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, $[\alpha]^{24}\text{D}$ −23.4° (*c* 2.69, EtOH) (lit.[10] $[\alpha]^{20}\text{D}$ −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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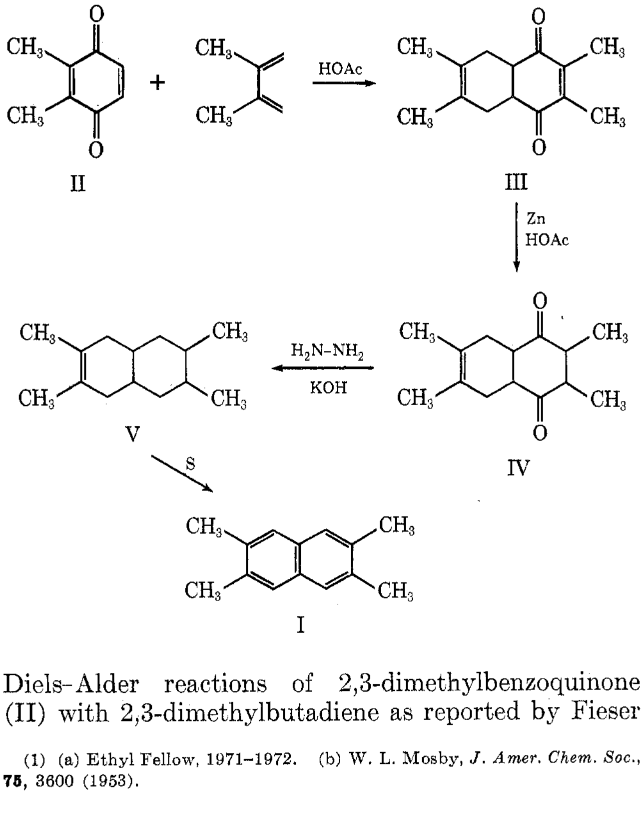
2,3,6,7-Tetramethylnaphthalene (I) was first prepared by Mosby[1b] from 2,3,6,7-tetramethylnaphthalene-1,4-dinitrile. The synthesis of this compound involved a rather long and tedious route. As we needed this compound in rather large quantities, a more convenient route was desired. The resultant synthesis 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
$E_{\text{c peak}} - E_{\text{a peak}}$	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).

the butadiene moiety would determine the 6 and 7 substituents in the naphthalene product.

Electrochemistry.—Qualitatively the reduction and oxidation potentials of I correlate with the electron-donating effects of methyl groups (Table III). The peak potential (E_{peak}) for the oxidation of I exhibits a large amount of solvent dependence. The reference electrode used in these studies was an aqueous saturated calomel electrode (sce). Use of the sce introduces an unknown liquid–liquid junction potential between the sce and the electrolytic solution. Differences in the junction potential between the sce and the various solvent systems probably account for the major portion of solvent dependence of I.[4a]

TABLE III

MOLECULAR ORBITAL ENERGIES OF NAPHTHALENIC COMPOUNDS WITH THEIR REDUCTION AND OXIDATION POTENTIALS[f,g]

	Naphthalene	Dimethyl-naphthalene	Tetramethyl-naphthalene
LUMO[a,c]	−0.6180	−0.6480	−0.6770
HFMO[b,c]	+0.6180	+0.5617	+0.5083
Reduction potential	−2.58	−2.68	−2.71
Oxidation potential	+1.72[e]	+1.56[d]	1.44[d]

[a] Lowest unoccupied molecular orbital. [b] Highest filled molecular orbital. [c] These values in units of β_0. [d] These values are cyclic voltametry peak potentials taken at 0.5 V/sec. [e] Estimated from $E_{1/2}$ of +1.70 at a rotated platinum disk as determined in R. D. Rieke, W. E. Rich, and T. H. Ridgway, *J. Amer. Chem. Soc.*, **93**, 1962 (1971). [f] Data for the LUMO of naphthalene and dimethylnaphthalene are from ref *e*. The energies for the remaining MO's were determined as in ref *e*. [g] Data in volts *vs.* sce.

Experimental Section

Cyclic voltametric (CV) experiments were performed with a solid state three-electrode instrument. The cell used has been described elsewhere.[4b] The platinum bead electrode used for the oxidation work was pretreated with aqua regia for 2 min, washed with distilled water, and dried before each experiment. Melting points were taken on an oil bath type instrument and are uncorrected. Nuclear magnetic resonance spectra were recorded for solutions in carbon tetrachloride with tetramethylsilane internal reference on a JEOL-C-60-HL instrument. Gas chromatography was done with a Hewlett-Packard 5750 on a 6.5 ft × 0.25 in. 20% SE-30 on Chromosorb W column. Infrared spectra were obtained with a Perkin-Elmer 257 spectrometer.

