hexane/ethyl acetate) 50 mg (70%) of **28c**: IR (CCl_4) 1720, 1670, 1620, 1595, 1490 cm^{-1}; NMR (CCl_4) δ 2.0 (3 H, s), 2.84 (2 H, d, $J = 8$ Hz), 4.04 (1 H, q, $J = 6$ Hz), 6.68 (1 H, d, $J = 16$ Hz), 6.75–7.8 (11 H, m); exact mass calcd for $C_{19}H_{18}O_2$ 278.1307, found 278.1312.

4-Phenyl-11,11-(ethylenedioxy)dodec-(*E*)-5-ene-2,7-dione (28d). To 3 mL of dry THF containing 2.45 mmol of *tert*-butyllithium in pentane at −78 °C was added dropwise 320 mg (1.25 mmol) of 2,2-(ethylenedioxy)-5-iodopentane in 4 mL of THF. After 1 h, the clear solution was added to a −40 °C slurry of 125 mg (0.600 mmol) of cuprous bromide–dimethyl sulfide in 7 mL of ether. After the black mixture was stirred at −40 °C for 1 h and cooled to −78 °C, a solution of 154 mg (0.500 mmol) of 1,4-dithiacycloheptan-2-one in 4 mL of ether was added and the resultant mixture was stirred for 2 h. After workup as described for **28a**, acetylation with 0.2 mL of acetic anhydride in 3 mL of pyridine and 3 mL of ether, and purification by TLC (3:2 hexene/ethyl acetate), 111 mg (46%) of **27d** was isolated: IR ($CHCl_3$) 1700, 1660, 1600, 1490 cm^{-1}; NMR ($CDCl_3$) δ 1.28 (3 H, s), 2.0 (3 H, s), 2.18 (3 H, s), 1.2–3.6 (18 H, m), 3.88 (4 H, s), 7.0–7.4 (5 H, m); exact mass calcd for $C_{25}H_{36}O_5S_2$ 480.2004, found 480.1986.

Oxidation of 80 mg (0.17 mmol) of **27d** with 36 mg (0.18 mmol) of MCPBA in 3 mL of methylene chloride and elimination at 120 °C in 3 mL of toluene generated, after TLC (3:2 hexane/ethyl acetate), 22 mg (40%) of **28d**: IR (CCl_4) 1710, 1680, 1620, 1490 cm^{-1}; NMR (CCl_4) 1.2 (3 H, s) 1.92 and 2.0 (3 H, 2 s), 1.4–2.5 (6 H, m), 2.58 and 2.80 (2 H, 2 d, $J = 7$ Hz), 3.8 (4 H, s), 3.9 (1 H, m), 5.88 (1 H, d, $J = 16$ Hz), 6.72 (1 H, dd, $J = 16, 6$ Hz), 6.9–7.3 (5 H, m).

Treatment of 2-Benzylidene-1,3-dithiane with Lead Tetraacetate. A solution of 208 mg (1 mmol) of 2-benzylidene-1,3-dithiane in 4 mL of benzene was added to 576 mg (1.3 mmol) of lead tetraacetate which had been washed free of acetic acid. After the mixture was heated at 55 °C for 5 min, a white powdery precipitate formed. Stirring continued for 1 h at 55 °C. The mixture was diluted with ether, washed with 5% aqueous sodium thiosulfate and brine, dried ($MgSO_4$), and evaporated in vacuo to give 264 mg (99%) of 2-(1′-acetoxybenzylidene)-1,3-dithiane **36**, pure by TLC and spectroscopy: IR (CCl_4) 1765, 1600 cm^{-1}; NMR (CCl_4) δ 1.96–2.3 (2 H, m), 2.12 (3 H, s), 2.82 (2 H, t, $J = 6.5$ Hz), 2.92 (2 H, t, $J = 7$ Hz), 7.16–7.54 (5 H, m); exact mass calcd for $C_{13}H_{14}O_2S_2$ 266.0435, found 266.0436.

To a solution of 264 mg (0.992 mmol) of **36** in 4 mL of toluene at −78 °C was added 1.1 mmol of a solution of DIBAL in hexane. After 6.5 h at −78 °C, 1 mL of methanol was added and the reaction allowed to warm to ambient temperature. A 1-mL aliquot of saturated aqueous sodium sulfate solution followed by 30 mL of ether was added, and the mixture was stirred 10 min. Excess solid sodium sulfate was added for drying, and the mixture was filtered and evaporated in vacuo. Purification by preparative TLC (7:3 hexane/ethyl acetate) gave 156 mg (70%) of **37** as an amorphous solid: mp 94–95 °C; IR (CCl_4) 1690, 1595, 1580 cm^{-1}; NMR ($CDCl_3$) δ 1.96–2.32 (2 H, m), 2.56–2.84 (2 H, m), 3.24–3.56 (3 H, m), 5.17 (1 H, s), 7.3–7.7 (3 H, m), 7.9–8.1 (2 H, m); exact mass calcd for $C_{11}H_{12}OS_2$ 224.0329, found 224.0330.

A solution of 35 mg (0.16 mmol) of **37** in 1 mL of absolute ethanol was refluxed for 4 h with 1 mL of W-2 Raney nickel. The solution was analyzed by TLC and VPC and showed only a single compound corresponding to acetophenone. The mixture was filtered through Celite and the filter cake washed with pentane. The filtrate was washed with water and dried, and the solvent was removed by distillation to give 16 mg (85%) of acetophenone, identical by NMR and IR spectroscopy, VPC, and TLC with an authentic sample.

Acknowledgment. We thank the National Science Foundation and the General Medical Sciences Institute of the National Institutes of Health for their most generous support of our programs. We also thank Mr. Patrick McDougal who carried out some preliminary experiments to clarify the mechanism of the reaction.

