

as the Wittig olefin synthesis, for the further elaboration of the carbon skeletons of several important classes of natural products. Work is in progress to optimize the yields of our reactions, to investigate the stereochemistry thoroughly,<sup>23</sup> to study the reaction of the intermediate vinylcopper complex with other electrophilic substrates besides  $\alpha,\beta$ -unsaturated carbonyl compounds,<sup>24</sup> and to apply our route to the synthesis of naturally occurring compounds.

**Acknowledgments.** We wish to thank Professor Alan B. Levy of this department for many fruitful discussions concerning this work. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Joint Awards Council and University Awards Committee, administered by the Research Foundation of the State University of New York, for support of this research.

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- We do not intend to imply any specific structures for the intermediate copper complexes such as **6** involved in this work.
- The efficiency of formation of the vinylcopper complexes under various conditions was determined by quenching the reaction mixtures with aqueous ammonium chloride and analyzing the crude products by GLC (6ft  $\times$   $\frac{1}{8}$  in, 5% OV-1, 110-240  $^{\circ}$ C) to determine the yields of the simple olefin ( $R^2R^4C=CH_2$ ) and the diene. At this time, we cannot exclude the possibility that the increased yields of vinylcopper complexes are due to stabilization of these species by the coordination of dimethyl sulfide rather than the absence of impurities that may promote the coupling reaction.
- Products from our small-scale reactions were conveniently isolated by bulb-to-bulb distillation and HPLC using a Waters 1 ft  $\times$  0.25 in.  $\mu$ -Porasil column. All products exhibited satisfactory NMR, IR, and mass spectra and microanalytical data.
- Unlike many reports in which large excesses of organocopper species are used in various reactions, the yields reported here are very representative of the efficiency of the overall process because of the use of equimolar quantities of all reactants.
- The improvement of yields of conjugate addition products upon using cuprates in place of alkylcopper complexes has been noted previously: see ref 5c, p 20.
- In further preliminary studies, the use of mixed cuprates has also led to improved yields of desired products from 1-acetylcyclohexene, 1-phenyl-2-buten-1-one, and methyl vinyl ketone but not from ethyl acrylate.
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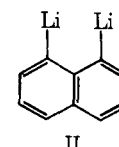
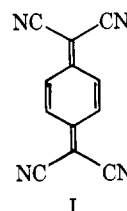
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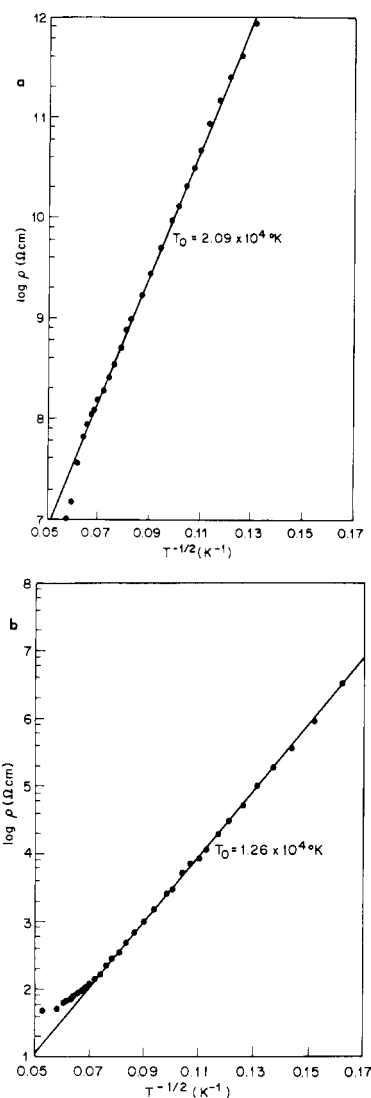
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## Peri-Bridged Naphthalenes from 1,8-Dilithionaphthalene

Sir:

In recent years there has been an increasing interest in planar, aromatic compounds containing several sulfur or selenium atoms, largely in connection with the possibly useful electrical, magnetic, and optical properties that charge transfer complexes involving these donor molecules and acceptors such as 7,7,8,8-tetracyanoquinodimethane (TCNQ, I) may have.<sup>1</sup>

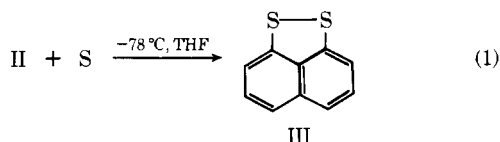




**Figure 1.** (a) Plot of  $\log R$  vs.  $T^{-1/2}$  (kelvin) for NDSe-TCNQ compressed pellet.  $\rho(RT) = 1 \times 10^7 \Omega \text{ cm}$ . (b) Plot of  $\log R$  vs.  $T^{-1/2}$  (kelvin) for NDTe-TCNQ compressed pellet.  $\rho(RT) = 50 \Omega \text{ cm}$ .

