and 0.1 M NaOH) containing a 5 M excess of BPA were placed in clear Pyrex tubes. These were irradiated for 15 h at 32 °C at a distance of 1 cm from a 450 W UV lamp (Hanovia water-cooled immersion well, Pyrex filter). The product distributions were determined by LC analysis of the reaction mixtures and the results are listed in Table III.

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Registry No.—BPA, 107-71-1.

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Substituent Effect on the Electrochemical Oxidation of Trityl Anions

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The reversible one-electron oxidations of triaryl anions and the irreversible second oxidative processes were examined for a series of sequentially substituted *p*-methyl anions. The cycle voltammograms of the lithium salts prepared in dimethoxyethane reveal that each of the potentials depends upon the substituent in the para positions. The relative effect of substituent on the stability of the several species is compared with other known measurements. Additionally, the relationship between carbanion stability and reduction potential is discussed.

The use of electrochemical data to provide entries into the thermodynamic stabilities of cations and anions is based on the interrelationship with the corresponding radical as shown below:

$$\mathrm{ROH} \rightleftarrows \mathrm{R}^+ \overset{e}{\rightleftarrows} \mathrm{R}\cdot \overset{e}{\rightleftarrows} \mathrm{R}^- \rightleftarrows \mathrm{RH}$$

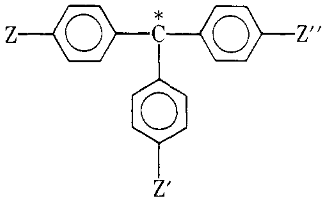
The important successes of the method are attested to by the recent contributions of Breslow and co-workers[1] and the extensive work by Henglein on the electrochemical properties of radical intermediates determined by pulse radiolysis polarography.[2]

In this study we utilize this approach to investigate the oxidation potentials of triaryl anions with two objectives: first, to provide information on the factors that govern carbanion and free-radical energy differences; second, to assess the relative substituent effect on the stability of anions, radicals, and carbonium ions. The first relates to the contributions of one and two electron transfer processes to nucleophilicity.[3] In a homologous series knowledge of anion stability and reduction potential can be used to probe relationships with nucleophilicities. The second relates to the types of contributions substituents can and do make on stability.

Accordingly, we have investigated the electrochemistry of a series of triaryl anions with a systematic substituent variation. Included in this work are the reversible and irreversible oxidation potentials of the series of para methyl substituted anions.

Results and Discussion

The lithium anions Ia → IVa were generated from the corresponding hydrocarbons and reaction with *n*-butyllithium in dimethoxyethane (DME).[4] The triaryl methanes IId and IIId were obtained via Grignard syntheses. Compound IVd was prepared from the corresponding chloride following the method of Gomberg.[5] To minimize decomposition of the air-moisture sensitive anions the freshly prepared solutions were generated on a No-Air system directly in the electrochemical cell.



I, Z = H; Z' = H; Z'' = H
II, Z = CH_3; Z' = H; Z'' = H
III, Z = CH_3; Z' = CH_3; Z'' = H
IV, Z = CH_3; Z' = CH_3; Z'' = CH_3
a, * = 2 electrons
b, * = 1 electron
c, * = 0 electrons
d, * = H
e, * = OH
f, * = Cl

The voltammogram of Ia depicted in Figure 1 reveals the reversible one-electron oxidation at −1.20 V and the irreversible oxidation at +0.57 V. These results are in agreement with those obtained by others for this same anion.[1a,b] Additionally the degree of reversibility and reproducibility, ±0.007 mV, of the measurements are acceptable. Accordingly, we investigated the corresponding electrochemical behavior of the substituted anions IIa → IVa. These data are depicted in