Registry No. 5a, 108-94-1; **5b**, 3350-30-9; **5c**, 830-13-7; **6a**, 823-45-0; **6b**, 1009-12-7; **6c**, 949-07-5; **7a**, 51310-03-3; **7b**, 73194-43-1; **7c**, 73194-44-2; **8a** (R = H), 60450-09-1; **8a** (R = CH_3), 60450-20-6; **8b** (R = H), 60450-12-6; **8c** (R = H), 60450-13-7; **9**, 946-33-8; **10**, 20795-53-3; 11, 73194-45-3; **12**, 73194-46-4; **13**, 60450-11-5; **14**, 73194-47-5; **16a** (R = H), 60450-07-9; **16a** (R = CH_3), 60450-08-0; **16b** (R = H), 60450-14-8; **16c** (R = H), 60450-15-9; **17**, 60450-10-4; **18**, 73194-48-6; **20**, 2046-21-1; **22a** (R = H), 2018-74-8; **22a** (R = CH_3), 60450-18-2; **22b** (R = H), 60450-16-0; **22b** (R = CH_3), 1189-64-6; **22c** (R = H), 60450-17-1; **23**, 60450-19-3; **24**, 73194-49-7; **25**, 73194-50-0; **26**, 1189-64-6; **27a**, 73194-51-1; **27b**, 73194-52-2; **27c**, 73194-53-3; **27d**, 73194-54-4; **28a**, 73194-55-5; **28b**, 73194-56-6; **28c**, 73194-57-7; **28d**, 73194-58-8; **33**, 17590-58-8; **36**, 72019-01-3; **37**, 21504-07-4; 1,3-propanedithiol bis(*p*-toluenesulfonate), 3866-79-3; methyl 9-hydroxy-2-decenoate, 40979-98-4; 2,2-(ethylenedioxy)-5-iodopentane, 3695-28-1; acetophenone, 98-86-2.

Synthesis of 1,8-(6′,7′-Dioxododecamethylene)phenanthrene[1]

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Received August 16, 1979

The synthesis of the title compound (1) is described starting from *o,o′*-stilbenedicarboxylic acid which was converted to *o,o′*-bis[(carbomethoxy)pentyl]stilbene which underwent acyloin cyclization and oxidation to give 1 in 9.5% overall yield. Spectroscopic properties of 1 are presented.

α-Diketones possess a variety of desirable properties for study of photophysical and photochemical phenomena.[2] The most extensively investigated member of this family of compounds is biacetyl, which has weak ($\epsilon \sim 30$), solvent-dependent, absorption maxima at about 275 and 420 nm (cf. Figure 1), exhibits both fluorescence and phosphorescence in fluid solution at room temperature, and undergoes a variety of photochemical reactions. It thus seemed that substances incorporating both an α-diketone moiety and an additional chromophore would be good candidates for investigation of intramolecular energy transfer[3] and might also exhibit photochromic properties.

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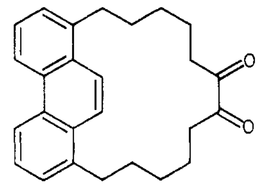
(1) From the D.Sc. dissertation of S. Welner, Technion, 1978.

(2) For review articles see M. B. Rubin, *Top. Curr. Chem.*, 13, 257 (1969); B. M. Monroe, *Adv. Photochem.*, 8, 77 (1971).

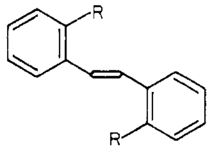
(3) For a general discussion see D. O. Cowan and R. L. Drisko, "Elements of Organic Photochemistry", Plenum, New York, 1976, Chapter 6.

An attractive choice for a second chromophore was the phenanthrene system whose absorption and emission spectra do not, for the most part, overlap those of typical α-diketones. Examination of molecular models suggested that construction of a phenanthrene derivative bridged at positions 1 and 8 by a 12-carbon chain incorporating an α-diketone function would be synthetically feasible and would provide a compound suitable for the purposes described above. This expectation has been realized. We have reported[4] novel results obtained in an investigation of intramolecular energy transfer in 1,8-(6′,7′-dioxododecamethylene)phenanthrene (**1**) and now wish to describe its synthesis.

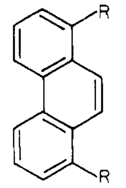


1

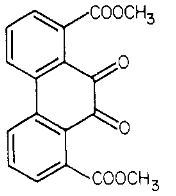
Among the plethora of methods for synthesis of phenanthrenes,[5] the oxidative photocyclization of stilbenes seemed to offer the advantages of simplicity and flexibility. This procedure has been used for preparation of a wide variety of substituted phenanthrenes,[6] but only a few examples of reaction of *o,o′*-disubstituted stilbenes have been reported.[7] Accordingly, the photocyclizations of *o,o′*-dimethyl- (**2a**) and *o,o′*-bis(methoxycarbonyl)stilbenes (**2b**) were investigated first. Both compounds were converted to the corresponding phenanthrenes (**3a,b**) in about 50% yield; **3b** was further characterized by oxidation to the quinone **4**.



