chloroform to yield, after hydrolysis, tricyclic heteroaromatics **8a** (72%, mp 285.5 °C) and **8b** (44%, mp 280 °C), respectively. These preliminary data indicate the potential of these new azadienes for direct synthesis of highly functionalized aromatic nitrogen heterocycles.

The utility of compounds **3a** and **3b** for the synthesis of nonaromatic heterocycles is demonstrated in the examples shown in Scheme III. Diene **3a** and maleic anhydride form a 1:1 adduct after 1 h in chloroform at room temperature. Addition of methanol to the crude adduct resulted in the regeneration of the lactam function by monodesilylation. The crystalline piperidone **9** is obtained in 82% yield; mp 249.5 °C; ν_{max} (KBr) 3320, 1830, 1780, 1765, 1675 cm^{-1}. The configuration of **9** follows from a detailed analysis[13] of the NMR spectrum at 200 MHz and decoupling experiments.

The reaction of **3a** with methyl acrylate further illustrates the potential for direct synthesis of functionalized piperidines. The adduct, upon hydrolysis with aqueous hydrogen fluoride,[14] gave a 65% yield of **10**, mp, 93.6 °C. The regiochemical assignment for **10** was confirmed by the presence of a doublet at δ 7.29 corresponding to one olefinic proton couplet (J = 4.7 Mz) with the proton of the NH group.

We believe that these readily prepared[15] reactive azadienes should find a place on the chemist's panoply. Further applications of the use of this methodology for natural product synthesis are currently under way.

Acknowledgment. This research was supported by S.P.P.S. Grant 79/84-13. S.-P. gratefully acknowledges an I.R.S.I.A. graduate fellowship. We thank Professor D. Ginsburg for reading and discussing the manuscript.

Registry No. 1a, 80658-26-0; **2**, 21684-59-3; **3a**, 80658-27-1; **3b**, 80658-28-2; **4a**, 21163-79-1; **4b**, 625-77-4; **5a**, 80658-29-3; **5b**, 29341-16-0; **6**, 66171-50-4; **7**, 80662-18-6; **8a**, 80658-30-6; **8b**, 80658-31-7; **9**, 80658-32-8; **10**, 80658-33-9; ethyl propiolate, 623-47-2; dimethyl acetylene dicarboxylate, 762-42-5; methyl propiolate, 922-67-8; *p*-benzoquinone, 106-51-4; 1,4-napthoquinone, 130-15-4; maleic anhydride, 108-31-6; methyl acrylate, 96-33-3.

(12) Meyer, H. *Monatsh. Chem.* **1902**, *22*, 440.

(13) NMR (Me_2SO-d_6) δ 0.025 and 0.04 (2s, 6 H), 0.76 (s, 9 H), 2.42–2.72 (m, 2 H), 3.56 (dd, 1 H), 4.06–4.22 (m, 1 H), 5.22 (dd, 1 H), 8.94 (d, 1 H).

(14) Newton, R. F.; Reynolds, D. P.; Finch, M. A. W.; Kelly D. R.; Roberts, S. W. *Tetrahedron Lett.* **1979**, 3981.

(15) Azadienes of type **3** can also be conveniently prepared from imidates by acylation followed by enol silylation.

New Methods for Alkaloid Synthesis: α-Acylamino Radical Cyclizations

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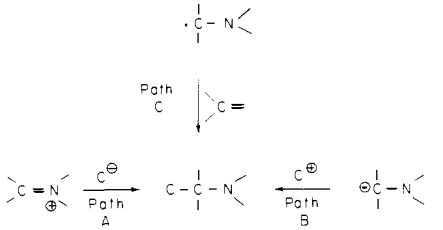
Received November 2, 1981

Construction of carbon–carbon bonds adjacent to nitrogen plays a central role in alkaloid chemistry (Scheme I). Both biosynthetic and laboratory pathways to these natural products rely heavily on variants of the Mannich reaction (path A) for construction of these bonds.[1] Recently, methods which couple α-amino-carbanion equivalents with electrophiles have been developed to accomplish the same task (path B).[2] The use of α-amino and α-acylamino radicals for assembling these bonds, however, has been largely ignored (path C).[3] We report here a new approach