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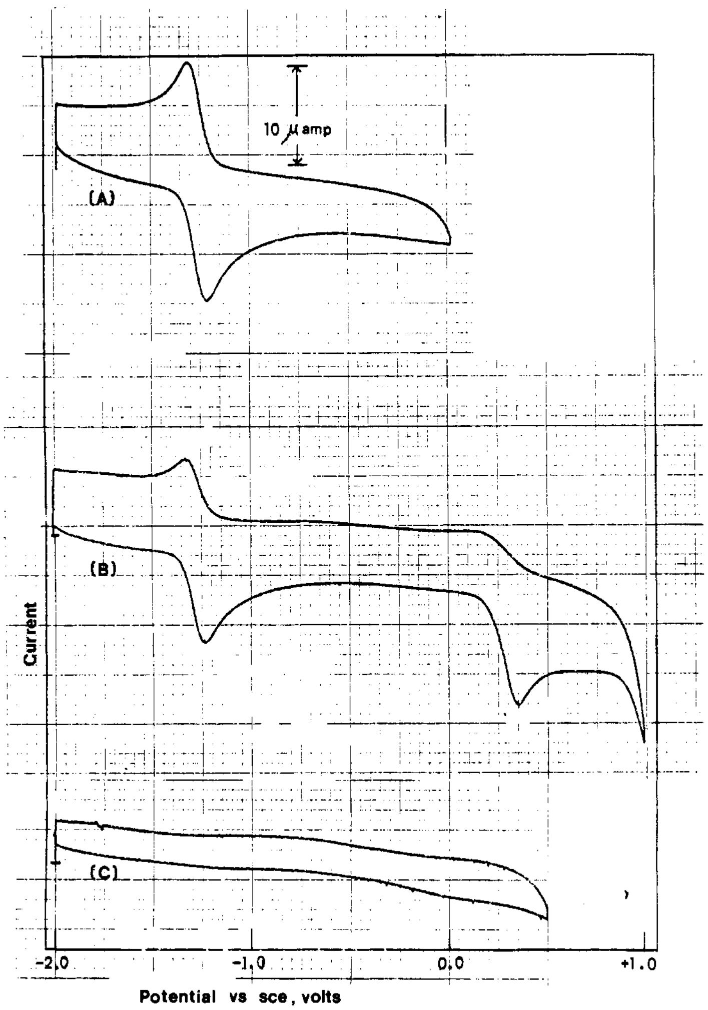

Figure 1. Cyclic voltammograms of 10^{-3} M $(CH_3C_6H_4)(C_6H_5)_2C^-$ in 0.1 M TBAP in dimethoxyethane solution at a scan rate of 200 mV s^{-1}: (A) scan range −2.0 to 0.0 V, isolating the reversible one-electron oxidation; (B) scan range −2.0 to +1.0 V, showing the successive one-electron oxidations; (C) scan range −2.0 to 0.5 V after quenching the solution with dry oxygen for 30 s followed by a 2 min argon purge.

Figure 2 and presented in Table I.

Since the second cathodic processes are clearly irreversible, displaying limited, but measurable, sweep rate and concentration dependence,[6] these data are not truly thermodynamic. The kinetic effects will be minimized, however, in a comparison of relative redox potentials for a series of compounds. That a similar electrode process is involved for compounds I–IV is clear from the data: the number of electrons transferred in the redox process is the same; the degree of reversibility of the processes is similar; and the character of the limiting currents is similar.[7] Additional support for the validity of the treatment is found in footnote *g* of Table I.

Each of the oxidation potentials depend upon the substituents in the para position. For triphenylmethyl and tritolylmethyl there is sufficient data on anion and cation stability from other sources to permit the evaluation of the substituent effect in detail. Accordingly Figures 3 and 4 represent the relative energetics of the anions and cations, respectively. Focusing first on Figure 3, the greater stability of the Ia compared to IVa comes from the pK_a measurements of Streitweiser.[8] Utilizing the data in Table I, the difference in radical stability Ib and IVb is estimated as 1.5 kcal/mol. This value and the oxidation potentials in Table I are then utilized to construct the energy diagrams in Figure 4 for the cations. The