2a, R = CH_3
b, R = $COOCH_3$
c, R = COOH
d, R = COCl



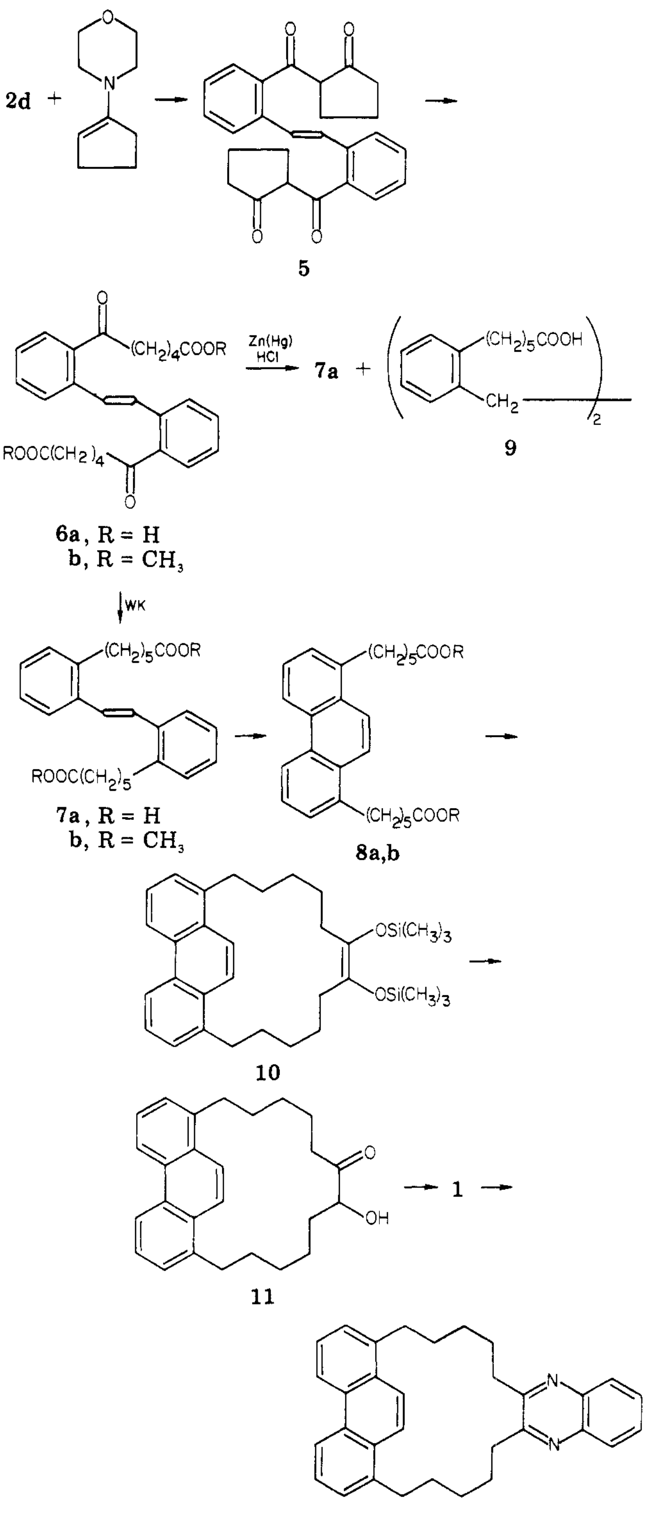
3a,b,c



4

The major limitation of the stilbene photocyclization procedure is the necessity of irradiating very dilute solutions in order to minimize photodimerization reactions. Thus, while either **3a** or **3b** might have served as starting material for introduction of the ten additional carbon atoms required, it was desirable to carry the synthesis as far as possible before the photocyclization step. As outlined in Scheme I, reaction of *o,o′*-stilbenedicarboxylic acid dichloride (**2d**) with the morpholine enamine of cyclopentanone followed by acid-catalyzed hydrolysis[8] gave the tetraketone **5** which underwent base-catalyzed cleavage to *o,o′*-bis(5-carboxypentyl)stilbene (**6a**) in 64% overall yield.

Scheme I



Wolff–Kishner reduction of **6a** afforded 48% of the diacid **7a**; esterification with diazomethane gave the diester **7b**. Clemmensen reduction of **6a** was also investigated and yielded about 20% of the desired **7a**, but the major product was 1,2-bis(*o*-carboxypentylphenyl)ethane (**9**). Stilbene **7a** was recovered unchanged after treatment under Clem-

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[4] S. Speiser, R. Katraro, S. Welner, and M. B. Rubin, *Chem. Phys. Lett.*, **61**, 199 (1979); D. Getz, A. Ron, M. B. Rubin, and S. Speiser, *J. Phys. Chem.*, **84**, 768 (1980).

[5] For a recent review see A. J. Floyd, S. F. Dyke, and S. E. Ward, *Chem. Rev.*, **76**, 509 (1976).

[6] (a) R. F. Stermitz, *Org. Photochem.*, **1**, 247 (1967); (b) E. V. Blackburn and C. J. Timmons, *Q. Rev., Chem. Soc.*, **23**, 482 (1969); (c) T. Kametani and K. Fukumoto, *J. Heterocycl. Chem.*, **8**, 341 (1971).

[7] Stilbenes substituted at ortho positions can, a priori, undergo cyclization at either the unsubstituted or substituted carbons. In the latter case, oxidation to a phenanthrene is possible only if loss (or migration) of substituent occurs and mixtures of phenanthrenes can be formed. This result was observed with 2,2′,3,3′-tetramethylstilbene (W. Carruthers and H.N.M. Stewart, *J. Chem. Soc. C*, 556 (1967)) and with methoxy-substituted stilbenes (R. G. F. Giles and M. V. Sargent, *J. Chem. Soc., Perkin Trans. 1*, 2447 (1974)). We have reproduced the result obtained with *o,o′*-dimethoxystilbene. No products involving loss of alkyl side chain were observed in the present work.

[8] Cf. S. Hunig and W. Lendle, *Chem. Ber.*, **93**, 909 (1960), and references contained therein.

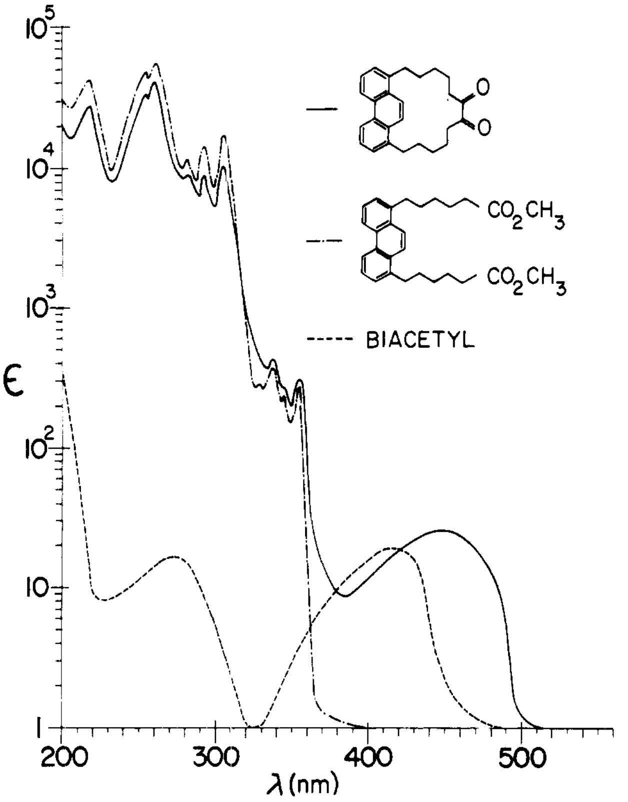

Figure 1. Absorption spectra of 1, **8b**, and biacetyl in acetonitrile.

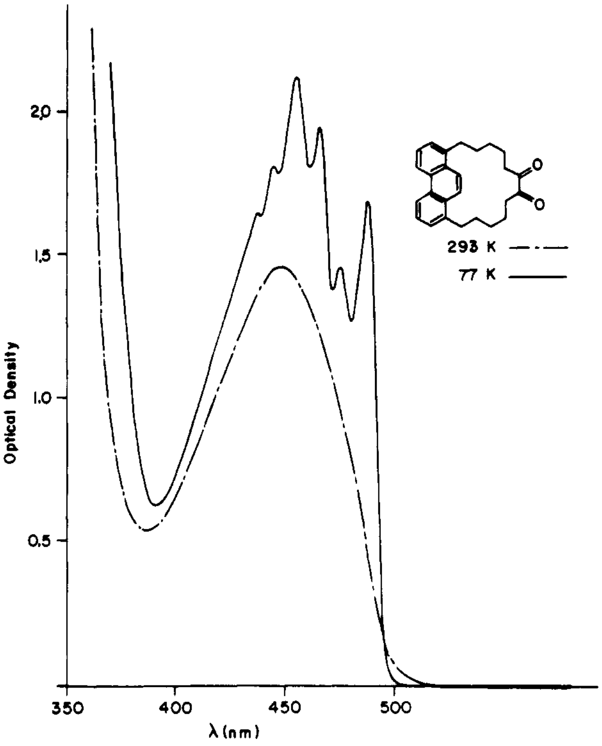

Figure 2. Absorption spectra of 1 in 2-methyltetrahydrofuran at 293 and 77 K.

mensen conditions; these results provide another example of reduction of the double bond of enones in reactions with zinc.[9] The reaction mixture containing **7a** and **9** could be carried through the photocyclization step since the desired 1,8-bis(5-carboxypentyl)phenanthrene (**8a**) precipitated during the course of irradiation. The technical problems resulting from coating of the immersion well did not arise when the diester (**7b**) was subjected to photocyclization, and the corresponding phenanthrene (**8b**) was obtained in 70% yield. Esterification of **8a** also afforded **8b**.

