reaction of the ammonium thioether with the triiodide ion itself.

Reaction Products. Procedures have been described previously.[1a,2c]

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Registry No. 1, 5932-57-0; 2, 76429-53-3; 3, 16220-69-2; 4, 44826-69-9; 5, 35332-10-6; 6, 14143-85-2; 7, 5947-17-1; 8, 76429-54-4; 9, 38280-81-8; 10, 76429-55-5; 10 perchlorate, 76429-56-6; 11, 76429-57-7; 12, 76429-58-8; 13, 76429-59-9; 14, 76429-61-3; 15, 76429-62-4; 1-thiacyclohexan-4-one, 1072-72-6; 1-thiacyclohexan-4-one oxime, 6309-59-7; 1,4-thiazepin-5-one, 2896-98-2.

Substituent Effect on the Electrochemical Oxidation of Trityl Anions. 2. Effect of an Electron-Withdrawing Group

Shelton Bank,* Clifford L. Ehrlich, Mark Mazur, and Jon A. Zubieta

Department of Chemistry, State University of New York at Albany, Albany, New York 12222

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The reversible one-electron oxidations of triarylmethyl anions and the irreversible second oxidative processes were examined for a series of sequentially substituted *p*-trimethylsilyl anions. The cycle voltammograms of the lithium salts prepared in dimethoxyethane reveal that the reversible potentials depend upon the substituent in the para positions. In contrast the second oxidative process is only slightly affected. Comparison with similarly substituted methyl triarylmethyl anions leads to estimates of the effect of a trimethylsilyl group on carbanion, radical, and cation stability.

In a previous study[1] we obtained and utilized electrochemical data to provide information about the several equilibria among triarylmethyl anions, radicals, and cations as shown in eq 1.

$$R^- \underset{e}{\rightleftarrows} R\cdot \underset{e}{\rightleftarrows} R^+ \qquad (1)$$

The reversible one-electron oxidation of lithium triarylmethyl anions and the irreversible second oxidative process were examined for a series of sequentially substituted *p*-methyl anions. The substituent effect on stability of the several species was assessed and compared with other estimating methods.

The electron-donating properties of the methyl group have a larger stabilizing effect on the energy of cations than the destabilizing effect on the energy of anions which in turn was larger than the moderate stabilizing effect on the energy of radicals. Additionally, sequential substitution revealed the effect for a single methyl group to be different for the two oxidative processes. For the reversible anion to radical oxidation the single methyl substitution brought about the smallest change. In contrast the radical oxidation process reveals the greater change for substitution by a single methyl group.

These effects are consonant with the known propeller geometry of the aryl rings in these species.[2] Of great interest for the anion, the twist angles for the phenyl rings are 19.7°, 30.6°, and 44.8°, respectively.[2a] Thus there is significant differential in the degree of conjugation of the several rings. For the electron-deficient cation the greatest stabilizing effect is realized when the donor methyl group is in the maximally conjugated ring. Similarly for the electron-rich anion the great stabilizing effects are achieved when the maximally conjugated ring is unsubstituted. This analysis is based on the electron-donor properties of methyl and the differential ring conjugation.

Differential ring conjugation is inherent in the geometrical requirements of the triaryl methyl system but maximum preference should be determined by substituent. In fact an electron-withdrawing group should reverse the pattern of sequential substituent effect; thus for the anion greater stabilization would be realized when a substituted ring is maximally conjugated. For the cation the prediction is exactly opposite.

The trimethylsilyl group was selected as representative of electron-withdrawing groups. Accordingly this study concerns a quantitative assessment of the effect of the trimethylsilyl group on the reversible and irreversible oxidation potentials of a series of para-substituted anions. The method permits direct comparison with the previous study of a representative electron-donor group. Additionally, the results can be compared to related studies of trimethylsilyl groups to delocalization energies and restricted rotation in diarylmethyl anions.[3]

Results and Discussion

The triarylmethanes Id, IId, and IIId were obtained via Grignard syntheses. The lithium anions Ia, IIa, and IIIa were prepared from the reaction of the corresponding triarylmethane and *n*-butyllithium in dimethoxyethane (DME). Freshly prepared anion solutions were generated and transferred to the electrochemical cell in a No-Air system.

Improvements in reversibility and reproducibility of the voltammograms were realized by a change to a nonaqueous reference electrode. The voltammogram of Ia depicted in Figure 1 reveals the one-electron oxidation at −1.068 V and the irreversible oxidation at +0.516 V. For direct comparison the reversible anion oxidation of the triphenylmethyl anion was obtained with this reference electrode.

