esr signal in toluene, but no half-field transitions have as yet been detected. Conceivably any $(CH_3)_2SnCl_2$ present may cause the borole to form a radical cation, as has been observed for many aromatic compounds in contact with Lewis acids.[9]

In conclusion, pentaphenylborole is a highly reactive nucleus, undergoing readily oxidation, partial protolysis, and the Diels–Alder reaction with a dienophile of low reactivity. Although a low-lying triplet has not been established, this borole seems to deserve further consideration as a potential antiaromatic system. In any event, previous claims about the inertness of this nucleus must be rectified.[10]

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(9) *Cf.* I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, **43**, 2712 (1965), and references cited therein.

(10) The procedure previously described in ref 5 was repeated faithfully, but the pale yellow solids isolated were air stable and unreactive to pyridine or to alkynes and had molecular weights >800 (mass spectroscopy). Such solids were identical by mass spectral, infrared, and tlc criteria with a sample generously provided by Dr. Braye.

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Stabilities of Trivalent Carbon Species. I. Aromatic and Antiaromatic Species Related to Triphenylmethyl

Sir:

The striking success of the Hückel approximation in the prediction of stabilities of nonalternant trivalent carbon species is generally recognized.[1] However, comparisons of various systems have been made using widely different experimental techniques, as illustrated by 9-phenylfluorenyl and triphenylmethyl species. Thus, the relative stabilities of the cations were first derived from conductivity measurements in liquid SO_2,[2] the anions from hydrocarbon acidity measurements,[3] and the free radicals from dimer dissociation equilibria[4] which were subsequently reinvestigated by thermochemical[5] and kinetic techniques.[6] The triphenylcyclopropenyl species have likewise been studied by a variety of methods.[7,8] We present here results for several systems which are structurally related to triphenylmethyl, for which relative stabilities of the various trivalent species are measured under identical conditions and may be referred to a single standard.

The stabilities of a large number of triarylcarbonium ions have been established by means of the H_R acidity function[9] and confirmed by potentiometric measurements.[10] The free energy of a triarylcarbonium ion (R^+) relative to triphenylcarbonium (R_0^+) is given by ΔF for reaction 1, which is readily obtained from pK_{R^+}

$$ROH + R_0^+ \rightleftharpoons R_0OH + R^+ \qquad (1)$$

values. The stabilities of the corresponding free radicals and anions, relative to the cation, may be determined from potentiometric measurements[11,12] (reactions 2 and 3). Thus, the series of trivalent carbon

$$R^+ + e \rightleftharpoons R\cdot \qquad (2)$$

$$R\cdot + e \rightleftharpoons R^- \qquad (3)$$

species may be related to the triphenylcarbinol ionization.

We have measured the reduction peak potentials of a group of cations which are structurally related to triphenylmethyl, and consequently should have nearly equal solvation energies, using triangular wave cyclic voltammetry. The cations were generated from the corresponding alcohols in aqueous sulfuric acid, and the reductions were carried out in this medium. Voltammograms were recorded with a Chemtrix SSP-2 instrument which was modified to permit the scan rate to vary from 1 to 200 V/sec. A three-electrode cell was used, with a dropping mercury working electrode, a platinum wire counter electrode, and a reference electrode of $Hg|Hg_2SO_4$–17 *M* H_2SO_4.[13] With the exception of triphenylcyclopropenium, the cations are reduced in successive one-electron steps, corresponding to reversible formation of the radical (eq 2) and irreversible reduction to the hydrocarbon (eq 4). For

$$R\cdot + e + H^+ \longrightarrow RH \qquad (4)$$

the series of structurally related radicals, we assume the potential obtained for reaction 4 measures *approximately* the free energy difference between the carbanion and radical.