Scheme I



Scheme II

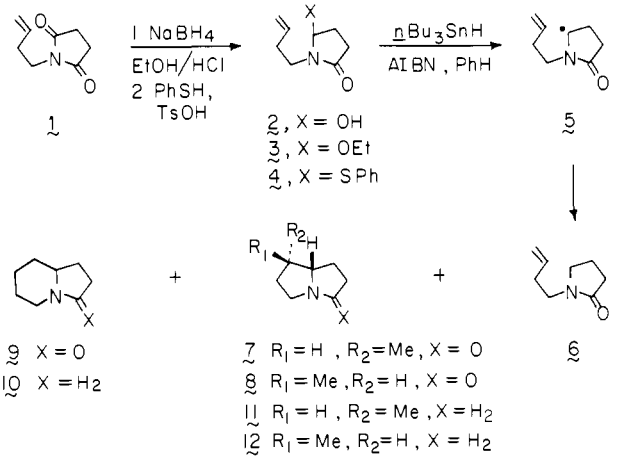


Table I. Treatment of α-Thiophenoxylactams with Tri-*n*-butyltin Hydride[a]

entry	thiophenoxylactam	products (% yield; ratio)[b]
1	13a	14a (12), 17 + 18 (70; 3.7:1)[c,e]
2	13b	14b (13), 15 + 16 + 19 (69; 7:61:33)[d]
3	13c	14c (25), 15 + 16 + 19 (56; 12:81:7)[d]

[a] A mixture of *n*-Bu_3SnH (1.1–1.5 mmol) and AIBN (0.05 mmol) in 10 mL of benzene was added dropwise to 13a–c (1.0 mmol) in 12 mL of benzene at reflux over a 2–4 h period followed by heating for an additional 2–4 h. [b] Reduction products 14a–c were separated from cyclization products by column chromatography. The ratios of cyclization products are based on VPC and 300-MHz ^{1}H–NMR data collected on purified mixtures of cyclization products. [c] A pure sample of 17 was obtained by preparative VPC. [d] A pure sample of 19 was obtained by VPC and by independent synthesis. Lactams 15 and 16 were analyzed as a pure mixture of stereoisomers. The stereochemical assignments for 15 and 16 are tentative and based in part on analogy with results obtained in the cyclizations of 4 and 24. Similarities between ^{1}H NMR spectra of 15 and 16 and those of 8 and 7, respectively, support this assignment. [e] The stereochemistry of the major and minor indolizidinones was not determined. The ratio may be the reverse of that shown here.

to the synthesis of indolizidines and pyrrolizidines, important substructures found in many alkaloids, via α-acylamino radical cyclizations.

We began our studies by developing a site-specific method for generating α-acylamino radicals as outlined in Scheme II.[4] Thus

(1) Dalton, D. R. "The Alkaloids"; Marcel Dekker: New York, 1979.

(2) Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 239 and references cited therein.

(3) For a relevant synthesis of (±)-coniine see: Urry, W. H.; Juveland, O. O.; Stacey, F. W. *J. Am. Chem. Soc.* **1952**, *74*, 6155. Urry, W. H.; Juveland, O. O. *Ibid.* **1958**, *80*, 3322. For other brief accounts see: Julia, M.; Maumy, M. *Bull. Soc. Chim. Fr.* **1968**, 1603. Julia, M. *Pure Appl. Chem.* **1967**, *15*, 167.

(4) For other methods of generating α-acylamino radicals see; Friedman, L.; Shechter, H. *Tetrahedron Lett.* **1961**, 238. Nikishin, G. I.; Mustafaev, R. I. *Dokl. Akad. Nauk SSSR* **1964**, *158*, 1127. Elad, D.; Sinnreich, J. *Tetrahedron* **1968**, *24*, 4509.