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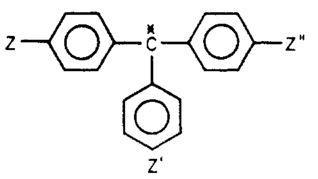
[1] S. Bank, C. L. Ehrlich, and J. A. Zubieta, *J. Org. Chem.*, 44, 1454 (1979).

[2] (a) J. J. Brooks and G. D. Stucky, *J. Am. Chem. Soc.*, 94, 7333 (1972); (b) H. Gomes de Mesquito, C. H. MacGillavry, and K. Eriks, *Acta Crystallogr.*, 18, 437 (1965); (c) P. Andersen and B. Klewe, *Acta. Chem. Scand.*, 21, 2599 (1967).

[3] S. Bank, J. S. Sturges, D. Heyer, and C. H. Bushweller, *J. Am. Chem. Soc.*, 102, 3982 (1980).

0022-3263/81/1946-1243$01.25/0



	Z	Z'	Z''
I	$Si(CH_3)_3$	H	H
II	$Si(CH_3)_3$	$Si(CH_3)_3$	H
III	$Si(CH_3)_3$	$Si(CH_3)_3$	$Si(CH_3)_3$
IV	H	H	H
V	CH_3	H	H
VI	CH_3	CH_3	H
VII	CH_3	CH_3	CH_3

a, * = 2 electrons; b, * = 1 electron; c, * = 0 electrons; d, * = H; e, * = OH; f, * = Cl

This value of −1.12 V compared to the value of −1.20 V obtained for this same anion with the saturated calomel electrode[1] agrees with reasonable estimates for the change in reference electrodes.[4] Most importantly the use of this same anion, cation, solvent, and concentration with both reference electrodes calibrates the scale for comparison of the present and the previous studies. Table I records the electrochemical behavior of the substituted anions.

The reversible oxidation of the anions depends upon the substituent in the para position. The data are displayed and compared with methyl substitution in Figure 2. Several features emerge from inspection of this diagram. All para-substituted trimethylsilyl triarylmethyl anions have oxidation potentials less negative than trityl anion whereas all para-substituted methyl triarylmethyl anions have oxidation potentials more negative than trityl. For the trimethylsilyl substituent the greatest differential change (50 mV) occurs upon single substitution. For methyl the maximum differential change (70 mV) occurs when all para hydrogens are replaced. The trimethylsilyl group is significantly stabilizing for the anion. Some quantitative estimate of this effect will be considered after discussion of the other process.

The second cathodic processes while clearly irreversible are comparable for this series of compounds. The similarity of the electrode process is warranted by similarity of the number of electrons transferred, the degree of reversibility, and the character of the limiting currents. These data are presented in Table I and displayed in Figure 3. The most significant feature is the contrasting magnitude dependencies for the trimethylsilyl and methyl groups. Three para tri-methylsilyl groups lead to an oxidation potential 20 mV more positive compared to 260 mV change to less positive potential for three para methyl groups. This process is clearly less sensitive to para trimethylsilyl substitution.

Analysis of the data in somewhat greater detail rests on the construction of energy relationships as shown in Figure 4. Central to both anion and cation stability considerations is the assumption that the stability of the tris[*p*-(trimethylsilyl)phenyl]methyl radical and the tri-*p*-tolylmethyl radical have comparable stabilities. Data obtained for ethyl-substituted radicals reveal an adjacent $Si(Et)_3$ group is about as stabilizing as an adjacent $C(Et)_3$ group.[5] The implication is that silicon stabilizes radical intermediates similar to carbon and quite different from hydrogen. Support for this assumption is obtained by comparing the derived and the experimentally determined pK_a differences of the corresponding anions (vide infra).