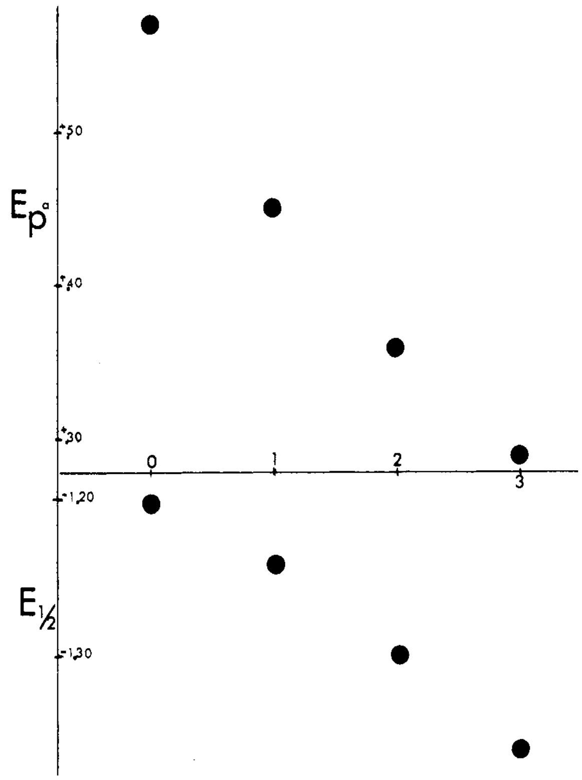

Figure 2. Relationship between $E_p(a)$ and $E_{1/2}$ in volts with the number of methyl groups in the para position.

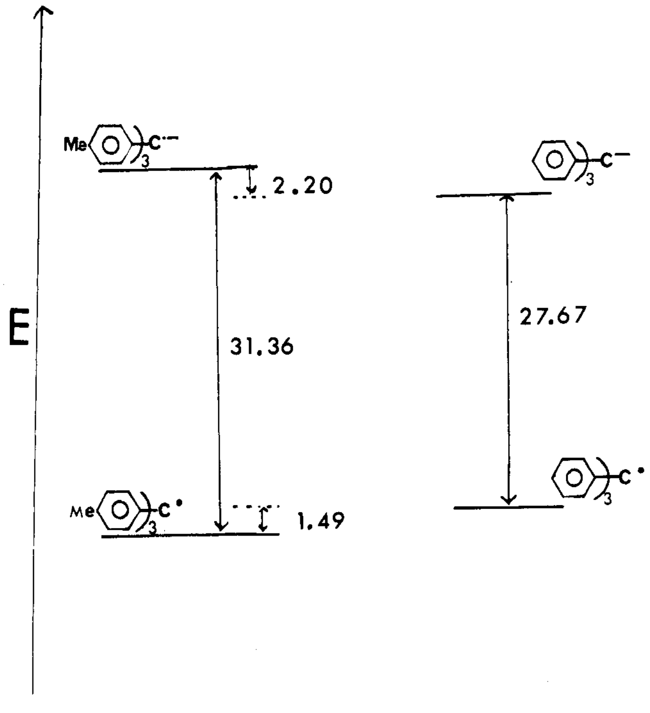

Figure 3. Energy relationship for the stabilities of tritolylmethyl and triphenylmethyl anions and radicals in kcal/mol.

estimated difference in cation stability is therefore 8.0 kcal/mol.

Two features of this analysis are noted. First, the estimated values can be compared with those obtained by other methods. Second, the relative effects of the substituents on each of the species can be assessed. For the former, the relative carbocation stability is in fair agreement with that obtained from carbocation alcohol equilibrium in sulfuric acid.[9] The ΔG_R^+ value of 4.1 kcal/mol for tri-*p*-tolylmethyl relative to tri-

