Novel Electrohydrodimerization of N-Substituted Maleimides in Aqueous Media

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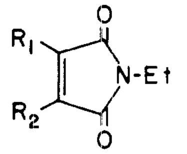
The electroreduction of N-substituted maleimides in neutral aqueous media is shown to yield hydrodimers via electrohydrodimerization, EHD. Previous studies on the electroreduction of diactivated olefins have concluded that an aprotic environment is necessary for EHD to occur. This novel behavior of N-substituted maleimides is examined by polarography, coulometry, bulk electrolysis, and product analysis. The reduction products were identified on the basis of microanalysis, ^{1}H NMR, ^{13}C NMR, mass spectrometry, and gas chromatography retention data. Several possible mechanisms are examined and a radical–radical coupling mechanism is proposed as the predominant pathway. *N*-Ethylmaleimide (**1a**), *N*-ethylcitraconimide (**1b**), and 3,4-dimethyl-*N*-ethylmaleimide (**1c**) were selected as representative N-substituted maleimides for this study.

There have been a number of recent reports describing detailed studies of the formation of hydrodimers from the electrolytic reduction of diactivated olefins, in a process called electrohydrodimerization (EHD). The available evidence suggests that in most cases EHD involves the direct coupling of anion radicals followed by protonation of the resulting dianion.[1–4] To obtain a high yield of the dimer an aprotic solvent must be used. If the concentration of water (or other proton donors) is significant, the anion radical is rapidly protonated forming a neutral radical. Since the neutral radical is normally easier to reduce than the starting material, it rapidly accepts another electron and then a proton to form a dihydromonomer. Hence, if protons are readily available, no dimer is formed.

Alternately, a good yield of dimer may be obtained by using a high concentration of a large organic ion, e.g., tetraethylammonium *p*-toluenesulfonate, as a supporting electrolyte. It has been argued that these relatively hydrophobic ions produce a "water poor" region at the surface of the electrode, approximating aprotic conditions.[5]

Studies on the interaction of *N*-ethylmaleimide, **1a**, with sulhydryl compounds led to our discovery that maleimides form hydrodimers in high yield in aqueous media at neutral pH. The unique behavior of N-substituted maleimides, compared with previously studied diactivated olefins, is the subject of this paper.

There has been little previous work on the electrochemistry of the maleimides. A classical, dc polarographic study noted the influence of different N-substituents on the reduction potential of maleimides, but no product analysis was carried out.[6] The exhaustive electrolysis of maleimide itself has been described.[7] This report noted that the reduction product at low pH (below pH 5) was succinimide. At intermediate pH values (pH 5–8) an unidentified product was obtained. We report here the isolation of the reduction product of *N*-ethylmaleimide, **1a**, as the hydrodimer of **1a**, bis[3,3′-(*N*-ethylsuccinimide)], **3a**.



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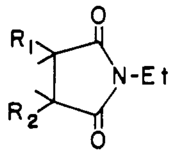

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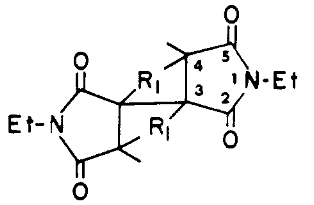
1a: $R_1 = R_2 = H$
1b: $R_1 = CH_3, R_2 = H$
1c: $R_1 = R_2 = CH_3$

2a: $R_1 = R_2 = H$
2b: $R_1 = CH_3, R_2 = H$
2c: $R_1 = R_2 = CH_3$



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3a: $R_1 = H$
3b: $R_1 = CH_3$

To aid in identifying the reduction products and elucidating the mechanism, two additional substrates were synthesized, 3-methyl-*N*-ethylmaleimide, **1b**, (*N*-ethylcitraconimide), and 3,4-dimethyl-*N*-ethylmaleimide, **1c**. The electrochemical behavior of these compounds as a function of pH was explored. Half-wave potentials, apparent *n* values (number of electrons consumed per substrate molecule), gas chromatographic retention data, and spectroscopic information have been analyzed in terms of the reduction mechanism.