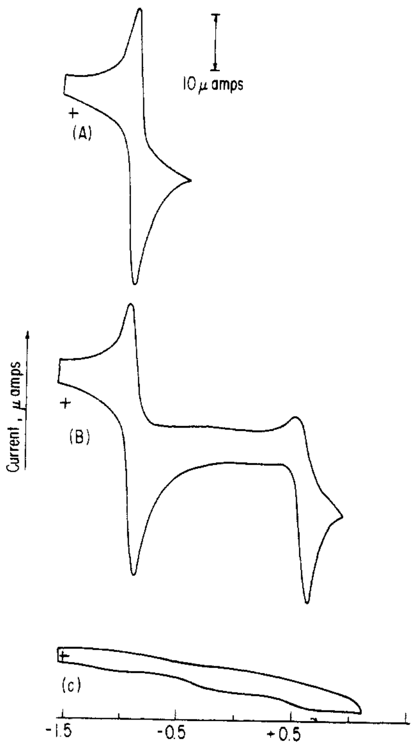


Figure 1. Cyclic voltammograms of 3.0×10^{-3} M $(Me_3SiC_6H_4)(C_6H_5)_2C^-$ in 0.1 M TBAP in dimethoxyethane solution at a scan rate of 200 mV s^{-1}: (A) scan range −1.5 to −0.5 V, isolating the reversible one-electron oxidation; (B) scan range −1.5 to +0.75 V, showing the successive one-electron oxidations; (C) scan range −1.5 to +0.75 V after quenching the solution with dry oxygen for 30 s followed by a 2-min argon purge.

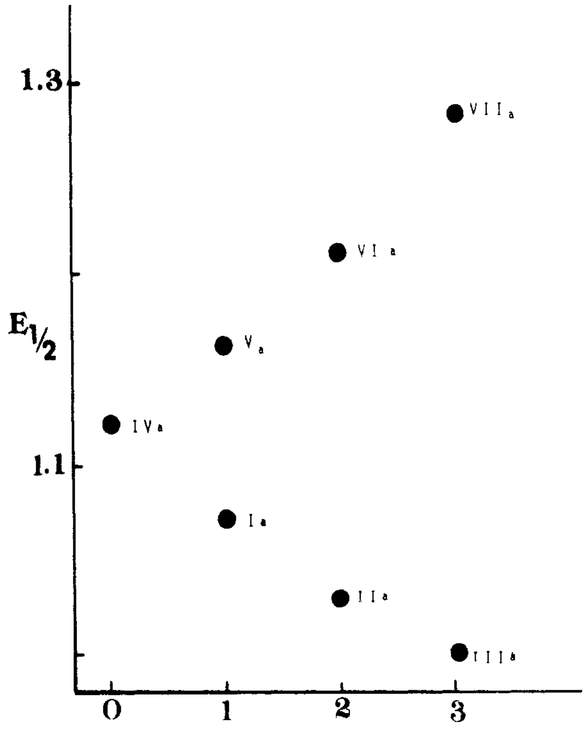


Figure 2. Relationship between $E_{1/2}$ in volts and the number of groups in the para position.

Focusing first on Figure 4 a variety of interesting points emerges. Three trimethylsilyl groups have a significant stabilizing effect on the anion (4.3 kcal/mol, 3.1 pK_a units).

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[4] D. T. Sawyer and J. L. Roberts, Jr., "Experimental Electrochemistry for Chemists", Wiley, New York, 1974, pp 34–58.

[5] P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 91, 6161 (1969).

Table I. Summary of Electrochemical Data[a] for Triaryl Anions

	$R^- \rightleftarrows R$			$R \rightarrow R^+$		
compd	Δ, mV[b]	$E_{1/2}$, V[c]	$(i_p(a)/V^{1/2}C) \times 10^{-4}$ [d]	$E_p(a)$[e]	$E_{p/2}$[f]	$(i_p(a)/V^{1/2}C) \times 10^{-4}$
$(C_6H_5)_3C^-$	74	-1.12_1	2.1	$+0.50_0$	$+0.42_5$	1.9
$[(CH_3)_3SiC_6H_4](C_6H_5)_2C^-$	72	-1.06_8	2.3	$+0.51_6$	$+0.43_8$	2.0
$[(CH_3)_3SiC_6H_4]_2(C_6H_5)C^-$	70	-1.03_0	2.0	$+0.53_3$	$+0.45_3$	1.8
$[(CH_3)_3SiC_6H_4]_3C^-$	79	-1.00_3	2.1	$+0.54_5$	$+0.46_7$	1.8

[a] Determined by cyclic voltammetry at 200 mV s^{-1} at a platinum wire electrode in dimethoxyethane solution, 0.5 M in $[n\text{-}C_4H_9]_4NClO_4$ at 21 ± 1 °C. [b] Peak potential separation indicating the reversibility of the electrode process. The theoretical value for a fully reversible one-electron process is 59.5 mV; under the conditions employed in this study, the reversible one-electron reduction of anthracene exhibited Δ = 66 mV. [c] $E_{1/2} = E_p(a) - E_p(c)/2$ vs. Ag/AgI reference electrode. [d] $\mu A(V\ s^{-1})^{-1/2}\ M^{-1}$. *Comparison of these values to that observed for the known one-electron reduction of anthracene,* 2.4, confirms that these are one-electron oxidations. [e] No cathodic wave was observed on the reverse sweep for $(C_6H_5)_3C^-$. The trimethylsilyl derivatives exhibited an ill-defined cathodic peak as illustrated in Figure 1. [f] Measured at 200 mV s^{-1}. Half-peak heights have been reported conventionally for the totally irreversible process (see R. N. Adams, "Electrochemistry at Solid Electrodes", Marcel Dekker, New York, 1969).