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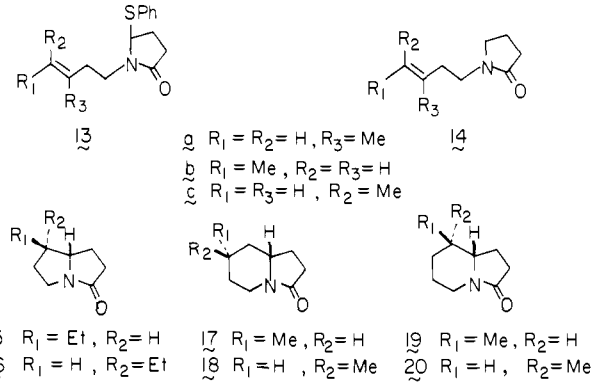
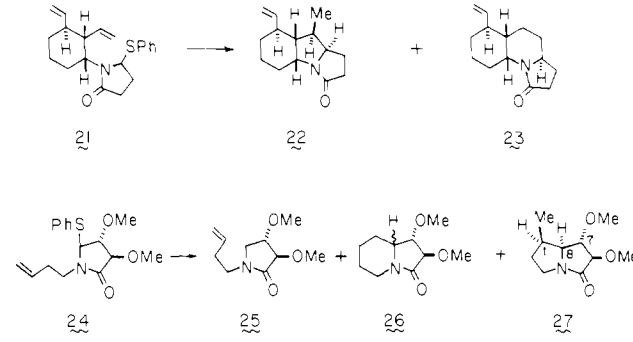
Chart I



imide **1** was reduced with sodium borohydride[5] to give a mixture of hydroxy and alkoxylactams **2** and **3**. The crude mixture of lactams was treated with an excess of thiophenol containing 0.04 equiv of *p*-toluenesulfonic acid (25 °C, 10 min) to afford thiophenoxylactam **4** in an 88% yield from **1**. Treatment of **4** with tri-*n*-butyltin hydride (1.4 equiv) and AIBN (0.04 equiv) in benzene at reflux gave an 84% yield of lactams **6**, **7**, **8**, and **9** in a 12:40:4:20 ratio, presumably via the intermediacy of α-acylamino radical **5** (see Table I, footnote *a* for conditions).[6-8] The structure of **6** was proven by independent synthesis[9] while the structures of **7** and **9** were proven by conversion to (±)-heliotridane (**11**) and (±)-δ-coniceine (**10**), respectively.[10-12]

Several aspects of the results presented in Scheme II are noteworthy. The combined yield of monomeric products obtained from α-acylamino radical **5** is very high. We attribute this in part to the site-selective method of radical generation employed herein. In addition, radical **5** gives a 2:1 ratio of exo and endo cyclization products, respectively, contrary to the considerably larger exo:endo ratios usually observed in simple hexenyl radical systems.[13] Whether this product distribution reflects the kinetic behavior of **5** or is influenced by the relative thermodynamic stabilities of the radicals derived from exo and endo cyclization remains to be determined.[14] Due to geometric constraints imposed by the sp^2 character at nitrogen, however, it is possible that the rates of endo and exo cyclization are similar. Finally, cyclization of **5** to pyrrolizidinones **7** and **8** proceeds with high stereoselectivity which parallels results obtained in related carbocyclic systems.[15]

Scheme III



In an attempt to delineate the effect of olefin substitution on the regiochemical course of this radical cyclization, thiophenoxylactams **13a–c** were prepared[16] and treated with tri-*n*-butyltin hydride. The results are shown in Table I. Entry 1 shows that internal olefin substitution leads to endo cyclization with modest stereoselectivity. Entry 2 shows that terminal *E*-alkyl substitution gives the same endo:exo cyclization ratio as observed for the parent radical **5**. On the other hand, terminal *Z*-alkyl substitution (entry 3) leads to almost exclusive formation of exo cyclization products. Once again, good stereoselectivity is observed in the exo cyclizations (**13b,c** → **15**, **16**; see Table I, footnote *d*). In addition, high stereoselectivity is observed in the endo cyclization process (**13b,c** → **19**).[17-19] Thus, by controlling olefinic substitution patterns, it is possible to guide the regiochemical course of α-acylamino radical cyclization toward indolizidinone or pyrrolizidinone formation.