The key reaction for formation of the 1,8-bridged phenanthrene system, acyloin cyclization of **8b** in the presence of excess trimethylchlorosilane,[10] proceeded in close to quantitative yield. This undoubtedly reflects the fact that 8 of the 18 atoms involved in ring formation are constrained to a coplanar relationship. The resulting enediol bis(trimethylsilyl ether) **10** was very sensitive to hydrolysis but exhibited the appropriate spectroscopic properties, particularly the molecular ion in the mass spectrum and an 18-proton singlet close to zero parts per million in Me_4Si-free deuteriochloroform. Attempts to convert **10** directly to the desired α-diketone **1** by reaction with bromine[11] or with cupric acetate[11a] produced complex mixtures which contained **1** in low yield. Accordingly, **10** was hydrolyzed under acidic conditions to the crystalline acyloin **11** (80% overall yield from **8b**). Finally, oxidation of **11** with dimethyl sulfoxide/acetic anhydride[12] produced **1** in 55% yield. The overall yield of **1** from **2c** was 9.5%. The structure assigned to **1** was in full agreement with all of the observed spectroscopic properties. It was further characterized by conversion to the quinoxaline **12** whose ultraviolet spectrum was closely approximated by summation of the absorption spectra of diester **8b** plus the quinoxaline of biacetyl. Repeated attempts to obtain **1** in crystalline form were unsuccessful; it was purified by repeated preparative-scale TLC to constant spectroscopic properties.

The ultraviolet-visible spectra of **1**, **8b**, and biacetyl in acetonitrile are reproduced in Figure 1. Very close superposition of the spectra of **8b** and **1** in the region of phenanthrene absorption (200–350 nm) is observed. The long-wavelength maximum of **1** showing a bathochromic shift of 30 nm relative to biacetyl appears at 448 nm. The observed value of 448 nm is remarkably close to the range of 442–446 nm reported[13] for 13–15-membered cyclic α-diketones and differs markedly from the value of 384 nm reported[14] for α,α,α′,α′-tetramethylcyclooctadecanedione. Comparison of the long-wavelength absorption of **1** in 2-methyltetrahydrofuran at 293 and 77 K is shown in Figure 2. In addition to the expected appearance of fine structure, a new maximum appears at 486 nm. Spectra taken at intermediate temperatures showed continuous enhancement of absorption in the 486-nm region; no sudden effect in the region of the glass-forming temperature of the solvent was observed. The position of the long-wavelength maximum of α-diketones has been shown[14] to be sensitive to the torsional angle between the vicinal carbonyl groups; it seems most probable that the observed spectra of **1** reflect such conformational effects rather than interaction with the phenanthrene moiety. Possibly, conformational mobility is frozen out to an appreciable

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(9) Cf. J. G. St. C. Buchanan and P. Woodgate, *Q. Rev., Chem. Soc.*, **23**, 522 (1969); I. Elphimoff-Felkin and P. Sarda, *Tetrahedron Lett.*, 3045 (1969); E. Vedejs in "Organic Reactions", W. G. Dauben, Ed., Wiley, New York, 1975, Chapter 3.

(10) J. J. Bloomfield, D. C. Owsley, and J. M. Nelke, *Org. React.*, **23**, 1 (1976).

(11) (a) K. Ruhlmann, *Synthesis*, 236 (1971); (b) J. Strating, S. Reiffers, and H. Wynberg, *ibid.*, 211 (1971); (c) J. M. Conia and J. M. Denis, *Tetrahedron Lett.*, 2845 (1971); (d) H. G. Heine, *Chem. Ber.*, **104**, 2869 (1971).

(12) J. D. Albright and L. Goldman, *J. Am. Chem. Soc.*, **89**, 2416 (1967); M. van Dyke and N. D. Pritchard, *J. Org. Chem.*, **32**, 3204 (1967).

(13) T. Mori, T. Nakahari, and H. Nozaki, *Can. J. Chem.*, **47**, 3266 (1979).

(14) N. J. Leonard and P. M. Mader, *J. Am. Chem. Soc.*, **72**, 5388 (1950).

extent at low temperature and the two carbonyl groups are, in part, very close to a coplanar (probably s-cis) arrangement.

Full details of the fluorescence spectra of 1 under a variety of conditions have been published.[4] Phosphorescence was also observed; excitation in the region of absorption of the diketone (450 nm) gave a phosphorescence spectrum with a maximum at 540 nm. A more complex phosphorescence spectrum was observed upon excitation at 337.1 nm (nitrogen laser); this spectrum appeared to be a combination of phenanthrene and dione emissions. Unfortunately, considerable overlap of the two sets of emissions prevented a detailed analysis.

Photolysis of 1 was expected, on the basis of previously reported[2,15] intramolecular reactions of α-diketones, to afford a cyclobutanolone. In this event, the product formed by irradiation of degassed benzene solutions of 1 at 436 nm was a complex mixture (at least six components as determined by TLC examination); the acyloin 11 was not formed. The quantum yield for disappearance of 1 at 436 nm in degassed benzene or benzene/2-propanol solution was 0.16; at 313 nm in benzene solution the quantum yield was reduced by one-half in agreement with the partial energy transfer observed in emission studies. In view of the complexity of the reaction product, investigation of the photochemistry of 1 was not continued.

Experimental Section

Infrared spectra were determined in potassium bromide pellets and NMR spectra in deuteriochloroform solution (internal standard tetramethylsilane) at 60 MHz unless noted otherwise. Preparative-scale photoirradiations employed a 450-W Hanovia immersion lamp in a water cooled Pyrex well. A 200-W Osram (HBO 200) point source together with Schott interference filters was used for quantum yield determinations.

1,8-Dimethylphenanthrene (3a). A mixture of *cis-* and *trans-o,o′*-dimethylstilbenes[16] (0.52 g) dissolved in 5×10^{-4} M iodine in cyclohexane (250 mL) was irradiated, while air was bubbled through the solution, for 11 h and then worked up as described below (for **2b**) to give crude **3a** (0.566 g), which was crystallized from methanol to give material (0.254 g, 49%), mp 189–190 °C (lit[17] mp 191–2 °C). Two crystallizations raised the melting point to 191–192 °C. Spectroscopic properties were in full agreement with the proposed structure.

