Credance for this explanation is gained by comparison of the vicinal coupling constants of **2** with those of the *p*-NO$_2$- and *p*-CH$_3$O-phenyl derivatives of **2** (*p*-NO$_2$-**2** and *p*-CH$_3$O-**2**, respectively) given in Table II. Granted that remote (para) substitution does not markedly alter the adjacent methylene groups electronegatively which in turn could alter the magnitudes of the observed vicinal coupling constants,[10] qualitative analysis indicates that as conformer population **2b** is diminished relative to **2a**, J_{12} should increase and J_{13} should decrease; conversely, as conformer population **2b** is increased relative to **2a**, J_{12} should decrease and J_{13} should increase. The electron-donating methoxy group causes J_{13} to increase while the electron-withdrawing nitro group causes J_{13} to decrease relative to the unsubstituted molecule **2**. Although only small conformer population changes are observed, the coupling constant and conformer population trends are what should be expected for an attractive electronic interaction.

Finally, it should be noted that the angle between two aryl rings on contiguous carbons of an ethane-like fragment (assuming idealized carbon hybridization) is 39° and the centers of the two rings are separated by ca. 3.5 Å (in an eclipsed conformation). Neither the inter-ring angle nor the inter-ring separation is optimal for charge-transfer interaction;[13] for maximum charge transfer the rings should be coplanar.

Experimental Section

All melting points are uncorrected. Micro analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. All NMR spectra were determined on 5% (wt/vol) D$_2$O solutions containing DSS as internal standard. Theoretical spectra were calculated with the LAOCN 3 program.[14]

(±)-Amphetamine was prepared by a previously reported procedure[15] as was dideuterioamphetamine (**3**-*d*$_2$).[3]

1-(2,4-Dinitrophenyl)nicotinamide chloride was prepared by the method of Lettre[16] and was used without further purification.

p-Nitroamphetamine was prepared by the method of Patrick[17] and exhibited bp 115–117 °C (Kugelrohr) at 1.0 mm (lit.[17] bp 115–116 °C at 1.0 mm). The ¹H NMR spectrum is consistent with the structure.

p-Methoxyamphetamine was prepared by lithium aluminum hydride reduction[18,19] of 1-(*p*-methoxyphenyl)-2-nitroprop-1-ene[19] which exhibited bp 142–146 °C at 1 mm and mp 42–44 °C (lit.[20] bp 176.2–178.8 °C at 8 mm and mp 43–44 °C). The product exhibited bp 87–89 °C at 0.6 mm (lit.[18] bp 141 °C at 14 mm; lit.[19] bp 129–132 °C at 8 mm). The ¹H NMR spectrum is consistent with the structure.

N-(1-Phenyl-2-propyl)nicotinamide chloride was prepared by adding 5.4 g (0.04 mol) of amphetamine to a solution of 13.0 g (0.04 mol) of 1-(2,4-dinitrophenyl)nicotinamide chloride in 65 mL of methyl alcohol cooled to 0 °C. Upon addition of the amine the solution turns red-black. The reaction mixture was stirred for 18 h at room temperature during which time the color of the mixture changed to yellow-orange. The solvent was removed on a rotary evaporator and the solid residue was extracted with 100

mL of water; the remaining solid was removed by filtration and was discarded. The aqueous filtrate was decolorized with activated carbon and filtered, and the solvent was removed on a rotary evaporator. The residue was crystallized from methanol–ether; after three crystallizations the melting point of the colorless solid is 206.5–208 °C; yield 9.3 g (84% of theoretical). Anal. Calcd for C$_{15}$H$_{17}$N$_2$OCl: C, 65.10; H, 6.15. Found: C, 65.07; H, 6.09.

N-[1-(4-Nitrophenyl)-2-propyl]nicotinamide chloride was prepared analoguously to the unsubstituted derivative (above). Product crystallized from ethanol–ether exhibited mp 192–194 °C. Anal. Calcd for C$_{15}$H$_{16}$N$_3$O$_3$Cl: C, 55.99; H, 4.98; N, 13.06; Cl, 11.04. Found: C, 56.20; H, 5.28; N, 13.10; Cl, 11.00.