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

		$R^- \rightleftarrows R\cdot$			$R\cdot \rightarrow R^+$		
compd	registry no.	Δ, mV[b]	$E_{1/2}$, V[c]	$(i_p(a)/V^{1/2}C) \times 10^{-4}$ [d]	$E_p(a)$[e]	$E_{p/2}$, V[f]	$(i_p(a)/V^{1/2}C) \times 10^{-4}$
$(C_6H_5)_3C^-$	40006-86-8	71	-1.20_3	3.2	$+0.57_4$	$+0.46_2$	3.4
$(CH_3C_6H_4)(C_6H_5)_2C^-$	16298-58-1	73	-1.24_0	2.6	$+0.45_4$	$+0.34_0$	2.9
$(CH_3C_6H_4)_2(C_6H_5)C^-$	13948-06-6	74	-1.29_7	2.7	$+0.36_3$	$+0.24_1$	2.8
$(CH_3C_6H_4)_3C^-$	69239-34-5	72	-1.36_4	3.1	$+0.29_0$	$+0.18_5$	3.6

[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 similar condition the reversible one-electron reduction of anthracene exhibited $\Delta = 64$ mV. [c] $E_{1/2} = E_p(a) = E_p(c)/2$; $E_{1/2}$ vs. saturated calomel electrode. [d] μA $(V\ s^{-1})^{-1/2}\ M^{-1}$. Comparison of these values to that observed for the known one-electron reduction of anthracene, 2.9, confirms that these are one-electron oxidations. [e] No cathodic wave was observed on the reverse sweep. [f] Measured at 200 mV s^{-1}. Half-peak heights have been reported conventionally for the totally irreversible process.[27] [g] In acetonitrile/0.1 M TBAP solution, the reversible reductions of trityl cation and trimethyl trityl cation have been observed. Volz and Lotsch[28] report values of +0.27 and +0.05V vs. SCE, respectively, for the reduction of the triarylmethyl cations under these conditions. Although the values reported herein (0.46 and 0.19 V for $E_{p/2}$) are quite at variance, it should be noted that the conditions under which the experiments were run are substantially different. The differences between the observed potentials for the processes (0.22 V in the reversible system vs. 0.27 V reported herein) are in substantial agreement.

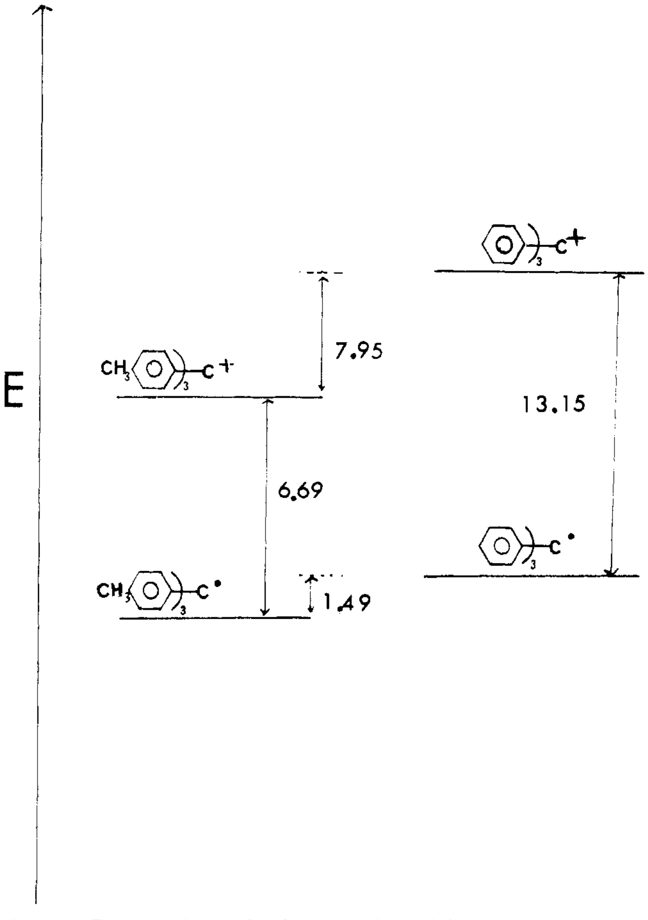

Figure 4. Energy relationship between the stabilities of the tritolylmethyl and the triphenylmethyl cations and radicals in kcal/mol.

phenylmethyl corresponds to the value of 8.0 kcal/mol obtained in this work. Similarly the estimated relative radical stabilities of 1.5 kcal/mol may be similarly compared with the value of 2.3 kcal/mol calculated from the radical dissociation constants of the corresponding dimers.[10] Given the uncertainty of these latter numbers the agreement is acceptable. Accordingly, in magnitude and direction the substituent effects derived from this work and from others are in fair agreement.

