Octahydroanthracene as a Bridging Unit for Juxtaposed Aromatic Rings

William C. Christopfel and Larry L. Miller*

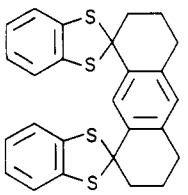
Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received June 25, 1984

The syntheses of two bis-dithioketal derivatives of 3,4,5,6-tetrahydro-1(2*H*),8(7*H*)-anthracenedione are described. The X-ray structure of the compound from 1,2-dimercaptobenzene is reported.

Molecules with enforced juxtaposition of aromatic rings have held special fascination for chemists. The long and continued interest in the properties and detailed structures of cyclophanes, in which the rings are stacked, most thoroughly reveals this fascination.[1] The utility of these structural types may be realized in the cofacial porphyrins where juxtaposition of the rings provides a unique catalyst for the reduction of oxygen to water.[2] Related phenomena of importance in biochemistry as well as solid state chemistry are stacking and intercalation of planar molecules.

On this basis, other molecular modules which would allow the juxtaposition of aromatic rings would be useful. We point out that an octahydroanthracene unit can provide a regiospecific bridge between two attached rings. In compounds like 1, the two rings are held close together



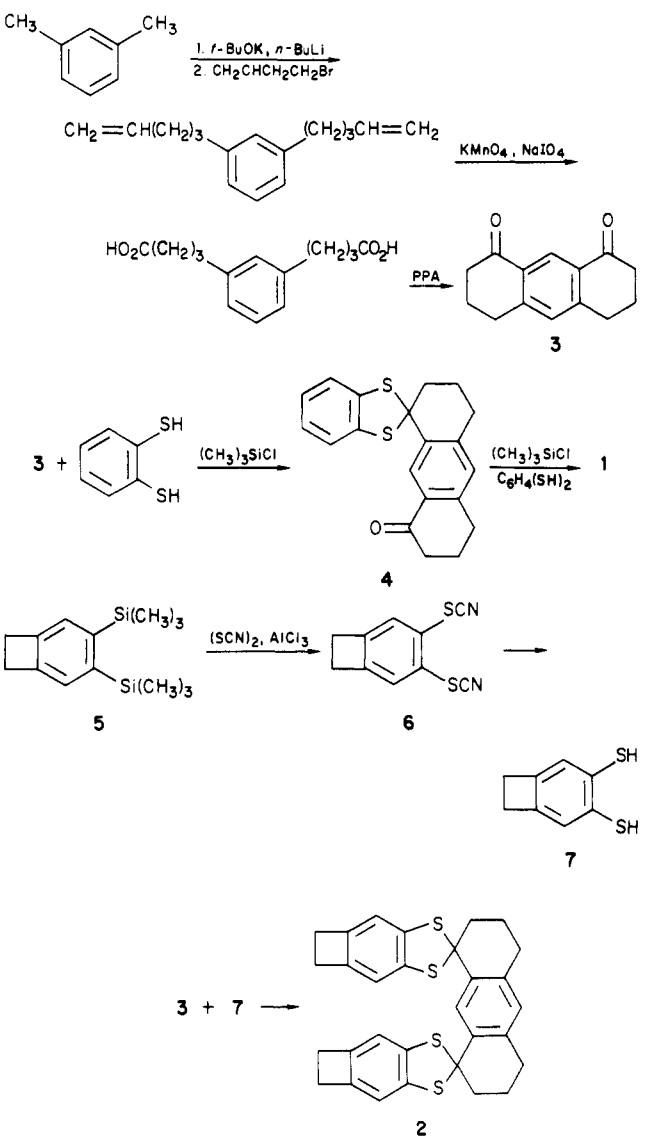
1

without the possibility of internal rotations as a consequence of the two spiro linkages at the 1 and 8 positions of the octahydroanthracene bridge. These positions are about 5 Å apart. 1,8-Disubstituted anthracenes have been prepared recently[3] for similar purposes. By comparison, compound 1 does not allow rotation of the aromatic groups attached to the anthracene unit. Since compounds like 1 should be synthetically accessible, the octahydroanthracene bridging module may prove useful in a variety of fields. The preparation of two such compounds is reported here. It is an additional intellectual curiosity that these compounds may be considered orthocyclophanes. The two bridges are incorporated in the octahydroanthracene structure, but it is obvious that the ortho substituents are joined as they should be in an orthocyclophane.

Results and Discussion

Compounds 1 and 2 were chosen as initial synthetic targets because a plausible and generalizable synthetic approach could be designed. The approach involved as the last step the bis-thioketalization of 3,4,5,6-tetrahydro-1(2*H*),8(7*H*)-anthracenedione (3). This previously unknown diketone was, therefore, prepared and, indeed, thioketalized as shown. A transformation of particular synthetic interest in the synthesis of 2 was the two-step replacement of trimethylsilyl groups with thio groups, i.e. 5 → 6 → 7. This procedure could have general utility.