N-[1-(4-Methoxyphenyl)-2-propyl]nicotinamide chloride was similarly prepared (above). Product crystallized from ethanol–ether exhibited mp 185–187 °C. Anal. Calcd for C$_{16}$H$_{19}$N$_2$O$_2$Cl: C, 62.64; H, 6.20; N, 9.14; Cl, 11.58. Found: C, 62.56; H, 6.11; N, 9.31; Cl, 11.49.

Synthesis of Methyl 3,5,9,11,13-Pentaoxotetradecanoate, a "Skipped" Heptaketide, via Ozonolysis of a Hydroaromatic System

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The synthesis of carbon chains possessing alternating methylene and carbonyl groups ("polyketides", **1**) has provided valuable materials for verification of the acetate–malonate pathway of biosynthesis[1] as well as useful precursors to certain acetate-derived natural products.[2] As synthetic entities, higher order polyketides present difficult objectives due to their inherent instability, the limited access to unprotected versions, and a proclivity, when unmasked, for these systems to undergo indiscriminate, internal condensation. Notable success in counteracting these properties has been achieved by Harris, who developed a stepwise, iterative process for homologation of polyketides via their polyenolate anions,[3] and by Money and Scott, who succeeded in deploying polyketides within cleverly contrived pyrone structures.[4]
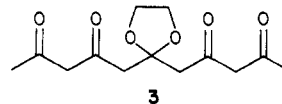
Our approach to the synthesis of polyketides had, as its antecedent, a report by Birch, which described an attempt to prepare **3** by ozonolysis of the dihydroaromatic system **2**.[5] Although **3** was not fully characterized in that study,

$$CH_3(COCH_2)_n CO_2R$$
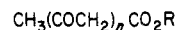
1
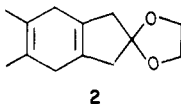
2

3

it was clear that this tactic offered a potentially valuable means for construction of extended polyketide (**1**, $n \geq 4$)

(13) Mulliken, R. *J. Am. Chem. Soc.* **1950**, *72*, 600; **1952**, *74*, 811.

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(20) Lerner, O. M. *Zh. Priklad. Khim.* **1958**, *31*, 663; *Chem. Abstr.* **1959**, *52*, 18271.

(1) Birch, A. J. *Science (Washington, D.C.)* **1967**, *156*, 202. Birch, A. J. *Fortschr. Chem. Org. Naturst.* **1957**, *14*, 186.

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and derivative structures. Two significant attributes of this methodology are its mildness, which should assure preservation of the polyketide once formed, and its ability to accommodate an unsymmetrical variant which permits a distinction between the "head" and "tail" units of the polyketide.

As a test of this strategy we chose for our objective a keptaketide (1, n = 6), modified by replacement of the C-7 keto function by a methylene group. This "skipped" heptaketide (18) was considered to be a potentially more tractable substrate for future condensation studies, since the discontinuity resulting from removal of the central carbonyl group substantially reduces the number of possible aromatization pathways. In devising a route to 17, the projected precursor of 18, we first sought a preparation of 2-methoxy-3-methylbenzoquinone (4), in anticipation that this would serve as a dienophile in a Diels–Alder reaction with a suitably constituted diene. Although 4 had been obtained previously by oxidation of 2,6-dimethoxytoluene with sodium dichromate,[6] a more satisfactory protocol was found in the oxidation of 3-methoxy-2-methylphenol with potassium nitrosodisulfonate (Fremy's salt).[7]