Experimental Section

Sampled dc polarography was performed on a Princeton Applied Research Model 174 polarographic analyzer using 0.5 mM samples. The supporting electrolyte consisted of a 3:1 (by volume) mixture of the appropriate McIlvaine buffer and 95% ethanol. A 1 s drop time, and 1 mV/s scan rate were used. The reference electrode for all electrochemical experiments was either a saturated sodium calomel (SSCE) or an aqueous Ag/AgCl (3 M NaCl) electrode (Bioanalytical Systems Model RE-1).

Coulometric experiments were carried out using a conventional operational amplifier potentiostat. The current was measured using an operational amplifier current-to-voltage converter and the resulting voltage was integrated via a voltage-to-frequency converter and a digital counter. A Pyrex cell (i.d. 34 mm; height, 8.0 cm) having a capacity of 50 mL was used with a mercury pool electrode of approximately 9.0 cm^2. Contact to the mercury pool was made via a platinum wire which entered the cell through a small side arm. The reference electrode, a glass stirrer, a coarse frit for solution degassing (Ace Glass No. 9435-08), and a central auxiliary electrode compartment (terminated with a 10-mm diameter coarse glass frit) were inserted through a tightly fitting Teflon top. A 7-mm spectroscopic-grade graphite rod was used for the auxiliary electrode.

A similar but larger cell was used for preparative electrolyses (i.d. 47 mm, height 10 cm, auxiliary electrode compartment—15 mm coarse frit, working electrode area approximately 17.0 cm^2, capacity 100 mL). Electrolysis was conducted using a locally constructed 0.5-A potentiostat and the current measured by observing the potential drop across a small resistor in the auxiliary electrode circuit using a high impedance digital voltmeter.

^{1}H and ^{13}C NMR spectra in $CDCl_3$ were obtained using a Perkin-Elmer R32 90-MHz instrument and a Varian CFT-20, respectively.

Electron impact (22.5 eV) mass spectrometry was performed on either an LKB-9000 with a gas chromatograph sample inlet system or a Varian MAT-CH5 with a direct probe inlet system.

Microanalyses were carried out by the Microanalysis Laboratory, Department of Chemistry, Purdue University.

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A Hewlett-Packard HP-5700 and a Varian Aerograph 2400 gas chromatograph were used with flame ionization detectors. A 6 ft × 1/8 in. stainless steel column of 3% SE-30 on Chromosorb W-AW-DCMS (100/120 mesh) was used in the HP-5700. The operating conditions were as follows: He flow = 20 mL/min, H_2 flow = 20 mL/min, air flow = 200 mL/min, detector temperature = 250 °C, injector temperature = 200 °C, temperature program (T_i) = 100 °C (4 min), rate = 32 °C/min, T_f = 230 °C (4 min). A 6 ft × 1/8 in. stainless steel column of 1.5% OV-101 on Gas Chromosorb Q (100/120 mesh) was used in the Varian 2400 with He flow = 30 mL/min, H_2 flow = 30 mL/min, air flow = 250 mL/min, detector temperature = 250 °C, injector temperature = 200 °C, temperature program (T_i) = 100 °C (4 min), rate = 30 °C/min, T_f = 220 °C (4 min).

Preparative gas chromatography was carried out using a Varian Aerograph 920. A 10 ft × 3/8 in. aluminum column packed with 15% SE-52 on Chromosorb G (70/80 mesh) was used. Up to 100 μL (~100 mg) of the crude product mixture was injected. Samples were collected over liquid nitrogen.

Coulometry. In a typical experiment 20 mL of solution was used to conserve materials and time. The cell was filled with the supporting electrolyte solution. This was deoxygenated and electrolyzed until the background current was below the threshold of the integrator. The purpose of this step was to help purify the mercury. The solution was then aspirated out of the cell with a glass capillary (Pasteur pipet). The cell was rinsed twice with doubly distilled water and emptied by aspiration. Twenty milliliters of supporting electrolyte solution containing a known amount of the compound of interest was then added to the cell. The fritted auxiliary electrode compartment was refilled with fresh electrolyte. The cell was deoxygenated with bubbling nitrogen for 15 min prior to electrolysis and throughout the experiment. A typical electrolysis required 1 to 2 h, for the current to decay to less than 5% of its initial value, depending on the concentration of the reactant. Two electrolyses were carried out before the mercury was replaced and the preelectrolysis step repeated.