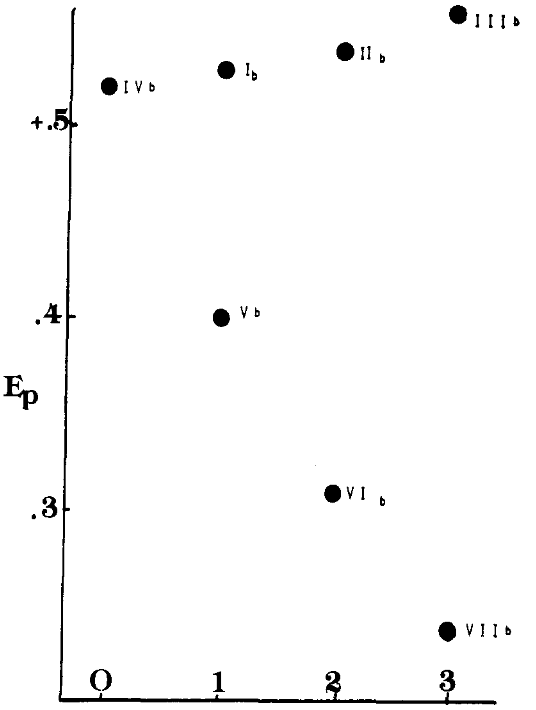

Figure 3. Relationship between E_p(a) and the number of groups in the para position.

Anion equilibration studies provide an independent value, and for IIId, 29.4 > pK_a IIId > 28.6. By comparison with IVd, the stabilizing effect is 3.8 ± 0.7 kcal/mol (2.8 ± 0.5 pK_a units). The large effect of silicon in stabilizing the anion is consonant with the results obtained on the substituent effect to restricted aryl rotation in diarylmethyl anions.[3] Interestingly the calculations reported in that work reveal a larger effect for silicon relative to methyl by a factor of ~2. Additionally there is fair agreement between these pK_a values and the σ^- values of trimethylsilyl of +0.17 and methyl −0.11.[6]

Figure 4 depicts the energy relationship of the tris-substituted cations and radicals. Of greatest note the effect of silyl substituents is minor. This contrasts with the effect of methyl which is now major. The relative magnitudes are in accord with the σ^+ constants of 0.093 and −0.256 for trimethylsilyl and methyl, respectively.[7] The derived differences between the unsubstituted and the tris(trimethylsilyl) cations of 0.5 kcal/mol is certainly within the experimental error and the assumptions of the treatment. What is clear is that cation stability is not markedly affected. Thus both methyl and trimethylsilyl groups stabilize radicals to similar extents, for anions, the silyl substituent has a more pronounced effect, and for cations the methyl substituent has a more pronounced effect.

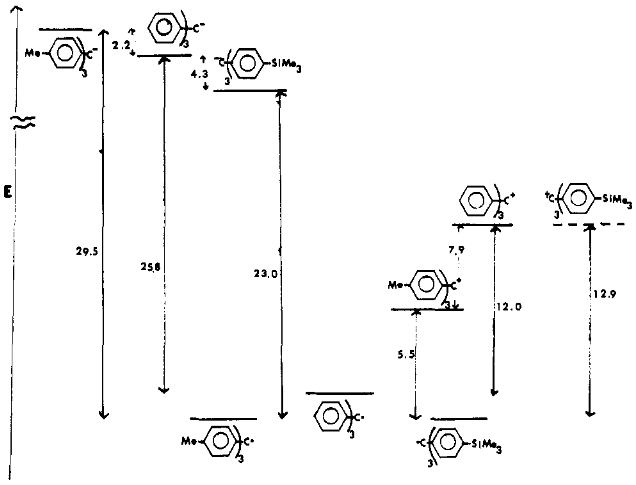

Figure 4. Energy relationship for the stabilities of tri-*p*-tolymethyl, triphenylmethyl and tris[*p*-(trimethylsilyl)phenyl]methyl anions, radicals, and cations in kilocalories/mole.