Scheme I



Initial forays to produce 3 directly by oxidation of 1,2,3,4,5,6,7,8-octahydroanthracene were unsuccessful and in practice, *m*-xylene was converted to its dianion by using potassium *tert*-butoxide and *n*-butyllithium.[4] The dianion was alkylated with 4-bromo-1-butene to give a mixture of mono- and dialkylated products (Scheme I). The desired dipentenylbenzene was separated by distillation (66% yield) and then oxidized to the dicarboxylic acid. The oxidation method of Lemieux and von Rudolf[5] involves the

(1) *Top. Current Chem.* **1983**, *113*, 115.
(2) Collman, J. P.; et al. *J. Electroanal. Chem.* **1979**, *101*, 117.
(3) Chang, C. K.; Abdalmuhdi, I. *J. Org. Chem.* **1983**, *48*, 5388. Chang, C. K.; Abdalmuhdi, I.; Liu, H. Y. *J. Am. Chem. Soc.* **1984**, *106*, 2725.
(4) Bates, R. B.; Hess, B. A., Jr.; Ogle, C. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1981**, *103*, 5052.
(5) Lemieux, R. U.; von Rudloff, E. *Can. J. Chem.* **1955**, *33*, 1701. Von Rudloff, E. *Ibid.* **1956**, *34*, 1413. ApSimon, J. W.; Chau, A. S. Y.; Craig, W. G.; Krehm, H. *Ibid.* **1967**, *45*, 1439.

0022-3263/84/1949-5198$01.50/0

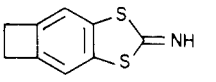
alkene, permanganate, and periodate in a rather complex catalytic cycle. Solvent mixtures of *tert*-butyl alcohol and water were employed in order to accommodate the disparate solubilities of olefin and their inorganic oxidants. Too much water gave no oxidation and too little water quenched the catalytic cycle producing only manganese dioxide.

The diacid was cyclized to the diketone with hot polyphosphoric acid to give an isolated yield of 34%.[6] In this Friedel–Crafts acylation one would expect the first ring forming acylation to proceed readily and the second (now on a deactivated aromatic nucleus) to proceed with difficulty. Although diacylations of aromatic rings are often discussed as impractical, the literature does include examples of good yields for such reactions.[6]

The thioketalization reaction between **3** and 1,2-dimercaptobenzene to give **1** was found to proceed almost quantitatively in chloroform in the presence of excess trimethylsilyl chloride.[7] The trimethylsilyl chloride probably facilitates this reaction because of its greater affinity for oxygen than sulfur. Thus, the trimethylsilyl chloride can activate the ketone functions by coordination with the ketone oxygen without deactivating the sulfur by reaction with the thiol groups.

At short reaction times for the thioketalization procedure the monoadduct **4** could be prepared. This is of potential interest because two different aromatic groups could be attached by sequential reactions. The ^{1}H NMR spectra of **4**, **3**, and **1** are of interest in that the 9′-hydrogen located on the central ring between the two functional groups shows large changes in chemical shift. Going from **3** to **4** to **1** the δ values are 8.63, 9.13, and 9.66. ^{13}C NMR spectra of compound **1** were also instructive. In the aromatic region of the wide-band proton-decoupled spectrum there were seven peaks as expected. A combination of relative peak intensities, APT pulse sequence, and a comparison of chemical shifts with 1,2-dimercaptobenzene indicated that the 9′-carbon resonance was at δ 132.73. This is shifted from 129.04 in the diketone **3**. The assignment was confirmed by a set of specific proton-decoupled spectra. When the 9′-H was irradiated the ^{13}C line at 132.73 was a singlet. When it was not irradiated the 132.73 peak split into a doublet. It can be seen that, like the 9′-hydrogen, the 9′-carbon peak is shifted to lower field in going from **3** to **1**. Since the through bond inductive effects of replacing ketone with dithioketal should not produce this shift, it is proposed to come from a through space effect. In particular it most likely arises from the induced aromatic ring current of the dithiobenzene rings. If these rings are "butterflied" out, it will place the 9′-hydrogen in their deshielding plane. The X-ray structure (see below) confirms this conformational feature.

Compound **2** was prepared starting with a cobalt-catalyzed cyclotrimerization to **5**. The aromatic electrophilic ipso substitution of the two trimethyl silyl groups of 1,2-dihydro-4,5-bis(trimethylsilyl)benzocyclobutene (**5**)[13] with thiocyanato groups to give **6** was accomplished using thiocyanogen[14] in chloroform with aluminum chloride.[15] The 1,2-dihydro-4,5-dithiocyanobenzocyclobutene (**6**) was obtained in 54% yield. This substitution reaction was also carried out by using thiocyanogen chloride[16] in acetic acid as the electrophilic reagent. This reagent gave a cleaner reaction but the reaction did not go to completion, giving a considerable amount of the monothiocyanation product. Over all, the reactions with thiocyanogen and aluminum chloride gave a better yield than that using thiocyanogen chloride. The dithiocyano compound was successfully reduced to 1,2-dihydro-4,5-dimercaptobenzocyclobutene (**7**) in greater than 90% yield with sodium borohydride in refluxing ethanol[17] or with sodium metal in liquid ammonia.[18] The sodium metal/liquid ammonia procedure offered no advantage over sodium borohydride and was not subsequently used. Reduction with triphenylphosphine in aqueous methanol was unsuccessful. A partially reduced compound, tentatively identified as **8**,



8

was formed. The thioketalization of diketone **3** with 1,2-dihydro-4,5-dimercaptobenzocyclobutene (**7**) to give **2** was accomplished in two ways; first, in low yield, by the treatment of a mixture of the two in refluxing benzene with *p*-toluenesulfonic acid,[19] and second, in 98% isolated yield, by the reaction of **7** and **3** in chloroform with excess trimethylsilyl chloride in the same way as for **1**. Compound **2** was a white crystalline solid that was thermally stable up to approximately 250 °C and seems to be quite air-stable. In the ^{1}H NMR spectrum of **2** the cyclobutyl hydrogens appear as a doublet because of the different chemical environments of the "inside" and "outside" hydrogens, and the 9′ hydrogen, as in compound **1**, is shifted downfield.

