pounds. Lepidopterene (7) yields were determined from ^{1}H NMR spectra of the reaction mixture (high-conversion runs).

Control Experiments. Treatment of 9-anthracenemethanol with 2 equiv or more of 9-methylanthracene and heating at reflux in 0.1 M $HClO_4$ (70/30 (v/v) CH_3CN/H_2O) resulted in quantitative formation of 7 (70% isolated).[22] If only a trace of acid was present or the solvent was changed to CH_3CN/HOAc (70/30 v/v), then no dimer was formed. The acetate **5a** when heated under the same conditions as entry 3 in Table II underwent no reaction. If **5a** and a 10-fold molar excess of 1 were heated together under these same conditions (except without peroxydisulfate present), then a trace of 7 was detected. The diacetate **13a**, when heated under the conditions discussed above, resulted in only formation of **4a** and **5a**. No dimer was detected. If a 10-fold excess of 1 was present, and the conditions of entry 4, Table VI were employed, then the dimer 7 was formed along with **5a** and **4a**. These results appear consistent with the dimer arising from the reaction of 9-anthracenylmethyl cation with 1. See Scheme II.

Registry No. 1, 779-02-2; 2, 17104-31-3; 3, 4159-04-0; **4a**, 31688-72-9; **5a**, 16430-32-3; **5c**, 72169-49-4; 7, 55614-27-2; $(NH_4)_2S_2O_8$, 7727-54-0; $Cu(OAc)_2$, 142-71-2; $Cu(ClO_4)_2$, 13770-18-8.

Notes

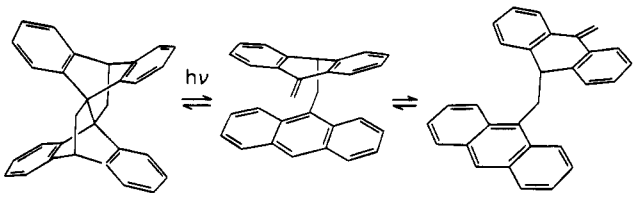
A New Synthesis of Lepidopterenes[1]

Larrie A. Deardurff[2] and Donald M. Camaioni*

Battelle, Pacific Northwest Laboratories, Richland, Washington 99352

Received March 4, 1986

The recent interest in lepidopterene (1) and its derivatives for their ability to undergo adiabatic photoinduced cycloreversion reactions[3,4] has prompted us to report a new synthesis of these compounds. This new method should facilitate the preparation of a wider variety of substituted derivatives.

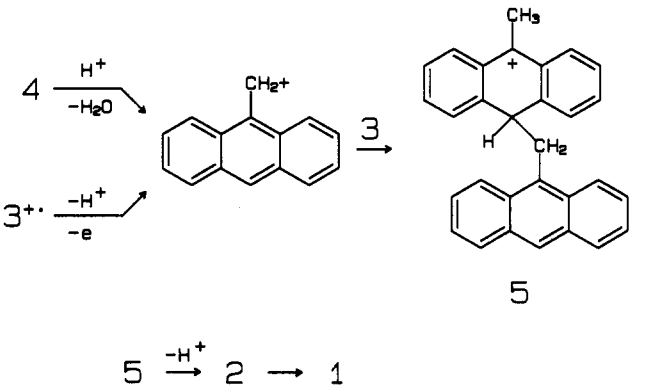


1 2

During the study[5] of the oxidation of 9-methylanthracene (3) with copper(II) peroxydisulfate, a "dimeric" compound identified as lepidopterene[6-8] (1) was formed. Depending on the conditions employed, 1 could be either a minor or the major product of oxidation. Thus, treatment of 3 with 0.9 mol equiv of peroxydisulfate in 0.03 M Cu(II) and 0.02 M sodium acetate in acetonitrile/acetic acid (7/3, v/v) at 90 °C gave an 80% yield of 1. The same reaction performed in acetonitrile/water (7/3, v/v) without added sodium acetate produced 1 in 30% yield.

