A solution of "racemic" hexahelicene in DMB (absorbance at λ_{max} 310 nm in the 0.1-mm cell of 0.45, concentration approximately 10^{-3} M) exhibited ellipticity at 322 nm of $+0.5 \times 10^{-3}$ degrees. This small peak is reproducible to less than 0.2×10^{-3} degrees. It arises not from a difference of interaction of DMB with the enantiomers of hexahelicene but rather from the fact that the starting material was not perfectly racemic. A solution of the starting material in benzene exhibited the same circular dichroism as in DMB.[5]

After the first brief contact of the above solution with a potassium mirror, the ellipticity at 322 nm changed sign becoming -1.3×10^{-3} degrees. After the second contact with the potassium mirror the ellipticity became -3.5×10^{-3} degrees. After a third contact the peak diminished to 0.8×10^{-3} degrees, and disappeared after a fourth contact. The shape of the peak was the same as that of resolved neutral hexahelicene. (The mononegative anion does not exhibit a circular dichroism peak at 322 nm.) No changes with time of the properties of the solution were observed during each interval of about 1 h between reductions.

In the early stages of the reduction only neutral molecule and mononegative ions are present.[6] The appearance of the circular dichroism peak of neutral (−) hexahelicene must result from a selective reduction of the (+) enantiomer. The effect is remarkably small. From the magnitude of the circular dichroism and the best estimate which I could make of the extent of reduction, the equilibrium constant for the reaction

$$(+)^\circ + (-)^- = (+)^- + (-)^\circ$$

$$K = \frac{[(+)^-]\,[(-)^\circ]}{[(+)^\circ]\,[(-)^-]} = 1.005 \pm 0.002$$

The symbols (+) and (−) stand for the enantiomers, the superscripts for the charges. The standard free energy for the reaction is only −3 cal/mol.

In the succeeding equilibria involving the more highly charged species, much larger effects are observed, but their quantitative interpretation awaits measurements of the absolute values of the circular dichroism of the species involved. The circular dichroism of only the neutral hexahelicene is required for estimation of the equilibrium constant for the reaction.

A number of control experiments were carried out. No circular dichroism peaks were found at either the absorption maxima of triphenylene (a related but nonchiral hydrocarbon) or anions on reduction in DMB. This experiment suggests that the large but as yet unanalyzed peaks at the absorption maxima of the anions of hexahelicene arise from selective reductions rather than from different induced optical activities in the anions. Finally, reduction of racemic hexahelicene in nonchiral dimethoxyethane yielded no observable optical rotation or circular dichroism.[7]

Although the effect here reported corresponds to a free-energy difference of only 3 cal/mol, it is nevertheless easily measured. Clearly the data do not permit unique determination of the nature of the interaction between the solute and solvent, but they eliminate all models in which the stereochemistry requires differences between free energy of reduction of the two enantiomers greater than 3 cal/mol.[8]

Acknowledgment. I am indebted to Professor Melvin Newman for a gift of racemic hexahelicene and to Dr. Douglas Daniel for preparation of (+)-2,3-dimethoxybutane from (+)-2,3-butanediol. The work has been supported by the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No.—(+)-2,3-Dimethoxybutane, 1565-60-2; (−)-hexahelicene, 19253-33-9; (+)-hexahelicene, 17486-32-7.

References and Notes

(1) H. L. Cohen and G. F. Wright, *J. Org. Chem.*, **18**, 432 (1953).

(2) A. G. Brook, H. L. Cohen, and G. F. Wright, *J. Org. Chem.*, **18**, 447 (1953).

(3) N. Allentoff and G. F. Wright, *J. Org. Chem.*, **22**, 1, (1957).

(4) N. Allentoff and G. F. Wright, *Can. J. Chem.*, **35**, 900 (1957).

(5) The sample was selected by Professor Melvin Newman after my complaint that the earlier samples of "racemic" hexahelicene which he had generously provided departed even more from being racemic.

(6) S. I. Weissman and R. Chang, *J. Am. Chem. Soc.*, **94**, 8683 (1972).

(7) This experiment may not be quite as silly as the reader would be justified in thinking it is. Recent work on the effect of the non-parity-conserving neutral current interaction on atomic and molecular properties suggests that all materials may have chiral properties. Professor Henry Primakoff has kindly made an estimate of this effect on the reduction of hexahelicene and concludes that at best for the reaction here considered $K - 1 = 5 \times 10^{-11}$, far below the sensitivity of the present measurement. However, the effect depends strongly on the atomic numbers of the elements involved and may yet become measurable. For references to work on this subject and a recent attempt at an experimental observation see D. C. Soreide, D. E. Roberts, E. G. Lindahl, L. L. Lewis, G. R. Apperson, and E. N. Fortson, *Phys. Rev. Lett.*, **36**, 352 (1976).

(8) One could interpret the difference to a difference in the anion charge–solvent dipole interaction. For a mean distance of 3 Å between a singly charged ion and a dipole of 0.5 D, a difference in distance greater than 0.01 Å would lead to a difference in free energy greater than the observed 3 cal/mol.

