other electron, or it may couple with itself or the starting material (refer to Scheme I). The fact that only monomer is produced at low pH indicates that the radical anion first picks up a proton. The protonated radical, **5**, being easier to reduce than the starting material, is immediately reduced to **6**, which picks up another proton to form the monomer **2**. This represents the most probable pathway to monomer formation at low pH.

The major differences between the pathways leading to the dimer are found in the coupling step. This step may be radical–radical coupling (rrc, species **4** to **8**), radical–substrate coupling (rsc, species **4** to **9**), or ion-substrate coupling (isc, species **7** to **8**). Previous work in nonaqueous solvents with activated and diactivated olefins has generally led to the conclusion that rrc is the predominate pathway.[1-4] This conclusion has been reached via several electrochemical techniques, including cyclic voltammetry, chronoamperometry, and rotating ring-disk voltammetry. In the present case, rrc again appears to be the predominate mechanism. The structure of **3b** where both methyl groups are found exclusively on the bridging carbons favors rrc and isc or rsc would favor formation of some dimer with one methyl group on the bridging carbon and one methyl group on the nonbridging carbon.

While the location of the methyl groups in **3b** is not due to steric effects, the complete lack of dimer formation with **1c** is attributable to steric hindrance. The steric effect of the methyl groups is also illustrated by the lower percentage of dimer that is produced from **1b** compared to **1a**.

Scheme I shows only the structures of intermediates formed by C–C interactions. The carbonyl oxygens also exhibit radical and ionic character, and thus could be involved in the initial coupling reaction. Such an intermediate could then rearrange to give the observed products. The likelihood of this scheme is favored by the fact that the tautomeric form of the radical anion in which the unpaired electron is on an oxygen is the form that has 6 π electrons available to the ring. Comparison to the electrochemical reduction mechanism of phthlamide and N-substituted phthlamides where the carbonyl group is reduced strengthens the case for the direct participation of oxygen in the coupling step.[10] Nevertheless, the authors favor the proposed mechanism involving the direct coupling of the carbon radicals.

Registry No.—Citraconic anhydride, 616-02-4; ethylamine, 75-04-7; dimethylmaleic anhydride, 766-39-2.

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Anodic and Photochemical Oxidation of Triphenylmethanes

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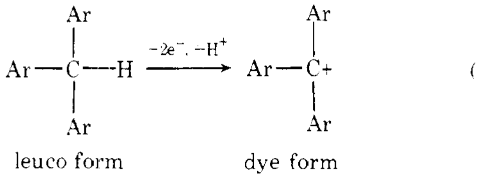
Cyclic voltammetry was used to study the effect of chemical structure on the anodic oxidation of 15 triphenylmethanes and related compounds. Two-electron oxidation leads irreversibly to formation of the corresponding dye except in those compounds where C–H bond cleavage at the central methine carbon atom is impossible. Ease of oxidation is enhanced by electron-releasing substituents and by increasing solvent polarity. Relative rates of photochemical oxidation of the compounds in air-saturated methylene chloride when irradiated at 366 nm were found to increase logarithmically with decreasing oxidation potential.

Triarylmethane dyes are among the oldest synthetic dyes and find application in the textile and printing industries and as indicators in analytical chemistry.[1,2] The formation of the dye cations from their leuco forms may be represented formally by eq 1.



$$\begin{array}{c}\mathrm{Ar}\\|\\\mathrm{Ar{-}C{-}H}\\|\\\mathrm{Ar}\end{array}\xrightarrow{-2e^-,\,-H^+}\begin{array}{c}\mathrm{Ar}\\|\\\mathrm{Ar{-}C{+}}\\|\\\mathrm{Ar}\end{array}\qquad(1)$$

It was recognized early by Fischer[3] that the chemical oxidation of leucotriarylmethanes is hindered by the presence of appropriate substituents, in particular, substitution of the aryl rings by methyl groups ortho to the central methine carbon atom. Subsequently, it was found that chemical oxidation is favored by the presence of acid,[4] and more recently the rate of oxidation of leucotriphenylmethanes was found to follow roughly the increasing ease of reduction of the oxidant.[5]

The photochemical oxidation of triphenylmethanes was studied by Shigorin and co-workers.[6-9] Based on quantum yields at 77 K, the primary photochemical step was thought to be a two-photon process leading to the radical cation $\mathrm{Ar_3CH^{+\cdot}}$ and a solvated electron. Upon warming of an irradiated sample in hydrocarbon glass, recombination occurs accompanied by luminescence, while warming of an alcohol glass leads to dye formation accompanied by negligible luminescence. The authors further remarked that while dye formation occurs via a two-photon process, in the presence of oxygen this becomes a one-photon process and in the presence of even stronger electron acceptors such as chloranil dye formation occurs via a no-photon (i.e., dark) process.