Dimethyl Phenanthrene-1,8-dicarboxylate (3b). A solution of *o,o′*-stilbenedicarboxylic acid diester **2b**[18] (0.74 g) in cyclohexane (500 mL), 5×10^{-4} M in iodine, was irradiated, while air was bubbled through the solution, for 3 h. Progress of reaction was monitored by UV spectroscopy. After distillation of the solvent, the residue was dissolved in chloroform (50 mL) which was washed with dilute sodium thiosulfate solution and saturated salt solution, dried, and concentrated to give a yellow solid (0.7 g). Crystallization from methanol gave material (0.385 g, 51%), mp 145–146 °C, which was homogeneous by TLC (1:2 benzene/hexane, silica gel). The analytical sample of **3b** was obtained by further crystallization from methanol: mp 146–147 °C; UV max (ethanol) 251 (34000), 257 (38000), 284 (19000), sh 305 (15000) nm; IR max, 1724 cm^{-1}; NMR δ 8.80 (d, J = 4 Hz, 4 H), 8.29 (d, J = 4 Hz, 2 H), 7.60 (t, J = 4 Hz, 2 H), 4.05 (6 H); mass spectrum, *m/e* 294 (M$^+$).

Anal. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.80. Found: C, 73.28; H, 4.78.

The diacid (**3c**) was obtained by saponification of **3b** (40 mg) with 0.5 M methanolic potassium hydroxide (10 mL) at reflux for 2 h. Acidification afforded solid diacid (35 mg) which crystallized from acetic acid (80 mL) to give the analytical sample: mp 365 °C dec; IR max 1500, 1600, 1670, 2500–3200 cm^{-1}.

Anal. Calcd for $C_{16}H_{10}O_4$: C, 72.18; H, 3.79. Found: C, 72.3; H, 3.85.

1,8-Bis(methoxycarbonyl)-9,10-phenanthrenequinone (4). A solution of phenanthrene diester **3b** (0.25 g) in acetic acid (7 mL) at 60 °C was treated dropwise with stirring with a solution of chromium trioxide (0.34 g) in acetic acid (1.7 mL) and water (1 mL). Heating was continued for 1 h after completion of addition and the solution allowed to stand for 1 h at room temperature. The product (0.140 g, 51%) which precipitated after addition of water (25 mL) was filtered and dried. Crystallization from methanol gave material (0.120 g), mp 218 °C, homogeneous by TLC (chloroform eluant). The analytical sample of **4** was obtained by crystallization from benzene-hexane mp 219 °C; UV max (benzene) 325 (3200), 412 (2000) nm; IR max 1680, 1720 cm^{-1}; NMR δ 8.20 (dd, $J_{3,4}$ = 4, $J_{2,4}$ = 1 Hz, 2 H), 7.85 (t, J = 4 Hz, 2 H), 7.50 (dd, $J_{2,4}$ = 1, $J_{2,3}$ = 1 Hz, 2 H), 4.0 (6 H); mass spectrum, *m/e* 324 (M$^+$).

Anal. Calcd for $C_{18}H_{12}O_6$: C, 66.67; H, 3.73. Found: C, 66.50; H, 3.69.

***o,o′*-Bis(2-oxocyclopentanoyl)stilbene (5).** Small portions of 2,2′-dicarboxystilbene dichloride (**2d**, 4.9 g total) were added over 0.5 h with stirring under nitrogen to an ice-cooled solution of 2-(*N*-morpholino)-1-cyclopentene[8] (10.5 g) in dry chloroform (150 mL). Stirring and cooling were continued for an additional 0.5 h and the solution was then allowed to stand overnight at room temperature. The yellow solution was transferred to a 2-L flask and 10% hydrochloric acid (20 mL) added with vigorous stirring which was continued for 1.5 h. The layers were separated, the aqueous layer was washed twice with chloroform, and the combined chloroform layers were washed, dried, and concentrated to give an oil which crystallized on standing. Trituration with methanol gave 4.56 g (70%) of **5**, mp 154–158 °C, which was sufficiently pure for subsequent steps.

The analytical sample of **5** was obtained by crystallization from methanol: mp 158–160 °C; UV (ethanol) 288 nm (ϵ 30000); IR 1350, 1480, 1600, 1700, 2900 cm^{-1}; NMR δ 11.0 (2 H, br, disappeared upon addition of deuterium oxide), 7.2–7.9 (m, 10 H), 2.2–2.8 (m, 8 H), 1.95 (q, J = 4 Hz, 2 H); mass spectrum, *m/e* 400 (M$^+$).

Anal. Calcd for $C_{26}H_{24}O_4$: C, 77.98; H, 6.04. Found: C, 78.23; H, 6.17.

***o,o′*-Bis(5-carboxypentanoyl)stilbene (6a).** **5** (2.5 g) was dissolved in 5% methanolic potassium hydroxide (250 mL), water (250 mL) added, and the resulting yellow-orange solution refluxed for 1 h and allowed to stand for 1 h at room temperature. White crystals separated upon acidification with 10% hydrochloric acid. These were filtered, washed with water, air-dried, and finally dried at 110 °C to give 2.49 g (91%) of **6a**, mp 152–153 °C, which was sufficiently pure for subsequent steps.

The analytical sample of **6a** was obtained by crystallization from benzene–methanol: mp 159–160 °C (mp with **5** 143–148 °C); UV (ethanol) 290 (ϵ 14000), sh 315 (12000) nm; IR, 3280, 2900, 2820, 1730, 1660 cm^{-1}; NMR (dimethyl-d_6 sulfoxide) δ 7.2–7.8 (m, 10 H), 3.0 (t, J = 3 Hz, 4 H), 2.2 (t, J = 3 Hz, 4 H), 1.4–1.8 (m, 8 H); mass spectrum, *m/e* 436 (M$^+$).

Anal. Calcd for $C_{26}H_{28}O_6$: C, 71.54; H, 6.47. Found: C, 71.7; H, 6.32.

The dimethyl ester (**6b**), mp 96–97 °C was prepared in 87% yield by reaction of a methanolic solution of **6a** with excess ethereal diazomethane. The analytical sample of **6b** was obtained by three crystallizations from cyclohexane and one from methanol: mp 97–99 °C; UV 291 (ϵ 15500), 313 sh (13800) nm; IR 1670, 1725 cm^{-1}; NMR δ 7.4–8.0 (10 H), 3.70 (6 H), 3.00 (t, J = 3 Hz, 4 H), 2.40 (t, J = 3 Hz, 4 H), 1.9 (quintet, 8 H); mass spectrum, *m/e* 464.