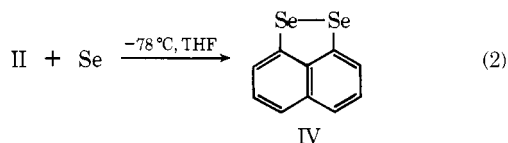
We wish to report a convenient, one-step synthesis of a group of naphthalene derivatives in which the peri positions of 1,8-dilithionaphthalene<sup>2</sup> are bridged by a pair of identical group 6 atoms.

The method is illustrated by the facile preparation of the well-known naphtho[1,8-*c,d*]-1,2-dithiole<sup>3</sup> (III) by the reaction of II with sublimed sulfur, as summarized in eq 1. This reaction proceeds readily in tetrahydrofuran solution at  $-78^\circ\text{C}$  to give III in 35–40% yield.<sup>4</sup> The properties of III obtained in this way agree well with those of an authentic sample of III prepared independently.<sup>3</sup> Its 220-MHz  $^1\text{H}$  NMR spectrum shows the expected AMX pattern, and its 70 eV mass spectrum shows the anticipated parent ion as its base peak at  $m/e$  190.

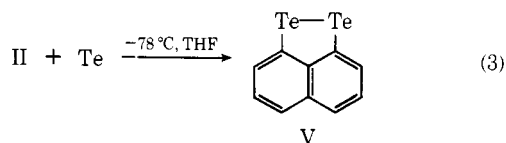


As summarized in eq 2, II reacts analogously with amorphous, gray selenium to give naphtho[1,8-*c,d*]-1,2-diselenole<sup>5</sup> (IV) as lustrous, purple crystals, mp  $127\text{--}129^\circ\text{C}$  (from hexane/methylene chloride) in 18–22% yield. The 220-MHz  $^1\text{H}$  NMR spectrum of IV bears a close resemblance to that of III, and the characteristic ion intensity ratios of the parent molecular ions in its 70 eV mass spectrum ( $m/e$  (int.) observed,

278 (4), 279 (5), 280 (18), 281 (10), 282 (47), 283 (32), 284 (88), 285 (23), 286 (100), 287 (19), 288 (39), 289 (5); calculated, 278 (4), 279 (5), 280 (20), 281 (14), 282 (51), 283 (31), 284 (88), 285 (15), 286 (100), 287 (11), 288 (32), 289 (4)) confirms the presence of two selenium atoms.<sup>6</sup>

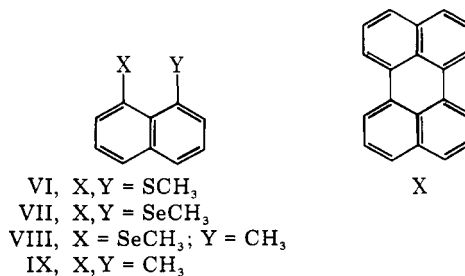


The reaction between II and powdered tellurium, as summarized in eq 3, produces naphtho[1,8-*c,d*]-1,2-ditellurole<sup>7</sup> (V) as metallic, greenish needles, mp  $212\text{--}214^\circ\text{C}$  (from hexane/carbon disulfide) in 8–12% yield. Once more, the  $^1\text{H}$  NMR shows an AMX pattern, and the 70 eV mass spectrum of the molecular ion cluster of V ( $m/e$  (int.) observed, 373 (2), 374 (7), 375 (5), 376 (17), 377 (16), 378 (36), 379 (26), 380 (67), 381 (30), 382 (100), 383 (11), 384 (92), 385 (9), 386 (50), 387 (5); calculated, 373 (2), 374 (6), 375 (5), 376 (17), 377 (15), 378 (36), 379 (25), 380 (66), 381 (28), 382 (100), 383 (11), 384 (93), 385 (10), 386 (51), 387 (6)) provides good support for its composition.<sup>6</sup>



Deeply colored 1:1 donor-acceptor complexes of IV and V are formed readily with I by mixing hot equimolar solutions of the components in acetonitrile and allowing the adducts to crystallize. The compressed pellet conductivities of these new TCNQ adducts were measured at low fields, thus yielding ohmic results. Plots of resistivity vs. temperature are shown in Figures 1a and 1b. A straight line plot of the logarithm of resistance vs.  $T^{-1/2}$  is observed over a large temperature range by the diselenole complex (NDSe-TCNQ) but not by the ditellurole analogue (NDTe-TCNQ). The slope of the line yields  $T_0$ , a measure of activation energy for conductivity.<sup>8</sup> Figure 1b reveals that NDTe-TCNQ appears to be metallic at room temperature.<sup>9</sup> Measurements on single crystals should verify this preliminary observation.