4

5

6   **7**

8   **9**
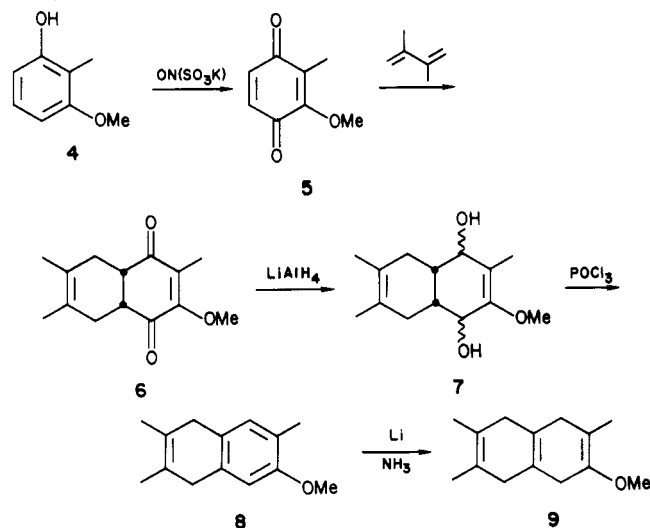
The Diels–Alder reactivity of 5 was first explored with a simple partner, 2,3-dimethylbutadiene, and the structure of the crystalline adduct 6, obtained in 72% yield, confirmed our expectation that cycloaddition had occurred selectively at the less substituted (and more electrophilic) double bond of 5.[8] The cycloadduct 6 also provided a convenient vehicle for charting a course to the requisite dihydro aromatic system 17.

Attempted reduction of 6 with sodium borohydride or with aluminum isopropoxide and 2-propanol gave mainly the aromatized product 10, whereas treatment of 6 with

10
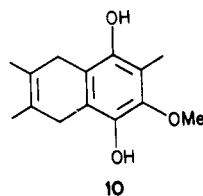
lithium aluminum hydride at 0 °C afforded 7 in only 22% yield. However, it was found that the efficiency of this latter conversion could be raised to 82% when reduction

**Table I. Ultraviolet Spectral Data for 18 and Related Polyketides**

compd	λ_{max}, nm	
	EtOH	NaOH
3[a]		294
18	273	298, 358 (sh)
19[a]	274	293
20[a]		295, 342 (sh)

[a] Data from ref 5.

was carried out at –50 °C. The resultant diol 7 was cleanly dehydrated with phosphorus oxychloride in pyridine to dihydronaphthalene 8 and the latter underwent smooth reduction with lithium–ammonia to furnish 9 in 74% yield.

With the model sequence successfully concluded, attention was turned toward the diene required for 17. The unstable 1,2-dimethylenecyclopentane (13) was acquired via a ten-step pathway beginning from pimelic acid. This entailed preparation of cyclopentane-1,2-dicarboxylic acid (11)[9] and its subsequent conversion to 13 by pyrolysis of the bis(amine oxide) 12, as described by Bartlett et al.[10] The Diels–Alder addition of 13 to 5 was conducted at room temperature and gave the crystalline adduct 14 in 30% yield. A sequence analogous to that employed with 6 led in good yield to diol 15 and, after dehydration, to the aromatic system 16. A Birch reduction of the latter furnished 17 in 86% yield.

Exhaustive ozonolysis of 17 was carried out in dichloromethane solution at –78 °C, and subsequent reduction of the presumed trisozonide intermediate was effected with hydrogen in the presence of palladium on charcoal. The polyketide 18 was obtained as a relatively stable, pale yellow oil which, as judged from its ^{1}H NMR spectrum, consisted of multiple keto/enol tautomers. It

11, R = CO$_2$H
12, R = CH$_2$NMe$_2$
              |
              O$^-$

13

14   **15**

16   **17**

18
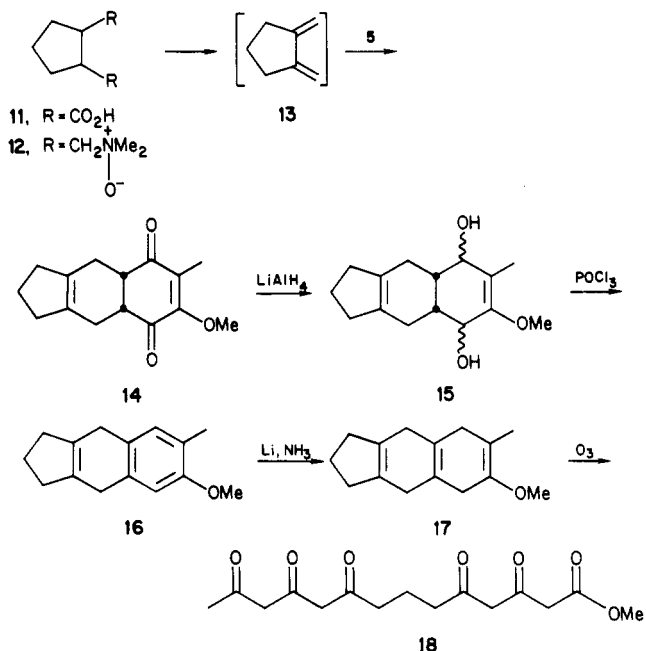
was, nevertheless, possible to discern the presence of the all-keto form 18 in this tautomeric mixture from two singlets at δ 3.67 and 3.80 (ratio 3:8, respectively). Comparison of the UV spectrum of 18 with the spectra of other polyketide structures (Table I) was especially informative. In neutral solution 18 displayed an absorption maximum

