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ADDITION OF BROMINE GAS TO CRYSTALLINE DIBENZOBARRELENE: AN ENANTIOSELECTIVE CARBOCATION REARRANGEMENT IN THE SOLID STATE

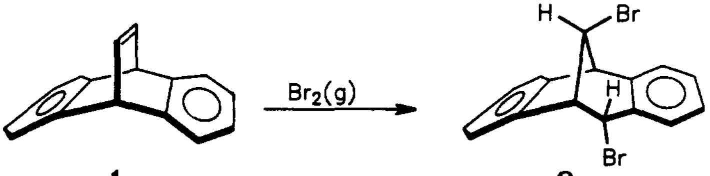
Miguel Garcia-Garibay, John R. Scheffer,* James Trotter* and Fred Wireko
Department of Chemistry, University of British Columbia, Vancouver, V6T 1Y6, Canada

Abstract. Treatment of chiral crystals of 2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5,7-triene (dibenzobarrelene, 1) with bromine vapor results in the formation of the rearranged product syn-8-bromo-endo-4-bromo2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-diene (2) in up to 8% enantiomeric excess.

The situation in which a molecule is achiral in solution owing to rapid conformational motions but is frozen in a homochiral conformation in the solid state is well documented,[1] and several studies have shown that chemical reactions of such crystals can lead to products of high optical activity.[2] An interesting question in such reactions is to what extent the overall chiral crystal lattice environment, as opposed to the disymmetric molecular conformation, determines the product optical activity. In one study where this question was addressed,[2a,3] it was concluded that molecular conformation was the dominant factor in inducing optical activity. One way of assessing the chiral influence of the crystal environment alone would be to study the enantioselectivity of a solid state reaction of a compound that crystallizes in a chiral space group even though the constituent molecules are conformationally rigid and highly symmetrical. Several such compounds are known[4] including dibenzobarrelene (1), the title compound; a recent X-ray crystallographic study has shown that dibenzobarrelene crystallizes in the chiral space group C2 while deviating only very slightly from C_{2v} molecular symmetry.[5]

The process chosen for study was the reaction of crystalline dibenzobarrelene with bromine vapor. Gas-solid reactions involving bromine are well established,[2a,3,6] and the product of trans-addition of bromine to dibenzobarrelene, if formed, would be chiral. Interestingly, bromination of dibenzobarrelene in solution is known[7] to afford the carbocationic rearrangement product syn-8-bromo-endo-4-bromo-2,3:6,7-dibenzobicyclo-bicyclo[3.2.1]octa-2,6-diene (2), which is also chiral. A second point of interest, therefore, was to see whether the solid state bromination would occur with or without rearrangement.[8]

Large (20 - 100 mg) single crystals of dibenzobarrelene[9] (1) were grown from ethanol, thoroughly powdered, and then exposed to excess bromine vapor at room temperature in a dessicator. Under these conditions, only a slight discoloration and liquefaction of the crystals was evident. After two hours, gas chromatography indicated the nearly complete consumption of starting material and the formation of one major volatile product in 85-90% yield plus one minor product in approximately 5% yield.[10] Isolation and characterization of the major



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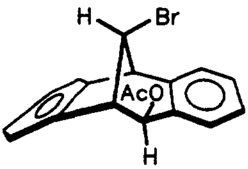
product showed it to be identical in every respect to the rearranged dibromide 2 formed by bromination of dibenzobarrelene in solution.[7] When the solid state bromination was carried out on large single crystals of dibenzobarrelene, there was a rapid transformation of the sample into a reddish-brown liquid. Gas chromatographic analysis of this material indicated a considerably reduced yield of dibromide 2 along with the formation of a large number of byproducts. This mixture was not studied further.