Preparative Electrolysis. For a typical electrolysis 100–400 mg of compound was dissolved in 25 mL of 95% ethanol and added to 75 mL of McIlvaine buffer containing 0.3 M KNO_3 for additional ionic strength. The solution was deoxygenated for 15 min with N_2 and the N_2 bubbling continued throughout the electrolysis. The solution was stirred by a magnetic stir bar (7/8 in. × 5/16 in.) floating on top of the Hg. Electrolysis was continued until the current decayed to less than 5% of the initial current. After an electrolysis was completed, the electrolyte solution was extracted three times with chloroform (1 × 25 mL, 2 × 15 mL). The combined chloroform extracts were back extracted twice with 25 mL of doubly distilled water to remove residual supporting electrolyte and then dried over anhydrous Na_2SO_4. The chloroform was then stripped off using a rotary evaporator. The isolated product mix was purified further or taken up again in a known amount of chloroform for product distribution studies by gas chromatography.

***N*-Ethylsuccinimide (2a).** *N*-Ethylsuccinimide (**2a**) was produced via controlled potential electrolysis of *N*-ethylmaleimide (1a) at pH 2.2 and E = −0.8 V vs. Ag|AgCl. The product was recrystallized from ether in a 2-propanol/dry ice bath. **2a** is a liquid at room temperature: ^{1}H NMR δ 3.54 (q, 2 H, J = 7.5 Hz), 2.69 (s, 4 H), 1.14 (t, 3 H, J = 7.5 Hz); m/e (rel intensity) 127 (100), 113 (12), 112 (11), 99 (13), 84 (36), 56 (56).

3-Methyl-*N*-ethylsuccimide (2b). 2b was produced by electrolysis of 3-methyl-*N*-ethylmaleimide (**1b**) at pH 2.2 and E = −0.9 V vs. Ag|AgCl. The product was recrystallized from ether in a 2-propanol/dry ice bath and is a liquid at room temperature: ^{1}H NMR δ 3.54 (q, 2 H, J = 7.5 Hz), 2.90 (m, 2 H), 2.28 (q, 1 H), 1.34 (d, 3 H), 1.16 (t, 3 H, J = 7.5 Hz); m/e (rel intensity) 141 (88), 113 (15), 98 (20), 72 (33), 42 (100).

3,3′-Bis(*N*-ethylsuccinimide) (3a). 3a was produced by electrolysis of *N*-ethylmaleimide (**1a**) at pH 5.9 and E = −1.0 V vs. Ag|AgCl. The product was recrystallized from ether in a 2-propanol/dry ice bath: ^{1}H NMR δ 3.53 (q, 4 H, J = 7.5 Hz), 3.33 (m, 2 H), 2.75 (t, 4 H), 1.13 (t, 6 H, J = 7.5 Hz); m/e (rel intensity) 252 (49), 180 (19), 153 (15), 127 (100), 99 (7), 54 (66).

Anal. Calcd for $C_{12}H_{16}N_2O_4$: C, 57.13; H, 6.39; N, 11.10. Found: C, 57.22; H, 6.58; N, 10.90.

3,3′-Bis(3,3′-methyl-*N*-ethylsuccinimide) (3b). 3b was produced by electrolysis of 3-methyl-*N*-ethylmaleimide (**1b**) at pH 6.0 and E = −1.1 V vs. Ag|AgCl. The product was recrystallized from cyclohexene: ^{1}H NMR δ 3.47 (q, 4 H, J = 7.5 Hz), 2.48 (s, 1 H), 2.29 (s, 1 H), 1.37 (s, 6 H), 1.08 (t, 6 H, J = 7.5 Hz); m/e (rel intensity) 280 (4), 265 (2.4), 141 (100), 126 (7.5).

Anal. Calcd for $C_{14}H_{20}N_2O_4$: C, 59.99; H, 7.19; N, 9.99. Found: C, 59.82; H, 7.37; N, 10.01.

