protons. The C-22 proton gives a signal at 210 Hz while the C-23 protons give a broader signal centered at 220 Hz.

Based on the above examples, this method of assignment of conformation at C-22 appears to be sufficiently general to be considered whenever the C-20, C-22 diol system is present.

The author wishes to thank Dr. Marcel Gut for supplying most of the samples. Compound II,[4] and the epimeric pairs III and IV,[5] have previously been reported in the literature. The chemistry of the remaining compounds (V–XII), which were obtained from Dr. Gut, has not yet been published. Their nmr spectra agreed fully with the assigned structures.

Registry No.—I, 57-88-5; II, 516-72-3; III, 17954-98-2; IV, 22348-64-7; V, 38379-54-3; VI, 38379-55-4; VII, 38379-56-5; VIII, 38379-57-6; IX, 38379-58-7; X, 38379-59-8; XI, 38379-60-1; XII, 38379-61-2.

[4] V. Petrow and I. A. Stewart-Webb, *J. Chem. Soc.*, **46**, 75 (1956).

[5] N. K. Chaudhuri, R. Nickolson, H. Kimball, and M. Gut, *Steroids*, **15**, 525 (1970).

Sulfonation of Terpene Derivatives. Aluminum Hydride Desulfurization of Sultones

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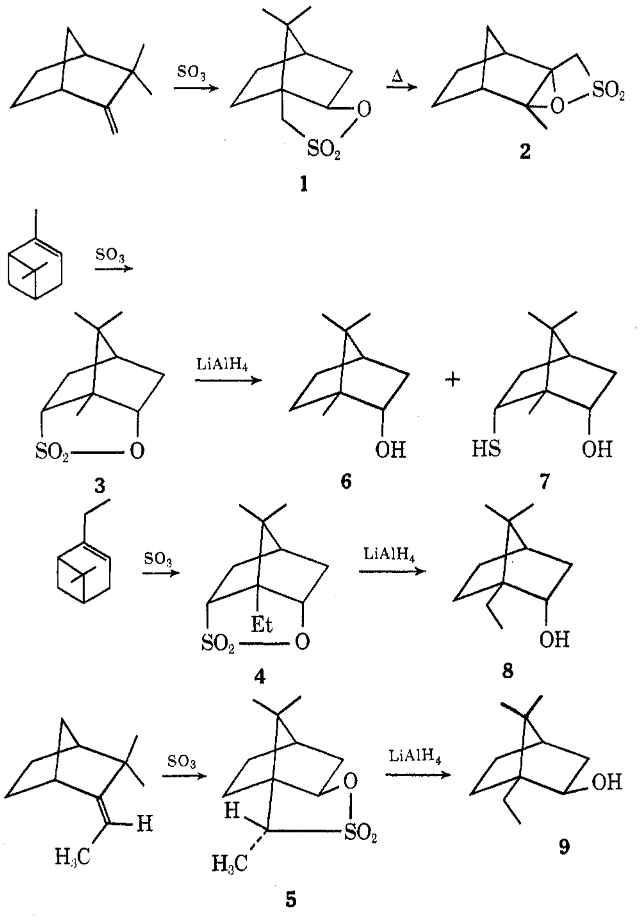
The reaction of camphene with sulfur trioxide–dioxane complex[1] in methylene chloride affords 10-isobornylsultone (**1**), which rearranges thermally at 150–170° to camphenesultone (**2**).[2] Herein we report that sulfonation of α-pinene, α-ethylapopinene, and 8-methylcamphene afford 6-bornylsultone (**3**), 10-methyl-6-bornylsultone (**4**), and 10-methyl-10-isobornylsultone (**5**), respectively, in poor to good yield.

6-Bornylsultone (**3**) exhibits normal sulfonate ester infrared absorption at 7.6 and 8.7 μ. The nmr spectrum, in addition to showing three methyl singlets, displays a broadened one-proton doublet centered at 4.60 ppm assigned to the C-2 proton and a broadened doublet of doublets centered at 3.15 ppm attributed to the C-6 proton.