The second point to note is the relative substituent effects for the three species. The stabilizing effect of para methyls in cations is larger than the destabilizing effect of the *p*-methyl in the anions which in turn is larger than the stabilizing effect of *p*-methyls in the radicals. The substituent effect is greater in the charged species and is considerably larger for cations than for anions. In direct analogy cation stabilities are correlated with σ^+ values, whereas anion and radical stabilities are correlated with σ or σ^- values.[11] In this regard it appears as if substituents affect the cation with resonance and/or hyperconjugation terms in addition to inductive and polarizability terms, whereas only the latter contribute substantially to radical and anion stability. These views are supported by the differing sequential effects of methyl substitution.

Attention is now focused on the effects of sequential methyl substitution on the several oxidation potentials. As revealed by Figure 2 and Table I the effects are monotonic and in the expected direction for each process. Interestingly, they differ in pattern, thus for the reversible anion to radical oxidation the smallest change is observed for a single methyl substitution that is in going from Ia to IIa. In contrast the radical oxidation to cation shows the largest change (0.12 V) for a single methyl substitution, that is in going from Ic to IIc.

These effects are consonant with the known propeller geometry of the aryl rings. Steric and conjugative effects are balanced in each to provide the greatest stabilities. Interestingly, the degree of twist for the three species is known from experiment[12] and calculation[13] and is similar for the anion, cation, and radical. Importantly, varying substituent effects are therefore not likely to be due to conformational difference in the species but rather differing substituent contributions.

For the cations the decreasing effects of methyl substitution of 0.12, 0.09, and 0.07 V respectively are an example of the saturation phenomenon.[14] One viable mechanism to account for this effect involves varying abilities of the rings to be planar. Thus for the cation with a single *p*-methyl group the maximum stabilizing effect is realized when this ring is conjugated at the expense of the others. In this vein the contribution of the third methyl group is essentially nonhyperconjugative. Significantly, the magnitude of this effect is the same as that observed for anions. The differential effect of adding the third methyl group of 0.07 V in the cation compares closely with the corresponding differential effect of 0.06 V in the anion. Thus the evidence points to varying and different roles for the contribution of a methyl group to cation stability. Finally the magnitudes of the contributions are quite similar in analogy with the effects in other reactions and substituents.[15]

The pattern of sequential methyl substitution for the anions is consonant with the above analysis but of a much smaller

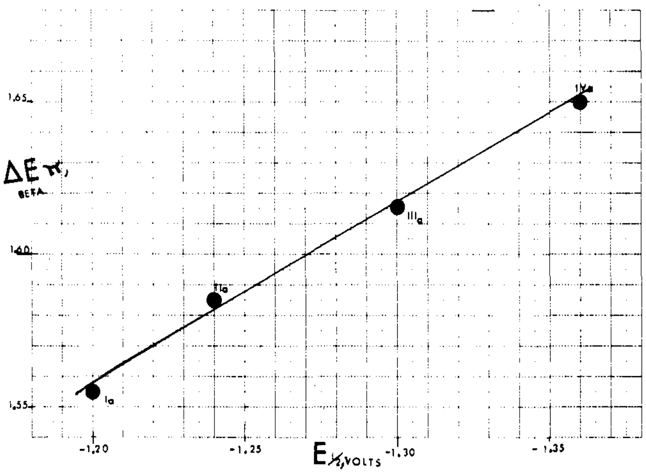

Figure 5. Relationship between the SCF calculated energy differences for the triaryl anions and radicals and the reversible oxidation of the lithium salts in DMF.

magnitude. For the anion with one methyl group the greatest stabilizing resonance effect is realized when an unsubstituted ring is maximally conjugated. In agreement, the first methyl substitution has the smallest effect. Although indicative and directionally correct it is not strong evidence since the resonance effect in anions is expected to be small and the observed change is less than half of that observed with the cations.