Table I. Half-Wave Potential as a Function of pH

pH	1a[c]		1b[d]		1c[e]
	1st wave	2nd wave	1st wave	2nd wave	1st wave[a]
2.21	−0.51[b]		−0.60		−0.69
2.69	−0.56		−0.67		−0.77
3.06	−0.61		−0.72		−0.81
3.51	−0.66		−0.77		−0.87
4.04	−0.71		−0.81		−0.90
5.00	−0.75	−1.20	−0.86	−1.27	−0.96
6.00	−0.77	−1.19	−0.90	−1.26	−1.02
7.00	−0.77	−1.19	−0.91	−1.25	−1.04
8.07	−0.78	−1.19	−0.91	−1.24	−1.06

[a] A second wave was not observed for **1c** over the entire pH range studied. [b] Potential vs. the sodium saturated calomel electrode. [c] Registry no., 128-53-0. [d] Registry no., 31217-72-8. [e] Registry no., 34316-72-4.

3,4-Dimethylsuccinimide (2c). Electrolysis of 3,4-dimethylmaleimide (**1c**) at any pH (from pH 2–8) and any potential more negative than −1.0 V vs. Ag|AgCl results in the production of two forms of 3,4-dimethyl-*N*-ethylsuccinimide, designated **2c** and **2c′**. Both are liquids at room temperature. The isomers were purified by preparative gas chromatography. (**2c** has the shorter retention time.) For a mixture of **2c** and **2c′**, mass spectrometry gives m/e (rel intensity) 155 (18), 140 (100), 82 (7), 56 (32).

2c: ^{1}H NMR δ 3.52 (q, 2 H, J = 7.5 Hz), 2.38 (m, 1 H), 1.32 (d, 3 H), 1.15 (t, 3 H, J = 7.5 Hz). Anal. Calcd for $C_8H_{13}N_1O_2$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.69; H, 8.47; N, 8.81.

2c′: ^{1}H NMR δ 3.52 (q, 2 H, J = 7.5 Hz), 2.90 (m, 1 H), 1.21 (d, 3 H), 1.14 (t, 3 H, J = 7.5 Hz). Found: C, 61.70; H, 8.43; N, 8.83.

Synthesis of *N*-Ethylcitraconimide (1b) and 3,4-Dimethyl-*N*-ethylmaleimide (1c). The general procedures of Coleman, Bork, and Dunn[8] and Miyadera and Kosower[9] were used for the synthesis of **1b** and **1c**. Rather than use a reduced pressure distillation, a Dean–Stark condenser was used to collect the water that is driven off during ring closure.

***N*-Ethylcitraconimide (1b) [or 2-Methyl-*N*-ethylmaleimide].** Citraconic anhydride, 18.0 mL (0.2 mol) (Aldrich), was dissolved in 250 mL of xylene in a 500-mL three-neck round-bottom flask. Anhydrous ethylamine (Eastman) (15.0 mL, 0.2 mol) was dissolved in 100 mL of benzene. These were reacted according to the published procedure.[9] After reducing the volume by removing some xylene, the reaction mixture was transferred to a 100 mL Bantamware round-bottom flask. The product was vacuum distilled at 86–90 °C (12 mm Hg) (lit.[9] 93 °C (13 mm Hg)) through a 150-mm Vigreux column using a short path distilling head and a cow receiver. The yield was ca. 40%: ^{1}H NMR δ 6.35 (d, 1 H, ν = 2 Hz), 3.53 (q, 2 H, ν = 7.5 Hz), 2.08 (d, 3 H, ν = 2 Hz), 1.17 (t, 3 H, ν = 7.5 Hz); m/e (rel intensity) 139 (58), 124 (100), 69 (6), 68 (16), 67 (14), 56 (15).

3,4-Dimethyl-*N*-ethylmaleimide (1c). Dimethyl maleic anhydride, 1.89 g (0.015 mol) (Aldrich), was added to 25 mL of benzene in a 100 mL three-neck round-bottom flask. Ethylamine, 1.0 mL (0.015 mol), was diluted with 15 mL of benzene and added to the reaction mixture. The product was vacuum distilled at 93–95 °C (13.5 mm Hg) (lit.[9] 105 °C (15 mm Hg)): ^{1}H NMR δ 3.52 (q, 2 H, ν = 7.5 Hz), 1.94 (s, 6 H), 1.15 (t, 3 H, ν = 7.5 Hz); m/e 153 (46), 139 (7), 138 (100), 110 (4.3), 54 (17), 53 (11).