The structure of **1** was elcuidated by single-crystal X-ray diffraction. Two conformers were present in the crystal. The "syn" conformer had the two dimercaptobenzene rings tilted by 9° from the plane determined by the anthracene central ring (see Figure 1A). The "anti" conformer had the two dithiobenzene rings tilted by 12° and 16° from the anthracene plane (Figure 1C). In each case this feature results from the nonplanar conformation of the "cyclohexene" rings. In addition, both conformers have a "butterfly" shape in which the dimercaptobenzene rings are tilted away from each other (Figures 1B and 1D). It seems likely that this feature is due to the hybridization at sulfur. This noncofacial arrangement might allow complexation of certain nonplanar acceptor species like carbon tetrachloride. Cofacial stacking of the two rings will be enhanced by a structure with an attractive, e.g., donor–acceptor, interaction between the rings.

Experimental Section

General Methods. Melting points were determined on a Mel-Temp capillary melting point apparatus and were uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 297 infrared spectrophotometer and were calibrated with the 1601.8-cm^{-1} absorption of polystyrene. ^{1}H NMR spectra were measured at 79.5 Hz on a Varion CFT-20 instrument and at 300 Hz on a Nicholet NT-300-WB instrument. Chemical shifts are

(6) Snyder, H. R.; Werber, F. X. *J. Am. Chem. Soc.* **1950**, *72*, 2965. Mosby, W. L. *J. Org. Chem.* **1954**, *19*, 294. Popp, F. D.; McEwen, W. E. *Chem. Rev.* **1958**, *58*, 321.
(7) Omg, B. S.; Cham, T. H. *Synth. Commun.* **1977**, *7*, 283. Caine, D.; Frobese, S. A. *Tetrahedron Lett.* **1978**, 883.
(8) Carlson, R. M.; Oyler, A. R. *Tetrahedron Lett.* **1974**, 2615.
(9) Pendarvis, R. O.; Hampton, K. G. *J. Org. Chem.* **1974**, *39*, 2289.
(10) Klein, J.; Medlik-Balan, A. *J. Am. Chem. Soc.* **1977**, *99*, 1473.
(11) Klein, J.; Medlik, A.; Meyer, A. Y. *Tetrahedron* **1976**, *32*, 51.
(12) Syper, L. *Tetrahedron Lett.* **1966**, 4493.
(13) Hillard, R. L., III; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1977**, *99*, 4058.
(14) Wood, J. L.; Fieser, L. F. *J. Am. Chem. Soc.* **1941**, *63*, 2323. Wood, J. L. *Org. React. (N.Y.)* **1946**, *3*, 255.
(15) Soderback, E. *Acta. Chem. Scand.* **1954**, *8*, 1851.
(16) Bacon, R. G. R.; Guy, R. G. *J. Chem. Soc.* **1960**, 318.
(17) Olsen, R. K.; Snyder, H. R. *J. Org. Chem.* **1965**, *30*, 184.
(18) Degani, I.; Fochi, R. *Synthesis* **1976**, 471. Ferretti, A. *Org. Synth.* **1973**, *5*, 419.
(19) Degani, I.; Fochi, R. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1133.