Anal. Calcd for $C_{28}H_{32}O_6$: C, 72.39; H, 6.94. Found: C, 72.50; H, 6.89.

***o,o′*-Bis(5-carboxypentyl)stilbene (7a).** A stirred mixture of diketo diacid **6a** (3.47 g), hydrazine hydrate (98%, 25 mL), and potassium hydroxide (2.5 g) in diethylene glycol (30 mL) was heated at reflux under nitrogen for 8 h. A solution of potassium hydroxide (12 g) in diethylene glycol (80 mL) was added, the reflux condenser removed, and the stirred solution heated to 197 °C and

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[15] W. H. Urry and D. J. Trecker, *J. Am. Chem. Soc.*, **84**, 118 (1962); W. H. Urry, D. J. Trecker, and D. H. Winey, *Tetrahedron Lett.*, 609 (1962).

[16] O. H. Wheeler and H. N. Battle de Pabon, *J. Org. Chem.*, **30**, 1473 (1965).

[17] R. D. Haworth, C. R. Mavin, and G. Sheldrick, *J. Chem. Soc.*, 454 (1934); F. E. King and T. J. King, *ibid.*, 1373 (1954).

[18] P. Ruggli and R. E. Meyer, *Helv. Chim. Acta*, **5**, 28 (1922).

then refluxed under nitrogen for 14 h. After cooling, the dark solution was acidified to pH 1 with concentrated hydrochloric acid and the cooled solution allowed to stand for 1 h. The resulting solid was filtered and dried to give crude **7a** (2.35 g), mp 107–110 °C. One crystallization from aqueous methanol gave **7a** (1.55 g, 48%), mp 138–141 °C, homogeneous by TLC. The analytical sample was obtained by crystallization from cyclohexane: mp 140–141 °C; UV (methanol) 288 (ϵ 21 700) nm; IR 1600, 1700, 2800, 2840, 3000 cm^{-1}; NMR δ 9.1 (2 H, the singlet disappeared upon addition of deuterium oxide), 7.1–7.8 (10 H), 2.80 (t, J = 3 Hz, 4 H), 2.30 (t, J = 3 Hz, 4 H), 1.3–2.0 (12 H); mass spectrum *m/e* 408.2259 (M$^+$), 390.2210 (M$^+$ – 18), 362.2236 (M$^+$ – 44).

Anal. Calcd for $C_{26}H_{32}O_4$: C, 76.44; H, 7.90. Found: C, 76.1; H, 8.28.

The dimethyl ester **7b** was prepared in quantitative yield by reaction of a methanol solution of the diacid with excess ethereal diazomethane. The crude product, obtained as an oil, was homogeneous by TLC and GLC and was used directly in the photocyclization: UV (cyclohexane) 288 (ϵ 19 500) nm; IR (CCl_4) 1730 cm^{-1}; NMR δ 7.1–7.8 (10 H), 3.60 (6 H), 2.80 (t, J = 3 Hz, 4 H), 2.30 (t, J = 3 Hz, 4 H), 1.3–2.0 (12 H); mass spectrum, *m/e* 408.2259 (M$^+$), 390.2210 (M$^+$ – 18), 362.2236 (M$^+$ – 44).

1,8-Bis(5-methoxycarbonylpentyl)phenanthrene (8b). A solution of diester **7b** (0.548 g) in 5 × 10^{-4} M iodine in cyclohexane (500 mL) was irradiated for 10 h while air was bubbled through the solution; progress of reaction was monitored by measurement of the UV spectrum of aliquots. The solvent was evaporated and the vessel washed with warm chloroform which was then used to dissolve the residue from cyclohexane. The chloroform was washed with sodium thiosulfate solution and water, dried, and concentrated to give an oil (0.59 g) which crystallized on standing. Crystallization from methanol gave **8b** (0.38 g, 70%), mp 81–82 °C, which was homogeneous by TLC and GLC. The analytical sample of **8b** was obtained by further crystallization from methanol: mp 82 °C; UV (methanol) 253 (ϵ 49 300), 260 (63 000), sh 267 (28 000), 287 (12 000), 293 (15 200), 306 (19 000), 330 (256), 338 (320), 345 (214), 353 (214) nm (low intensity maxima were determined in 2-methyltetrahydrofuran); IR 1730 cm^{-1}; NMR δ 8.60 (dd, $J_{3,4}$ = 4 Hz, $J_{2,4}$ = 1 Hz, 2 H), 8.0 (2 H), 7.3–7.7 (m, 4 H), 3.65 (6 H), 3.10 (t, J = 3 Hz, 4 H), 2.35 (6, J = 3 Hz, 4 H), 1.35–2.0 (12 H); mass spectrum, *m/e* 434.

Anal. Calcd for $C_{28}H_{34}O_4$: C, 77.39; H, 7.89. Found: C, 77.80; H, 7.91.

1,8-Bis(5-carboxypentyl)phenanthrene (8a). Irradiation as described above of a solution of diacid **7a** (0.22 g) in 5 × 10^{-4} M iodine in methanol (500 mL) for 10 h afforded a suspension of the desired product. The vessel was washed with a total of 500 mL of hot methanol, the combined material concentrated, 1:1 cyclohexane/benzene (100 mL) added, and the solution concentrated to remove traces of iodine to yield **8a** (0.127 g, 58%), mp 218–222 °C. The highly insoluble product could be dissolved in a large volume of boiling methanol or acetic acid: UV (methanol) 253 (ϵ 22 000), 260 (23 000), sh 267 (11 000), 281 (5500), 292 (6300), 305 (7200) nm; IR 1680, 2620 (br), 2910 cm^{-1}.

A suspension of **8a** in methanol was esterified with excess ethereal diazomethane to afford diester **8b**, identical with the material described above by comparison of UV, IR, and NMR spectra.

1,8-[6′,7′-Bis(trimethylsilyloxy)-$\Delta^{6'}$-dodecamethylene]-phenanthrene (10). Sodium (1 g) was added to a three-necked, round-bottomed flask fitted with a reflux condenser, Hershberg stirrer, and Hershberg dropping funnel and containing dry toluene (50 mL) under nitrogen. The toluene was heated to reflux while the stirrer operated at maximum speed (2500–2700 rpm). After 1–2 min, slow addition of a mixture of diester **8b** (0.50 g) and trimethylchlorosilane (13 mL) in dry toluene (15 mL) was begun and continued over a period of 1.5-2 h. Refluxing and stirring were continued for an additional 2 h. After cooling, the suspension was filtered and washed with dry toluene without allowing it to become dry. Evaporation of the solvent gave crude **10** (0.79 g) which was not stable on silica gel and was used directly in the next step.