Since we are interested in the fate of the intermediate radical cations formed in these oxidations,[9] studies were undertaken to determine the mechanism for the formation of 1. We suspected that subsequent reactions of $3^{\bullet+}$ could lead to the 9-anthracenylmethyl cation. Thus, control experiments were designed to test whether the cation would react with 3 to produce 1. It was found by ^{1}H NMR spectroscopy that 1 was formed in quantitative yield (70% isolated) when 9-anthracenemethanol (4) and 2 equiv of 3 were heated in 0.1 M perchloric acid in acetonitrile/water (7/3, v/v). Thus, we suggest the mechanism shown in Scheme I. The anthracenylmethyl cation forms and adds to 3, giving 5 which due to steric factors preferentially loses a proton from the methyl group to form the *exo*-methylene compound 2. Intramolecular [2 + 4] cycloaddition of compound 2 yields compound 1. Becker et al.[6] have shown that 1 is favored in its equilibrium with 2 (K_{eq} = 630).

Scheme I



Previous synthetic approaches[3,6,7] have mainly yielded symmetrical lepidopterenes. Our observations suggest that solvolysis of substituted anthracenemethanols in the presence of substituted 9-methylanthracenes can provide a convenient general approach to unsymmetrical and ring-substituted derivatives. For example, the new derivative 9-methyllepidopterene (6) was produced in ca. 33% yield (by ^{1}H NMR) when 1 equiv of 9-anthracenemethanol and 2 equiv of 9,10-dimethylanthracene (7) were heated at reflux in benzene with a catalytic amount of *p*-toluenesulfonic acid. (Benzene was used as a solvent to enhance the solubility of dimethylanthracene.) Since isolation of 6 from unreacted 7 proved difficult, an excess of 10-methyl-9-anthracenemethanol and 3 were allowed to

(1) This work was supported by the Gas Research Institute, Basis Coal Science Program, Contract No. 5081-260-0536.

(2) University of Washington—Northwest College and University Association for Science (NORCUS) Postdoctoral Research Associate.

(3) Becker, H. D. *Pure Appl. Chem.* **1982**, *54*, 1589–1604. Becker, H. D.; Andersson, K. *J. Org. Chem.* **1983**, *48*, 4542–4549. Becker, H. D.; Hall, S. R.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1984**, *37*, 1313–1327.

(4) Ferguson, J.; Robbins, R. J.; Wilson, G. J. *J. Phys. Chem.* **1984**, *88*, 5193–5197.

(5) Deardurff, L. A.; Alnajjar, M. S.; Camaioni, D. M. *J. Org. Chem.*, accompanying paper in this issue.

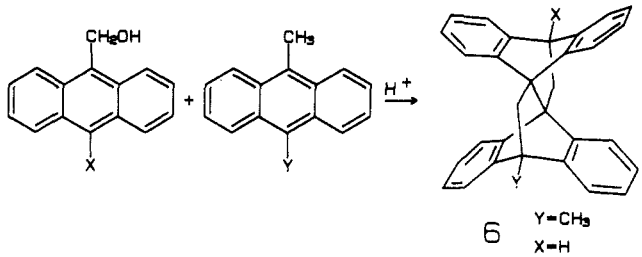
(6) Becker, H. D.; Sandros, K.; Arvidsson A. *J. Org. Chem.* **1979**, *44*, 1336–1338. Becker, H. D.; Andersson, K.; Sandros, K. *J. Org. Chem.* **1980**, *45*, 4551–4555.

(7) Felix, G.; Lapouyade, R.; Castellan, A.; Bouas-Laurent, H.; Gaultier, J.; Hauw, C. *Tetrahedron Lett.* **1975**, 409.

(8) Henderson, W. W. Ph.D. Thesis, University of Minnesota, 1962.

(9) Camaioni, D. M.; Franz, J. A. *J. Org. Chem.* **1984**, *49*, 1607–1613. Camaioni, D. M.; Alnajjar, M. S. *J. Org. Chem.* **1985**, *50*, 4456–4461.

0022-3263/86/1951-3693$01.50/0



react as described above. This resulted in the isolation of **6** in 28% yield. Thus, the synthesis of a series of unsymmetrical lepidopterenes appears to be possible.