The structure of **3** was confirmed by aluminum hydride[3] or lithium aluminum hydride reduction[2] to borneol (**6**). 6-*endo*-Mercaptoborneol (**7**) was also isolated from the lithium aluminum hydride reduction[4] and exhibited two eight-line nmr signals, after trifluoroacetic acid was added to remove the spin coupling of the –SH proton, consistent with the di-endo-configurational assignment.[5]

Sulfonation of 8-methylcamphene[6] yields a single isomer of 10-methyl-10-isobornylsultone (**5**), which is assigned an *endo*-10-methyl configuration on the assumption that sulfonation of the camphene double bond occurs from the more accessible exo face of the molecule.

10-Methyl-10-isobornylsultone (**5**) is transformed into 10-methyl-isoborneol (**9**) on reduction with aluminum hydride, while 10-methyl-6-bornylsultone affords 10-methylborneol (**8**) under the same conditions.



The sulfonation–desulfurization sequence described above provides a convenient method for the preparation of 10-substituted borneol and isoborneol derivatives. Although the sulfonation of pinene and camphene derivatives involve Wagner–Meerwein shifts, the reaction is free of Nametkin methyl migration, which plays an important role in the addition of acetic acid derivatives to 8-substituted camphene derivatives.[7] Desulfurization of sultones with lithium aluminum hydride proceeds slowly, and, at best, gives poor to fair yields of sulfur-free alcohol. Reduction with aluminum hydride, on the other hand, is relatively rapid and affords good yields of alcohols.

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[1] For the sulfonation of olefins see F. Bordwell, R. D. Chapman, and C. E. Osbourne, *J. Amer. Chem. Soc.*, **81**, 2002 (1959); F. Pueshal and C. Kaiser, *Chem. Ber.*, **98**, 735 (1965), and references cited therein.

[2] J. Wolinsky, D. R. Dimmel, and T. W. Gibson, *J. Org. Chem.*, **32**, 2087 (1967).

[3] J. Wolinsky and R. Lau, *Syn. Commun.*, **2**, 327 (1972).

[4] The lithium aluminum hydride reduction of terpene sultones will be described in a forthcoming publication.

[5] We attribute the absence of eight-line signals in sultone **3** to the presence of the sultone ring which distorts the bond angles of the bornane ring.

[6] 8-Methylcamphene consists of a mixture of *anti*-8-methyl and *syn*-8-methyl isomers in a ratio of 13:1, respectively.[7]

[7] J. Wolinsky and E. J. Eustace, to be published.

Experimental Section[8]

6-Bornylsultones (3).—To a freshly prepared solution of 266 g (1.52 mol) of sulfur trioxide–dioxane complex in 400 ml of methylene chloride at −78° was added (2 hr) a solution of 184 g (1.35 mol) of α-pinene (practical grade, 90% $[\alpha]_D$ +46°) in methylene chloride. The solution was allowed to warm to room temperature and stirred for 17 hr. Ether was added and the solution was washed with saturated salt solution, dried ($MgSO_4$), and concentrated to leave 165 g of a dark brown oil, which slowly deposited crystals. Recrystallization of the solid from methanol, sublimation *in vacuo*, and chromatography of the mother liquors on neutral alumina yielded a total of 21.0 g (7.3%) of 6-bornylsultone (**3**). The analytical sample of **3** was obtained by recrystallization from 2:1 hexane–THF and showed mp 198–199°; $[\alpha]_D$ −12.6° (*c* 6.28, $CHCl_3$); ir (CCl_4) 7.4 and 8.6 μ; nmr (CCl_4) 0.93 and 1.00 (s's, 6, CH_3CCH_3), 1.37 (s, 3, CH_3), 3.15 (d of d, 1, $-CHSO_2-$), and 4.60 ppm (broadened d, 1, –CHO–); mass spectrum (70 eV) *m/e* (rel intensity) no parent ion, 148 (9.0), 137 (5), 109 (23), 108 (100), 93 (29), 67 (19), and 41 (20).

Anal. Calcd for $C_{10}H_{16}O_3S$: C, 55.53; H, 7.46; S, 14.83. Found: C, 55.61; H, 7.42; S, 14.71.