Spectroscopic properties: UV (cyclohexane) 255 (ϵ 35 000), 262 (43 500), sh 270 (24 000), 293 (10 400), 307 (11 900) nm; NMR (deuteriochloroform without internal standard) δ 8.75 (dd, $J_{3,4}$ = 4, $J_{2,4}$ = 1 Hz, 2 H), 8.25 (2 H), 7.3–7.9 (4 H), 3.30 (t, J = 3 Hz, 4 H), 1.0–2.0 (16 H), 0.2–0.4 (18 H); mass spectrum, *m/e* 518 (M$^+$).

1,8-(6′-Hydroxy-7′-oxododecamethylene)phenanthrene (11). The bis(trimethylsilyl ether) **10** (0.79 g) in tetrahydrofuran (50 mL) and hydrochloric acid (1 N, 5 mL) was refluxed with stirring under nitrogen for 3 h. After cooling, the solution was treated with solid calcium carbonate (5 g) and filtered, and the solvent evaporated. The residue was taken up in chloroform, dried, and concentrated to give an oily solid (0.54 g) which afforded crude acyloin **11** (0.343 g, 80% based on diester), mp 153–156 °C after trituration with ether; this was used directly in the next step.

The analytical sample of **11**, mp 170–171 °C, was obtained by preparative-scale TLC (silica gel) using chloroform as eluant: UV (methanol) 253 (ϵ 32 500), 260 (41 500), 282 (7850), 293 (8800), 305 (11 200) nm; UV (2-methyltetrahydrofuran) 331 (ϵ 282), 337 (356), 346 (234), 355 (252) nm; IR 1700, 2900, 3400 cm^{-1}; NMR δ 8.50 (dd, $J_{3,4}$ = 4, $J_{2,4}$ = 1 Hz, 2 H), 8.0 (2 H), 7.3–7.8 (4 H), 3.9 (d, J = 4 Hz, 1 H), 3.4 (1 H, disappeared upon addition of deuterium oxide), 3.2 (t, J = 3 Hz, 4 H), 0.9–2.1 (16 H); mass spectrum, *m/e* 374.2209 (M$^+$), 356.2097 (M$^+$ – 18), 346.2302 (M$^+$ – 28).

Anal. Calcd for $C_{26}H_{30}O_2$: C, 83.38; H, 8.07. Found: C, 83.18; H, 8.27.

The substance was slowly oxidized in air.

The material soluble in ether (0.23 g) contained some **11** (by TLC) and could be carried through the next step.

1,8-(6′,7′-Dioxododecamethylene)phenanthrene (1). A mixture of acyloin **11** (0.343 g), dimethyl sulfoxide (10 mL), and acetic anhydride (8 mL) was allowed to stand for 60 h at room temperature in the dark. Water (20 mL) was added and the system extracted with chloroform (2 × 20 mL). The chloroform extracts were washed with water and 5% sodium bicarbonate, dried, and concentrated (final concentration under high vacuum) to give crude **1** (0.370 g) as a yellow glass. The product (0.190 g, 55%) was isolated in pure form by preparative-scale TLC on silica gel by using 1:1 benzene/hexane as eluant. A center cut (60 mg) was rechromatographed by developing successively with 1:1 benzene/hexane, benzene, 3:7 chloroform/hexane, and 3:2 chloroform/hexane; the product was recovered almost quantitatively. The ratio between absorbance at λ_{max} 448 nm and λ_{min} 392 nm was 2.88 and was not changed by further chromatography. Repeated attempts to crystallize the product were unsuccessful: UV (acetonitrile) 253 (ϵ 42 000), 261 (52 500), 282 (11 000), 293 (11 000), 306 (13 300), 337 (290), 354 (212), 448 (25.2) nm; IR 1710, 2890 cm^{-1}; NMR δ 8.50 (dd, $J_{3,4}$ = 4, $J_{2,4}$ = 1 Hz, 2 H), 7.9 (2 H), 7.3–7.8 (4 H), 3.2 (t, J = 3 Hz, 4 H), 2.45 (t, J = 3 Hz, 4 H), 0.6–1.8 (12 H); mass spectrum, *m/e* 372.2188 (M$^+$, 20%), 344.2087 (M$^+$ – CO) (calcd for $C_{26}H_{28}O_2$ (M$^+$) 372.2089).

The quinoxaline (**12**) was prepared by treating diketone **1** (30 mg) in ethanol (0.5 mL)–benzene (5 mL) with *o*-phenylenediamine (9 mg) dissolved in a few drops of ethanol. After 5 drops of acetic acid was added and the solution boiled for 5 min, a white solid (10 mg) separated. A pure sample (7 mg) of **12**, mp 245 °C, was obtained by preparative TLC by developing first with chloroform–hexane (6:4) and then with chloroform: UV (methanol) 238 (ϵ 32 000), 252 (26 000), 260 (29 000), sh 268 (16 000), 292 (8800), 305 (10 000), 316 (3200) nm; IR 2860 cm^{-1}; mass spectrum, *m/e* 444.2621 (calcd for $C_{32}H_{32}N_2$ 444.2565).

Clemmensen Reduction of 6a. *o,o′*-Bis(5-carboxypentyl)-1,2-diphenylethane (9). A suspension of zinc dust (30 g) and mercuric chloride (2.25 g) in water (37 mL) was treated with concentrated hydrochloric acid (1.5 mL). After the solution was stirred for 5 min, the liquid was decanted and the amalgam covered with a mixture of concentrated hydrochloric acid (30 mL) and water (22 mL). The diketo diacid **6a** (2.25 g) dissolved in hot acetic acid (100 mL) was added, and the mixture was stirred at reflux for 10 h with addition of portions (15 mL) of concentrated hydrochloric acid every 2 h. Refluxing and stirring was continued overnight, and the solution was allowed to cool slowly. The resulting crystals were filtered, washed with water, and air-dried to give a mixture (1.57 g) of stilbene **7a** and diarylethane **9**. One crystallization from aqueous methanol gave a purified mixture (1.1 g, 52%), mp 99–101 °C. TLC on silica gel with chloroform–methanol (2:3) gave a single spot.

Photocyclization of a portion of the mixture as described above for pure **7a** gave phenanthrene **8b** (20%) identical with material described above. Evaporation of the methanol-soluble portion and crystallization gave **9** (75%), mp 99–100 °C. The analytical sample of **9** was obtained by crystallization from cyclohexane: mp 102–103 °C; UV (methanol) 262 (8900), 271 (6900), 291 (1700), 303 (1600) nm; IR 1710, 2900, 3000 cm^{-1}; NMR δ 10.30 (2 H, disappeared upon addition of deuterium oxide), 7.30 (8 H), 2.90 (4 H), 2.2–2.8 (8 H), 1.3–2.0 (12 H); mass spectrum, *m/e* 410.2448 (M$^+$), 392, 374.