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(10) Bartlett, P. D.; Wingrove, A. S.; Owyang, R. J. Am. Chem. Soc. 1968, 90, 6067.

similar to that observed for 2,4-pentanedione (19)[5] and, in the presence of base, the spectra of these two substances exhibited virtually identical bathochromic shifts. In fact, the wavelength of the absorption maximum of 18 in basic solution closely parallels that observed for 3 and also 2,4,6-heptanetrione (20), as well as 19. The presence of an absorption (shoulder) at ca. 350 nm in 18 and 20 is thought to be due to formation of a dienolate anion of these structures. Finally, although it was not possible to obtain a crystalline derivative of 18, the latter gave a strongly positive response to ferric chloride solution.

The synthesis of modified heptaketide 18 via ozonolytic cleavage of 17 extends the earlier work of Birch[5] and exemplifies a potentially general entry to this important class of structures. Furthermore, our approach should provide access to substrates whose modes of intramolecular condensation can be studied in a systematic fashion.

Experimental Section

General Methods. Infrared spectra (IR) were obtained with a Perkin-Elmer 137 infrared spectrophotometer. Ultraviolet spectra (UV) were obtained with a Carey 15 spectrophotometer. Nuclear magnetic resonance spectra (NMR) were obtained with either a Varian HA-100 or a Varian EM-360 spectrometer and are reported in δ units with tetramethylsilane (Me$_4$Si) as the internal standard. Coupling constants (J) are given in hertz; s = singlet, d = doublet, t = triplet, q = quartet, and p = pentuplet. Elemental analysis were performed by Dr. Susan Rottschaefer, Department of Chemistry, University of Oregon. Mass spectra were obtained by using a CEC Model 21-110 double-focusing mass spectrometer equipped with a direct inlet system at 70 eV ionization potential. Ozone was generated by a Welsbach Ozonator. Thin-layer chromatography (TLC) was carried out with Merck silica gel PF-254 plates. Column chromatography was done with neutral aluminum oxide or neutral silica gel which were used as activity II. All boiling points (bp) and melting points (mp) are uncorrected. Extracts of reaction mixtures were dried over magnesium sulfate.

3-Methoxy-2-methylphenol (4). To a solution of 12.40 g (0.10 mol) of 2,6-dihydroxytoluene and 4.00 g (0.10 mol) of sodium hydroxide in 50 mL of water was added slowly 12.80 g (0.10 mol) of dimethyl sulfate. The solution was refluxed for 8 h and cooled, and an additional 4.00 g (0.10 mol) of sodium hydroxide was added. The mixture was washed with ether, and the aqueous portion was then acidified with dilute hydrochloric acid and extracted with ether. The ether extract was washed with saturated aqueous sodium bicarbonate, dried, and evaporated, and the residual oil was distilled to give 9.20 g (67%) of 4: bp 58–68 °C (0.04 mm); IR (neat) 3400, 1580, 770 cm^{-1}; NMR (CDCl$_3$) δ 2.05 (2 H, s), 3.72 (3 H, s), 5.02 (1 H, s, exchanged with D$_2$O), 6.38 (1 H, d, J = 7 Hz), 6.42 (1 H, d, J = 7 Hz), 6.97 (1 H, t, J = 7 Hz).