The electrochemical oxidation of triphenylmethanes appears to have received less attention than have their chemical or photochemical oxidation. Galus and Adams[10] reported that leuco crystal violet [$(p\text{-}(\mathrm{CH_3})_2\mathrm{NC_6H_4})_3\mathrm{CH}$] in acetonitrile undergoes a two-electron oxidation step ($E_{p/2}$ = +0.51 V vs. SCE) leading to crystal violet dye and a second oxidation step

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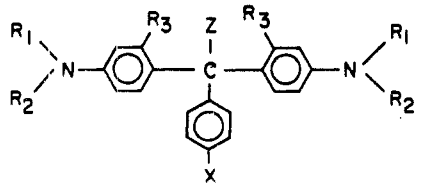

COMPOUND	R1	R2	R3	X	Z
I	C_2H_5	C_2H_5	CH_3	H	H
II	C_2H_5	$C_6H_5CH_2$	CH_3	H	H
III	$C_6H_5CH_2$	$C_6H_5CH_2$	CH_3	H	H
IV	C_2H_5	C_2H_5	Cl	H	H
V	$C_6H_5CH_2$	$C_6H_5CH_2$	Cl	H	H
VI	CH_3	CH_3	H	H	CH_3
VII	C_2H_5	C_2H_5	CH_3	NO_2	H
VIII	C_2H_5	C_2H_5	CH_3	CN	H
IX	C_2H_5	C_2H_5	CH_3	Br	H
X	C_2H_5	C_2H_5	CH_3	$(C_2H_5)_2N$	H

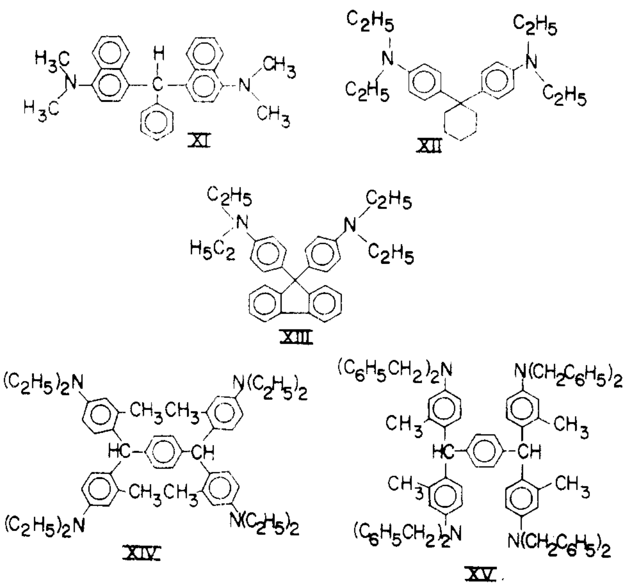

Figure 1. Structures of compounds examined in this study.

($E_{p/2}$ = +0.87 V) for which the product was not identified.

In this paper we report the anodic oxidation of the series of triphenylmethanes and related compounds shown in Figure 1 as studied by cyclic voltammetry, and consider the effect of chemical structure on ease of oxidation and dye formation. In addition, the photochemical oxidation of selected members is reported and the relation of this process to anodic oxidation discussed.

Results

A. Anodic Oxidation of Compound I. The anodic oxidation of bis[4-(diethylamino)-2-methylphenyl]phenylmethane (I) was studied in somewhat greater detail than the rest of the series. The cyclic voltammogram (CV) of I in acetonitrile (AN) is shown in Figure 2. The anodic scan is characterized by two closely spaced peaks, O_I (+0.72 V vs SCE) and O_{II} (+0.80 V), followed by a third peak, O_{III} (+1.08 V), whose current height is about half that of $O_I + O_{II}$. The appearance of the corresponding reduction peak R_{III} (+1.01 V) upon reversal of scan direction and the 70-mV separation between O_{III} and R_{III} indicate that O_{III} is due to a reversible one-electron process.[11] The reduction peak R_I corresponding to O_I is barely detectable, and a reduction peak corresponding to O_{II} is totally absent. After repeated scans between +0.4 and +1.2 V, the solution around the working electrode becomes intensely green and scanning to negative potentials reveals the presence of a reversible one-electron couple R_{IV} (−0.54 V)/O_{IV} (−0.48 V), which is absent in the voltammogram of I prior to the anodic scans.

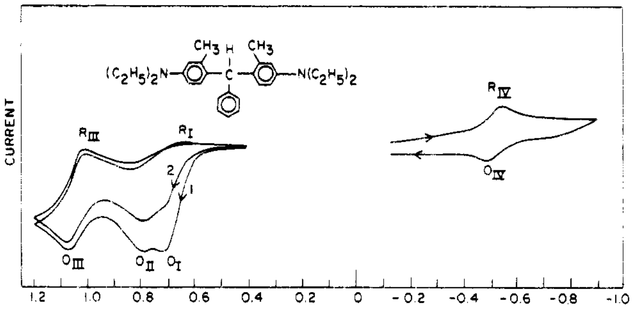

Figure 2. Cyclic voltammogram of compound I in AN: (left) first two anodic scans; (right) cathodic scan after several anodic scans.

Redox couples O_{III}/R_{III} and R_{IV}/O_{IV} were identified as follows. When I is subjected to chemical oxidation using ceric ammonium nitrate, the product may be isolated as the oxalate salt which is colored an intense green [λ_{max} (AN) 650 nm (log ϵ 4.57), 443 (4.20)]. Cyclic voltammetry of this dye derived from I shows that it undergoes oxidation at the same potential as O_{III}/R_{III} in the CV of I and reduction at the same potential as R_{IV}/O_{IV}. These redox potentials are in fact quite similar to those reported[12] for the structurally related dye Malachite Green [$(p\text{-}(CH_3)_2NC_6H_4)_2C(C_6H_5)^+Cl^-$], which in AN undergoes oxidation to the radical dication at +0.97 V and reduction to the neutral radical at −0.64 V. The visible absorption spectrum in AN of the dye produced by anodic oxidation of I is identical with that of the chemically oxidized sample.