For the reversible oxidation of the anions the sequential trimethylsilyl substitution is revealing. As depicted in Figure 2 the effect is monotonic with the largest effect (53 mV) observed for the single trimethylsilyl substitution and the smallest (27 mV) observed for replacement by the third trimethylsilyl substituent. These effects are in direct agreement with the differential ring conjugation of the triarylmethyl system and the electron-withdrawing effect of the trimethylsilyl group. Interestingly, in magnitude the differential parallels that found for the corresponding cations and the electron-donating methyl group. Accordingly the conclusion that in solution there is a single maximally conjugated ring as is found in the solid is reinforced.

The relationship between anion oxidation potentials and computed energies of the highest occupied molecular orbitals for the anions calculated by using an ω SCF treatment was examined. Coulomb and resonance integrals for silicon from the literature[8] give rise to values of E_m in units of β of 0.143, 0.154, 0.175, and 0.187 for IIIa, IIa, Ia, and

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[6] J. Hine, "Structural Effects on Equilibria in Organic Chemistry", J. Wiley and Sons, New York, 1975, p 73.

[7] A. J. Gordon and R. A. Ford, "The Chemists Companion", J. Wiley & Sons, New York, 1972, p 152-3.

[8] J. Réffy, J. Karger-Kucsis, and J. Nagy. *Period. Polytech. Chem. Eng.*, 20, 77 (1976).

IVa, respectively. If a linear relationship is assumed the resulting slope of $\beta = 2.2$ V is in good agreement with other values.[9]

Experimental Section

The proton NMR were recorded on a Varian A60A spectrometer in $CDCl_3$ solutions. The carbon-13 NMR were recorded on a Bruker WH90 spectrometer in $CDCl_3$. Chemical shifts are reported in parts per million downfield from Me_4Si. The mass spectra were obtained by using an AEI MS-902 high-resolution electron-impact mass spectrometer. Gas chromatographic analyses were performed on a Hewlett-Packard HP-5750 instrument. A 10 ft × $^1/_8$ in. stainless-steel column packed with 10% Carbowax, 20M, 60–80-mesh, and a 2 ft × $^1/_8$ in. silicone-rubber column were used. Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. The solvent, dimethoxyethane (DME), was distilled prior to use from the sodium benzophenone ketyl. Tetrabutylammonium perchlorate (TBAP) recrystallized from ethyl acetate was used as the supporting electrolyte.

4-(Trimethylsilyl)bromobenzene. To 300 mL of a Grignard solution prepared from 118 g (0.50 mol) of *p*-dibromobenzene and 12.0 g (0.50 mol) of magnesium in ether was added 54.0 g (0.497 mol) of trimethylsilyl chloride. After being refluxed for 24 h the reaction mixture was poured over ice and acidified with ammonium chloride. After standard workup 88.4 g (0.386 mol) of crude product was obtained. After fractional distillation, 94–100 °C (12 mm), and removal of solid impurities, 34.2 g (0.149 mol) of pure *p*-(trimethylsilyl)bromobenzene was obtained; NMR ($CDCl_3$) δ 0.25 (9 H, s), 7.4 (4 H, m).

[4-(Trimethylsilyl)phenyl]diphenylmethane. A Grignard reagent was prepared from 2.0 g (0.32 mol) of magnesium and 12.1 g (0.053 mol) of 4-(trimethylsilyl)bromobenzene in ether. To this solution was added 9.7 g (0.053 mol) of benzophenone in benzene. After reflux for 12 h the mixture was hydrolyzed with ice and ammonium chloride. Standard workup gave rise to 19.0 g of crude [4-(trimethylsilyl)phenyl]diphenylcarbinol. Reaction of 14.4 g (0.043 mol) of this material with 25 mL of benzene and 5 mL of acetyl chloride by the method of Bachmann[10] gave rise to 12.9 g of a brown oil ([4-(trimethylsilyl)phenyl]diphenylchloromethane) which was used directly in the final step. Reaction of the crude [4-(trimethylsilyl)phenyl]diphenylchloromethane, 12.5 g (0.036 mol), with 29.3 g (0.775 mol) of sodium borohydride in 123 mL of diglyme and 67 mL of water at 60 °C for 12 h gave 8.70 g (0.025 mol) of crude [4-(trimethylsilyl)phenyl]diphenylmethane. Attempted recrystallization from methanol led to the recovery of a low-melting solid. GLC analysis on a 2-ft, silicone rubber column at 220 °C revealed a single sharp peak at 4.2 min in addition to solvent peaks: ^1H NMR δ 0.25 (9 H, s), 5.62 (1 H, s), 7.0–7.6 (14 H, m); ^{13}CNMR δ 1.19, 56.7, 126.0, 128.0, 128.6, 129.2, 133.1, 137.7, 143.6, 144.2; mass spectrum, calcd for $C_{22}H_{24}S_1$ 316.1647, obsd 316.1684.