The potential utility of this method in alkaloid synthesis is underscored by the examples presented in Scheme III. Thus, treatment of thiophenoxylactam **21**[20] with *n*-Bu_3SnH gave exo cyclization product **22** (51%)[21] and endo cyclization product **23** (31%), an intermediate in a synthesis of the Dendrobatid alkaloid gephyrotoxin.[22] It is noteworthy that no reduction product was obtained and that both cyclizations proceed with high stereoselectivity at the radical center. We attribute these observations to pronounced conformational preferences expected for the intermediate radical.[22,23]

Finally, cyclization of lactam **24**, prepared from tartaric acid, gives a separable mixture of lactams **25** (24%), **26** (28%),[24] and **27** (31%).[25] Pyrrolizidinone **27** contains C-1, C-7, and C-8

(5) Hubert, J. D.; Wijnberg, J. B. P. A.; Speckamp, W. N. *Tetrahedron* **1975**, *31*, 1437.

(6) After the completion of this work, the method of α-acylamino radical generation independently developed herein was reported by others: Bachi, M. D.; Hoornaert, C. *Tetrahedron Lett.* **1981**, 2693.

(7) Lactam **6** (12%) was separated from lactams **7–9** (74%) by column chromatography. Lactams **7–9** were obtained as a preparatively inseparable mixture and were analyzed by a combination of 300-MHz ^1H NMR spectrometry and analytical VPC. An independent synthesis of **9** via an alternate route aided our analysis.

(8) The possibility that indolizidinone **9** arises from an ionic cyclization followed by *n*-Bu_3SnH reduction of an intermediate sulfide is unlikely. Thiol **4** is stable to (i) PhH (reflux, 1.0 equiv *n*-Bu_4Sn, 7 h) and (ii) $NaBH_3CN$ (pH 4, MeOH, 4 h) and is reduced to **6** only slowly by TFA–Et_3SiH ($t_{1/2}$ = 35 min). Thus ionization of **4** under the conditions employed here is unlikely.

(9) Treatment of **3** with either TFA–Et_3SiH or $NaBH_3CN$ (pH 4) gave **6**.

(10) A mixture of **7**, **8**, and **9** was reduced with either BH_3·THF or $LiAlH_4$ to afford mixtures of **10** and **11**. Pure samples of **10**, **10**·picrate, and **11**·picrate were isolated from these product mixtures. An authentic sample of (±)-**10**, prepared via an alternate route for the purpose of comparison, was identical with the **10** prepared here [90-MHz ^1H NMR, IR mp (picrate), and 300-MHz ^1H NMR (picrate)].[11] An authentic sample of (±)-**11**·picrate, prepared by a known procedure (Schweizer, E. E.; Light, K. K. *J. Org. Chem.* **1966**, *31*, 870) was identical with the **11**·picrate prepared here (300-MHz ^1H NMR, mp, IR). Although (±)-pseudoheliotridane (**12**) was not isolated, the presence of small amounts of **8** in the cyclization mixture was apparent from NMR analyses of mixtures **7–9** and partially purified samples of **8** obtained by preparative gas chromatography.

(11) For other syntheses of (±)-**10** see: Weinreb, S. M.; Khatri, N. A.; Shringarpure, J. *J. Am. Chem. Soc.* **1979**, *101*, 5073 and references cited therein.

(12) For other syntheses of **10** and **11** see: Miyano, S.; Fujii, S.; Yamashita, O.; Toraishi, N.; Sumoto, K.; Satoh, F.; Masuda, T. *J. Org. Chem.* **1981**, *46*, 1737 and references cited therein.

(13) For a summary of regiochemical guidelines for radical cyclizations see: Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482. For a relevant review see: Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; deMayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, p 161; For a recent example of a 5-hexen-1-yl type radical that undergoes an unusually large amount of endo cyclization see: Wilt, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 5251.