All three of these bridged naphthalenes react rapidly with methylolithium in tetrahydrofuran; subsequent alkylation of the products, however, revealed that the reactions followed somewhat different courses. In the case of III, 1,8-bisthiomethylnaphthalene (VI), (mp  $84\text{--}85^\circ\text{C}$ , lit.  $84^\circ\text{C}$ )<sup>10</sup> is the sole organic product. Under the same conditions IV yields 1,8-bisselenomethylnaphthalene (VII) and 1-selenomethyl-8-methylnaphthalene<sup>11</sup> (VIII) in a ratio of 4:1. In the case of V, the major product is 1,8-dimethylnaphthalene<sup>11,12</sup> (IX); a trace of perylene (X) is also formed.<sup>13</sup>



There are several mechanistic questions raised by this work, and many opportunities for synthesis present themselves; we are continuing our studies in this area.

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## References and Notes

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- (4) The yields of compounds III, IV, and V have not been optimized.
- (5) Anal. Calcd for  $C_{10}H_6Se_2$ : C, 42.28; H, 2.12; Se, 55.59. Found: C, 42.26; H, 2.12; Se, 55.46. IR (KBr): 3060, 1901(w), 1748(w), 1595, 1534, 1481, 1413, 1345, 1188, 1142, 1043, 959, 891, 859, and 751  $cm^{-1}$ . UV  $\lambda_{max}$  (cyclohexane) 212 ( $\epsilon$   $3.9 \times 10^4$ ), 255 (shoulder) ( $\epsilon$   $1.1 \times 10^4$ ), 262 ( $\epsilon$   $1.5 \times 10^4$ ), 367 (shoulder) ( $\epsilon$   $1.2 \times 10^4$ ), and 380 nm ( $\epsilon$   $1.6 \times 10^4$ ). 220-MHz  $^1H$  NMR spectrum: 2 H, d of d; 2 H, d of d; 2 H, t; extending from  $\delta$  7.20 to 7.51.  $^{13}C$  NMR: Chemical shift values 121.12, 123.75, 127.62, 137.50, 137.89, 140.91 ppm relative to  $Me_4Si$ .
- (6) The calculated mass spectra were obtained by use of the MASH computer program, which is a local version of ISOW developed by W. A. G. Graham, University of Alberta, and modified by R. C. Winterton and R. S. Weber, Cornell University. The results are an average of two scans.
- (7) Anal. Calcd for  $C_{10}H_6Te_2$ : C, 31.49; H, 1.59; Te, 66.92. Found: C, 31.31; H, 1.60; Te, 67.12. IR (KBr): 3060, 1925(w), 1777(w), 1531, 1481, 1412, 1343, 1189, 1136, 1040, 959, 890, 794, and 752  $cm^{-1}$ . UV  $\lambda_{max}$  (cyclohexane) 257 ( $\epsilon$   $7.5 \times 10^3$ ), 267 ( $\epsilon$   $7.7 \times 10^3$ ), 383 (shoulder) ( $\epsilon$   $7.6 \times 10^3$ ), and 410 nm ( $\epsilon$   $1.0 \times 10^4$ ). 220-MHz  $^1H$  NMR spectrum: 2 H, d of d; 2 H, d of d; 2 H, t; extending from  $\delta$  7.12 to 7.67.  $^{13}C$  NMR: Chemical shift values 127.22, 128.18, 129.41, 132.58, 142.02, 147.83 ppm relative to  $Me_4Si$ .
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- (11) Compounds VII, VIII, and IX gave satisfactory IR, NMR, and mass spectral data.
- (12) This product was found to be identical with 1,8-dimethylnaphthalene prepared by allowing 1,8-dithionaphthalene to react with methyl iodide.
- (13) Perylene was identified by direct comparison with an authentic sample.