Bis[4-(trimethylsilyl)phenyl]phenylmethyl Chloride. This material was prepared via bis[4-(trimethylsilyl)phenyl]phenylcarbinol which was not purified. A Grignard reagent prepared from 5.01 g (0.20 mol) of magnesium and 30.0 g (0.13 mol) of 4-(trimethylsilyl)bromobenzene in 90 mL of ether was reacted with 10.8 g (0.072 mol) of ethyl benzoate in 90 mL of benzene. After 4 h of reflux and workup there was obtained 28.8 g of yellow oil. The crude alcohol was dissolved in 30 mL of benzene and reacted with 20 mL of acetyl chloride. After solvent removal and addition of petroleum ether there was obtained 13.4 g (0.032 mol) of bis[4-(trimethylsilyl)phenyl]phenylmethyl chloride, mp 133–136 °C. The mass spectrum had peaks at *m/e* 387 (100, M – Cl), 388 (43.6), and 389 (20.6) which agree with the formula $C_{25}H_{31}Si_2Cl$; ^1H NMR δ 0.25 (18 H, s), 7.1–7.4 (13 H, m).

Bis[4-(trimethylsilyl)phenyl]phenylmethane. Reduction of 3.0 g (0.007 mol) of bis[4-trimethylsilyl)phenyl]phenylmethyl chloride with 2.15 g (0.057 mol) of sodium borohydride in aqueous diglyme at 65 °C for 24 h gave rise to 1.977 g (0.005 mol) of bis[4-(trimethylsilyl)phenyl]phenylmethane: mp 60–62 °C; ^1H NMR δ 0.36 (18 H, s), 5.5 (1 H, s) 7.0–7.5 (13 H, m); ^{13}CNMR δ 0.161, 58.0, 127.3, 128.4, 129.3, 129.9, 130.5, 133.0, 135.8, 139.0, 144.8, 145.4; mass spectrum, calcd for $C_{25}H_{32}Si_2$ 388.2043, found 388.2070.

Ethyl *p*-(Trimethylsilyl)benzoate. A Grignard solution (25 mL) prepared from 11.5 g (0.05 mol) of *p*-bromo(trimethylsilyl)benzene and 1.22 g (0.05 mol) of magnesium in ether was added to a solution of 8.85 g (0.075 mol) of diethyl carbonate in 5 mL of ether. After 14 h at room temperature the reaction mixture was hydrolyzed. After distillation at 89 °C (0.35 mm) [lit.[11] 105–106 °C (2.7 mm)] 4.08 g (0.0183 mol) of ethyl *p*-(trimethylsilyl)benzoate was obtained; ^1H NMR δ 0.25 (9 H, s), 1.35 (3 H, t), 4.35 (2 H, q), 7.75 (4 H, m).

Tris[4-(trimethylsilyl)phenyl]methane. This material was prepared via the corresponding carbinol and chloride which were directly reacted. To 20 mL of Grignard solution prepared from 1.128 (0.465 mol) of magnesium and 9.51 g (0.415 mol) of *p*-(trimethylsilyl)bromobenzene in ether was added 4.00 g (0.018 mol) of ethyl *p*-(trimethylsilyl)benzoate in 7 mL of dry benzene. After reflux for 2 h the reaction mixture was hydrolyzed and worked up in the usual way to provide 8.90 g (0.018 mol) of crude carbinol. From 4.77 g (0.01 mol) of carbinol and 3 mL of acetyl chloride in dry benzene, using the method of Bachmann,[10] was obtained 4.59 g (0.01 mol) of crude chloride. Reduction of 4.59 g of chloride (~0.01 mol) with 3.01 g (0.08 mol) of sodium borohydride and 0.80 g (0.02 mol) of sodium hydroxide in 13 mL of diglyme and 7 mL of water gave 2.47 g (0.005 26 mol) of crude product. Recrystalization from methanol gave a material with a sharp melting point, 150–151 °C. Gas chromatography (2-ft silicone-rubber column at 220 °C) revealed a single sharp peak at 9.7 min in addition to solvent peaks: ^1H NMR δ 0.28 (27 H, s), 5.40 (1 H, s), 7.07–7.55 (12 H, m); ^{13}C NMR δ 1.08, 57.05, 128.8, 133.3, 137.9, 144.3, 151.9; mass spectrum, calcd for $C_{28}H_{40}Si_3$ 460.2438, found 460.2463.