The CV of I is quite sensitive to purity of the compound and solvent. In the less polar solvent methylene chloride, the CV has the appearance shown in Figure 3a, with oxidation peaks O_I and O_{II} better resolved than in AN and the corresponding reduction peaks R_I and R_{II} clearly visible upon reversing the scan direction. If increasing amounts of benzoic acid are added to the sample, the CV changes as shown in Figures 3b and 3c. The second oxidation peak O_{II} shifts to more negative potential and merges with O_I as shown in Figure 4, while R_I decreases in height and R_{II} changes in appearance from a peak to a step, indicating increased kinetic character associated with the electron transfer step.

We defer until the Discussion section a consideration of the mechanistic implications of these observations, but note at this point that CV's resembling Figures 3b and 3c were obtained with samples of I which had been prepared several months previously, with freshly purified samples of I in reagent grade CH_2Cl_2 or with freshly prepared I in prepurified CH_2Cl_2 following brief irradiation by a low-pressure mercury lamp or upon addition of a polar solvent such as butanol. For these reasons the remainder of the voltammetric experiments reported here were done using freshly purified samples, prepurified CH_2Cl_2, and with the exclusion of light during preparation and handling of solutions.

B. Effect of Structural Variation on Anodic Oxidation. Substituents on Nitrogen. That the first oxidation step involves removal of an electron from an orbital centered on one of the amino nitrogen atoms is supported by the marked influence of substituents attached to nitrogen upon the ease of

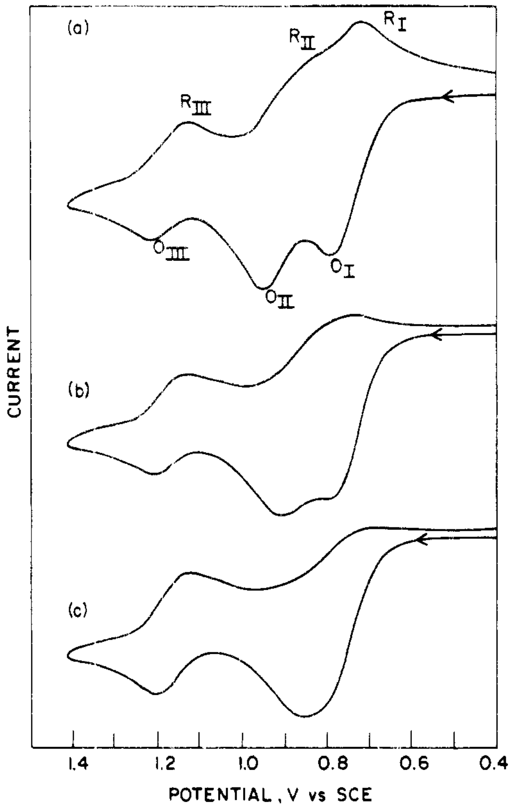

Figure 3. Effect of added proton donor on CV of I in CH_2Cl_2; *iR* drop compensated: (a) compound I only; (b) same sample but 5.8×10^{-2} M in benzoic acid; (c) same sample but 2.1×10^{-1} M in benzoic acid.

oxidation. The CV's of compounds II–V have the same appearance as that of compound I; however, as seen in Table I, the peak potentials are shifted by substitution. For compounds I–III these shifts may be correlated by means of the Taft substituent constants[13] σ^* or their sum, $\Sigma\sigma^*$. The successive substitution of *N*-ethyl groups (σ^* − 0.10) by more strongly electron-withdrawing benzyl groups (σ^* +0.22) is reflected in the shifts of 0.09–0.1 V per benzyl group, not only for O_I and O_{II} but also for O_{III}, which involves oxidation of the dye cation. These shifts are described by $E_p(\mathrm{I}) = 0.30(\Sigma\sigma^*) + 0.85$ ($r = 0.999$), $E_p(\mathrm{II}) = 0.28(\Sigma\sigma^*) + 1.01$ ($r = 1.000$), and $E_p(\mathrm{III}) = 0.30(\Sigma\sigma^*) + 1.28$ ($r = 0.999$). (By comparison, photoelectron spectroscopy[14] gives the following values for ionization potentials: I, 6.92 eV; II, 6.86 eV; III, 6.97 eV.)

The replacement of a ring methyl group by a chloro substituent results in IV (from I) and V (from III), which may also be considered in the present context since the electronic effects of the substituent are transmitted to the amino nitrogen atom via the benzene ring. The CV patterns are the same as for I; however, the replacement of CH_3 by Cl (IV vs. I and V vs. III) increases the difficulty of oxidation by 0.2 V in each of the three oxidation steps.

Phenyl Ring Substituents. The ease of removal of an electron is also influenced by para substituents on the phenyl ring not bearing amino groups. Oxidation potentials for these compounds (I and VII–X, Table I) are a linear function of the Hammett substituent constant σ_p as described by $E_p(\mathrm{I}) = 0.056\sigma_p + 0.79$ ($r = 0.996$). The small value of the reaction constant ($\rho = 0.056$ V) reflects the decreased transmission of substituent effects through the sp^3 carbon atom as compared with the effects of substituents on the aniline rings or on nitrogen itself. The reaction constant becomes even smaller and the correlation more tenuous for O_{II} ($\rho = 0.032$ V, $r = 0.895$) and O_{III} ($\rho = 0.015$ V, $r = 0.565$). With $(C_2H_5)_2N$ as a phenyl substituent (compound X), of course, an additional reactive center is introduced into the molecule. The second oxidation peak O_{II} is seen only as an inflection in the CV of X, and the absence of R_I indicates that the first oxidation step is irreversible. Although one might expect that the rate of the C–H cleavage step leading to the dye cation would be influenced by the phenyl ring substituent, any trend between the height of O_{III} and substituent was not apparent in these studies.