Experimental Section

Lepidopterene (1). Method I. 9-Methylanthracene (0.10 g, 0.52 mmol), ammonium peroxydisulfate (0.10 g, 0.46 mmol), copper(II) acetate (0.03 g, 0.15 mmol), and 5 mL of 0.02 M sodium acetate in acetonitrile/acetic acid (7/3, v/v) were combined and heated at 90 °C for 1 h under argon. A 1-mL aliquot of 0.05 M phenanthrene was added as an internal GC standard. The reaction mixture was poured into 50 mL of water and extracted four times with methylene chloride. The combined extracts (50 mL) were dried over sodium sulfate. GC and NMR indicated an 80% yield of **1** (based on **3** consumed).

Method II. 9-Anthracenemethanol (0.10 g, 0.5 mmol) and 9-methylanthracene (0.19 g, 1.0 mmol) were heated at 90 °C under argon in 0.1 M perchloric acid in acetonitrile/water (7/3, v/v) for 1 h. The reaction mixture was then worked up as above. Gas chromatography showed the absence of 9-anthracenemethanol and the disappearance of 0.52 mmol of **3**. After solvent removal, NMR of the residue indicated only **3** and **1** present. Addition of benzene to the residue and filtering gave 0.13 g (70%) of **1** as a white solid: mp 330–335 °C (lit.[3b] mp 317–323 °C); HRMS, *m/e* calcd for $C_{30}H_{22}$ (M^+) 382.17215, found 382.1731; ^1H NMR (300 MHz, $CDCl_3$) δ 2.91 (d, J = 2.7 Hz, 4 H), 4.65 (t, J = 2.7 Hz, 2 H), 6.74 (d, J = 7.5 Hz, 4 H), 6.82 (td, J = 7.5, 1.5 Hz, 4 H), 7.01 (td, J = 7.5, 1.5 Hz, 4 H), 7.35 (d, J = 7.5 Hz, 4 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 143.59, 143.59, 125.48, 125.22, 122.64, 122.35, 54.01, 45.58, 28.93; IR (KBr) 3080, 3020, 2990, 2980, 2950, 1460, 990, 760, 740, 635, 585 cm^{-1}; UV–vis [cyclohexane; λ_{max}, nm ($\epsilon \times 10^{-3}$)] 272 (2), 264 (1.9), 257 (1.7), 253 (1.7).

10-Methyl-9-anthracenemethanol. 10-Methyl-9-anthraldehyde (0.13 g, 1.4 mmol) in 50 mL of anhydrous ether was added in portions to a stirred suspension of 0.57 g (1.5 mmol) of lithium aluminum hydride in 15 mL of ether. After 2 h, the reaction was quenched by the slow addition of water. The reaction mixture was poured into 50 mL of dilute H_2SO_4 and extracted with methylene chloride. The organic phase was washed with aqueous sodium bicarbonate and water and dried over sodium sulfate. Solvent was removed under reduced pressure and the residue recrystallized from benzene/hexane to give 0.24 g (77%) of yellow crystals, mp 224–228 °C (lit.[10] mp 222.5–223 °C).

9-Methyllepidopterene (6). Method 1. 9,10-Dimethylanthracene (0.052 g, 0.025 mmol), 9-anthracenemethanol (0.052 g, 0.25 mmol), and a catalytic (1-mg) amount of p-toluenesulfonic acid were refluxed in 10 mL of deoxygenated benzene for 45 min. The reaction mixture was poured into 50 mL of water, and the layers were separated. The aqueous phase was extracted three times with 15-mL volumes of CH_2Cl_2. The organic phases were combined, dried over Na_2SO_4, and then evaporated to give a solid residue. Attempts to isolate **6** in pure form from this material were unsuccessful. However, liquid chromatography performed by adsorbing the material to silica gel (Fisher grade 150, 60–100 mesh) and eluting with hexane through a 1 × 14 cm column of silica gel provided a fraction that consisted mainly of **6** and unreacted **7** (by ^1H NMR). Integration of the methyl NMR peaks for **6** and **7** showed the ratio of **6**/**7** to be ca. 1/2.