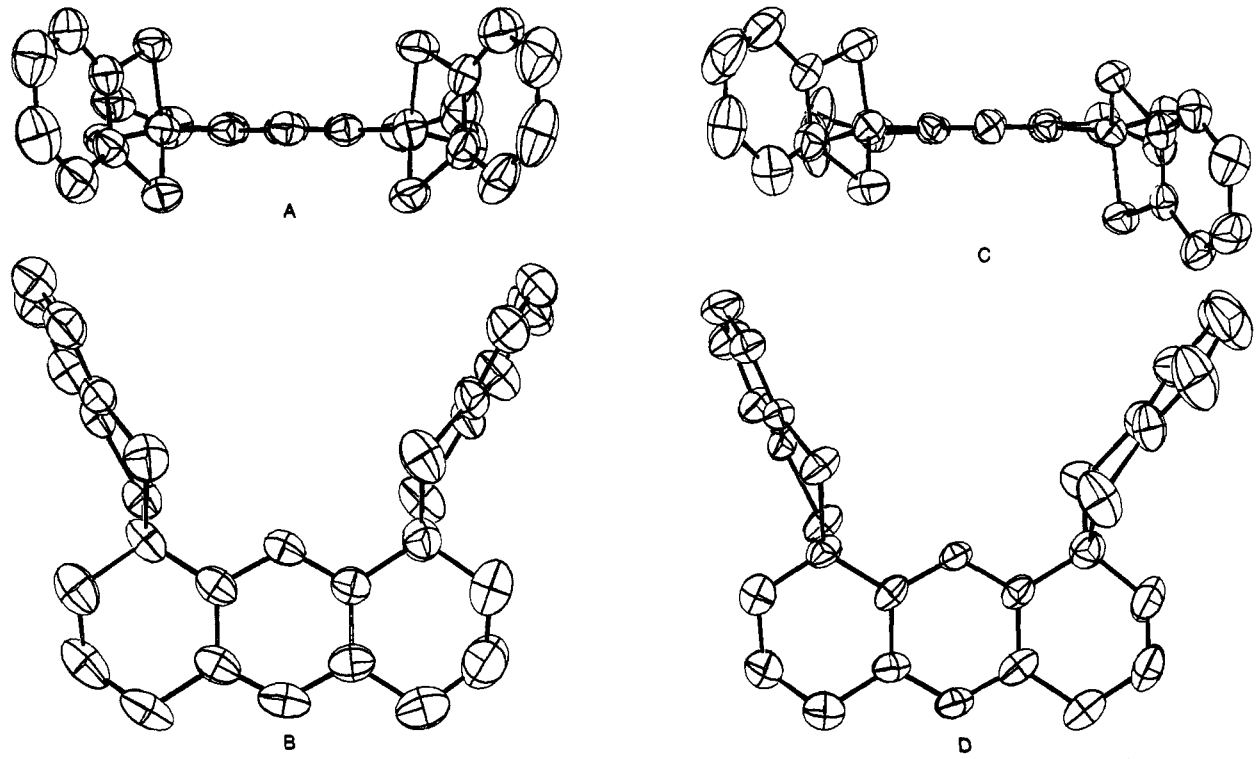


Figure 1. ORTEP drawing of 1 with hydrogen atoms omitted. Ellipsoid volumes show 50% probability of enclosure: (A, B) symmetrical conformer; (C, D) anti conformer.

reported in δ units relative to internal Me_4Si. Mass spectra were measured at 70 eV on an AEI MS-30 instrument. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Analytical vapor-phase chromatography data were obtained on a Varian Model 3700 gas chromatograph.

1,3-Bis(4-pentenyl)benzene. A dry 500-mL three-necked round-bottomed flask was fitted with a nitrogen bubbler, a reflux condenser, a magnetic stirring bar, and a 125-mL pressure equalizing dropping funnel. To this flask were added potassium *tert*-butoxide (16.8 g, 0.15 mol), hexane (250 mL, distilled from sodium metal), and *m*-xylene (8.52 mL, 0.070 mol, dried over 4-Å molecular sieves). With stirring at room temperature *n*-butyl lithium (2.1 M in hexane, 72.97 mL, 0.153 mol) was added dropwise over 20 min via the addition funnel. The reaction mixture was then heated at reflux for 1 h and let cool to room temperature to give a yellow/brown suspension of the dipotassium salt of *m*-xylene.[4]

This mixture was cooled in a dry ice/acetone bath and 4-bromo-1-butene (54.2 g, 40.75 mL, 0.4 mol) was added in one portion. The reaction mixture was stirred with cooling for 10 min, and then the cooling bath was removed and the mixture allowed to warm to room temperature. The reaction mixture became colorless upon warming, at which point the reaction was probably complete, but for convenience it was stirred at room temperature overnight.

The reaction mixture was gently washed with two portions of water (vigorous shaking caused an emulsion), and the hexane phase was dried over sodium sulfate and concentrated under reduced pressure to give a light yellow liquid. This liquid was shown by gas chromatography, using a 16 ft Ni column with 10% Carbowax 20M on 80/100-mesh Chrom W AWDMCS and a temperature program from 90 °C at a rate of 8°/min, to be composed mostly of the desired diolefin and the monoolefin resulting from partial alkylation. The total yield of diolefin as determined by gas chromatography was 9.88 g (66.3%). Purification was effected by fractional distillation. The purest cut of diolefin (96.3% by GC) distilled between 90 and 95 °C at 0.05 torr. All of the fractions were analyzed by GC and the middle fractions were combined to give a mixture containing greater than 90% of diolefin which was used satisfactorily for the following reactions: NMR acetone-d_6, 79.5 mHz) δ 7.0 (m, 4 H), 5.82 (m, 1 H), 5.05 (d, J = 12 Hz, 1 H), 4.87 (d, J = 4 Hz, 1 H), 2.57 (t, J = 15.2 Hz, 2 H), 2.27–1.57 (m, 4 H); IR ($CHCl_3$) 2850, 1639, 1605, 1587, 1440 cm^{-1}; mass spectrum, m/e 214 (parent ion); high-resolution mass spectrum calcd for $C_{16}H_{22}$ 214.1722, found 214.1724.