Anal. Calcd for $C_{26}H_{34}O_4$: C, 76.06; H, 8.34. Found: C, 76.23; H, 7.97.

The stilbene **7a** was recovered unchanged in 90% yield from treatment with zinc amalgam as described above.

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Registry No. 1, 70161-78-3; *cis*-**2a**, 20657-42-5; *trans*-**2a**, 36888-18-3; **2b**, 56526-10-4; **2c**, 73049-16-8; **2d**, 73049-17-9; **3a**, 15815-47-1; **3b**, 73049-18-0; **3c**, 38378-77-7; **4**, 73049-19-1; **5**, 73049-20-4; **6a**, 73049-21-5; **6b**, 73049-22-6; **7a**, 73049-23-7; **7b**, 73049-24-8; **8a**, 73049-25-9; **8b**, 70161-79-4; **9**, 73049-26-0; **10**, 73061-94-6; **11**, 73049-27-1; **12**, 73049-28-2; 2-(*N*-morpholino)-1-cyclopentene, 936-52-7; *o*-phenylenediamine, 95-54-5.

Vinylphosphonium Bicycloannulation of Cyclohexenones and Its Use in a Stereoselective Synthesis of Trachyloban-19-oic Acid[1]

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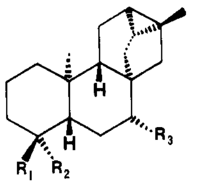
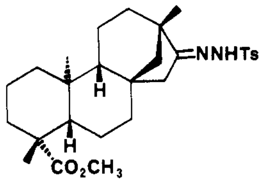
Tricyclo[3.2.1.0^{2,7}]octan-6-ones are prepared in a single step from α-cyclohexenones by reaction of the α' enolates of the latter with vinyl- or isopropenyltriphenylphosphonium bromide. The α-substituted vinylphosphonium salt generally gives higher yields and faster reaction rates than the parent compound. With 4,4-dimethylcyclohex-2-en-1-one, the major products result from the condensation of 2 mol of phosphonium salt per mol of enone; this anomaly can be ascribed to steric hindrance. In a model study, the ring system of the sesquiterpene ishwarane is constructed in one step from Δ^2-1-octalone and the isopropenyl salt. Podocarpic acid is converted to trachyloban-19-oic acid, the enantiomer of a sunflower diterpene, by using this bicycloannulation method as the key step.

The common sunflower (*Helianthus annuus* L.)[2] contains in its flower head,[3] roots,[4] and shoots[4] large amounts of *ent*-trachyloban-19-oic acid[5] (**1**), a member of the rare pentacyclic (trachylobane) diterpene class. Not long after Pyrek reported[3] the discovery of this natural product in 1970, the closely related derivative ciliaric acid (**2**) was found in two other sunflower species, *H. ciliaris*[6] and *H. laciniatus*,[7] and was correlated by conversion[6] to **1**. The trachylobane terpenes[8] as a whole are biogenetically important in that their carbon skeleton represents a deprotonated form of a key intermediate proposed[9] by Wenkert for the biosynthesis of the tetracyclic diterpenes, and the discovery[10] of this system in nature (trachylobanic acid **3**) helped to confirm his hypothesis.[11,12] The recent isolation[13] of trachylobane itself (**4**) together with all the basic types of tetracyclic diterpenes from one source, the monkey



1 $R_1 = CH_3$, $R_2 = CO_2H$, $R_3 = H$
2 $R_1 = CH_3$, $R_2 = CO_2H$, $R_3 = OH$
3 $R_1 = CO_2H$, $R_2 = CH_3$, $R_3 = H$
4 $R_1 = R_2 = CH_3$, $R_3 = H$
5 $R_1 = CH_3$, $R_2 = CO_2CH_3$, $R_3 = H$



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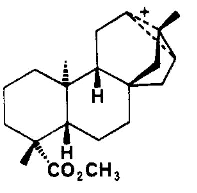

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(1) Bicycloannulation. 5. For the previous paper in this series, see R. M. Cory, L. P. J. Burton, and R. G. Pecherle, *Synth. Commun.*, **9**, 735 (1979).

(2) C. B. Heiser, "The Sunflower", University of Oklahoma Press, Norman, OK, 1976.

(3) (a) J. St. Pyrek, *Tetrahedron*, **26**, 5029 (1970); (b) O. Achmatowicz, Jr., A. Ejchart, L. Kozerski, and J. St. Pyrek, *J. Chem. Soc., Chem. Commun.*, 98 (1971).

(4) Z. Kasprzyk, W. Janiszewska, and M. Papaj, *Bull. Acad. Pol. Sci., Ser. Sci. Biol.*, **22**, 1 (1974).

(5) In the original name for this compound[3] the prefix ent was omitted.

(6) L. F. Bjeldanes and T. A. Geissman, *Phytochemistry*, **11**, 327 (1972).

(7) A. Ortega, A. Ayala, C. Guerrero, and A. Romo de Vivar, *Rev. Soc. Quim. Mex.*, **16**, 191 (1972).

(8) J. R. Hanson in "Chemistry of Terpenes and Terpenoids", A. A. Newman, Ed., Academic Press, New York, 1972, Chapter 4, p 155; R. McCrindle and K. H. Overton in "Advances in Organic Chemistry, Methods and Results", Vol. 5, R. A. Raphael, E. C. Taylor, and H. Wynberg, Eds., Interscience, New York, 1965, p 47.

(9) E. Wenkert, *Chem. Ind.* (*London*), 282 (1955).

(10) G. Hugel, L. Lods, J. M. Mellor, D. W. Theobald, and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1974 (1963); 2882, 2888, 2894 (1965).

(11) A. C. Oehlschlager and G. Ourisson in "Terpenoids in Plants", J. B. Pridham, Ed., Academic Press, New York, 1967, Chapter 5, p 83.

(12) For further work in this area see: R. A. Appleton, A. J. McAlees, A. McCormick, R. McCrindle, and R. D. H. Murray, *J. Chem. Soc. C*, 2319 (1966); A. J. McAlees, R. McCrindle, and S. T. Murphy, *J. Chem. Soc., Perkin Trans. 1*, 1042 (1976); D. R. Robinson and C. A. West, *Biochemistry*, **9**, 70, 80 (1970); J. W. ApSimon and S. F. Hall, *Can. J. Chem.*, **56**, 2156 (1978).

0022-3263/80/1945-1852$01.00/0