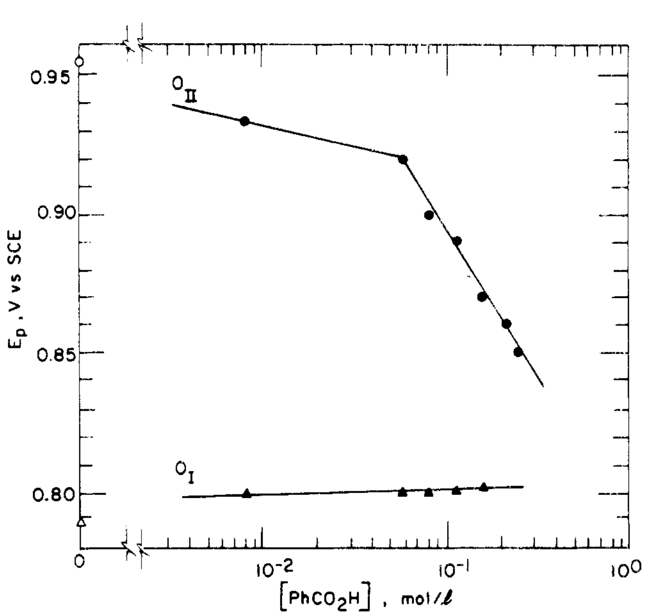

Figure 4. Peak potentials for the first and second oxidation peaks of I in CH_2Cl_2 as a function of benzoic acid concentration. Open symbols (○, △) = no acid.

Table I. Anodic Oxidation Data [a]

compd	peak potentials, V vs. SCE O_I/R_I	O_{II}/R_{II}	O_{III}/R_{III}
I	0.79/0.72	0.95–	1.22/1.15
II	0.88/0.82	1.04–	1.31/1.22
III	0.98/0.92	1.13/–	1.41/1.31
IV	1.01/0.96	1.15/–	1.40/1.32
V	1.20/1.14	1.31/–	1.60/1.51
VI	0.92/0.85		
VII	0.84/0.79	0.97/–	1.24/1.17
VIII	0.83/0.77	0.98/–	1.23/1.16
IX	0.81/0.75	0.96/–	1.24/1.15
X	0.75/–		1.09/1.02
XI	0.85/–		1.59/–
XII	0.79/0.67	0.89/0.80	
XIII	0.88/0.78	1.00/0.91	
XIV	0.78/0.73	0.94/–	1.21/1.13
XV	0.96/0.91	1.13/–	1.39/1.32

[a] Sweep rate 100 mV/s; *iR* drop compensated.

Substituents on the Central Carbon Atom. Since dye formation is associated with C–H bond cleavage, it was of interest to examine the electrode behavior of compounds in which the central methine C–H group is replaced by C–alkyl. The difference in behavior is clearly seen with compounds VI, XII, and XIII, whose CV's show no evidence of the couple O_{III}/R_{III}, in keeping with the absence of any dye formation at the indicator electrode. Compound VI differs from XII and XIII in that while the latter show two oxidation steps (O_I/R_I and O_{II}/R_{II}), compound VI shows only a single oxidation step. All three differ from the compounds described previously, however, in having peak currents on reversal of scan direction (R_I or R_I and R_{II}) which approach in height those due to the primary oxidation steps observed on the forward scan.

Compound XI. This compound is unique in the present

Table II. Spectral and Photooxidation Data for Compounds I-V

compd	λ_{max} (ϵ) of dye, nm	% conversion after 16-min exposure	relative % conversion after 16 min
I	650 (31 000)	51.0	100
II	646 (24 900)	3.4	6.67
III	644 (21 200)	2.35	4.61
IV	645 (25 440)	0.25	0.49
V	663 (15 640)	0	0

series. As with leuco crystal violet[10] and compound VI, which also have the amino nitrogen atoms substituted by CH_3 rather than C_2H_5 groups, only a single primary oxidation peak O_I is observed. However, unlike the other compounds having C–H rather than C–alkyl at the central carbon atom, dye formation following initial oxidation is not observed, nor is the O_{III}/R_{III} couple seen in the CV.

Compounds XIV and XV. Compound XIV may be regarded as the "double-barrelled" analogue of I, with XV as the "double-barrelled" analogue of III. The shape of the CV's of XIV and XV and the oxidation peak potentials are identical with those of the corresponding "single-barrelled" analogues. The peak currents, normalized for concentration, are about twice as great, however. Thus, each electroactive end of XIV or XV loses electrons independently of the other, with twice the number of electrons per molecule being given up as occurs with their "single-barrelled" analogues. Since the molecules are probably too large to approach the electrode perpendicularly and still permit oxidation at the distant reactive center, the observation of simultaneous electron transfer from both centers may be taken as evidence that the molecules are oriented parallel to the electrode in the charge exchange step.