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## Redox Reactions of Di- $\mu$ -oxo Bridged Binuclear Manganese(IV) and -(III) Complexes

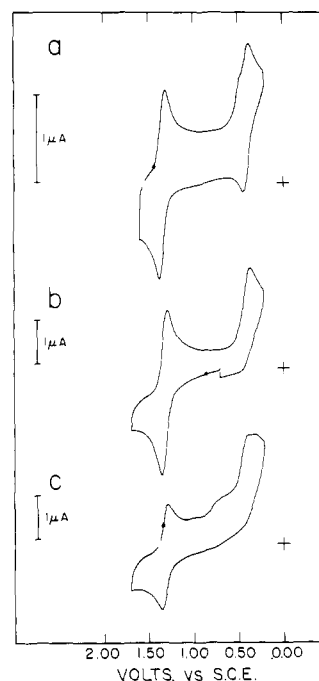
Sir:

Although manganese is essential for the oxygen evolution process in photosynthesis,<sup>1</sup> its chemical role in photosystem-II remains uncertain. Furthermore, the chemical environment around the manganese ion is not known, which precludes the rational design of model compounds.

In the mechanism proposed by Kok<sup>2</sup> and supported by flash photolysis data,<sup>3</sup> four discrete one-electron steps lead to oxygen evolution. Because of a multiplicity of oxidation states for manganese and the associated coordination chemistry, most investigators<sup>4</sup> believe its essential role is as a redox catalyst.

Several model ligand systems have been suggested for manganese in photosystem-II, including one with manganese bound to an  $N_4$  macrocyclic ligand.<sup>5</sup> Various di- $\mu$ -oxo, di- $\mu$ -hydroxo, and  $\mu$ -oxo- $\mu$ -hydroxo binuclear manganese species also have been proposed as photosystem-II models.<sup>6-10</sup> An important test of the merit of model systems is the thermodynamics of their redox reactions.

The di- $\mu$ -oxo bridged binuclear manganese complexes, te-



**Figure 1.** Cyclic voltammograms in 0.1 M TPAP-acetonitrile at a platinum electrode of (a) 0.5 mM  $[Mn_2^{IV,IV}O_2(phen)_4](ClO_4)_4$  (**1**), (b) 0.5 mM  $[Mn_2^{III,IV}O_2(bpy)_4](ClO_4)_3$  (**2**), and (c) 0.5 mM **2** after electrolysis at +1.45 V vs. SCE. Scan rate, 0.1 V/s.

trakis(1,10-phenanthroline)di- $\mu$ -oxo-dimanganese(IV, IV) perchlorate,  $[Mn_2^{IV,IV}O_2(phen)_4](ClO_4)_4$  (**1**), and tetrakis(2,2'-bipyridyl)di- $\mu$ -oxodimanganese(III, IV) perchlorate,  $[Mn_2^{III,IV}O_2(bpy)_4](ClO_4)_3$  (**2**), have been prepared and partially characterized.<sup>11-13</sup> Such complexes have proven to be useful starting materials for the present oxidation-reduction investigations. The crystal structure<sup>12</sup> of **2** includes distinct manganese-oxygen bond lengths for the trivalent and tetravalent manganese ions. The magnetic susceptibilities of **1**<sup>13</sup> and **2**<sup>12</sup> are less than expected for the spin-only condition and indicate antiferromagnetic coupling of the manganese ions across the di- $\mu$ -oxo bridge. The electrochemical redox reactions and solution magnetic susceptibilities of **1** and **2** are the subject of the present communication.

The cyclic voltammogram of **1** (Figure 1a) exhibits two electrochemically reversible redox reactions. Controlled potential coulometry establishes that each wave is a one-electron process; these reactions are summarized in Scheme I. Electrochemical reduction of  $[Mn_2^{III,IV}O_2(phen)_4]^{3+}$  (**3**)<sup>14</sup> to  $[Mn_2^{III,III}O_2(phen)_4]^{2+}$  is followed by a coupled chemical reaction. Electrolysis of **1** (a red solution) at +1.00 V vs. SCE yields a green solution that appears identical with a solution of **3**.

The cyclic voltammogram for **2** (Figure 1b) includes a reversible anodic couple; the redox reactions are summarized in Scheme I and are supported by controlled potential coulometric measurements. The coupled chemical reaction that occurs after reduction of **2** is much faster than in the corresponding reaction after the second reduction of **1**. Comparison of anodic and cathodic peak currents confirms that a coupled chemical reaction also follows the oxidation of **2**. The pseudo-first-order rate constant, measured by the method of Nicholson and Shain,<sup>15,16</sup> is 0.02  $s^{-1}$ . Anodic electrolysis of **2** (a green solution) at +1.45 V causes some decomposition, indicated by the cyclic voltammogram of the product solution (Figure 1c), and yields a reddish brown solution.

The solution-phase magnetic susceptibilities of **2** and of **3**<sup>14</sup> have been determined by the NMR method<sup>17,18</sup> at ambient temperature; for **2**,  $\mu_{eff} = 2.56 \pm 0.11 \mu_B$  (uncorrected) com-