Lithium Aluminum Hydride Reduction of 6-Bornylsultone (3). A. 6-*endo*-Mercaptoborneol (7).—To a stirred slurry of 0.53 g (14 mmol) of $LiAlH_4$ in 20 ml of freshly distilled THF was added 1.0 g (4.6 mmol) of sultone **3**. The solution was heated at reflux for 50 hr and then the excess hydride was destroyed with water. The solids were dissolved in 5% HCl and extracted with ether. The ethereal solution was dried ($MgSO_4$) and evaporated to yield 0.62 g of an oil, which on glpc analysis proved to be a mixture of borneol (**6**), 6-mercaptoborneol (**7**), and 6-bornylsulfinate ester[3] in the ratio of 5:55:40. Preparative glpc yielded 6-*endo*-mercaptoborneol (**7**): mp 149–151° (sublimes, sealed tube); ir (CCl_4) 2.80, 3.90, 8.9 and 9.4 μ; nmr (CCl_4) 0.88 and 0.95 (s's, 9, 3 CH_3), 1.71 (t, 1, J = 4.7 Hz, C_1H), 1.97 (d, 1, J = 6.5 Hz, CHS**H**), 3.17 (s, 1, OH), 3.25 (m, 1, –C**H**SH), and 4.12 ppm (A portion of AMNX, 1, $J_{2\text{-exo},3\text{-endo}}$ = 10 Hz, $J_{2\text{exo-},3\text{-exo}}$ = 4.5 Hz, $J_{2\text{-exo},6\text{-exo}}$ = 2.1 Hz, –C**H**OH). Addition of F_3CCO_2H causes the signal at 3.25 to shift to 3.47 ppm ($J_{5\text{-endo},6\text{-exo}}$ = 10.5 Hz, $J_{5\text{-exo},6\text{-exo}}$ = 5.7 Hz, $J_{2\text{-exo},6\text{-exo}}$ = 2.5 Hz) and the signal at 4.12 to shift to 4.37 ppm ($J_{2\text{-exo},3\text{-endo}}$ = 10.0, $J_{2\text{-exo},3\text{-exo}}$ = 5.0 Hz, and $J_{2\text{-exo},6\text{-exo}}$ = 2.5 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 186 (5.4), 153 (3.8), 152 (7.8), 135 (8.6), 134 (7.4), 108 (100), 93 (28).

Anal. Calcd for $C_{10}H_{18}OS$: C, 64.46; H, 9.74. Found: C, 64.21; H, 9.55.

B. Borneol (6).—A solution of 700 mg (3.2 mmol) of sultone **3** in 5 ml of dry THF was added to a slurry of 700 mg (17.9 mmol) of $LiAlH_4$ in 10 ml of dry THF. The mixture was refluxed for 60 hr, cooled, and worked up in the normal fashion to yield an oil which by glpc analysis contained 39% borneol (**6**), 45% **7**, and 16% 6-bornylsulfinate ester.[3] The isolated product and authentic borneol had identical retention times on two glpc columns (SE-30, 160°, and Carbowax 20M, 200°). In addition, the reduction product has ir, mass, and nmr spectra identical with those of the authentic borneol.

Aluminum Hydride Reduction of 6-Bornylsultone (3).—A mixture of 1.38 g (36.6 mmol) of lithium aluminum hydride, 1.46 g (11.00 mmol) of aluminum chloride, and 790 mg (3.66 mol) of **3** was refluxed for 40 hr. The usual work-up gave 0.34 g (35%) of borneol, $[\alpha]^{24}_D$ +31.1° (EtOH) {lit.[9] $[\alpha]_D$ +37.4° (EtOH)}.

10-Methyl-10-isobornylsultone (5).—To a solution of 10.7 g (0.064 mol) of sulfur trioxide–dioxane complex in 30 ml of methylene chloride at −78° was added slowly 8.55 g (0.057 mol) of (±)-8-methylcamphene[6] in 20 ml of methylene chloride. The solution was allowed to warm to room temperature and stirred for 18 hr. Ether was added and the solution was washed with 10% sodium bicarbonate solution and saturated salt solution and dried ($MgSO_4$); the solvent was removed to yield an oil. Crystallization from hexane–THF (10:1) and chromatography of the mother liquors on silica gel afforded a total of 5.89 g (44.9%) of (±)-10-methyl-10-isobornylsultone (**5**): mp 91–94°; ir (CCl_4) 7.57 and 8.56 μ; nmr ($CDCl_3$) 0.96 and 1.01 (s's, 6, CH_3CCH_3), 1.37 (d, 3, J = 7 Hz, CH_3CH-), 3.25 (q, 1, J = 7 Hz, CH_3CH-), and 4.24 ppm (d of d, –CHO–); mass spectrum (70 eV) *m/e* (rel intensity) no parent ion, 149 (34), 122 (90), 107 (80), 105 (49), 93 (42), 81 (44), 67 (40), 41 (100), and 39 (53).