C. Effect of Structural Variation on Photooxidation. The effect of structural variation on ease of photooxidation was studied by irradiating compounds I-V in air-saturated CH_2Cl_2 solutions at 366 nm in the tail of the long wavelength absorption band. The optical densities at this wavelength of equimolar solutions do not differ by more than about 10%. The course of the reaction was monitored by following the change in absorption spectrum with time as determined for aliquots withdrawn from the photolysis vessel. Typically, the absorption band near 320 nm due to the leuco compound decreases as peaks near 440 and 650 nm due to the dye appear and increase in height. The presence of an isosbestic point at about 330 nm may be taken as evidence[15] that the rate of dye formation is directly proportional to the rate of disappearance of the leuco form.

Knowing the molar absorptivities of the dyes obtained by Ce(IV) oxidation of I-V, it is possible to compare their rates of formation from the absorption spectra. This is done in Table II, where the comparison is given in terms of percent conversion (or relative percent conversion) after a 16-min irradiation. Clearly the efficiency of photooxidation is dramatically affected by the structural variations in this series and in the case of V is vanishingly small.

Discussion

We now review briefly the qualitative features of the voltammograms which bear on the mechanism of dye formation resulting from the anodic oxidation of the leucotriarylmethanes observed in the present series. Formation of the dye species, which is evidenced by the appearance of O_{III}/R_{III} and R_{IV}/O_{IV}, involves the loss of two electrons as required by stoichiometry and as previously reported[10] for leuco crystal violet. The two oxidation peaks O_I and O_{II} are absent in the CV of the dye and may be associated with successive one-electron steps which lead to dye formation. Whether loss of the proton precedes the loss of the second electron (e^-, H^+, e^-) or follows it (e^-, e^-, H^+) cannot be stated conclusively, but may be argued as follows. If proton loss were to occur from the singly oxidized species ($Ar_3CH^{+\cdot} \rightarrow Ar_3C\cdot + H^+$), then it would follow that the second electron is removed from the neutral triarylmethyl radical ($Ar_3C\cdot$). However, if, as seems reasonable from the present study and previous work,[12] the couple R_{IV}/O_{IV} corresponds to the electrode reaction $Ar_3C\cdot \rightleftarrows Ar_3C^+ + e^-$, then only a single two-electron oxidation peak would be seen in the CV since oxidation of the neutral radical occurs more readily (at less positive potential) than the primary oxidation step. A disproportionation mechanism ($2Ar_3CH^{+\cdot} \rightarrow Ar_3CH + Ar_3CH^{2+}$) would similarly be evidenced by only a single oxidation peak. The stepwise mechanism shown in eq 2–4 for the overall process may then be suggested.

$$Ar_3CH \rightleftarrows Ar_3CH^{+\cdot} + e \qquad (2)$$

$$Ar_3CH^{+\cdot} \rightleftarrows Ar_3CH^{2+} + e \qquad (3)$$

$$Ar_3CH^{2+} \xrightarrow{k} Ar_3C^+ + H^+ \qquad (4)$$

Presumably, the proton loss is facilitated by the partial positive charges which develop on the phenyl rings adjacent to the central methine carbon atom following loss of electrons from the para nitrogen atoms. In the case of the naphthyl compound (XI), where neither reversible oxidation nor dye formation is observed, the positive charge density at the 4 position (adjacent to the methine carbon atom) may be insufficient to weaken the C–H bond for cleavage and instead reaction may occur at the 5 or 8 positions where there is also considerable positive charge density.

An additional factor contributing to C–H bond cleavage is the gain in delocalization energy as the central carbon atom changes from sp^3 to sp^2 hybridization. This is made more difficult in the case of compound XI by the greater steric requirements of the naphthyl group as compared with phenyl. Finally, even if steric and charge density requirements are satisfied, dye formation will not occur if, as with compounds VI, XII, and XIII, C–C rather than C–H bond breaking is required.

The effect of solvent on the electrode process may be rationalized as follows. On the one hand, the peak potential of O_{II} shifts with benzoic acid concentration in a manner reminiscent of protonation equilibrium prior to electron transfer.[16] The direction of this shift, however, is opposite to that normally encountered,[17] namely, that B is more easily oxidized than BH^+. Remembering that cathodic shifts in O_{II} and decreases in the height of R_I and R_{II} are also observed in AN or in CH_2Cl_2 plus butanol, it seems preferable to conclude that the C–H bond breaking is facilitated by changes in solvent polarity. The shift in O_{II} but not in O_I is then due to this irreversible chemical reaction which follows the second oxidation step and depletes the concentration of the doubly charged species at the electrode surface.[18]

In the case of the photochemical dye formation, it is necessary to consider not only the oxidative half-reaction of the triphenylmethane molecule but also the half-reaction of the electron-accepting species. Under the present conditions this could be either CH_2Cl_2 ($E_{1/2} = -2.33$ V vs. SCE[19]) or more likely oxygen ($E_{1/2} = -0.79$ V vs. SCE[20]). While the dye formation could involve a two-electron loss followed by heterolytic C–H bond cleavage as in the anodic reaction, here it is possible that dye formation occurs via a one-electron transfer to form superoxide, followed by hydrogen atom abstraction either by superoxide itself or by hydroperoxyl radical,[21] which results from the reaction of superoxide and trace amounts of acid in the solvent. This is consistent with Shigorin's finding[9] that dye formation is a two-photon process in the absence of oxygen but a one-photon process in the presence of oxygen if we assume one electron transferred per photon.