2-Methoxy-3-methylbenzoquinone (5). To a solution of 43.0 g (0.21 mol) of potassium nitrosodisulfonate (Fremy's salt) and 16.2 g (0.20 mol) of sodium acetate in 2.5 L of water was added a solution of 10.0 g (0.072 mmol) of 4 in 20 mL of ether. The mixture was stirred for 2 h at room temperature and extracted with ether (3 × 300 mL). The organic solution was dried and the ether was removed, leaving a dark red oil. This was distilled to give 4.20 g (42%) of 5 as an orange oil, which solidified upon refrigeration: bp 55–60 °C (0.04 mm); IR (neat) 1680, 1665, 1620, 840 cm^{-1}; NMR (CDCl$_3$) δ 2.02 (3 H, s), 4.10 (3 H, s), 6.65 (2 H, m); mass spectrum, m/z 136.0522 (M$^+$, calcd for C$_8$H$_8$O$_2$ 136.0524).

***cis*-5,8,8a-Tetrahydro-2-methoxy-3,6,7-trimethyl-1,4-naphthoquinone (6).** A solution of 3.28 g (0.022 mol) of 5 and 1.90 g (0.023 mol) of 2,3-dimethylbutadiene in 50 mL of petroleum ether was heated at 65 °C for 8 h under a nitrogen atmosphere. Upon cooling the reaction mixture to –78 °C, the product crystallized and was collected by filtration. Recrystallization from petroleum ether at –78 °C gave 3.66 g (72%) of 6: IR (Nujol) 1680, 1660, 1608 cm^{-1}; NMR (CDCl$_3$) δ 1.60 (6 H, s), 1.88 (3 H, s), 2.0–2.6 (6 H), 3.00–3.24 (2 H, m), 3.96 (3 H, s); mass spectrum, m/z 234 (M$^+$).

Anal. Calcd for C$_{14}$H$_{18}$O$_3$: C, 71.79; H, 7.70. Found: C, 71.53; H, 7.74.

***cis*-1,4,5,8,8a-Hexahydro-1,4-dihydroxy-2-methoxy-3,6,7-trimethylnaphthalene (7).** A solution of 150 mg (0.64 mmol) of 6 in 15 mL of anhydrous ether was slowly added to 10 mL of ether containing 27 mg (0.70 mmol) of lithium aluminum hydride at –50 °C. The mixture was stirred for 0.5 h, and 40 mL of ethyl acetate was added, followed by careful addition of 1 mL of water. The mixture was filtered, and the filtrate was washed with 50 mL of ethyl acetate. The combined organic solutions were dried, and the solvent was removed by evaporation, with the temperature maintained below 35 °C. This produced a yellow solid which was decolorized by washing repeatedly with petroleum ether to give 126 mg (82%) 7: mp 146–149 °C; IR (Nujol) 3400, 1660, 1310 cm^{-1}; NMR (Me$_2$SO) δ 1.52 (9 H, s), 1.55–1.83 (2 H), 1.96–2.20 (4 H), 2.48–2.58 (2 H, exchanged with D$_2$O), 3.50 (3 H, s), 4.38 (2 H, m). This material underwent conversion to a substance of undetermined structure upon attempted crystallization.

5,8-Dihydro-1,4-dihydroxy-2-methoxy-3,6,7-trimethyl-naphthalene (10). A mixture of 200 mg (0.86 mmol) of 6 and 34 mg (0.86 mmol) of sodium borohydride in 20 mL of *tert*-butyl alcohol was stirred at room temperature for 3 h. Water (30 mL) was added, and the solution was extracted with four 30-mL portions of ether. The organic layer was dried, and the solvent was removed by evaporation, leaving 186 mg (93%) of 10 as an off-white solid: IR (Nujol) 3400, 1100 cm^{-1}; NMR (Me$_2$SO) δ 1.74 (6 H, s), 2.10 (3 H, s), 3.12 (4 H, s), 3.4 (2 H, s), 3.64 (3 H, s); mass spectrum, m/z 234 (M$^+$).

