sir:

The synthetic usefulness of the tertiary amine–trichlorosilane combination has been demonstrated in a number of systems. This includes its use as a reducing agent[1] and as a method of silicon–carbon bond forma-

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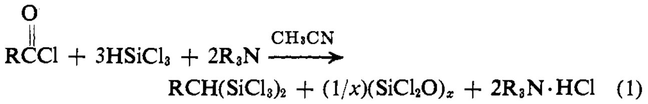
[1] R. A. Benkeser and W. E. Smith, *J. Amer. Chem. Soc.*, **90**, 5307 (1968).

Table I

Run	Reactants[a]	Conditions	Products[b–d]
1	$\mathrm{CH_3COCl}$ (1:4:2.4)	$\mathrm{CH_3CN}$ (solvent) 1 hr (room temperature) 1 hr (reflux)	$\mathrm{CH_3CH(SiCl_3)_2}$ (55%)
2	$\mathrm{C_2H_5COCl}$ (1:4:2.4)	$\mathrm{CH_3CN}$ (solvent) 1 hr (room temperature) 1 hr (reflux)	$\mathrm{CH_3CH_2CH(SiCl_3)_2}$ (57%)
3	$\mathrm{(CH_3)_2CHCOCl}$ (1:4:2.4)	$\mathrm{CH_3CN}$ (solvent) 1 hr (room temperature) 1 hr (reflux)	$\mathrm{(CH_3)_2CHCH(SiCl_3)_2}$ (41%)
4	$\mathrm{(CH_3)_3CCOCl}$ (1:4:2.4)	$\mathrm{CH_3CN}$ (solvent) 1 hr (room temperature) 1 hr (reflux)	$\mathrm{(CH_3)_3CCH(SiCl_2H)(SiCl_3)}$ (43%) (IV) $\mathrm{(CH_3)_3CCH(SiCl_3)_2}$ (19%) (V)
5	n-$\mathrm{C_5H_{11}COCl}$ (1:4:2.4)	$\mathrm{CH_3CN}$ (solvent) 1 hr (room temperature) 1 hr (reflux)	n-$\mathrm{C_5H_{11}CH(SiCl_3)_2}$ (72%)
6	$\mathrm{C_6H_5COCl}$ (1:5:2.0)[e]	$\mathrm{CH_3CN}$ (solvent) 18 hr (reflux)	$\mathrm{C_6H_5CH(SiCl_3)_2}$ (46%) $\mathrm{C_6H_5CH_2SiCl_3}$ (9%)

[a] Values in parentheses represent mole ratios of acid chloride : $\mathrm{HSiCl_3}$: $(n\text{-}\mathrm{C_3H_7})_3\mathrm{N}$. [b] In each case the amine hydrochloride was isolated in almost quantitative yield. [c] Satisfactory elemental analysis and spectral data (ir and nmr) were obtained for all compounds listed. [d] In each reaction $(\mathrm{SiCl_2O})_x$ described previously[2] remained behind after distillation. [e] $(\mathrm{C_6H_{11}})_2\mathrm{NCH_3}$ was used in place of $(\mathrm{C_3H_7})_3\mathrm{N}$ in the case of benzoyl chloride.

tion.[2,3] We now wish to report a novel reaction of this combination with acid chlorides. The over-all process can be represented by eq 1. The generality of the reaction is indicated by the results in Table I.

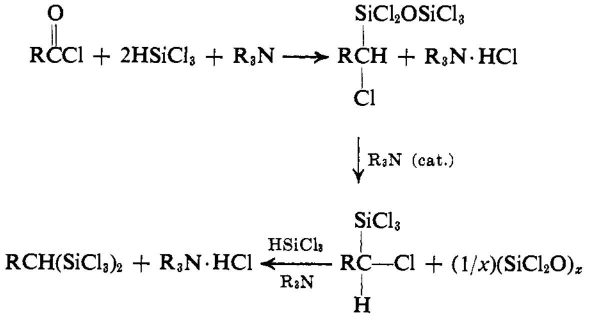


$$\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Cl} + 3\mathrm{HSiCl_3} + 2\mathrm{R_3N} \xrightarrow{\mathrm{CH_3CN}} \mathrm{RCH(SiCl_3)_2} + (1/x)(\mathrm{SiCl_2O})_x + 2\mathrm{R_3N\cdot HCl} \quad (1)$$

By way of an example, 480 mmol of tri-*n*-propylamine was added with stirring to a solution of 800 mmol of trichlorosilane, 200 mmol of propionyl chloride, and 100 ml of acetonitrile over a 2-hr period at −5 to 15°. The mixture was stirred for 1 hr at room temperature followed by 1-hr reflux. The amine hydrochloride, precipitated by the addition of 500 ml of ether, was removed by filtration. Distillation afforded 1,1-bis(trichlorosilyl)propane (56%) boiling at 86–90° (8 mm).