The relationship between the anion oxidation potentials and computed energies is shown in Figure 5. The energies were calculated by a ω SCF molecular orbital treatment. The relationship is monotonic and if assumed to be linear gives rise to a slope of $\beta = 1.80$ V, in reasonable agreement with other values.[16]

Finally we turn attention to the relationship between anion stability and electron transfer. As expected substitution of methyl in each para position increases the basicity and the reduction potential. Notably the effect on basicity of 2.20 kcal/mol is less than the 3.70 kcal/mol difference in reduction potentials. Thus the less stable anion is a more powerful reducing agent by a greater margin. In these systems this is the result of a reversal of the relative energies of the radicals and the anions. For this set of similar anions a clear relationship between these two contributors to nucleophilic reactivity is now available.

Experimental Section

The NMR spectra were recorded on a varian A60 A spectrometer in $CDCl_3$ solutions. Chemical shifts are reported in ppm downfield from Me_4Si. The melting points are uncorrected.

4-Methylphenyldiphenylcarbinol (IIe). To a Grignard solution prepared from 19.7 g (0.115 mol) of *p*-bromotoluene and 2.70 g (0.110 g-atom) of magnesium in ether was added 20.0 g (0.110 mol) of benzophenone in benzene. After being refluxed for 1 h and being hydrolyzed, 13.30 g (0.048 mol) of 4-methyltriphenylcarbinol was obtained: NMR ($CDCl_3$) δ 2.25 (3 H, s), 2.89 (1 H, s), 7.1 (4 H, s), 7.1 (4 H, s), 7.2 (10 H, s).

4-Methyltriphenylchloromethane (IIf). Reaction of 13.3 g (0.48 mol) of IIe with 15 mL of acetyl chloride in benzene in the method of Bachmann[17] gave rise to 11.0 g (0.0376 mol) of 4-methyltriphenylchloromethane: NMR δ 2.32 (3 H, s), 7.10 (4 H, s), 7.23 (10 H, s).

4-Methyltriphenylmethane (IId). Reaction of 11.0 g (0.376 mol) of IIf with 8.51 g (0.23 mol) of sodium borohydride in 200 mL of Me_2SO[18] gave 7.1 g (0.0275 mol) of 4-methyltriphenylmethane. The compound was recrystallized from methanol–chloroform: mp 68.5–69 °C (lit.[19] mp 72 °C); NMR δ 2.34 (3 H, s), 5.54 (1 H, s), 7.07 (4 H, s), 7.15–7.30 (10 H, m).

4,4′-Dimethyltriphenylcarbinol (IIIe). A Grignard reagent prepared from 9.0 g (0.37 g-atom) of magnesium and 65.8 g (0.384 mol) of *p*-bromotoluene was reacted with 25.0 g (0.17 mol) of ethyl benzoate. The melting point of the material was 75.5–77 °C (lit.[20] mp 80.0 °C): NMR δ 2.3 (6 H, s), 2.65 (1 H, s), 7.15 (8 H, s), 7.25 (5 H, s).

4,4′-Dimethyltriphenylmethyl Chloride (IIIf). From 11.1 g (0.385 mol) of IIIe and 6 mL of acetyl chloride in benzene there was obtained 6.80 g (0.022 mol) of 4,4′-dimethyltriphenylmethyl chloride. After recrystallization from benzene petroleum ether the melting point was 104–106 °C (lit.[21] mp 106–107 °C): NMR δ 2.30 (6 H, s), 7.11 (8 H, s), 7.22 (5 H, s).