1,3-Bis(3-carboxypropyl)benzene. A 250-mL three-necked round-bottomed flask was fitted with two 50-mL addition funnels, a magnetic stirring bar and a pH electrode. To this flask was added sodium metaperiodate (8.0 g, 37.38 mmol), water (150 mL), and potassium permanganate (220 mg, 1.40 mmol). This mixture was stirred until homogeneous and was then adjusted to pH 8 by the dropwise addition of a 5% aqueous potassium carbonate solution (w/w). A solution of 1,3-bis(4-pentenyl)benzene (1.0 g, 4.67 mmol) in *tert*-butyl alcohol (30 mL) was added in one portion to the reaction flask, and the resulting mixture was stirred vigorously. *tert*-Butyl alcohol was added to the vigorously stirred reactions mixture in 10-mL portions until the pH began to drop slowly (about 30–40 mL). The reaction mixture was maintained at approximately pH 8 by the periodic addition of 5% aqueous potassium carbonate solution. The reaction mixture underwent a color change from purple to burgundy to brown. When the mixture became brown no further oxidation was observed to occur.

The reaction mixture was cautiously acidified (pH $\leq$1) with concentrated hydrochloric acid and then sodium bisulfite was added until the mixture became a clear, homogeneous, light yellow solution. This solution was concentrated under reduced pressure to remove the *tert*-butyl alcohol and was then extracted 3 times with diethyl ether.

The diethyl ether extracts were concentrated under reduced pressure, and the residue was dissolved in 10% aqueous sodium hydroxide. This solution was washed twice with methylene chloride, acidified to pH 1 with concentrated hydrochloric acid, and extracted 3 times with diethyl ether. The combined ether extracts were dried over sodium sulfate and concentrated under reduced pressure to give the crude product as a white solid, 0.818 g (77.8%). This material was crystallized from toluene to give 0.58 g (55.4%) of a white powder: mp 132–136 °C [lit.[20] mp 135–136.2 °C); NMR (Acetone-d_6, 79.5 mHz) δ 7.08 (m, 4 H), 2.66 (t, 4 H), 2.25 (m, 4 H), 1.98 (m, 4 H); IR (KBR) 2950, 1686, 1428, 1407, 1339, 1274, 1205 cm^{-1}; mass spectrum, m/e 250 (parent ion). Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25; O, 25.57. Found: C, 66.96; H, 7.29; O, 25.33.

(20) Schimelpfenig, C. W. *J. Org. Chem.* **1975**, *40*, 1493.

3,4,5,6-Tetrahydro-1(2*H*),8(7*H*)-anthracenedione (3). Polyphosphoric acid (12.72 g) was added to a dry 25-mL two-necked round-bottomed flask under nitrogen which was then heated in an oil bath to 100 °C (oil bath temperature). The 1,3-bis(4-carboxypropyl)benzene (403.1 mg, 1.61 mmol) was then added in one portion with vigorous manual stirring using a glass rod to quickly give a brown mixture. The temperature of the oil bath was then increased to 135 °C over 15 min with frequent manual stirring of the reaction mixture. The reaction flask was then removed from the oil bath and the reaction mixture was quenched with crushed ice. Ether was added to dissolve the solid, and the ether phase was washed twice with 5% aqueous sodium hydroxide and then with water until the water washes were no longer basic. The ether phase was dried over sodium sulfate and concentrated under reduced pressure to give a pale yellow solid (252.3 mg) which was dissolved in acetone and decolorized with activated charcoal to give a white solid. This solid was crystallized from carbon tetrachloride (6 mL) to give 116.2 mg (33.6%) of a white crystalline solid: mp 198–199.5 °C; NMR ($CDCl_3$, 79.5 mHz) δ 8.63 (s, 1 H), 7.10 (s, 1 H), 2.93 (t, J = 6.0 Hz, 4 H), 2.62 (t, J = 6.0 Hz, 4 H), 2.11 (m, 4 H); IR (KBr) 2947, 2883, 1682, 1605, 1458, 1438, 1428, 1405 cm^{-1}; mass spectrum, m/e 214 (parent ion). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59; O, 14.93. Found: C, 78.62; H, 6.60; O, 14.74.

2′,3′,4′,5′,6′,7′-Hexahydrodispiro[1,3-benzodithiole-2,1′-anthracene-8′,2″-[1,3]benzodithiole] (1). A dry 10-mL two-necked round-bottomed flask was fitted with a nitrogen bubbler and a magnetic stirring bar. To this flask was added diketone **3** (170 mg, 0.79 mmol), 1,2-dimercaptobenzene[21] (395 mg, 2.78 mmol), $CHCl_3$ (4 mL), and trimethylsilyl chloride (distilled from tri-*n*-butylamine under nitrogen, 1.51 g, 1.8 mL, 13.9 mmol). The reaction mixture was stirred at room temperature for 113.5 h and then diluted with $CHCl_3$ (25 mL) and washed with 25 mL of 5% aqueous sodium carbonate. The chloroform phase was concentrated under reduced pressure to give a yellow/white solid. This solid was dissolved in hot carbon tetrachloride (6 mL), let cool to room temperature, and filtered. Storage in the freezer overnight gave a white powder (183.5 mg, 50.0%). More product was obtained from the mother liquor by preparative thin-layer chromatography on silica gel. The material was applied to the plate as a solution in methylene chloride, and then the plate was developed first in hexane and then in carbon tetrachloride to give a white solid (165 mg, 45%). The combined yield was 95% based on diketone **3**. A white crystalline material can be obtained from toluene.

