Elemental analysis was performed at the Elemental Analysis Center of Kyoto University, Kyoto.

Ethyl 2-Amino-2-deoxy-D-glucopyranoside (Iab). The anomeric mixture of ethyl 2-acetamido-2-deoxy-D-glucopyranoside was prepared by refluxing 2-acetamido-2-deoxy-D-glucose in the presence of dry IRA 120 (H^+) resin in anhydrous ethanol for 5 h. The anomeric mixture (500 mg), $[\alpha]^{23}D$ +35.7° (c 1.02, water), was dissolved in 10 ml of 2.0 N NaOH and the solution was kept in a boiling water bath for 3 h. After cooling to room temperature, the reaction mixture was neutralized with 2.0 N HCl and diluted with distilled water to ~150 ml.

Ethyl 2-Amino-2-deoxy-α-D-glucopyranoside (Ia) and Ethyl 2-Amino-2-deoxy-β-D-glucopyranoside (Ib). The diluted solution of **Iab** obtained above was applied to a column (2.7 × 52 cm) of Amberlite CG 120 (H^+). The column was eluted with 0.3 N HCl at a flow rate of 30 ml/h, and fractions of 7.0 g each were collected. A screening test was carried out by the ninhydrin reaction. Each of the peaks was combined and concentrated in vacuo to dryness. Crystallization was performed from a mixture of water, ethanol, and ethyl ether, and two recrystallizations from the same solvent. Ethyl 2-amino-2-deoxy-α-D-glucopyranoside hydrochloride (Ia) was isolated from fractions 139–157, yield 213 mg (42.6%): mp 199–203 °C; $[\alpha]^{23}D$ +135° (c 0.48, water) [lit.[15] mp 197–198 °C; $[\alpha]^{19}D$ +129.2° (c 0.4, water)]. The β anomer (Ib) was isolated from fractions 123–135, yield 199 mg (39.8%): mp 227–228.5 °C; $[\alpha]^{24}D$ −18.7° (c 0.48, water) [lit.[16] mp 213–214 °C; $[\alpha]D$ −27.8° (water)].

Ethyl 2-Acylamino-2-deoxy-α-D-glucopyranosides (IIa) and Ethyl 2-Acylamino-2-deoxy-β-D-glucopyranosides (IIb). Each of Ia and Ib (72.9 mg each) was placed in 0.5 ml of anhydrous methanol involving 7 mg of Na. Upon gentle swirling, NaCl separated and was removed by filtration and washed with 0.5 ml of anhydrous methanol. An amount of carboxylic anhydride (1.2 molar equiv to Ia or Ib) was added at room temperature with stirring. In the case of the anhydride of the fatty acids higher than C_{12}, an additional 2.0 ml of methanol was added to the mixture and the mixture was warmed at ~60 °C for a few seconds. The mixture was allowed to stand at room temperature overnight, and ethyl ether and petroleum ether (bp 30–70 °C) were added. The mixture was kept in a refrigerator to give crystals, and two recrystallizations were performed from ethanol, ethyl ether, and petroleum ether. It was essential for analysis to remove a trace of NaCl contaminated through the recrystallizations. The crystalls were filtered, washed with ethyl ether, and dried over P_2O_5 in vacuo at 100 °C for 2 h. Table I shows the anomerically pure *N*-acyl derivatives thus prepared in the reaction with the anhydrides of fatty acids.

Ethyl 2-Benzamido-2-deoxy-α-D-glucopyranoside. The above procedure was applied to the preparation of the title compound by using benzoic anhydride, yield 93.2%: mp 199–202 °C; $[\alpha]^{20}D$ +85.4° (c 0.48, methanol); ir (KBr) 3500–3300 (OH, NH), 1630 (C=O in *N*-benzoyl), 1540 (N–H in *N*-benzoyl), 1140–1030 (C–O–C), 850 cm^{-1} (the α-D configuration).

Anal. Calcd for $C_{15}H_{21}O_6N$: C, 57.86; H, 6.80; N, 4.50. Found: C, 57.63; H, 7.00; N, 4.40.