4,4′-Dimethyltriphenylmethane (IIId). From 6.80 g (0.0385 mol) of IIIf, 680 g (0.180 mol) of sodium borohydride, and 1.80 g (0.045 mol) of sodium hydroxide in 30 mL of diglyme and 15 mL of water[22] there was obtained 4.24 g (0.0192 mol) of 4,4′-dimethyltriphenylmethane: NMR δ 2.27 (6 H, s), 5.42 (1 H, s), 7.00 (8 H, s), 7.10–7.25 (5 H, m); mp 50–53 °C (lit.[23] mp 53 °C).

4,4′,4″-Trimethyltriphenylmethyl Chloride (IVf). From 121 g (1.22 mol) of toluene and 111.7 g (0.726 mol) of carbon tetrachloride in 200 mL of carbon disulfide and 70 g (0.525 mol) of aluminum chloride[24] there was obtained 12.2 g (0.0383 mol) of brown crystals: mp 158–160 °C (lit.[24] 173 °C); NMR δ 2.32 (9 H, s), 7.13 (12 H, s).

Tri-*p*-tolylmethane (IVd). Reduction of 12.0 g (0.0375 mol) of IVf with 11.3 g (0.300 mol) of sodium borohydride and 3.0 g (0.75 mol) of sodium hydroxide in 44 mL of diglyme and 26 mL of water gave 3.00 g (0.0105 mol) of tri-*p*-tolylmethane: mp 56–58 °C (lit.[25] mp 63 °C); NMR δ 2.31 (9 H, s), 7.02 (12 H, s).

The solvent, dimethoxyethane (DME), was distilled prior to use from the sodium benzophenone ketyl. Tetrabutylammonium perchlorate (TBAP), recrystallized from ethyl acetate, was used as a supporting electrolyte. The cell was prepared and sealed under a dry argon atmosphere.

The anions were prepared in the following manner. A weighed amount of the parent hydrocarbon was placed in a dry flask which was subsequently evaporated and filled with dry argon. DME was added through a rubber septum. Into this mixture was injected a 1.58 M solution of *n*-butyllithium (in hexane) in slightly over a twofold excess. The colored anion solution was transferred via a double pointed syringe needle into a flask containing the correct amount of TBAP sealed under dry argon. This mixture was then shaken to achieve a homogeneous solution. The anion/electrolyte solution was then transferred to the cell by a double pointed needle. The voltammagram of the anion was taken immediately. Following this, the anion was then quenched and another voltammagram was taken.

Electrochemical measurements were performed in DME|0.5 M $[n\text{-}Bu_4]NClO_4$ vs. an isolated saturated calomel electrode. A three-electrode, IR compensated system with a platinum auxiliary electrode was used throughout. Cyclic voltammetry was performed at a platinum wire electrode on the PAR Model 170 electroanalytical system at 21 °C.

The cyclic voltammogram confirmed the reversibility of the first oxidation step ($R^- \rightarrow R\cdot + 1e$, at approximately −1.20 to −1.30 V) in all cases.[26] Potential sweep rates from 5 to 500 mV s^{-1} were used. The minimum value allowed by connection 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 ~71 mV. The reversible one-electron reduction of anthracene, observed at −1.95 V in this system, exhibited a peak separation of 64 mV under similar conditions.

The second oxidative process, occurring at approximately +0.3 to +0.6V 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}.

Registry No.—IId, 603-37-2; IIe, 5440-76-6; IIf, 23429-44-9; IIId, 603-39-4; IIIe, 6266-56-4; IIIf, 69239-35-6; IVd, 16845-02-6; IVf, 971-93-7; *p*-bromotoluene, 106-38-7; benzophenone, 119-61-9; ethyl benzoate, 93-89-0; toluene, 108-88-3; carbon tetrachloride, 56-23-5.