The white powder obtained from carbon tetrachloride was characterized spectroscopically: ^1H NMR ($CDCl_3$, 300 mHz) δ 9.66 (s, 1 H), 7.05 (m, 8 H), 6.80 (s, 1 H), 2.78 (t, J = 6.3, 4 H), 2.60 (m, 4 H), 1.99 (m, 4 H); ^{13}C NMR 138.55, 137.61, 132.73, 132.15, 129.58, 125.63, 122.09, 71.126, 41.93, 29.22, 20.01; IR (KBr) 2941, 1563, 1492, 1443, 1115 cm^{-1}; mass spectrum, m/e 462 (parent ion); high-resolution mass spectrum calcd for $C_{26}H_{22}S_4$ 462.0602, found 462.0590.

Plate-like crystals suitable for X-ray diffraction studies were obtained by crystallization from toluene. The crystals were monoclinic, space group $C2/c$, with a = 41.442 (6) Å, b = 14.594 (2) Å, c = 14.983 (2) Å, β = 97.42 (1)°; 16 molecules/unit cell; calculated density 1.368 g/cm^3. Data were collected for $0 < \phi < 62°$; 7051 independent reflections were measured, of which the 3568 with $I > 3\sigma(I)$ were used in the calculations. A combination of direct methods and difference Fourier syntheses was used to locate all non-hydrogen atoms. Anisotropic thermal refinement was applied to all non-hydrogen atoms. Hydrogen atoms were included at idealized positions with isotropic thermal parameters one unit larger than those of the carbon atoms to which they were attached. The R factor for the structure was 0.060. An ORTEP drawing is shown in Figure 1 where the hydrogen atoms are left out for clarity. Positional parameters, thermal parameters, and interatomic distances and angles are available as supplementary material.

2′,3′,4′,5′,6′,7′-Hexahydrospiro[1,3-benzodithiole-2,1′-anthracen]-8′-one (4). Into a 1.5-mL reaction vial containing a magnetic stirring bar was added diketone **3** (31.5 mg, 0.147 mmol), 1,2-benzenedithiol (62.6 mg, 0.441 mmol), and chloroform (0.5 mL). The vial was purged with nitrogen, and chlorotrimethylsilane (0.2 mL, 1.58 mmol, distilled from tri-*n*-butylamine under N_2) was added at room temperature in one portion. The reaction mixture was stirred at room temperature under nitrogen and followed by TLC (silica gel developed in methylene chloride and stained with iodine). The spot corresponding to starting diketone **3** (R_f ~0.2) slowly faded and two new spots appeared (R_f 0.7 and 0.9). After about 70 h the spot corresponding to starting material was completely gone. At this time the reaction mixture was quenched with about 10 mL of 5% aqueous sodium carbonate, then more chloroform was added (4 mL) and after agitation the phases were separated. The chloroform phase was concentrated under reduced pressure and the residue was purified by preparative TLC using silica gel with methylene chloride. The material with R_f 0.9 was a white solid and was identified as the dithioketaled product **1** (20.5 mg). The material with R_f 0.7, also a white solid, was identified as the monothioketal product **4**: NMR ($CDCl_3$, 79.5 MHz) δ 9.13 (s), 7.17–6.97 (m), 2.94–2.74 (m), 2.69–2.49 (m), 2.19–1.94 (m); IR (CH_2Cl_2) 1680 cm^{-1}; mass spectrum, m/e 338 (parent ion); high-resolution mass spectrum calcd for $C_{20}H_{18}OS_2$ 338.0799, found 338.0795.

1,2-Dihydro-4,5-dithiocyanobenzocyclobutene (6). Preparation of Thiocyanogen.[14] A dry 250-mL three-necked round-bottomed flask was fitted with a nitrogen bubbler, a magnetic stirring bar, and a 60-mL pressure equalizing addition funnel. To this flask was added lead(II) thiocyanate (9.79 g, 30.28 mmol, crystallized in the dark from water (5 g from 300 mL) and dried in the dark under high vacuum at refluxing ethanol temperatures) and chloroform (40 mL, distilled from phosphorous pentoxide). In the addition funnel a solution of dry chloroform (40 mL) and bromine (4.24 g, 1.36 mL, 26.5 mmol) was prepared. At room temperature with vigorous stirring the bromine solution was added portionwise to the reaction flask over about 30 min. After addition was complete vigorous stirring was continued until the bromine color had disappeared (usually about 1 h). The stirring was then stopped and when the solid had settled the chloroform solution of thiocyanogen was syringed off for use in the thiocyanation reaction.