(14) Julia, M. *Pure Appl. Chem.* **1974**, *40*, 553.

(15) Agosta, W. C.; Wolff, S. *J. Chem. Res.* (*C*) **1981**, 78.

(16) Lactams **13a–c** were prepared from the appropriate imides by using the reaction sequence outlined in Scheme II in 83%, 88%, and 89% overall yields, respectively.

(17) The olefin **13c** used in these experiments contained a small amount of olefin **13b**. Thus the exo–endo selectivity in the cyclization of **13c** may be greater than the 93:7 ratio reported in Table I.

(18) For the effect of substituents on the regiochemical course of simple hexenyl radicals see: Julia, M.; Descoins, C.; Baillarge, M.; Jacquet, B.; Uguen, D.; Groeger, F. A. *Tetrahedron* **1975**, *31*, 1737. Beckwith, A. L. J.; Phillipou, G.; Blair, I. A. *Tetrahedron Lett.* **1974**, 2251.

(19) Stereoisomeric indolizidinone **20** was not detected. Treatment of 1-(pent-4-en-1-yl)-5-thiophenoxy-2-pyrrolidinone with tri-*n*-butyltin hydride provided 1-(pent-4-en-1-yl)-2-pyrrolidinone (8%) and a mixture of 1-azabicyclo[5.3.0]decan-10-one (21%), **19** (24%; $J_{H_4H_5}$ = 9 Hz), and authentic **20** (30%; $J_{H_4H_5}$ = 3.7 Hz), separable by VPC.

(20) Prepared from the appropriate imide by using the reaction sequence outlined in Scheme II.

(21) The stereochemical assignment for **22** is tentative and based on analogy with results obtained in the cyclizations of **4** and **24**.

(22) Hart, D. J. *J. Org. Chem.* **1981**, *46*, 3576.

(23) Hart, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 397. Hart, D. J. *J. Org. Chem.* **1981**, *46*, 367.

(24) Obtained as a 5:4 mixture diastereoisomers. The structures of **26** were proven by independent synthesis.

substitution, which is similar to that of the more complex pyrrolizidine alkaloids.[26] Thus the methods described herein may provide an enantioselective entry to this important class of alkaloids. Studies directed toward this end as well as other synthetic ventures using radical carbon–carbon bond forming reactions will be reported in due course.

Acknowledgment. We thank Dr. C. E. Cottrell and Richard Weisenberger for their assistance in obtaining 300-MHz ^{1}H NMR and mass spectra, respectively, at The Ohio State University Chemical Instrument Center. Financial support from donors of The Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. 1, 58805-10-0; (±)-**2**, 80664-36-4; (±)-**3**, 80664-37-5; (±)-**4**, 80664-38-6; **5**, 80664-39-7; **6**, 52132-72-6; (±)-**7**, 80664-40-0; (±)-**8**, 80664-41-1; (±)-**9**, 71779-55-0; (±)-**10**, 62279-67-8; (±)-**10** picrate, 62318-95-0; (±)-**11**, 17463-81-9; (±)-**11** picrate, 17463-80-8; (±)-**13a**, 80664-42-2; (±)-**13b**, 80664-43-3; (±)-**13c**, 80664-44-4; **14a**, 80664-45-5; **14b**, 80664-46-6; **14c**, 80664-47-7; (±)-**15**, 80664-48-8; (±)-**16**, 80664-49-9; (±)-**17**, 80664-50-2; (±)-**18**, 80664-51-3; (±)-**19**, 80664-52-4; **21**, 80664-53-5; (±)-**22**, 80664-54-6; (±)-**23**, 78308-08-4; **24**, 80664-55-7; (±)-**25**, 80664-56-8; **26**, 80664-57-9; (±)-**27**, 80664-58-0; (±)-**20**, 80664-59-1; (±)-1-(pent-4-en-1-yl)-5-thiophenoxy-2-pyrrolidinone, 80664-60-4; 1-(pent-4-en-1-yl)-2-pyrrolidinone, 80664-61-5.