Ethyl 2-Benzamido-2-deoxy-β-D-glucopyranoside. The same procedure was applied to prepare the title compound, yield 55%: mp 192–195 °C; $[\alpha]^{21}D$ −40.3° (c 0.62, water); λ_{max} (water) 230 nm (ε 6400); ir (KBr) 3450–3250 (OH, NH), 1630 (C=O in *N*-benzoyl), 1550 (N–H in *N*-benzoyl), 1070–1020 (C–O–C), 870 cm^{-1} (the β-D configuration); NMR (D_2O) δ 1.05 (t, 3 protons, CH_3), 3.72 (q, 2 protons, CH_2), 4.65 (d, 1 proton, $J_{1,2}$ = 7.0 Hz, H-1), 7.55 ppm (m, 5 protons, phenyl).

Anal. Calcd for $C_{15}H_{21}O_6N$: C, 57.86; H, 6.80; N, 4.50. Found: C, 57.77; H, 7.08; N, 4.54.

Registry No.—Ia, 57120-95-3; Ib, 6835-60-5; ethyl 2-benzamido-2-deoxy-α-D-glucopyranoside, 60538-40-1; benzoic anhydirde, 93-97-0; ethyl 2-benzamido-2-deoxy-β-D-glucopyranoside, 60538-41-2; propionic anhydride, 123-62-6; butyric anhydride, 106-31-0; caproic anhydride, 2051-49-2; caprylic anhydride, 623-66-5; capric anhydride, 2082-76-0; lauric anhydride, 645-66-9; myristic anhydride, 626-29-9; palmitic anhydride, 623-65-4; stearic anhydride, 638-08-4.

References and Notes

(1) S. Pope, R. M. Tomarelli, and P. György, *Arch. Biochem. Biophys.*, **68**, 326 (1957).
(2) C. S. Rose, R. Kuhn, F. Zilliken, and P. György, *Arch. Biochem. Biophys.*, **49**, 123 (1954).
(3) F. Zilliken, C. S. Rose, G. A. Braun, and P. György, *Arch. Biochem. Biophys.*, **54**, 329 (1955).
(4) R. Lambert and F. Zilliken, *Arch. Biochem. Biophys.*, **110**, 544 (1965).
(5) A. Gaube, P. György, J. R. E. Hoover, R. Kuhn, C. S. Rose, H. W. Rullius, and F. Zilliken, *Arch. Biochem. Biophys.*, **48**, 214 (1954).
(6) S. Hirano, H. Hayashi, T. Terabayashi, K. Onodera, S. Iseki, N. Kochibe, Y. Nagai, N. Yagi, T. Nakagaki, and T. Imagawa, *J. Biochem. (Tokyo)*, **64**, 563 (1968).
(7) (a) R. H. Pater, R. A. Coelho, and D. F. Mowery, Jr., *J. Org. Chem.*, **38**, 3372 (1973); (b) G. N. Bollenback, *Methods Carbohydr. Chem.*, **2**, 326 (1963).
(8) (a) Y. Matsushima, T. Miyazaki, and J. T. Park, *J. Biochem. (Tokyo)*, **54**, 109 (1963); (b) Y. Matsushima and T. Miyazaki, *Bull. Chem. Soc. Jpn.*, **38**, 1325 (1965); (c) A. Neuberger and B. M. Wilson, *Carbohydr. Res.*, **17**, 85 (1971); (d) S. Beychok, G. Ashwell, and E. A. Kabat, *ibid.*, **17**, 19 (1971).
(9) S. Hirano, N. Akimoto, M. Ishigami, and Y. Koga, *Anal. Biochem.*, **66**, 627 (1975).
(10) J. E. Stoddart, "Stereochemistry of Carbohydrates", Wiley-Interscience, New York, N.Y., 1971, pp 72–87.
(11) (a) A. Neuberger and A. P. Fletcher, *Carbohydr. Res.*, **17**, 79 (1971); (b) A. Neuberger and A. P. Fletcher, *J. Chem. Soc. B*, 179 (1969); (c) S. Inouye, *Chem. Pharm. Bull.*, **16**, 1134 (1968).
(12) (a) Y. Inouye, K. Onodera, S. Kitaoka, and S. Hirano, *J. Am. Chem. Soc.*, **78**, 4722 (1956); (b) Y. Inouye, K. Onodera, S. Kitaoka, and S. Hirano, *J. Org. Chem.*, **25**, 1265 (1960).
(13) R. Kuhn and W. Kirschenlohr, *Chem. Ber.*, **86**, 1331 (1953).
(14) (a) S. A. Barker, E. J. Bourne, M. Stacey, and D. H. Whiffen, *J. Chem. Soc.*, 171, 3468, 4211 (1954); (b) H. Spedding, *Adv. Carbohydr. Chem.*, **19**, 23 (1964).
(15) P. F. Lloyd and G. P. Roberts, *J. Chem. Soc.*, 2962 (1963).
(16) J. C. Irvine and J. C. Hynd, *J. Chem. Soc.*, 103 (1913).