$$\mathrm{Ar_3CH + O_2} + h\nu \rightarrow \mathrm{[Ar_3CH]^{+}\cdot + O_2^{-}\cdot}$$

$$\mathrm{[Ar_3CH]^{+}\cdot + O_2^{-}\cdot \rightarrow Ar_3C^{+} + HO_2^{-}}$$

$$\mathrm{H^{+} + O_2^{-}\cdot \rightarrow HOO\cdot}$$

$$\mathrm{[Ar_3CH]^{+}\cdot + HOO\cdot \rightarrow Ar_3C^{+} + H_2O_2}$$

Finally, we consider that variations in structure in the series I–V result in relative rates of dye formation which differ by several orders of magnitude. It has been suggested[22,23] that such excited state charge exchange reactions may be treated in terms of the free energy change for the reaction as estimated by $\Delta G = -\Delta E^* + [E(\mathrm{D^+/D}) - E(\mathrm{A/A^-})] - e^2/4\pi\epsilon_0\epsilon r$, where ΔE^* is the electronic excitation energy, $E(\mathrm{D^+/D})$ is the donor oxidation potential, $E(\mathrm{A/A^-})$ is the acceptor reduction potential, and $e^2/4\pi\epsilon_0\epsilon r$ is the free energy change on bringing the ions to encounter distance.

It has further been suggested[24-26] for fluorescence quenching involving electron donor–acceptor interactions that the rate of quenching follows the free energy change as estimated above, i.e., $\log k_q \,\alpha\, \Delta G$. The arguments are not beyond question, but in practice seem valid when comparing rates caused by systematic variations in structure of one member of the DA pair while the other member is held constant.

This line of reasoning seems to apply to the photochemical dye formation studied here since log (relative rate) decreases as the oxidation potential of the triphenylmethane increases. With the relative rate of I taken as 100, this trend is described by the least-squares equation log (relative rate) = $-8.81E_p(\mathrm{I}) + 8.85$ ($r = 0.932$). It is implied by this relation that the overall rate is determined by the rate of excited-state electron transfer to oxygen and that subsequent C–H bond breaking and rehybridization is rapid.

Experimental Section

A. Synthesis. With the exception of compounds VI, XII, and XIII, the compounds described were prepared according to the following general procedure. N-alkylation of the aromatic amines was carried out by allowing the appropriate alkyl halide to react with the amine in KOH/Me$_2$SO solution at room temperature. The product was isolated either by addition of water, in which case the product crystallized out or separated as an oil, or by addition of benzene and extraction of the water-soluble components into water. In this case, the solvent was evaporated and the product purified by crystallization and column chromatography. The aromatic amine and the aldehyde were then charged into a reaction vessel under an N$_2$ blanket. A solution of sulfuric acid in 1-butanol was added and the mixture refluxed for 18 h. The slurry was then cooled and carefully neutralized with sodium bicarbonate or a KOH solution. Methanol was added to assist the precipitation of the product. The product separated either as an oil or, in most cases, as a solid. The oil usually solidified when dispersed in methanol. The solid was then recrystallized from methanol, cyclohexane, or a mixture of benzene/alcohol after the decolorizing carbon treatment and was further purified by column chromatography on neutral alumina, generally using a benzene/hexane (1:1) mixture as eluent. Yields were typically 60–70%. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Bis[4-(diethylamino)-2-methylphenyl]phenylmethane (I): mp 112–113 °C (lit.[27] mp 110–112 °C).

Bis[4-(*N*-benzyl-*N*-ethylamino)-2-methylphenyl]phenylmethane (II): mp 80–82 °C. Anal. Calcd for $\mathrm{C_{39}H_{42}N_2}$: C, 86.94; H, 7.86; N, 5.20. Found: C, 87.23; H, 8.12; N, 5.07.

Bis[4-(dibenzylamino)-2-methylphenyl]phenylmethane (III): mp 100–101 °C. Anal. Calcd for $\mathrm{C_{49}H_{46}N_2}$: C, 88.78; H, 6.99; N, 4.23. Found: C, 88.50; H, 7.26; N, 4.07.

Bis[4-(diethylamino)-2-chlorophenyl]phenylmethane (IV): mp 164–165 °C. Anal. Calcd for $\mathrm{C_{27}H_{32}N_2Cl_2}$: C, 71.20; H, 7.08; N, 6.15. Found: C, 71.17; H, 7.12; N, 6.07.

Bis[4-(dibenzylamino)-2-chlorophenyl]phenylmethane (V): mp 97–98 °C. Anal. Calcd for $\mathrm{C_{47}H_{40}N_2Cl_2}$: C, 80.21; H, 5.73; N, 3.98. Found: C, 80.27; H, 5.85; N, 3.71.

Bis[4-(diethylamino)-2-methylphenyl]-4-nitrophenylmethane (VII): mp 152–153 °C. Anal. Calcd for $\mathrm{C_{29}H_{37}N_3O_2}$: C, 75.78; H, 8.11; N, 9.14. Found: C, 75.70; H, 8.34; N, 9.27.

Bis[4-(diethylamino)-2-methylphenyl]-4-cyanophenylmethane (VIII): mp 161–162 °C. Anal. Calcd for $\mathrm{C_{30}H_{37}N_3}$: C, 81.96; H, 8.48; N, 9.56. Found: C, 82.46; H, 8.58; N, 9.19.