Supplementary Material Available: Spectral data (NMR, IR, and mass) on compounds **4**, **6–11**, and **13–27** and schemes for independent syntheses of **9**, **10**, and **26** (10 pages). Ordering information is given on any current masthead page.

(25) The stereochemical assignments for **27** are based on NOE experiments performed at 300 MHz. For example, irradiation of the C-1 methyl group shows a 15% NOE at H-7.

(26) For an overview see: Robins, D. J. In "Advances in Heterocyclic Chemistry"; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1979; Vol. 24, p 247.

Design and Synthesis of an Amphoteric Four-Stage Redox Hydrocarbon Bearing Phenalenyl Moieties. 1,2-Bis(phenalen-1-ylidene)ethane[1]

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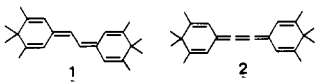
Received October 14, 1981

Recently a rich variety of multi-stage redox-type organic molecules has been synthesized, and their chemical and physical properties, redox potentials in particular, have been correlated with their structural characteristics.[2] One of the unique features of conjugated hydrocarbons is in the amphoteric redox property in which both multi-stage anodic oxidation and cathodic reduction steps are observed. Only a few examples of such redox systems known to date are polycyclic arenes[3] such as anthracene and perylene and cross-conjugated polyenes such as bis(3,4,4,5-tetramethyl-2,5-cyclohexadien-1-ylidene)ethane (**1**) and ethene (**2**).[4,5] However, there are almost no efforts to synthesize mol-



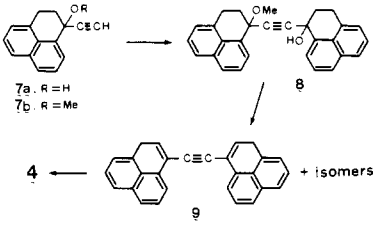
1 2

(1) The Chemistry of Phenalenium Systems. 32. For part 31; see: Hara, O.; Yamamoto,K.; Murata, I. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2036. A partial account of this work was presented at the Fourth International Symposium on the Chemistry of Novel Aromatic Compounds, Jerusalem, Israel, September 4, 1981.

(2) (a) Deuchert, K.; Hünig, S. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 875. Hünig, S.; Berneth, H. *Top. Curr. Chem.* **1980**, *92*, 1. (b) Perlstein, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 519.

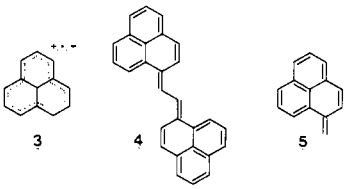
(3) Hammerich, O.; Parker, V. D. *J. Am. Chem. Soc.* **1974**, *96*, 4289. Jensen, B. S.; Parker, V. D. *J. Chem. Soc., Chem. Commun.* **1974**, 367. Jensen, B. S.; Parker, V. D. *J. Am. Chem. Soc.* **1975**, *97*, 5211.

Scheme I



ecules designed so as to reduce both oxidation potential (E^{ox}) and reduction potential (E^{red}). To date significant advances have been made on the correlation of E^{ox} and E^{red} with ionization potential and electron affinity of hydrocarbons.[6,7] Furthermore, the numerical sum of E^{ox} and E^{red}, i.e., $E^{sum} = E^{ox} + (-E^{red})$, is independent of the reference potential. Thus, E^{sum} values might be used as one of the convenient *experimental measures* estimating the extent of the amphoteric redox property of a hydrocarbon being considered. In this communication we report the design, synthesis, and some properties of a new class of compound that exhibits the *smallest E^{sum} value*.