The reaction scheme for this acid chloride reaction can be inferred, to a first approximation, from information already at hand. It has been shown previously[2] that benzoyl chloride can be made to yield $\mathrm{C_6H_5CHClSiCl_2OSiCl_3}$ (I) or $\mathrm{C_6H_5CHClSiCl_3}$ (II) instead of α,α-bis(trichlorosilyl)toluene (Table I) by carefully controlling the reaction conditions. We have shown further that II can be converted into $\mathrm{C_6H_5CH(SiCl_3)_2}$ (III) as shown below. It thus appears that both I and II are formed prior to the appearance of III when benzoyl chloride is treated with the tertiary amine–trichlorosilane combination. Assuming these specific data to be general for acid chlorides, a *possible* reaction scheme is outlined below. This scheme is consistent with that already reported[2] for reductive silylation of carbonyl compounds and silylation of alkyl halides.[3]

$$\mathrm{II} \xrightarrow[\substack{\mathrm{CH_3CN} \\ \text{reflux 8 hr}}]{\substack{1.67\ \text{equiv of HSiCl}_3 \\ 1.00\ \text{equiv of } (n\text{-}\mathrm{C_3H_7})_3\mathrm{N}}} \mathrm{III}$$



$$\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Cl} + 2\mathrm{HSiCl_3} + \mathrm{R_3N} \longrightarrow \mathrm{R}\overset{\mathrm{SiCl_2OSiCl_3}}{\underset{\mathrm{Cl}}{\mathrm{CH}}} + \mathrm{R_3N\cdot HCl}$$

$$\Big\downarrow \mathrm{R_3N\ (cat.)}$$

$$\mathrm{RCH(SiCl_3)_2} + \mathrm{R_3N\cdot HCl} \xleftarrow[\mathrm{R_3N}]{\mathrm{HSiCl_3}} \mathrm{R}\overset{\mathrm{SiCl_3}}{\underset{\mathrm{H}}{\mathrm{C}}}\text{—}\mathrm{Cl} + (1/x)(\mathrm{SiCl_2O})_x$$

The only major anomaly in Table I is $\mathrm{(CH_3)_3CCH(SiCl_3)(SiCl_2H)}$ (IV) which presumably arises from $\mathrm{(CH_3)_3CCH(SiCl_3)_2}$ (V) *via* an amine–amine hydrochloride catalyzed chlorine–hydrogen exchange involving V and trichlorosilane. Such exchanges are known in silicon chemistry,[4,5] and we have demonstrated that V is indeed converted to IV in the presence of tri-*n*-propylamine *or* tri-*n*-propylamine hydrochloride under reaction conditions listed for runs 1 through 6 (Table I). The driving force for the exchange in this particular case is probably the relief of steric strain in V.

It is clear from the data of Table I that the reaction of acid chlorides with trichlorosilane–tertiary amines leading to bis(trichlorosilyl) derivatives is a general one and certainly the most convenient method now available for preparing such silicon compounds.

Acknowledgment. The authors are grateful to the Purdue Research Foundation and the Petroleum Research Fund, administered by the American Chemical Society, whose financial assistance made this work possible.

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Received June 2, 1969

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(2) R. A. Benkeser and W. E. Smith, *J. Amer. Chem. Soc.*, **91**, 1556 (1969).

(3) R. A. Benkeser, J. M. Gaul, and W. E. Smith, *ibid.*, **91**, 3666 (1969).

(4) D. R. Weyenberg, A. E. Bey, and P. J. Ellison, *J. Organometal. Chem.*, **3**, 489 (1965).

(5) A. B. Burg, *J. Amer. Chem. Soc.*, **76**, 2674 (1954).