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Kinetics of Methanolysis of and of Sodium Methoxide Induced Elimination from Substituted Benzyldimethylcarbinyl Chlorides[1]

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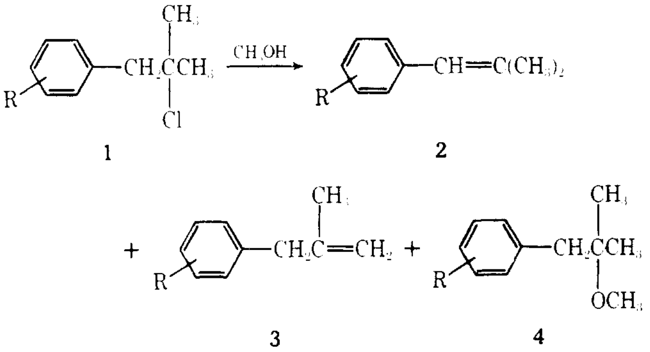
Rates of methanolysis of a series of substituted benzyldimethylcarbinyl chlorides at three temperatures obey the Hammett equation with ρ ca. -0.9. $\Delta S^{\ddagger}$ is in most cases about -4 gibbs/mol. Rates of reactions of *p*-nitro- and 3,5-dichlorobenzyldimethylcarbinyl chlorides with NaOMe in MeOH to form isomeric olefins have been measured. When taken in conjunction with literature data, our measurements for $ArCH{=}CMe_2$ formation necessitate use of σ^- for $p\text{-}NO_2$ to give good Hammett correlation, with ρ +1.2. For formation of $ArCH_2C(Me){=}CH_2$, ρ is essentially zero (-0.07). The data for the NaOMe reactions are successfully interpreted in terms of variable transition state E2 theory, but do not support an alternative theory that postulates attack of base on an ion pair.

The kinetics of solvolysis of benzyldimethylcarbinyl chloride (**1a**) and of elimination induced by NaOMe, both in methanol at 75.8 °C, were studied by Bunnett, Davis, and Tanida.[3] A few years later, Blackwell, Fischer, and Vaughan[4,5] extended such kinetic study to a number of ring-substituted benzyldimethylcarbinyl chlorides, all at 66.5 °C. We now report a further extension of these studies, to include two substrates not previously investigated and, for the first time, to include the influence of temperature and enable the calculation of activation parameters.

The solvolysis of substituted benzyldimethylcarbinyl chlorides in 80% aqueous ethanol has been reported by Landis and VanderWerf,[6a] Tessler and VanderWerf,[6b] and Brown and Kim.[7] However, these investigators did not determine product compositions or the kinetic effects of added bases.

Results

From either methanolysis or methoxide-induced elimination, the products are two olefins (**2** and **3**) and an ether (**4**).



a, R = H d, R = *p*-Cl
b, R = $p\text{-}CH_3$ e, R = 3,5-Cl_2
c, R = $p\text{-}OCH_3$ f, R = $p\text{-}NO_2$

Synthesis of Substrates. Although most of the substrates were obtained straightforwardly, the synthesis of one calls for special comment. *p*-Nitrobenzyldimethylcarbinyl chloride (**1f**) is conspicuously absent from the reports of Landis and VanderWerf[6a] and of Brown and Kim.[7] Blackwell et al.[4,5] mention specifically their inability to obtain it. We succeeded in synthesizing **1f** by nitration of **1a** with nitric acid in acetic anhydride at ca. 60 °C and in isolating it as a crystalline solid.

Products of types **2, 3,** and **4** were obtained by treating the various substrates with bases in methanol. They were isolated, ultimately by gas-liquid chromatography (GLC), characterized by their NMR and other spectra, and used for qualitative and quantitative calibration of the GLC product analyses on reactions under kinetic conditions.

Rate and Product Determinations. Inasmuch as the 1-aryl-2-methyl-1-propenes (**2**) strongly absorb ultraviolet light at about 250 nm, except that λ_{max} for **2f** is at 316 nm, while compounds of types **1, 3,** and **4** have little absorption at these wavelengths, it was possible to estimate the yield of **2** from any reaction by spectrophotometry. In most cases the photometric estimate agreed with the GLC determination within ±2%, but the GLC yield was used for treatment of data.

We determined rate constants for solvolysis of compounds **1a–f** at three temperatures except in the case of **1a**, and our determinations are summarized in Table I. In order to avoid acid-catalyzed interconversion of products, all solvolysis re-

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