Bis[4-(diethylamino)-2-methylphenyl]-4-bromophenylmethane (IX): mp 141 °C. Anal. Calcd for $\mathrm{C_{29}H_{37}N_2Br}$: C, 70.58; H, 7.56; N, 5.68. Found: C, 70.28; H, 7.62; N, 6.00.

Bis[4-(diethylamino)-2-methylphenyl]-4-(diethylamino)phenylmethane (X): mp 98.5–99.5 °C. Anal. Calcd for $\mathrm{C_{33}H_{47}N_3}$: C, 81.60; H, 9.75; N, 8.65. Found: C, 81.73; H, 10.03; N, 8.28.

Bis[4-(dimethylamino)-1-naphthyl]phenylmethane (XI): mp 191–192 °C. Anal. Calcd for $\mathrm{C_{31}H_{30}N_2}$: C, 86.47; H, 7.02; N, 6.51. Found: C, 86.23; H, 7.30; N, 6.30.

1,4-Bis(bis[4-(diethylamino)-2-methylphenyl]methyl)benzene (XIV): mp 216 °C. Anal. Calcd for $\mathrm{C_{52}H_{70}N_4}$: C, 83.15; H, 9.39; N, 7.46. Found: C, 83.26; H, 9.44; N, 7.17.

1,4-Bis(bis[4-(dibenzylamino)-2-methylphenyl]methyl)benzene (XV): mp 195–196 °C. Anal. Calcd for $\mathrm{C_{92}H_{86}N_4}$: C, 88.56; H, 6.95; N, 4.49. Found: C, 88.52; H, 7.12; N, 4.30.

1-Bis[4-(dimethylamino)phenyl]-1-phenylethane (VI). This compound was prepared by heating dimethylaniline and acetophenone saturated with dry HCl in a sealed stainless steel tube for 2 h at 185 °C. The reaction mixture, after cooling to room temperature, was treated with NaHCO$_3$ solution, and the product was extracted with ether. After removal of solvent and crystallization from ethanol, the product (8% yield) had mp 134 °C. Anal. Calcd for $\mathrm{C_{24}H_{28}N_2}$: C, 83.68; H, 8.19; N, 8.13. Found: C, 83.85; H, 8.31; N, 7.78.

1,1-Bis[4-(diethylamino)phenyl]cyclohexane (XII). This compound was prepared by the method of Rule and Riordan:[28] mp 89–90 °C (lit.[27] mp 89.5–90.5 °C).

9,9-Bis[4-(diethylamino)phenyl]fluorene (XIII). To a 100-mL round-bottom flask was added 18 g (0.1 mol) of fluorenone, 29.8 g (0.2 mol) of *N,N*-diethylaniline, 17 mL of HCl, and 5 mL of ethanol, and the mixture was heated to reflux for 48 h. After cooling, the unreacted fluorenone was removed by filtration. The filtrate was made basic with 10% NaOH and extracted with 3 × 100 mL of benzene. The benzene and excess amine were removed by distillation under vacuum. The desired product was an oil which solidified upon treatment with methanol. Recrystallization from EtOAc/MeOH (70:30) afforded a white crystalline product (10% yield) which had mp 163–164 °C. Anal. Calcd for $\mathrm{C_{33}H_{36}N_2}$: C, 86 06; H, 7.82; N, 6.08. Found: C, 86.06; H, 7.95; N, 6.01.

B. Chemical Oxidation of Leucotriarylmethanes I–V. To a solution of the leucotriarylmethane (1 mmol) in acetonitrile (5 mL) was added ceric ammonium nitrate (2 mmol), with the immediate formation of an intense green color. After stirring overnight at room temperature, ammonium oxalate (8 mmol) and water (50 mL) were added and the mixture was filtered. The filtrate was extracted with several portions of CH$_2$Cl$_2$, and the extract was taken to dryness under vacuum. The dyes were obtained by this procedure as the oxalate salts in about 50% yield. The long wavelength absorption maxima in CH$_2$Cl$_2$ of the five dyes prepared were as follows [$\lambda_{\max}$ nm (log ϵ)]: I, 650 (4.49); II, 646 (4.40); III, 644 (4.33); IV, 645 (4.40); V, 663 (4.19).

C. Photochemistry. Solution photolyses were carried out in spectral grade methylene chloride using a photochemical reactor made by Bradford Scientific, Inc., Marbelhead, Mass., containing a 366-nm mercury source. Solution concentrations were 10^{-3} M contained in quartz tubes which were continually oxygenated by a capillary air bleed.

UV/vis spectra were obtained on a Cary 15 spectrophotometer. For I the absorbance at 650 nm increased with time as follows [time (min), absorbance]: 0.5, 0.03; 1.0, 0.11; 2.0, 0.15; 4.0, 0.32; 8.0, 0.49; 25, 0.69; 55, 0.73.