In order to investigate the extent of asymmetric induction in the solid state brominations, ^{1}H NMR chiral shift reagent studies were undertaken. Encouragingly, preliminary optical rotation measurements had shown that samples of 2 from the solid state brominations *were* optically active, whereas those from solution brominations were racemic. Dibromide 2, however, proved to be ill-suited for shift reagent studies, and therefore 2 was converted by known methods into *exo*-acetate 3.[7] In one experiment, a sample of 2 with $[\alpha]_D$ = 17.7° was converted into bromo-acetate 3 ($[\alpha]_D$ = 10.9°) and analyzed by NMR at 400 MHz with 0.2 eq of the chiral shift reagent Eu(hfc)$_3$. Integration of the acetate methyl signals at 3.06 and 3.18 ppm indicated an enantiomeric excess of approximately 8%; a second run from a different solid state bromination gave an enantiomeric excess of 3%. As expected, solution-derived 3 was racemic.



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We conclude, therefore, that while a chiral molecular conformation is undoubtedly very important in bringing about enantioselective chemical transformations, the medium in which the reaction is carried out also plays a significant role and may, if chiral, *by itself* lead to product optical activity. Similar conclusions have been drawn for chemical reactions of symmetrical molecules in chiral solvents[11] and chiral inclusion complexes,[12] but as far as we are aware, our results are the first of their kind for homomolecular chiral single crystals. Results such as these have obvious implications for the prebiotic origins of optical activity,[13] and we are continuing our studies in this fascinating field.

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1. (a) A.C.D. Newman and H.M. Powell, *J. Chem. Soc.*, 3747 (1952); (b) E. Havinga, *Biochim. Biophys. Acta*, 13, 171 (1954); (c) R.E. Pincock and K.R. Wilson, *J. Am. Chem. Soc.*, 93, 1291 (1971); (d) R.E. Pincock, R.R. Perkins, A.S. Ma and K.R. Wilson, *Science*, 174, 1018 (1971).

2. (a) B.S. Green, M. Lahav and D. Rabinovich, *Acc. Chem. Res.*, 12, 191 (1979); (b) S.V. Evans, M. Garcia-Garibay, N. Omkaram, J.R. Scheffer, J. Trotter and F. Wireko, *J. Am. Chem. Soc.*, 108, 5648 (1986).

3. D. Rabinovich and Z. Shakked, *Acta Cryst., B*, 30, 2829 (1974).

4. J. Jacques, A. Collet and S.H. Wilen, "Enantiomers, Racemates and Resolutions," Wiley, New York, 1981, pp 14-18.

5. M. Garcia-Garibay, J.R. Scheffer, J. Trotter and F. Wireko, *Tetrahedron Lett.*, 28, 1741 (1987).

6. (a) K. Penzien and G.M.J. Schmidt, *Angew. Chem., Int. Ed. Engl.*, 8, 608 (1969); (b) E. Hadjoudis, E. Kariv and G.M.J. Schmidt, *J. Chem. Soc., Perkin Trans. II*, 1056 (1972).

7. I.G. Dinulescu, M. Avram, Gh.D. Mateescu and C.D. Nenitzescu, *Chem. Ind.*, 2023 (1964).

8. While photochemical rearrangements in the solid state are well established (review: J.R. Scheffer, M. Garcia-Garibay and O. Nalamasu in "Organic Photochemistry," A. Padwa, Ed., Marcel Dekker, New York, 1987, pp 249-347), crystalline phase carbocation rearrangements are extremely rare. One example is reported by G.I. Borodkin, S.M. Nagy, V.I. Mamatyuk, M.M. Shakirov and V.G. Shubin, *J. Chem. Soc., Chem. Commun.*, 1533 (1983).

9. Dibenzobarrelene was prepared by the method of H.P. Figeys and A. Dralanis, *Tetrahedron*, 28, 3031 (1972).

10. The spectra of the minor product are consistent with a structure that is the C(4) epimer of dibromide 2, namely *syn*-8-bromo-*exo*-4-bromo-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-diene.

11. J.D. Morrison and H.S. Mosher, "Asymmetric Organic Reactions," American Chemical Society, Washington, D.C., 1976, Ch. 10.

12. (a) V. Ramamurthy, Tetrahedron, **42**, 5753 (1986); (b) F. Toda and K. Tanaka, J. Chem. Soc., Chem. Commun., 1429 (1986).

13. (a) B.S. Green and L. Heller, Science, **185**, 525 (1974); (b) L. Addadi and M. Lahav in "Origins of Optical Activity in Nature," D.C. Walker, Ed., Elsevier, New York, 1979, Ch. 14.

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