Results

The half-wave potentials for **1a**, **1b**, and **1c** at various pH are listed in Table I. All three maleimides exhibit a single $2e^-$, pH-dependent wave at low pH (below 5). At neutral pH, **1a** and **1b** give two $1e^-$, pH-independent waves. Only one $2e^-$, pH-independent wave is observed for **1c** at neutral pH. The polarographic behavior of N-substituted maleimides above pH 8 is complicated by hydrolysis to the monoamide acids and will not be considered here.

The identity of the reduction product was established on the basis of microanalysis, ^{1}H NMR, ^{13}C NMR, and mass spectrometry. All results are consistent with the given structures. For all compounds, the mass spectra showed a significant molecular ion. Off-center resonance decoupling was employed in making the ^{13}C NMR assignments. The ^{13}C NMR results for all compounds are given in tabular form

Table II. Relative Yield of Monomer and Hydrodimer as a Function of pH

substrate	pH	concn, mM	E_{applied}[a]	% monomer	% dimer
1a	5.9	16	−1.0	1.3	98.7
	5.9	16	−1.4	18.3	81.7
	1.8	16	−0.8	96.6	3.4
1b	6.0	34	−1.1	18.4	81.6
	6.0	17	−1.1	21.0	79.0
	6.0	17	−1.4	52.0	48.0
	2.2	17	−0.9	99.4	0.6
	2.2	34	−0.9	99.0	1.0

[a] Potential vs. Ag|AgCl.

Table III. Apparent n Values Determined via Constant Potential Coulometry

compd	pH	concn, mM	E_{applied}[a]	n_{app}[b]
1a	2.2	5.02	−0.80	1.96 ± 0.02
	2.2	1.04	−0.80	1.86 ± 0.01
	6.0	10.4	−1.00	1.12 ± 0.03
	6.0	1.04	−1.00	1.33 ± 0.03
	6.0	10.4	−1.40	1.76 ± 0.01
	6.0	1.04	−1.40	1.76 ± 0.05
1b	2.1	4.40	−0.90	1.86 ± 0.03
	2.1	2.40	−0.90	1.83 ± 0.03
	2.1	0.51	−0.90	1.70 ± 0.02
	6.0	10.6	−1.10	1.31 ± 0.03
	6.0	1.06	−1.10	1.45 ± 0.13
	6.0	10.6	−1.40	1.61 ± 0.16
	6.0	1.06	−1.40	1.66 ± 0.05
1c	2.1	4.88	−1.00	1.98 ± 0.02
	2.1	0.61	−1.00	1.95 ± 0.02
	5.3	4.88	−1.15	1.73 ± 0.08
	5.3	0.94	−1.15	1.84 ± 0.03

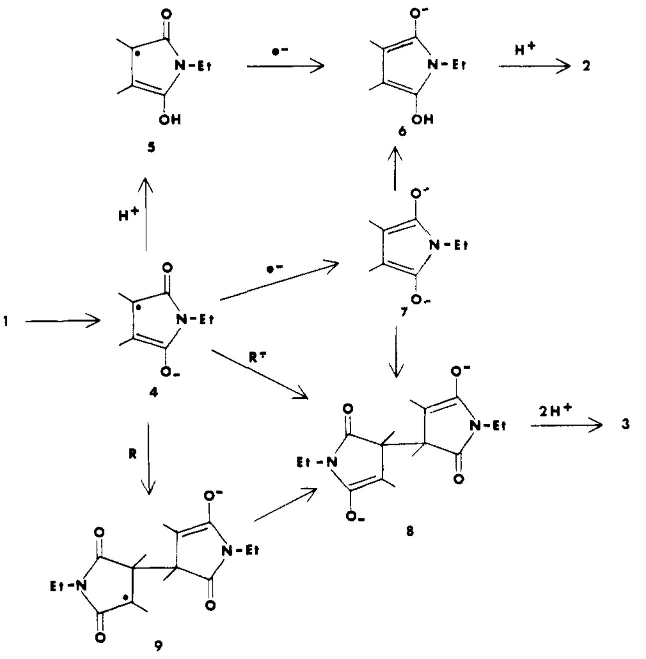
[a] Potential vs. Ag|AgCl. [b] Average of 4–10 runs ±1 standard deviation.