D. Electrochemistry. Electrochemical measurements were made using the PAR 170 electrochemistry system in the three-electrode mode. The working electrode was a Beckman planar platinum disk electrode (area 0.22 cm^2) for cyclic voltammetry. The reference electrode was a saturated NaCl calomel electrode (SCE), and the counter electrode was a platinum wire spiral. The solvents used were acetonitrile (Burdick & Jackson, distilled and dried over 5Å molecular sieves) and methylene chloride (either Burdick & Jackson as received or Baker Reagent grade percolated through a column of neutral alumina and then distilled from CaH$_2$). Tetraethylammonium fluoborate (TEAF, Southwestern Analytical Chemicals, dried under vacuum) served as supporting electrolyte. Sample solutions were 5×10^{-4} M in depolarizer and 0.1 M in supporting electrolyte and were prepared under argon in amber glass flasks. Current–potential curves were obtained at a scan rate of 100 mV/s after a 2-min purge with purified nitrogen. For precise determination of peak potentials, compensation of *iR* drop in the cell was made using feedback circuitry available with the instrument.

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Registry No.—I, 15008-36-3; II, 68582-39-8; III, 68582-40-1; IV, 68582-41-2; V, 68582-42-3; VI, 23308-55-6; VII, 40660-35-3; VIII, 68582-43-4; IX, 68582-44-5; X, 68582-45-6; XI, 68582-46-7; XII, 33978-57-3; XIII, 68582-47-8; XIV, 68582-48-9; XV, 68582-49-0; fluorenone, 486-25-9; *N,N*-diethylaniline, 91-66-7; dimethylaniline, 121-69-7; acetophenone, 98-86-2.

Supplementary Material Available: Peak potentials of oxidation steps O_{I}, O_{II}, and O_{III} for I–III vs. $\Sigma\sigma^*$ for substituents on nitrogen (Figure 5), peak potentials of oxidation steps O_{I}, O_{II}, and O_{III} for I and VII–X vs. σ for phenyl ring substituents (Figure 6), cyclic voltammograms of X, VI, XII, and XI (Figures 7–10), and absorption spectra of I as a function of length of irradiation (Figure 11) (8 pages). Ordering information is given on any current masthead page.

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Transfer Hydrogenation and Transfer Hydrogenolysis. 20. Dehydrogenation by 7,7,8,8-Tetracyanoquinodimethane

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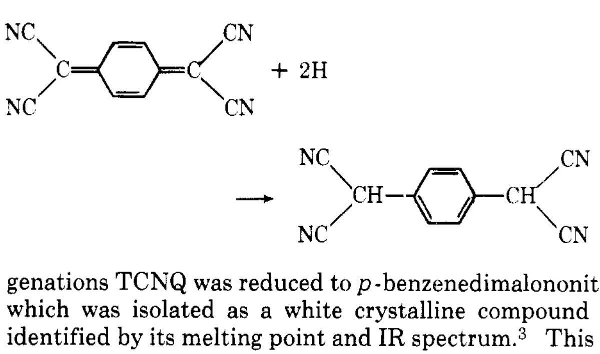
Benzyl-type alcohols and hydroaromatic compounds were dehydrogenated by 7,7,8,8-tetracyanoquinodimethane (TCNQ). The fact that the reactivity of 1,2-dihydronaphthalene was comparable to that of 1,2-dihydro-1,1-dimethylnaphthalene, which gave 1,2-dimethylnaphthalene, suggests that the dehydrogenation of 1,2-dihydrobenzenes proceeds via the formation of a carbonium ion by a rate-determining hydride abstraction (two-step ionic mechanism). The hydrogen transfer from 1-phenylpropanol was studied in detail. The yield of propiophenone increased when solvents which would be expected to increase the concentration of the complex between TCNQ and the alcohol were used. Initial rates of the reaction were proportional to the concentration of the hydrogen donor and the hydrogen acceptor. In the reaction of several para- or meta-substituted 1-phenylpropanols in dioxane at 140 °C, −3.76 was obtained as a value of the reaction constant. Relative rates of the reaction of PhCH(OH)Et, PhCH(OD)Et, PhCD(OH)Et, and PhCD(OD)Et were 4.0, 4.0, 1.0, and 1, respectively. This means that the transfer of the hydrogen attached to the α position of the alcohol is the rate-determining step. This and some other results support a two-step ionic mechanism for the dehydrogenation of alcohols.

The thermal hydrogen transfer from some types of organic compounds to high potential quinones is well known.[1] In the previous paper,[2] we reported the dehydrogenation by tetracyanoethylene (TCNE) and discussed the mechanism of the hydrogen transfer from benzyl-type alcohols to TCNE. 7,7,8,8-Tetracyanoquinodimethane (TCNQ) would also be expected to dehydrogenate organic compounds because it has structural similarity to both quinones and TCNE. Although dehydrogenations by TCNQ have not been reported, we find them to occur readily and have studied them in detail.

Results and Discussion

Hydrogen-Donating Ability. At first the susceptibility of organic compounds to dehydrogenation by TCNQ was investigated under the following reaction conditions. A hydrogen donor (0.1 M) and TCNQ (0.1 M) were heated at 140 °C for 6 h in dioxane. This was used as a solvent for dehydrogenation by dichlorodicyanobenzoquinone (DDQ). In these dehydrogenations TCNQ was reduced to *p*-benzenedimalononitrile, which was isolated as a white crystalline compound and identified by its melting point and IR spectrum.[3] This fact shows that the reaction in eq 1 proceeded.



(1)

TCNQ, like other hydrogen acceptors of thermal hydrogen transfer,[1,2] has been reported to react with compounds having active hydrogens.[4] In some cases extensive side reactions occur. We have determined not only the yield of dehydrogenation product but also the amount of starting material that

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