5,8-Dihydro-2-methoxy-3,6,7-trimethylnaphthalene (8). To a solution of 200 mg (0.84 mmol) of diol 7 in 20 mL of pyridine cooled to –5 °C was added slowly 8.40 g (55.0 mmol) of phosphorus oxychloride. The mixture was allowed to warm slowly to room temperature and was stirred for 24 h. The excess phosphorus oxychloride was destroyed by slow addition of water at –5 °C, and the mixture was added to 50 mL of water and extracted with ether. The ethereal layer was washed with dilute hydrochloric acid and saturated aqueous copper sulfate and dried. Upon removal of the ether, a solid residue was left which was crystallized from methanol to yield 105 mg (65%) of 8: mp 112–114 °C; IR (CCl$_4$) 1610, 1500, 1238 cm^{-1}; NMR (CDCl$_3$) δ 1.76 (6 H, s), 2.14 (3 H, s), 3.22 (4 H, s), 3.78 (3 H, s), 6.55 (1 H, s), 6.88 (1 H, s); mass spectrum, m/z 202 (M$^+$).

Anal. Calcd for C$_{14}$H$_{18}$O: C, 83.12; H, 8.97. Found: C, 82.89; H, 9.00.

1,4,5,8-Tetrahydro-2-methoxy-3,6,7-trimethylnaphthalene (9). A solution of 109 mg (0.54 mmol) of 8 in 20 mL of tetrahydrofuran was added to 80 mL of liquid ammonia and 20 mL of tetrahydrofuran, and to this solution was added 104 mg (14.9 mmol) of lithium wire containing 1% sodium. The mixture was stirred at –30 °C for 0.5 h, and ethanol was added dropwise until the blue color just disappeared. A further 50 mg (7.2 mmol) of lithium was added, and, after 0.5 h, the ammonia was allowed to evaporate. Ammonium chloride (1.00 g) was added, followed by 50 mL of water. The mixture was extracted with ether, and the extract was dried and evaporated. The solid residue was crystallized from methanol to give 82 mg (74%) of 9: IR (CCl$_4$) 1650 cm^{-1}; NMR (CDCl$_3$) δ 1.60 (9 H, s), 2.48 (4 H, s), 2.55 (4 H, s), 3.54 (3 H, s); mass spectrum, m/z 204 (M$^+$).

Anal. Calcd for C$_{14}$H$_{20}$O: C, 82.30; H, 9.87. Found: C, 82.46; H, 9.63.

1,2-Dimethylenecyclopentane (13). A mixture of 5.00 g (0.027 mol) of 1,2-bis((dimethylamino)methyl)cyclopentane[10] and 20 mL of 30% hydrogen peroxide was stirred for 48 h (initially, cooling was required to maintain the solution at room temperature). Unreacted peroxide was decomposed by addition of a catalytic amount of platinum black, and the mixture was stirred for a further 3 h. Water was removed from the mixture, first by evaporation (40 °C) and then at high vacuum (0.03 mm for 6 h) to yield 12 as a viscous oil. To this material was added 20 mg of hydroquinone, and the mixture was heated at 170–180 °C (150 mm) in a continuous stream of nitrogen. The distillate was collected in two dry ice-acetone traps and was taken up in 15 mL of ether. The ether was washed with 0.1 N hydrochloric acid until the washings were acidic and then with saturated sodium bicarbonate. The resulting ethereal solution of 13 was dried and was used without further purification.

***cis*-6,7-Cyclopenteno-5,8,9,10-tetrahydro-2-methoxy-3-methyl-1,4-naphthoquinone (14).** The ethereal solution of 13

prepared above was added to 2.50 g (16.4 mmol) of **5** in 50 mL of petroleum ether, and the solution was stirred for 16 h at room temperature under a nitrogen atmosphere. Upon cooling the solution to −78 °C, pale yellow crystals were obtained which were collected by filtration. This material was recrystallized from petroleum ether at −78 °C to give 1.2 g (30%) of **14**: mp 87–89 °C; IR (Nujol) 1690, 1655, 1600, 1280 cm⁻¹; NMR (CDCl₃) δ 1.88 (3 H, s), 1.70–2.10 (2 H, m), 2.10–2.60 (8 H, m), 3.10–3.35 (2 H, m), 3.96 (3 H, s); mass spectrum, *m/z* 246 (M⁺).

Anal. Calcd for C₁₅H₁₈O₃: C, 73.17; H, 7.32. Found: C, 73.23; H, 7.41.