Anal. Calcd for $C_{11}H_{18}O_3S$: C, 57.36; H, 7.68; S, 13.92. Found: C, 57.25; H, 7.60; S, 13.68.

Aluminum Hydride Reduction of 10-Methyl-10-isobornylsultone (5).—To a stirred slurry of 2.62 g (19.6 mmol) of aluminum chloride and 2.48 g (65.4 mmol) of lithium aluminum hydride in 100 ml of ether at 0° was added a solution of 1.5 g (6.54 mmol) of sultone **5** in 25 ml of ether. The solution was heated at reflux for 40 hr and cooled, and 25 ml of ethyl acetate, followed by 25 ml of water, was added. The salts were removed and washed with ether, and the combined ether solution was washed with water, dried ($MgSO_4$), and evaporated to leave a foul-smelling oil. Sublimation *in vacuo* gave 670 mg (61%) of 10-methylisoborneol (**9**): mp 52–54°, ir (CCl_4) 2.92 μ; nmr ($CDCl_3$) 0.99 (t, 3, CH_3), 0.80 and 1.08 (s's, 6, CH_3CCH_3), 2.30 (m, 1, OH), and 3.84 ppm (m, 1, –CHO–); mass spectrum (70 eV), *m/e* (rel intensity) 168 (3.5), 107 (29), 95 (100), 93 (23), 79 (26), 69 (25), 67 (32), 55 (37), 53 (28), 43 (46), and 41 (86).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.26; H, 12.10.

10-Methylcamphor (10).—To a solution of 200 mg of 10-methylisoborneol (**9**) in 10 ml of acetone at 0° was added 2 ml of Jones reagent over a 10-min period. The mixture was stirred for 1 hr, and 2 ml of isopropyl alcohol was added. The salts were removed by filtration and washed with ether. The combined filtrates were washed with water, dried ($MgSO_4$), concentrated, and evaporatively distilled *in vacuo* to yield 164 mg (83%) of 10-methylcamphor (**10**): ir (neat) 5.74 μ; nmr ($CDCl_3$) 0.86, 0.97 (s's, 6, CH_3CCH_3), and 0.97 ppm (t, 3, CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 166 (18), 122 (29), 109 (37), 95 (100), 83 (18), 69 (17), 67 (18), 55 (40), and 41 (31).

The oxime of 10-methylcamphor displayed mp 103–104° (lit.[10] mp 104°).

(+)-10-Methyl-6-bornylsultone (4).—To a stirred slurry of 21.8 g (0.14 mol) of sulfur trioxide–dioxane complex in 65 ml of methylene chloride at −78° was added (1 hr) a solution of 21.0 g (0.14 mol) of α-ethylapopinene,[11–13] $[\alpha]^{21}_D$ −49.8° ($CHCl_3$), in methylene chloride. The reaction mixture was stirred at −78° for 2 hr and at ambient temperature for 18 hr. The reaction was worked up in the usual manner affording a yellow oil which was chromatographed on silica gel. The early fractions yielded 5.8 g (28%) of *p*-ethylcumene: n^{25}_D 1.4898 (lit.[14] n^{25}_D 1.4900); nmr ($CDCl_3$) 1.19 (t, 3, J = 7.5 Hz, CH_3), 1.23 (d, 6, J = 7 Hz, $(CH_3)_2CH$), 2.58 (q, 2, J = 7.5 Hz, $-CH_2-$), 2.72 (septet, 1, J = 7.0 Hz, –CH–), and 7.08 ppm (m, 4, Ar H). The later fractions yielded 1.28 g (4%) of (+)-10-methyl-6-bornylsultone (**4**). The analytical sample of **4** was obtained by recrystallization from pentane and showed mp 178–179°; ir (CCl_4) 7.40 and 8.64 μ; $[\alpha]^{24}_D$ +15.3° (*c* 2.10, $CHCl_3$); nmr ($CDCl_3$) 0.99, 1.07 (s's, 6, CH_3CCH_3), 1.05 (t, 3, J = 7 Hz, CH_3), 3.48 (d of d, 1, $-CHSO_2$), and 4.81 ppm (broad d, 1, –CHO–); mass spectrum (70 eV) *m/e* (rel intensity) no parent ion, 123 (14), 122 (100), 107 (39), 95 (15), 55 (22), 43 (25), 41 (38), and 39 (14).