Thiocyanation.[15] A dry 250-mL two-necked round-bottomed flask was fitted with a nitrogen bubbler and a magnetic stirring bar. To this flask was added 1,2-dihydro-4,5-bis(trimethylsilyl)benzocyclobutene[13] (**5**, 1.88 g, 7.57 mmol) and chloroform (30 mL, distilled from phosphorous pentoxide) and then the flask was cooled in an ice bath. The chloroform solutions of thiocyanogen prepared above (approximately 80 mL) was then added with stirring via syringe, and the mixture was stirred until it cooled to ice-bath temperature. Aluminum chloride (1.0 g, 7.57 mmol) was added all at once and the reaction mixture was stirred at ice-bath temperatures for 1.5 h. The ice bath was then removed and the reaction mixture was stirred at room temperature for 4 h. The reaction mixture was then quenched with water and the chloroform phase washed with water until the aqueous extracts were no longer acidic. The chloroform phase was concentrated under reduced pressure to give an orange solid which was dissolved in hot ethanol (100 mL), stirred at room temperature for 1 h, and filtered. This ethanol solution was then stirred with activated charcoal (1.5 g) for 2 h, filtered, and concentrated under reduced pressure. Crystallization from ethanol gave 0.724 g (43.8%) of white crystalline product, mp 87–90.5 °C. The mother liquor was concentrated to give a second crop of slightly off-white crystals (0.168 g, 10.2%) for a combined yield of 54%: NMR ($CDCl_3$, 79.5 mHz) 7.51 (s, 2 H), 3.28 (s, 4H); IR (KBr) 2932, 2145, 1435, 1418, 1407 cm^{-1}; mass spectrum, m/e 218 (parent ions). Anal. Calcd for $C_{10}H_6N_2S_2$: C, 55.02; H, 2.77; N, 12.83; S, 29.38. Found: C, 55.12; H, 2.93; N, 12.80; S, 29.27.

1,2-Dihydro-4,5-dimercaptobenzocyclobutene (7). A 25-mL three-necked round-bottomed flask was fitted with a nitrogen bubbler, a magnetic stirring bar, and a reflux condenser. To this flask was added 1,2-dihydro-4,5-dithiocyanobenzocyclobutene (**6**, 100 mg, 0.458 mmol), ethanol (8 mL, nitrogen purged), and, portionwise with stirring at room temperature, sodium borohydride (80 mg, 2.06 mmol). This reaction mixture was heated at reflux for 3 h, then more sodium borohydride (25 mg) was added, and reflux was resumed for another 2.5 h. The reaction mixture was cooled to room temperature, diluted with water, and

(21) Ferretti, A. *Org. Synth.* **1973**, *5*, 419. Adams, R.; Reifschneider, W.; Ferretti, A. *Org. Synth.* **1973**, *5*, 107.

(under) nitrogen) washed twice with methylene chloride. The aqueous phase was acidified to pH 1 with 1 N hydrochloric acid and (still under nitrogen) extracted 3 times with chloroform. The combined chloroform extracts were dried over sodium sulfate and concentrated under reduced pressure to give 69.6 mg of a white solid (90.3%): NMR (C_6D_6, 79.5 mHz) δ 6.74 (s), 3.41 (s), 2.71 (s); NMR (C_6D_6/D_2O, 79.5 mHz) δ 6.74 (s), 2.72 (s), IR ($CHCl_3$) 2937, 2830, 1451, 1354, 1282 cm^{-1}; mass spectrum, *m/e* 168 (parent ion). This material was used without further purification or characterization.

2',3',4',5',6',7'-Hexahydrodispiro[cyclobuta[*f*]-1,3-benzodithiole-2,1'-anthracene-8',2''-cyclobuta[*f*]-1,3-benzodithiole] (2). A dry 10 mL two-nicked reacton flask was fitted with a nitrogen bubbler and a magnetic stirring bar. To this flask was added 1,2-dihydro-4,5-dimercaptobenzocyclobutene (**7**, 261 mg, 1.55 mmol), diketone **3** (111 mg, 0.518 mmol), chloroform (2.5 mL), and trimethylsilyl chloride (1.0 mL, 0.856 g, 7.88 mmol). This mixture was stirred at room temperature for 94 h and then diluted with chloroform and washed with 5% aqueous sodium carbonate. The chloroform phase was concentrated under reduced pressure to give a pink solid. This solid was dissolved in hot carbon tetrachloride, cooled to room temperature, and filtered. Storage in the freezer overnight gave 234 mg of white crystals (87.9%, based on **3**). The mother liquor was concentrated to dryness, dissolved in hot ethyl acetate, and filtered. The filtrate, after being concentrated under a stream of nitrogen, gave 29.1 mg of pale yellow crystals (10.9%) for a combined yield of 98.8%: mp > 250 °C; NMR ($CDCl_3$, 300 mHz) δ 9.70 (s, 1 H), 6.83 (s, 4 H), 6.78 (s, 1 H), 3.05 (d, J = 1.5 Hz, 8 H), 2.76 (t, J = 6.3, 4 H), 2.58 (m, 4 H), 1.97 (m, 4 H); IR ($CHCl_3$) 2943, 2876, 2844, 1489, 1448, 1272 cm^{-1}; mass spectrum, *m/e* 514 (parent ion); high-resolution mass spectrum calcd for $C_{30}H_{26}S_4$ 514.0917, found 514.0913.

Acknowledgment. This work was supported by the Office of Naval Research and the Center for Microelectronics and Information Science at the University of Minnesota. Dr. D. Britton performed the X-ray structure determination.