The reversibility of the first reduction is demonstrated at fast scan rates, where oxidation of the radical is faster than its dimerization.[14] The peak potential for this reduction is very sensitive to the composition of the solvent and shifts dramatically to more negative potentials with increasing acidity. At high acid concentrations, the first wave merges with the second, which is generally insensitive to solvent composition, and a two-electron wave is observed. Two-electron reduction of triphenylcarbonium ion has previously been noted in direct current polarography in 97% H_2SO_4[15] and methanesulfonic acid.[16] We shall present detailed results of the solvent effect on the reduction of these and other cations in a subsequent paper.

(1) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, Chapter 10.

(2) K. Ziegler and H. Wollschitt, *Ann.*, **479**, 104 (1930).

(3) J. B. Conant and G. W. Wheland, *J. Amer. Chem. Soc.*, **54**, 1212 (1932).

(4) S. T. Bowden and W. J. Jones, *J. Chem. Soc.*, 1149 (1928).

(5) H. E. Bent and J. E. Cline, *J. Amer. Chem. Soc.*, **58**, 1624 (1936).

(6) S. G. Cohen, F. Cohen, and C. H. Wang, *J. Org. Chem.*, **28**, 1749 (1953).

(7) A. W. Krebs, *Angew. Chem. Intern. Ed. Engl.*, **4**, 10 (1965).

(8) R. Breslow, *ibid.*, 7, 565 (1968).

(9) N. C. Deno, J. Jaruzelski, and A. Schriescheim, *J. Amer. Chem. Soc.*, 77, 3044 (1955).

(10) R. W. Taft, *et al.*, *ibid.*, **86**, 116 (1964); **87**, 2489 (1965); **88**, 4747 (1966).

(11) J. B. Conant, *et al.*, *ibid.*, **47**, 1959 (1925); **55**, 3752 (1933).

(12) H. E. Bent and N. B. Keevil, *ibid.*, **58**, 1228 (1936).

(13) The potential of this electrode is +0.256 V *vs.* sce; *cf.* A. A. Vlček, *Collection Czech. Chem. Commun.*, **16**, 373 (1951).

(14) R. Breslow, W. Baharry, and W. Reinmuth, *J. Amer. Chem. Soc.*, **83**, 1763 (1961).

(15) M. I. James and P. H. Plesch, *Chem. Commun.*, 508 (1967).

(16) S. Wawzonek, R. Berkey, and D. Thomson, *J. Electrochem. Soc.*, **103**, 513 (1956). Two one-electron waves are observed if water is added to the solvent.

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]

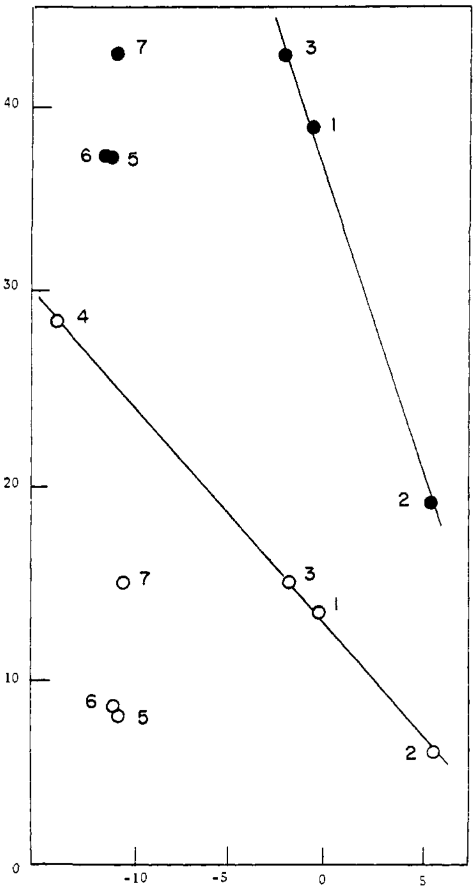

Figure 1. Relative stabilities of trivalent carbon species in 10.2 M H_2SO_4. Abscissa: $\delta_R F_{R^+}$; ordinate: $\delta_R F_R\cdot$ (open circles) and $\delta_R F_{R^-}$ (closed circles). Numbers correspond to those used in Table I.

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.

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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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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).