Method 2. 10-Methyl-9-anthracenemethanol (0.067 g, 0.3 mmol), 9-methylanthracene (0.048 g, 0.25 mmol), and a catalytic amount (ca. 2–3 mg) of p-toluenesulfonic acid were combined with 5 mL of deoxygenated benzene. The resultant suspension was heated to reflux under argon. After 40 min, an additional 0.02 g (0.09 mmol) of the alcohol and 5 mL of benzene were added. After an additional 2 h at reflux, the solution was allowed to cool. The reaction mixture was filtered and the solvent removed. The yellow residue was taken up in methylene chloride and chromatographed on a short column of silica gel, eluting with 10% CH_2Cl_2/hexane and neat CH_2Cl_2. The hexane eluates were combined, the solvent was removed, and the residue was recrystallized from benzene/hexane (2 days at ca. 0 °C) to give 0.028 g (28%) of **6** as yellow crystals: mp 261–263 °C (uncorrected); ^1H NMR (79.5 MHz, $CDCl_3$) δ 7.4–6.6 (ArH, 16 H), 4.60 (t, J = 2.8 Hz, 1 H), 2.91 (d, J = 2.8 Hz, 2 H), 2.68 (s, 2 H), 2.21 (s, 3 H). Anal. Calcd for $C_{31}H_{24}$: C, 93.9; H, 6.1. Found: C, 93.62; H, 6.02.

Acknowledgment. We thank Dr. David C. Lankin (Varian Associates) for obtaining the high-field ^1H and ^{13}C NMR spectra and Dr. Edward Chess (BNW) for performing the high-resolution mass spectral analyses reported here.

Registry No. **1**, 55614-27-2; **3**, 779-02-2; **3** (alcohol), 1468-95-7; **6**, 103692-67-7; **7**, 781-43-1; 10-methyl-9-anthraldehyde, 7072-00-6; 10-methyl-9-anthracenemethanol, 71339-55-4.

(10) Southern, P. F.; Waters, W. A. *J. Chem. Soc.* **1960**, 4340–4346.

Functionalization of Aromatic Systems: A Highly Chemoselective Synthesis of [(Trimethylsilyl)methyl]nitroarenes

Giuseppe Bartoli,* Marcella Bosco, Renato Dalpozzo, and Paolo E. Todesco

Istituto di Chimica Organica, Viale Risorgimento 4, I-40136 Bologna, Italy

Received March 11, 1986

In spite of the ready availability of aromatic nitro compounds, only few methods to introduce alkyl side chains, carrying useful functional groups, into these compounds have been developed. Makosza et al.[1] succeeded in realizing a "vicarious" substitution of hydrogen with α-cyano-, sulfonyl-, and carbalkoxy-substituted alkyl groups, by using weakly basic carbanions bearing a good leaving group on the anionic carbon. Although the occasional competitive displacement of substituents bound to one of the reactive positions of the aromatic ring may occur, this method showed interesting applications in organic synthesis.[2]

The discovery of the irreversible conjugate addition of highly basic carbanions such as Grignard reagents[3] provided a general and efficient tool to introduce regio-[4] and chemoselectively[5] alkyl groups into an aromatic ring. The Grignard reagent addition method shows a greater versatility than Makosza's vicarious substitution, since, in ethereal solution, the nitronate adducts are stable enough to be treated in situ with a large variety of selective reducing,[6]

(1) (a) Makosza, M.; Golinski, J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 451. (b) Makosza, M. In *Current Trends in Organic Synthesis*; Nozaki, H., Ed.; Pergamon: Oxford, 1983; p 401. (c) Makosza, M.; Winiarski, J. *J. Org. Chem.* **1984**, *49*, 1494.

(2) (a) Stahly, G. P.; Stahly, B. C.; Lilje, K. C. *J. Org. Chem.* **1984**, *49*, 578. (b) Makosza, M.; Golinsky, J.; Baran, J. *J. Org. Chem.* **1984**, *49*, 1488.

(3) (a) Bartoli, G.; Rosini, G. *Synthesis* **1976**, 270. (b) Bartoli, G.; Leardini, R.; Medici, A.; Rosini, G. *J. Chem. Soc., Perkin Trans. 1*, **1978**, 692.

(4) Bartoli, G. *Acc. Chem. Res.* **1984**, *17*, 109.

(5) Bartoli, G.; Bosco, M.; Dalpozzo, R.; *Tetrahedron Lett.* **1985**, *26*, 115.

0022-3263/86/1951-3694$01.50/0