Estimation of pK_a Value of Tris[*p*-(trimethylsilyl)phenyl]methane. The pK_a of tris[*p*-(trimethylsilyl)phenyl]methane was estimated by NMR methods. The lithium salt of IIId in tetrahydrofuran (THF) has a singlet at 0.21 ppm accounting for 27 protons and an AA′BB′ pattern in the aromatic region. This pattern was fit by using the LAOCOON III program to give δ 7.40 and 6.86, $J_{1,2} = 8.2$ Hz, and $J_{1,3} = 2.1$ Hz. Accordingly upon anion formation both the trimethylsilyl and aromatic protons move relative to the hydrocarbon.

The anion of triphenylmethane (IVa) was used at the upper end of the expected pK_a range. Of greatest importance the signal for the para protons at 5.96 ppm, $J_{p,m} = 6.6$ Hz, occurs in a region where there is no absorbtion in the silyl anion IIId. Similarly, the signals for the ortho and meta hydrogens at 7.31 and 6.52 ppm, respectively, with $J_{o,m} = 7.9$ Hz have a window at 6.86 ppm where the silyl anion absorbs.

When an equimolar mixture of IIId and IVd was treated with excess butyllithium both anions were formed. Reaction of 1 equiv of base with an equimolar mixture gave only the anion IIIa. Finally, 0.5 mL of a 0.1 M solution of IIIa in THF was reacted with 0.5 mL of a 1.0 M IVd solution in THF;[12] NMR analysis revealed no trityl anion from which we may conclude that the anion cannot be present in amounts greater than 10% of the hydrocarbon. Accordingly the pK_a of IIId must be at least 2 units less than that of triphenylmethane (pK_a 31.4[13]).

The anion of 1,1,3-triphenylpropene was used at the lower end of the expected pK_a range. The NMR of the lithium salt of 1,1,3-triphenylpropene has peaks at 5.22 and 5.48 ppm and a complex aromatic region centered at 6.82 ppm. Importantly the high-field signals occur in the region where there is no absorption for the anion IIIa. Similarly, the anion IIIa absorbtion at 7.40 ppm occurs in a region where neither the hydrocarbon nor the anion of 1,1,3-triphenylpropene absorb.

Reaction of IIId and 1,1,3-triphenylpropene with 2 equiv of butyllithium in THF gave rise to both anions. Sequential addition

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(9) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemistry", J. Wiley and Sons, New York, 1962, Chapter 7.

(10) W. E. Bachmann, "Organic Syntheses", Collect. Vol. III, Wiley, New York, 1955, p 841.

(11) J. D. Roberts and C. M. Regan, *J. Am. Chem. Soc.*, **75** 4102 (1953).

(12) Control experiments guarantee that these reactions were conducted under conditions known to establish equilibration. See also, S. Bank and J. S. Sturges, *J. Organomet. Chem.*, **156**, 5 (1978).

of aliquots of methanol in THF until 1 equiv had been added revealed that only the anion IIIa had been protonated. Finally, reaction of 10 equiv of IIId with I equiv of the anion of 1,1,3-triphenylpropene revealed a complete absence of the anion IIIa.[12] Since a minimum of 10% anion formation would be detectable and a 10-fold excess was used, we conclude that the pK_a of IIId is at least 2 pK_a units greater than that of 1,3,3-triphenylpropene (26.6).[13]

Electrochemical Measurements. Electrochemical measurements were performed in DME/0.5 M [$(n\text{-}C_4H_9)_4N$]ClO_4 vs. a Ag/AgI reference electrode. A three-electrode IR-compensated system with a platinum auxiliary electrode was used throughout. Details of the construction of the reference electrode are given in ref 14 and 15. Cyclic voltammetry was performed at a platinum wire electrode on a PAR Model 170 electroanalytical system at 21 °C.