Chemicals.—Spectro Grade acetonitrile (Matheson Coleman and Bell) was dried by addition of Al_2O_3 which had been dried at 400° for 24 hr. *n*-Butyronitrile was stirred with $KMnO_4$ and anhydrous Na_2CO_3 and heated to 70°. Fast distillation at 15 mm gave BN with an impurity evident in the uv spectrum which could not be removed by fractionation. However, this BN was acceptable, giving limits of +1.7 to −1.6 on platinum. Propylene carbonate was prepared by the method of Nelson and Adams.[5] Spectro Grade dimethylformamide obtained from Matheson Coleman and Bell was refluxed over copper sulfate through a Soxhlet containing Linde 4A molecular sieves under vacuum, not allowing the pot temperature to rise above 50°. The DMF was then distilled under vacuum into a receiver cooled to −78°, where it was stored under N_2.

Tetraethylammonium perchlorate (TEAP) was purchased from Eastman and purified by a standard procedure.[6] Tetra-*n*-butylammonium perchlorate (TBAP) was made according to a published procedure.[7]

All AN solutions were 0.1 *M* in TEAP, PC solutions were 0.25 *M* in TEAP, and BN solutions were 0.1 *M* TBAP.

In all experiments I was 1 mmol and was purified by gc.

2,3,6,7-Tetramethyl-4a,5,8,8a-tetrahydro-1,4-naphthaquinone (III).—Quinone II was prepared as described by Fieser and Ardao[2] and allowed to react with 2,3-dimethylbutadiene as has been described,[2] yielding III (73–84%), mp 104.5–105° (lit.[2] mp 103–104°), ir 1671 cm^{-1} (CH_2Cl_2).

2,3,6,7-Tetramethyl-2,3,4a,5,8,8a-hexahydro-1,4-naphthoquinone (IV).—Compound III (35.9 g, 0.165 mol) was dissolved in HOAc (180 ml) and added to a vigorously stirred suspension of activated[8] zinc dust in H_2O (100 ml). After 8 min the suspension was filtered, cooled, and diluted with H_2O to give a crop of white needles (7.0 g). The solution was then neutralized with $NaHCO_3$ and saturated with NaCl. A solid appeared at the top of the solution, and was skimmed off and extracted with acetone; the acetone was stripped off and the product was dried *in vacuo*, yielding IV (total of 21.9 g, 79%, 0.1 mol): mp 129–130° (CCl_4); ir 1708 cm^{-1} (CH_2Cl_2); mass spectrum *m/e* 220.1462 (calcd for $C_{14}H_{20}O_2$, 220.1553).

2,3,6,7-Tetramethyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene (V).—Diketone IV (28.9 g, 0.13 mol) was treated with hydrazine hydrate (115 ml, 99%) in diethylene glycol (500 ml) until all IV had dissolved. KOH (120 g) in diethylene glycol (480 ml) was added and the mixture was refluxed for 1 hr. The condenser was removed and the solution temperature was allowed to rise to 185°, at which point the condenser was replaced and the solution was refluxed for 5 hr, cooled, and extracted with petroleum ether (bp 30–60°) which was stripped off, leaving light yellow oil V (17.0 g, 67%, 0.089 mol). This product was chromatographed through a 2 × 15 cm column of Al_2O_3 with hexane, yielding a colorless liquid: nmr τ 8.175, 8.47, 8.68, 8.93, 9.05, 9.13, 9.25 (peaks overlap too much to allow valid integration); ir (neat) 2960 (w), 2904 (m), 1455 (w), 1378 (w) cm^{-1}; mass spectrum *m/e* 192.1884 (calcd for $C_{14}H_{24}$, 192.1878).

2,3,6,7-Tetramethylnaphthalene (I).—Octahydrodecalin V (3.54 g, 18 mmol) was mixed with sulfur (2.45 g, 76 mmol) and heated at 235° for 5 min. The reaction mixture was cooled and extracted with petroleum ether, which was evaporated and the residue was chromatographed on a 2 × 50 cm column of alumina (Merck) to yield I (1.51 g, 45%, 8.2 mmol). The product was light yellow, indicating an impurity: mp 188–190° (lit.[1] mp 191.0–191.5°); nmr τ 7.66 (12 H, methyl), 2.63 (4 H aromatic) (lit.[9] 7.64); mass spectrum *m/e* 184.1254 (calcd for $C_{14}H_{16}$, 184.1252).

Registry No.—I, 1134-40-3; III, 38312-84-4; IV, 38312-85-5; V, 38312-86-6.

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The Reaction of Bromomethylenecyclopropane with Potassium *tert*-Butoxide

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In continuation of our study of rearrangement reactions of terminal halo olefins,[1] we report here the reaction of bromomethylenecyclopropane (1) with potas-

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