Anal. Calcd for $C_{11}H_{18}O_3S$: C, 57.36; H, 7.88; S, 13.92. Found: C, 57.27; H, 7.80; S, 13.70.

Desulfurization of 10-Methyl-6-bornylsultone (4).—To an ice-cold slurry of 635 mg (16.7 mmol) of lithium aluminum hydride and 665 mg (5.0 mmol) of aluminum chloride in 20 ml of ether was added 384 mg (1.67 mmol) of sultone **4**. The reaction mixture was heated at reflux for 40 hr and worked up in the usual fashion to give 134 mg of crude 10-methylborneol contaminated by three minor unidentified materials. A pure sample of 10-methylborneol was isolated by vpc using a 15% Carbowax column at 180° and showed mp 59–60° (lit.[10] mp 57.5°); ir (neat) 2.92 μ; nmr ($CDCl_3$) 0.88 (s, 3, CH_3), 0.97 (s and t, 6, CH_3, and CH_3CH_2-), 2.57 (m, 1, OH), and 4.19 ppm (A portion of AMNX, 1, $J_{2\text{-exo},6\text{-exo}}$ = 1.5 Hz, $J_{2\text{-exo},3\text{-exo}}$ = 3.5 Hz, $J_{2\text{-exo},3\text{-endo}}$ = 10 Hz, –CHO–); mass

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[8] All melting and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Infracord, Model 137-B. Nmr spectra were measured with a Varian Associates A-60 spectrometer. Optical rotations were measured with a Zeiss polarimeter. Mass spectra were determined by the Purdue University Spectral Service employing a Hitachi RMU-6A mass spectrometer. Gas–liquid chromatography was performed on an Aerograph 90-P instrument using a 5-ft 20% SE-30 on Chromosorb column at 160–180°. Microanalyses were performed by Dr. C. S. Yeh and associates.

(9) E. Beckmann, *Justus Liebigs Ann. Chem.*, **250**, 353 (1889).

(10) G. Ohloff, G. Schade, and H. Farnow, *Chem. Ber.*, **90**, 113 (1957).

(11) Obtained in 67% yield by lithium aluminum hydride reduction of nopol tosylate: mp 49–50°, $[\alpha]^{24}_D$ −27.4° (*c* 5.23, $CHCl_3$), lit.[12] mp 49–50°.

(12) R. T. Arnold and M. J. Danzig, *J. Amer. Chem. Soc.*, **79**, 892 (1957).

(13) G. Ohloff, H. Farnow, and G. Schade, *Chem. Ber.*, **89**, 1549 (1956).

(14) J. P. Bain, *J. Amer. Chem. Soc.*, **68**, 638 (1946).

spectrum (70 eV) m/e (rel intensity) 168 (7.6), 124 (18), 109 (23), 95 (100), 67 (11), 55 (20), 43 (14), 41 (34), and 39 (14).

Oxidation of 10-methylborneol using the Jones procedure gave (−)-10-methylcamphor, $[\alpha]^{24}\mathrm{D}$ −23.4° (c 2.69, EtOH) (lit.[10] $[\alpha]^{20}\mathrm{D}$ −25°), whose ir and nmr spectra were identical with those of (±)-10-methylcamphor obtained by oxidation of 10-methylisoborneol (9).

Registry No.—**3,** 38359-42-1; **4,** 38359-43-2; **5,** 38359-44-3; **7,** 38359-45-4; **9,** 38359-46-5; **10,** 38359-47-6; α-pinene, 80-56-8; (±)-8-methylcamphene, 38359-48-7; α-ethylapopinene, 38359-49-8.