Registry No. **1**, 93304-13-3; **2**, 93304-14-4; **3**, 82817-90-1; **4**, 93304-15-5; **5**, 57297-31-1; **6**, 93304-16-6; **7**, 93304-17-7; 1,3-bis(4-pentenyl)benzene, 93304-18-8; *m*-xylene, 108-38-3; *m*-xylene dipotassium salt, 78831-97-7; 4-bromo-1-butene, 5162-44-7; 1,3-bis(4-carboxypropyl)benzene, 54698-75-8; 1,2-dimercaptobenzene, 17534-15-5; lead(II) thiocyanate, 592-87-0; thiocyanogen, 505-14-6; potassium *tert*-butoxide, 865-47-4.

Supplementary Material Available: X-ray data (11 pages). Ordering information is given on any current masthead page.

Enantioselective Processes. Reaction of Optically Active Amines with Photochemically Generated Ketenes

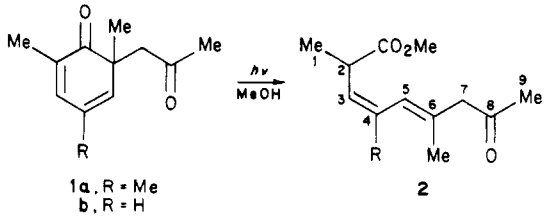
Arthur G. Schultz* and Yashwant S. Kulkarni

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181

Received May 29, 1984

The diastereoselectivity of the reaction of *d*- and *l*-ephedrine with ketenes photochemically generated from 6-(2-oxopropyl)-2,4,6-trimethyl-2,4-cyclohexadien-1-one (**1a**), 6-(2-oxopropyl)-2,6-dimethyl-2,4-cyclohexadien-1-one (**1b**), and 6-acetoxy-2,4,6-trimethyl-2,4-cyclohexadien-1-one (**3a**) is described. Configurational assignments at C(2) in the major products **5a** and **6** resulting from irradiation of **1a** in the presence of *d*-ephedrine and *l*-ephedrine, respectively, were made by chemical degradation and correlation studies with (*S*)-(+)-3-hydroxy-2-methylpropanoic acid (**7a**).

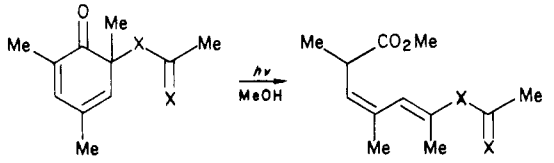
We recently reported[1] the near quantitative photoconversion of 6-(2-oxopropyl)-2,4,6-trimethyl-2,4-cyclohexadien-1-one (**1a**)[2] to 2-carbomethoxy-2,4-dimethyl-3,5-nonadien-8-one (**2a**). Remarkably, **2a** was isolated in 96% yield as a single geometric isomer. The conversion of **1b** to **2b** also occurs with similar stereoselectivity.



1a, R = Me
b, R = H

2

Diene carboxylic acid derivatives produced by photoreaction of 2,4-cyclohexadienones tend to be isomerically pure at the C(3)-C(4) double bond (*Z* configuration) but a mixture of *E* and *Z* configurations at the C(5)-C(6) double bond.[3] Only the 6-acetoxy-2,4-cyclohexadien-1-ones[4a-d] and two 6-(benzoyloxy)-2,4-cyclohexadien-1-ones[4d] had been reported to undergo highly stereoselective photoisomerization to diene ketenes. For example, photolysis of 6-acetoxy-2,4,6-trimethyl-2,4-cyclohexadien-1-one (**3a**) in methanol gives **4a** in 93% yield and the corresponding C(5)-C(6) isomer (2%).[4b] In marked contrast, the unsaturated hydrocarbon analogue **3b** gives **4b** (~70%) along with the C(5)-C(6) isomer (~30%).



3a, X = O
b, X = CH_2

4

During the conversion **1** → **2**, there also is the potential for enantioselection in the protonation of the diene ketene

(1) Schultz, A. G.; Ranganathan, R.; Kulkarni, Y. S. *Tetrahedron Lett.* **1982**, *23*, 4527.

(2) Nitta, M.; Omata, A.; Sugiyama, H. *Chem. Lett.* **1980**, 1615.

(3) For reviews of 2,4-cyclohexadienone photochemistry, see: (a) Quinkert, G. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 211. (b) Quinkert, G. *Agnew. Chem., Int. Ed. Engl.* **1972**, *11*, 1072. (c) Quinkert, G. *Pure Appl. Chem.* **1973**, *33*, 285.

(4) (a) Baldwin, J. E.; McDaniel, M. C. *J. Am. Chem. Soc.* **1968**, *90*, 6118. (b) Quinkert, G.; Bronstert, B.; Schmieder, K. R. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 637. The isomeric, fully conjugated diene carboxylic ester also is obtained (5%) from irradiation of **3a** in methanol. (c) Morris, M. R.; Waring, A. J. *J. Chem. Soc., Chem. Commun.* **1969**, 526. (d) Waring, A. J.; Morris, M. R.; Islam, M. M. *J. Chem. Soc. C* **1971**, 3274. The highly stereoselective photoisomerization of ten 6-acetoxy-2,4-cyclohexadien-1-ones are reported. (e) For discussions of factors which may control diene stereoselectivity, see ref 4a and 4d.

0022-3263/84/1949-5202$01.50/0