(Table IV) to facilitate comparisons between the different compounds.

The distribution of the reduction products of **1a** and **1b** as a function of pH, applied potential, and concentration is given in Table II. Clearly, only monomer is produced at low pH. The results of the coulometric study (Table III) also show that monomer production predominates at low pH. Monomer formation gives an n value of 2, while dimer formation gives an n value of 1. At low pH no n value lower than 1.70 was observed and most were above 1.85, indicating that monomer formation is predominant.

Table II shows that at neutral pH, dimer production is predominant and is favored by electrolysis on the first wave.

Scheme I



Dimer formation is also favored by increased concentration, as expected for a second-order reaction. Also, as expected, the n values approach 1 under the conditions favoring dimerization.

The reduction of **1c** leads exclusively to monomer regardless of the conditions. However, two diasteriomers, **2c** and **2c′**, are produced in approximately equal amounts. On the basis of differences in the ^1H and ^{13}C NMR spectra, **2c** and **2c′** tentatively have been identified as the *dl* pair and the meso isomer, respectively. This assignment is based on the upfield shift exhibited by the ^{13}C resonance of the methyl groups in the meso compound due to steric crowding.

Discussion

Scheme I shows the major pathways that the electrochemical reduction of N-substituted maleimides may follow. The first step is the formation of the radical anion via the addition of one electron. Due to electron delocalization this cyclic radical anion is a more stable radical anion than that formed from noncyclic compounds such as the dialkyl fumarates. This increased stability is clearly reflected in the fact that the electrohydrodimerization of N-substituted maleimides is observable in aqueous buffers at room temperature, conditions which yield only monomer for the dialkyl fumarates.[1,3,5]

The radical anion may react with a proton, or accept an-

Table IV. ^{13}C NMR Shifts and Assignments

	registry no.	C_2,C_5[a]	C_3	C_4	C_6	C_7	R_1	R_2
1a		170.69	134.18	134.18	32.64	13.87		
2a	2314-78-5	177.23	28.32	28.32	33.39	12.89		
3a	68630-19-3	177.25, 175.0	39.62	31.93	33.98	12.98		
1b		171.69, 170.70	145.98	127.34	32.83	13.97	10.85	
2b	65168-02-7	180.40, 176.28	36.49[b]	34.69[b]	33.67	13.02	16.72	
3b	68630-21-7	180.81, 174.58	46.45	40.22	33.68	12.74	21.71	
1c		172.12	137.15	137.15	32.81	14.06	8.5	8.58
2c	68630-21-7	179.30	43.19	43.19	33.70	13.09	15.10	15.10
2c′	68630-22-8	180.24	38.23	38.23	33.57	13.05	11.48	11.48

[a] Where the carbonyl carbons differ no absolute assignments could be made; however, it appears that the carbonyl carbon nearest to the bridge carbon and/or methyl group has the lower shift value. [b] Tentative assignments only, due to overlapping splitting peaks.

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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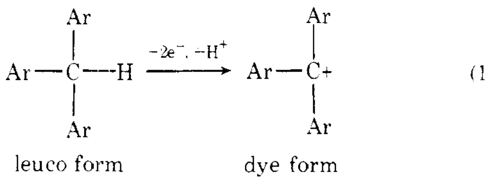
Cyclic voltammetry was used to study the effect of chemical structure on the anodic oxidation of 15 triphenylmethanes and related compounds. Two-electron oxidation leads irreversibly to formation of the corresponding dye except in those compounds where C–H bond cleavage at the central methine carbon 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.



$$Ar_3C\text{—}H \xrightarrow{-2e^-,\ -H^+} Ar_3C^+ \qquad (1)$$

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 $Ar_3CH^{+\cdot}$ 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 [$(p\text{-}(CH_3)_2NC_6H_4)_3CH$] 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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