***cis*-6,7-Cyclopenteno-1,4,5,8,9,10-hexahydro-1,4-di-hydroxy-2-methoxy-3-methylnaphthalene (15).** A solution of 150 mg (0.64 mmol) of **14** in 20 mL of anhydrous ether was slowly added to a stirred suspension of 28 mg (0.73 mmol) of lithium aluminum hydride in 25 mL of ether at −60 °C. The mixture was stirred for 1.5 h after the addition was complete, and 40 mL of ethyl acetate was added, followed by 2 mL of water. The solution was allowed to warm to room temperature, extracted with ethyl acetate, dried, and evaporated at 20 °C. The residual oil was washed with petroleum ether to yield 108 mg (68%) of unstable **15**: IR (Nujol) 3500, 3000, 1680, 1630 cm⁻¹. This material was used immediately for conversion to **16**.

6,7-Cyclopenteno-5,8-dihydro-2-methoxy-3-methyl-naphthalene (16). A solution of 928 mg (3.7 mmol) of **15** in 20 mL of pyridine at 0 °C was slowly added to 6.00 g (40 mmol) of phosphorus oxychloride. After addition was complete, the solution was heated at 65 °C for 18 h. The excess phosphorus oxychloride was destroyed by careful addition of water at 0 °C, and the mixture was extracted with three 50-mL portions of ether. The ether extract was washed with 1 N hydrochloric acid until acidic and then with aqueous sodium bicarbonate and dried. Removal of the solvent in vacuo left a colorless solid, which was chromatographed on alumina (elution with hexane) to give 434 mg (55%) of **16**: IR (CCl₄) 1500, 1235, 1205, 1090 cm⁻¹; NMR (CDCl₃) δ 1.80–2.20 (2 H, m), 2.19 (3 H, s), 2.22–2.50 (4 H, m), 3.31 (4 H, s) 3.80 (3 H, s), 6.60 (1 H, s), 6.91 (1 H, s).

Anal. Calcd for C₁₅H₁₈O: C, 84.07; H, 8.47. Found: C, 83.91; H, 8.58.

6,7-Cyclopenteno-1,4,5,8-tetrahydro-2-methoxy-3-methyl-naphthalene (17). To a solution of 198 mg (0.93 mmol) of **16** in 100 mL of dry tetrahydrofuran was added 80 mL of distilled ammonia, followed by 100 mg (14.9 mmol) of lithium. After 10 min, 2 mL of 100% ethanol was added, and after a further 15 min the solution became colorless, and the ammonia was allowed to evaporate. To the residue was added 50 mL of water, and the mixture was extracted with four 100-mL portions of ether. The extract was evaporated, and the residue was chromatographed on alumina. Elution with hexane gave 172 mg (86%) of **17**: IR (CCl₄) 1200, 1165, 1135 cm⁻¹; NMR (CDCl₃) δ 1.65 (3 H, s), 1.70–2.10 (2 H, m), 2.10–2.40 (4 H, m), 2.45–2.80 (8 H, two broad singlets of 4 H each), 3.52 (3 H, s), mass spectrum, *m/z* 216 (M⁺).

Anal. Calcd for C₁₅H₂₀O: C, 83.33; H, 9.25. Found: C, 83.33; H, 9.36.

Methyl 3,5,9,11,13-Pentaoxotetradecanoate (18). A stream of ozone was passed through a solution of 216 mg (1.0 mmol) of **17** in 150 mL of methylene chloride at −78 °C until a light blue coloration persisted. Nitrogen was then passed through the solution for 1 h to remove excess ozone, and the solution of ozonide was reduced with hydrogen over 30 mg of 10% palladium-on-charcoal at room temperature for 3 h. The solution was filtered, and the solvent was evaporated to leave 131 mg (42%) of **18** as a light yellow oil: IR (neat) 3500 (broad), 1730 (broad) cm⁻¹; NMR (CDCl₃) complex with singlets at δ 3.67 and 3.80 (1:3); UV (ethanol) λ_max 298 and 358 nm (shoulder); mass spectrum, *m/z* 312.120 (calcd for C₁₅H₂₀O₇ 312.121).