Enolate Route to 5,10-Disubstituted Indeno[2,1-*a*]indene

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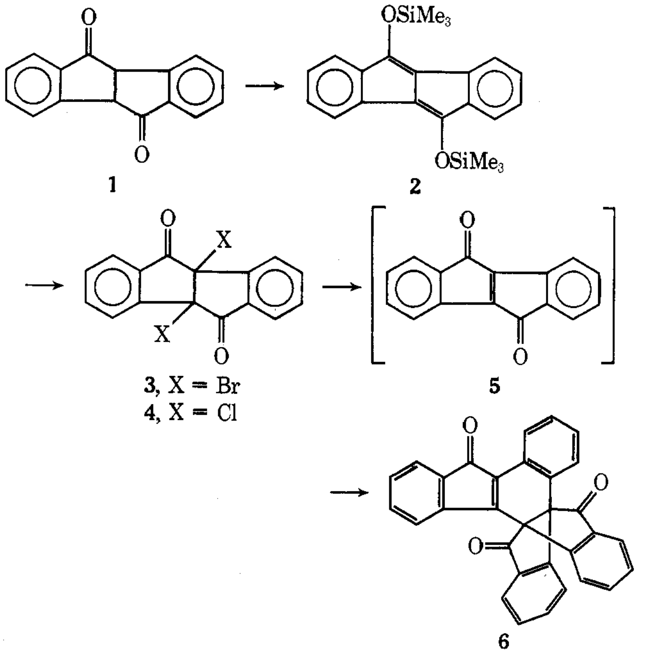
Although 5,10-dialkyl- and diarylindeno[2,1-*a*]indenes are readily prepared from the dione **1**,[1] reported attempts[2] to prepare these 4n π-electron systems by trapping the enolate of **1** have been less successful.



Direct conversion of **1** to the bis(silyl enol ether) can be accomplished by treating **1** with chlorotrimethylsilane in the presence of DBN.[3] The orange product **2** exhibits a uv–visible spectrum typical of an indeno[2,1-*a*]indene chromophore. Silyl ether formation does not occur in the presence of either triethylamine (method of House and co-workers[4]) or *N*-ethylpiperidine. Presumably the more basic amidine, DBN, is necessary to initiate the silylation by enolizing **1**. Alternatively, bis(silyl ether) **2** can be prepared by treating **1** with excess *N,O*-bis(trimethylsilyl)acetamide in the presence of a catalytic amount of DBN. Attempts to prepare the bisenamine, 5,10-bis(dimethylamino)indeno[2,1-*a*]indene, using trimethylsilyldimethylamine, a reagent reported[5,6] to convert ketones to enamines, led instead to the bis(silyl ether) **2**. Here, as in previous cases,[7] trimethylsilyldimethylamine gave a silyl enol ether rather than an enamine.

Bromination of **2** affords the dibromodione **3** while chlorination gives the dichlorodione **4**. Debromination of the **3** with zinc yields the known red trione **6**[8] previously shown to arise from the dimerization–decarbonylation of the enedione, **5**.[9]

Experimental Section

5,10-Bis(trimethylsiloxy)indeno[2,1-*a*]indene (2). To a warm solution (~50 °C) of 1.20 g (5 mmol) of dione **1** in 50 ml of benzene was added 10 ml of chlorotrimethylsilane followed by a solution of 1.5 g (12 mmol) of DBN in 25 ml of benzene. After 20 min at 50 °C the reaction mixture was allowed to cool to room temperature over 4 h. The DBN hydrochloride was filtered from the reaction mixture. After washing the filtrate with 2 × 25 ml of 4% aqueous HCl it was dried over Na_2SO_4 and then the benzene removed on a rotory evaporator. The orange residual solid was extracted with hot hexane (1 × 50 ml, 1 × 10 ml). Cooling in a freezer gave 0.512 g of orange crystals: mp 132–133 °C; λ_{max} (ether) 411 nm (ϵ 19 600), 387 (14 500), 366 (6700), 303 (32 800), 293 (32 100), 267 (29 700), 262 (27 700), 250 (24 000), 232 (17 200); ^1H NMR (CCl_4) δ 0.33 (9 H, s, $SiCH_3$), 6.76–7.17 (4 H, m, aromatic); mass spectrum M^+ *m/e* 378. Partial evaporation of the hexane mother liquor followed by cooling gave a second crop of 0.494 g. The yield base on 0.325 g of recovered **1** was 68%.

Anal. Calcd for $C_{22}H_{26}O_2Si_2$: C, 69.79; H, 6.92. Found: C, 70.26; H, 6.67.

Halogenation of 2. To a solution of 617 mg (1.6 mmol) of **2** in 20 ml of carbon tetrachloride was added 1.24 g (7.8 mmol) of bromine dissolved in 5 ml of carbon tetrachloride. After standing for 10 min, the reaction mixture was stripped of solvent. The pale yellow solid was air dried yielding 563 mg of **3** (90% yield). The analytical sample was prepared by crystallization from carbon tetrachloride: mp 206–208 °C (reported[10] mp 204–206 °C); ir (CCl_4) 1735 (C=O), 1595 cm^{-1} (aromatic C=C); mass spectrum $M^+ - Br$ *m/e* 311, 313.

Anal. Calcd for $C_{16}H_8Br_2O_2$: C, 49.01; H, 2.06. Found: C, 48.95; H, 2.18.

Chlorination of **2** affords **4**: mp 192–193 °C (white crystals from methanol); mass spectrum M^+ *m/e* 302, 304, 306.

Anal. Calcd for $C_{16}H_8Cl_2O_2$: C, 63.39; H, 2.67. Found: C, 63.32; H, 2.66.

Registry No.—**1**, 50703-54-3; **2**, 60428-11-7; **3**, 25117-53-7; **4**, 60428-12-8; chlorotrimethysilane, 75-77-4.

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(1) K. Brand et al., *Chem. Ber.*, **45**, 3071 (1912); **53**, 809, 815 (1920); **55**, 601 (1922); **69**, 2504 (1936).

(2) A. G. Osborne, Ph.D. Thesis, University of Washington, Seattle, Wash., 1955, reported that the reaction of **1** with isopropenyl acetate gave a trace amount of a red compound characterized only by a uv spectrum.

(3) DBN = 1,5-diazabicyclo[4.3.0]non-5-ene.

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