The cyclic voltammograms confirmed the reversibility of the first oxidation step ($R^- \rightarrow R\cdot + 1e$, at approximately -1.00 to -1.20 V in all cases.)[16] Potential sweep rates from 5 to 500 mV s^{-1} were used. The minimum value allowed by convection and diffusion was 5 mV s^{-1}. The ratios between the anodic and cathodic peak currents, $i_p(a)/i_p(c)$, were unity and independent of sweep rate. The potential separation between peaks was constant at ~72 mV. The reversible one-electron reduction of anthracene observed at -1.87 V in this system exhibited a peak separation of 66 mV under similar conditions.

The second oxidative process, occurring at approximately +0.4 to +0.6 V for the various compounds, is completely irreversible, probably due to rapid capture of the cation by another molecule of anion. This was independent of sweep rate, up to the maximum sweep rate available, 1000 mV s^{-1}. For this irreversible process use of E_p values as a measure of cation stability depends upon the condition that the rate of the chemical step following electron transfer be independent of substitution. This will be obeyed for the cation–anion recombination.[17]

Acknowledgment. We acknowledge with gratitude assistance in the preparation of compounds by Mr. R. Bruen and Mr. C. Migdal.

Registry No. Ia, 76429-99-7; Ib, 76430-00-7; Ic, 76430-01-8; Id, 68494-28-0; IIa, 76430-02-9; IIb, 76430-03-0; IIc, 76430-04-1; IId, 69340-84-7; IIIa, 76430-05-2; IIIb, 76430-06-3; IIIc, 76430-07-4; IIId, 76430-08-5; IVa, 40006-86-8; IVb, 2216-49-1; IVc, 13948-08-8; 4-(trimethylsily)bromobenzene, 6999-03-7; *p*-dibromobenzene, 106-37-6; trimethylsilyl chloride, 75-77-4; benzophenone, 119-61-9; [4-(trimethylsilyl)phenyl]diphenylcarbinol, 50653-05-9; [4-(trimethylsilyl)phenyl]diphenylchloromethane, 76446-92-9; bis[4-(trimethylsilyl)phenyl]phenylmethyl chloride, 76446-93-0; ethyl benzoate, 93-89-0; bis[4-(trimethylsilyl)phenyl]phenylcarbinol, 50653-06-0; ethyl *p*-(trimethylsilyl)benzoate, 18028-09-6; diethyl carbonate, 105-58-8; tris[4-(trimethylsilyl)phenyl]carbinol, 76430-09-6; tris[4-(trimethylsilyl)phenyl]methyl chloride, 76430-10-9.

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[17] We gratefully acknowledge the suggestion of a reviewer for this point.

Evidence for a Strong Through-Bond Interaction in *anti*-Tricyclo[6.4.0.0^{2,7}]dodecatetraene

Rolf Gleiter* and Klaus Gubernator

Institut für Organische Chemie der Universität, D-6900 Heidelberg, West Germany

Wolfram Grimme

Institut für Organische Chemie der Universität, D-5000 Köln, West Germany

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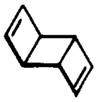
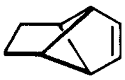
The He(I) photoelectron spectra of *anti*-tricyclo[6.4.0.0^{2,7}]dodecatetraene (6) and bicyclo[4.2.0]octa-2,4-diene (7) have been recorded. The first bands in the PE spectrum of 6 and 7 could be assigned based on a ZDO model and semiempirical calculations. The ZDO model reveals a resonance integral between the butadiene moiety and four-membered-ring fragment of $\beta = -1.5$ eV. In the case of 6 the first two bands are split by 0.6 eV which is due to through-bond interaction between the π system and the four-membered ring. A comparison with other systems showing two π systems in an anti arrangement to a σ system reveals a large through-bond effect.

Recent photoelectron (PE) spectroscopic investigations[1] and model calculations[2] indicate that a four-membered ring interacts strongly with a double-bond system connected in 1,2 and 1,3 positions. Relevant examples are the PE spectra of *syn*- and *anti*-tricyclo[4.2.0.0^{2,5}]octadienes[3,4] 1 and 2 as well as tricyclo[3.3.0.0^{2,6}]octene (3)[5] and bicyclo[4.1.1]octa-2,4-diene (4).[6] Missing links in this series are the *syn*- and *anti*-tricyclo[6.4.0.0^{2,7}]dodecatetraenes 5 and 6 as well as bicyclo[4.2.0]octa-2,4-diene (7). In this paper we report our PE spectroscopic investigations of 6 and 7.


1


2


3


4

Photoelectron Spectra. The He(I) PE spectra of 6 and 7 are shown in Figure 1. The recorded first vertical ion-

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