Selectivity in the Reduction of Enantiomers of Hexahelicene in an Optically Active Solvent

S. I. Weissman

Department of Chemistry, Washington University, St. Louis, Missouri 63130

Received August 10, 1976

The reduction of aromatic molecules to their anions by alkali metals is now a well-established chemical process. Soon after the identification of the reduction products as anions it was recognized that interactions involving the anions, the solvent, and the alkali metal counterions play an important part in the behavior of the systems. It has also been recognized for a long time that interactions between chiral solvents and solutes produce a variety of observable effects such as induced optical activity in nonchiral solutes and selective formation of enantiomers of chiral products in chemical reactions. Examples of the latter phenomena are provided by Wright's observations that reductions carried out in one of the enantiomers of dimethoxybutane are selective among the enantiomers of chiral products.[1-4]

In this note I describe experiments which were intended to isolate some features of solvent–anion interaction through a study of the selective reduction to their mononegative anions of the enantiomers of hexahelicene in the optically active solvent (+)-2,3-dimethoxybutane (DMB). Because of the stability of the anions of hexahelicene and the enormous rotation and circular dichroism of neutral hexahelicene the system is ideal for the observation of small effects. The reactions were followed by recording the circular dichroism spectra of a solution of hexahelicene in the optically active solvent subsequent to successive reductions by a potassium mirror. The standard high vacuum methods for handling solutions of radical anions were used. The apparatus was fitted with two quartz optical cells, one with a 0.10-mm light path, the other with a 1.00-mm path. Either cell could be inserted into the light beam of a Jasco J-20 spectropolarimeter. Readings were as reproducible on removal and reinsertion of the cells as they were on successive recordings during which the cells were not removed. For the experiments with the optically active solvent, the shorter light path was used in order to minimize contributions in the 300–350-nm region of the tail of the ultraviolet circular dichroism peak of DMB.

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.

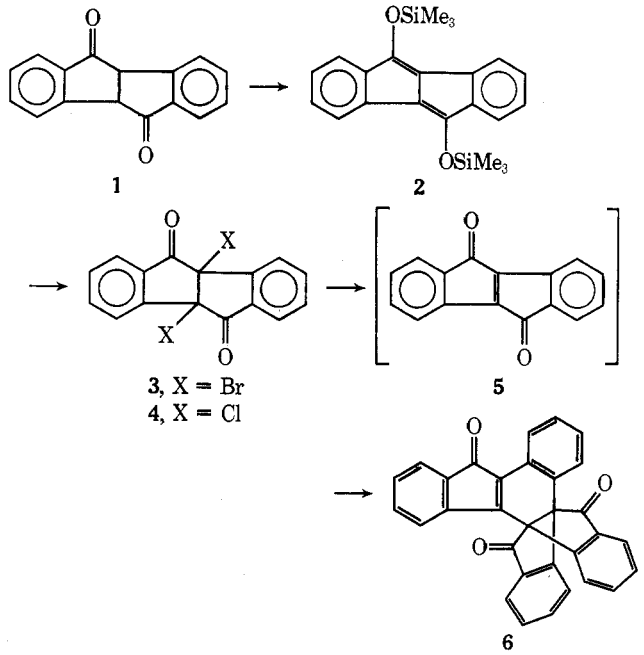
Enolate Route to 5,10-Disubstituted Indeno[2,1-*a*]indene

Eugene LeGoff

Department of Chemistry, Michigan State University, E. Lansing, Michigan 48824

Received June 11, 1976

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,