The odd alternant hydrocarbon phenalenyl appears to be a potential candidate to build up this class of redox systems[8] because it is known to exist in three electronically stable oxidation states:[9a,b] the cation (3^+),[9c] the radical ($3\cdot$),[9d] and the anion (3^-).[9c] However,



the serious disadvantage of the open-shell hydrocarbon $3\cdot$ is the lack of its stability, since it is known to dimerize in solution even at low temperature.[9a,10] In order to construct the closed-shell amphoteric four-stage redox hydrocarbons based on the phenalenyl system, two phenalenyl rings as the terminal groups are connected with two sp^2 carbons producing 1,2-bis(phenalen-1-ylidene)ethane (**4**). Although **4** consists of the phenafulvene moiety **5**, which has been shown to be an unstable transient species,[11] fortunately **4** proved to be a stable and isolable compound by our earlier studies.[11,12] However, extremely low yield of its formation prevented us from investigating the detailed properties of **4**. Thus, we synthesized **4** with an unequivocal procedure (Scheme I).[13]

(4) (a) Hünig, S.; Horner, M.; Schilling, P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 556. (b) Hünig, S.; Schilling, P. *Liebigs Ann. Chem.* **1976**, 1103. (c) Hagenbruch, B.; Hesse, K.; Hünig, S.; Klug, G. *Ibid.* **1981**, 256.

(5) (a) **1** is one of the first amphoteric four-stage redox hydrocarbons. (b) The first example of the amphoteric six-stage redox system, 9,9′-bianthryl-10,10′-dicarbonitrile, has recently been reported: Heinze, J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 202.

(6) Dewar, M. J. S.; Hashmall, J. A.; Trinajstić, N. *J. Am. Chem. Soc.* **1970**, *92*, 5555 and references cited therein. Streitwieser, A. Jr. "Molecular Orbital Theory for Organic Chemists"; Wiley: New York, **1961**; Chapter 7. Peover, M. E. "Electroanalytical Chemistry"; Bard, A. J., Ed.; Marcel Dekker: New York, **1967**; Vol. 2, p 40.

(7) Parker, V. D. *J. Am. Chem. Soc.* **1974**, *96*, 5656. **1976**, *98*, 98.

(8) (a) Haddon, R. C. *Nature (London)* **1975**, *256*, 394. (b) *Aust. J. Chem.* **1975**, *28*, 2343.

(9) (a) Reid, D. H. *Quart. Rev., Chem. Soc.* **1965**, *19*, 274. (b) Murata, I. "Topics in Non-Benzenoid Aromatic Chemistry"; Nozoe, T., Breslow, R., Hafner, K., Ito, S., Murata, I., Eds.; Hirokawa: Tokyo, **1976**; Vol. 1, p 159. (c) Pettit, R. *Chem. Ind. (London)* **1956**, 1306. *J. Am. Chem. Soc.* **1960**, *82*, 1972. (d) Reid, D. H. *Chem. Ind. (London)* **1956**, 1504. (e) Boekelheide, V.; Larrabee, C. E. *J. Am. Chem. Soc.* **1950**, *72*, 1245.

(10) (a) Reid, D. H. *Tetrahedron* **1958**, *3*, 339. (b) Gerson, F. *Helv. Chim. Acta* **1966**, *49*, 1463. Gerson, F.; Heilbronner, E.; Reddock, H. A.; Paskovich, D. H.; Das, N. C. *Ibid.* **1967**, *50*, 813. See also: (c) Haddon, R. C.; Wudl, F.; Kaplan, M.; Marshall, J. H.; Cais, R. E.; Bramwell, F. B. *J. Am. Chem. Soc.* **1978**, *100*, 7629. Haddon, R. C.; Wudl, F.; Kaplan, M. L.; Marshall, J. H.; Bramwell, F. B. *J. Chem. Soc., Chem. Commun.* **1978**, 429.

(11) (a) Murata, I.; Nakasuji, K.; Kume, H. *Tetrahedron Lett.* **1973**, 3401. (b) *Ibid.* **1973**, 3405.

(12) (a) Nakasuji, K.; Murata, I. *Tetrahedron Lett.* **1976**, 2155. (b) Murata, I.; Nakasuji, K. *Isr. J. Chem.* **1980**, *20*, 244.

0002-7863/82/1504-1432$01.25/0