A New Synthesis of 2,3,6,7-Tetramethylnaphthalene and Its Electrochemistry

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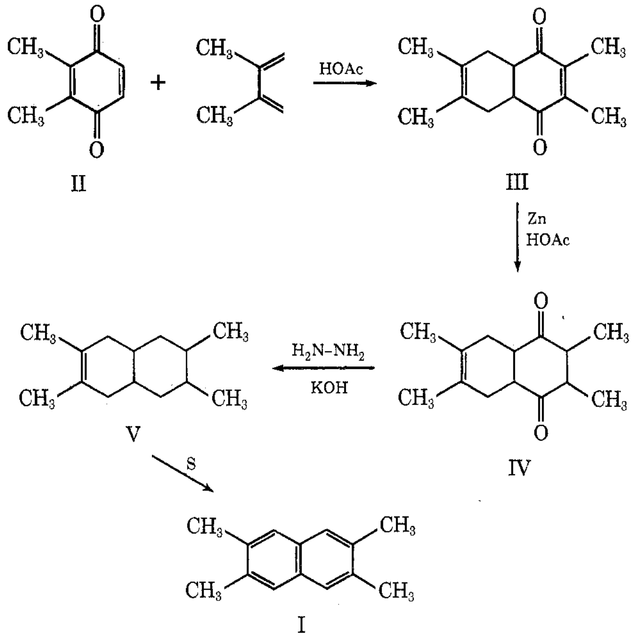
2,3,6,7-Tetramethylnaphthalene (I) was first prepared by Mosby[1b] from 2,3,6,7-tetramethylnaphthalene-1,4-dinitrile. The synthesis of this compound involved a rather long and tedious route. As we needed this compound in rather large quantities, a more convenient route was desired. The resultant synthesis is presented in this paper along with electrochemical data.

Results

Synthesis.—The synthesis of I is outlined in Scheme I. The unsaturated diketone III was synthesized by Diels–Alder reactions of 2,3-dimethylbenzoquinone (II) with 2,3-dimethylbutadiene as reported by Fieser and Ardao.[2] Attempted reduction of the carbonyl groups of III using Wolff–Kishner, Clemmenson, sodium, or chlorobenzoxazole methods under various conditions gave negative results. The aromatized hydroquinone appeared to be the typical product. It was thought that saturation of the quinone-type double bond in III might reduce the molecule's tendency to aromatize. Thus, when III was treated with zinc dust in glacial acetic acid, the desired reduction to IV occurred. Furthermore, IV was then reduced by the Wolff–Kishner procedure to V in 67% yield. Heating hydrocarbon V with sulfur produced I.

Scheme I



Electrochemistry.—I was reduced in dimethylformamide (DMF) and oxidized in acetonitrile (AN), n-butyronitrile (BN), and propylene carbonate (PC). I apparently reduced cathodic to solvent breakdown in AN, BN, and PC, while oxidizing anodic to the breakdown of DMF. Table I gives the data obtained from the reduction on mercury. Polarographic determination of the half-wave reduction potential ($E_{1/2}$) was impossible owing to the fact that the wave came at the foot of solvent breakdown. Therefore, an approximate $E_{1/2}$ was calculated from the cyclic voltametry data.[3]

Table I

Reduction of I in DMF at a Hanging Mercury Drop Electrode[a]

E_{peak}	−2.74 V
$E_{1/2}$[b]	−2.71 V
$E_{\mathrm{c\,peak}} - E_{\mathrm{a\,peak}}$	0.096 V
Sweep rate	200 mV/sec

[a] These values in volts *vs.* the saturated calomel electrode (sce). [b] Reference 3.

The results for the oxidation of I on platinum are shown in Table II. The oxidation waves from cyclic voltametry are chemically irreversible, showing no cathodic current in AN or BN up to 100 V/sec and only a barely noticeable cathodic current in PC at 20 V/sec. The peak potentials are also dependent on sweep rate.

Table II

Oxidation of I[a]

Solvent	E_{peak}	Sweep rate, mV/sec
AN	1.43	200
BN	1.53	200
PC	1.39	200

[a] Volts *vs.* sce.

Discussion

Synthesis.—The synthesis we have presented provides a more convenient alternative to the existing procedure. It utilized readily available starting materials and relatively simple reactions. In addition, it promises to provide a versatile route to other substituted naphthalenes. Thus, variations in the 2,3 substituents of the starting quinone would determine the substituents in the 2 and 3 position of the final naphthalene. Similarly, the 2 and 3 substituents on

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(1) (a) Ethyl Fellow, 1971–1972. (b) W. L. Mosby, *J. Amer. Chem. Soc.*, **75**, 3600 (1953).

(2) L. Fieser and M. I. Ardao, *ibid.*, **78**, 774 (1956).

(3) R. S. Nicholson and I. Shain, *Anal. Chem.*, **30**, 706 (1964).