Registry No. 4, 6971-52-4; 5, 2207-57-0; 6, 95274-99-0; 7, 95275-00-6; 8, 95275-02-8; 9, 95275-03-9; 10, 95275-01-7; 12, 95275-05-1; 13, 20968-70-1; 14, 95275-06-2; 15, 95275-07-3; 16, 95275-08-4; 17, 95275-09-5; 17 (ozonide), 95275-11-9; 18, 95275-10-8; 1,2-bis((dimethylamino)methyl)cyclopentane, 95275-04-0; 2,6-dihydroxytoluene, 608-25-3; 2,3-dimethylbutadiene, 513-81-5.

Formation of 6(2*H*)-Aceanthrylenones and Their Photochemical Conversion into Aceanthrylenes

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The photochemical decomposition of 10-diazoanthrone (**1**) in the presence of methyleneanthrone (**2**) gives the spiro-substituted anthrone **3**, which, in refluxing solvents
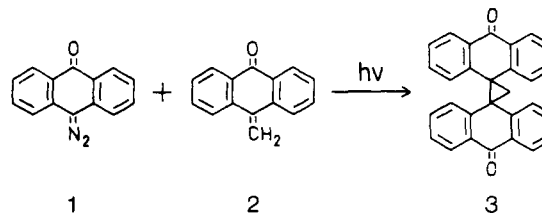
under nitrogen, had been found to be converted into the aceanthrylenone derivative **4**.[1] The apparently facile formation of **4** from **3** is intriguing insofar as it seems to involve the spontaneous loss of two hydrogen atoms. In conjunction with the present study dealing with the previously unnoticed photosensitivity of **4**, we have also investigated its formation from **3**.

Freshly prepared solutions of spirocyclopropane anthrone **3** in benzene or methylene chloride under nitrogen assume a transient red color which originates from a broad absorption around 500 nm. These red solutions give rise to a multiline ESR spectrum which may be attributable to biradical **5** (cf. Figure 1). Chemical evidence for the actual presence of **5** was obtained by trapping with molecular oxygen which gave peroxide **6** in 79% yield.[2]

The electron spectral changes associated with the disappearance of absorption around 500 nm under nitrogen are probably explicable by a homolytic rearrangement of **3** resulting in the formation of the hydroxy-substituted aceanthrene **7**, which is reversibly converted into its keto tautomer **8**. Treatment of the reaction mixture with acetic anhydride/pyridine affords the acetate **9** whose electronic absorption spectrum (see Experimental Section) supports the suggested formation of **7**.

Upon exposure to oxygen, **7**/**8** in methylene chloride solution is converted into the hydroperoxide **10**, which gives the 6(2*H*)-aceanthrylenone **4** by treatment with trifluoroacetic acid.[3] More conveniently, however, **4** can be obtained by stirring a suspension of **3** in benzene under argon in the presence of a hydrogen acceptor such as DDQ or silver oxide (see Scheme I). Consequently, the previously[1a] noted conversion of **3** into **4** under nitrogen is presumably due to the inadvertent presence of some oxidant.

Oxidation product **4** forms colorless crystals (mp 321–322 °C (lit.[1a] mp 303–304 °C) and exhibits a UV absorption in solution around 360 nm which we find to be characteristic of the 6(2*H*)-aceanthrylenone chromophore (see Experimental Section). The compound attracted our at-

(1) (a) Nakazawa, S.; Hirakawa, K.; Fujimori, S.; Iwazaki, K. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2052. (b) More recently, structure **3** has been assigned tentatively, and probably erroneously, to a compound that has a melting point of 240 °C and is stable in solution: Zitzmann Suits, J.; Applequist, D. E.; Swart, D. J. *J. Org. Chem.* **1983**, *48*, 5120.

(2) Analogous peroxides have been obtained in the autoxidation of bis(phenol)s (Colgate, S. M.; Hewgill, F. R. *Aust. J. Chem.* **1980**, *33*, 351). We are indebted to Dr. F. R. Hewgill of the University of Western Australia for recording the ESR spectrum shown in Figure 1.

(3) For an analogous reaction of TFA with an anthronyl hydroperoxide, see: Becker, H.-D.; Sanchez, D. *J. Org. Chem.* **1979**, *44*, 1787.