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On the Reaction of Sodium Methoxide with Perbromo-D_{2h}-bishomocubane. A Structural Reassignment

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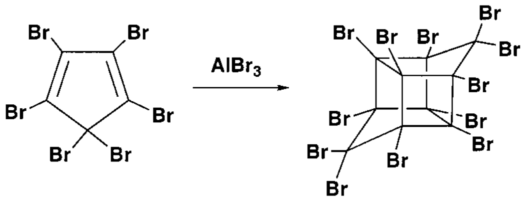
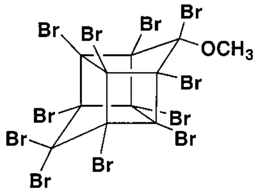
Hexabromocyclopentadiene reacts exothermically with AlBr$_3$ to give in excellent yield a cage dimer, C$_{10}$Br$_{12}$. This has been assigned[1] the centrosymmetric D_{2h}-bishomocubane cage structure **1** based on a tenuous analogy with the proposed structure[2] of Mirex, the perchloro analogue, once an important insecticide. We have now confirmed this assignment unambiguously using single-crystal X-ray analysis.[3]

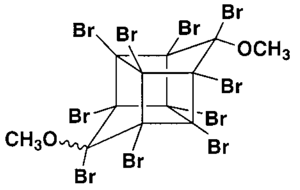


1

Ungefug, McGregor, and Roberts reported in 1971[4] that sodium methoxide in THF reacts with **1** at room temperature; first one bromine substituent is replaced with a methoxy group, and then, at a similar rate, a second is replaced likewise. The overall conversion is clean and yields >80% of a single dimethoxy compound. (Further reaction with NaOMe does occur, but more slowly, and gives a complex mixture of products.) Structures **2** and **3** were assigned originally to the first two products based primarily on mass spectroscopic arguments.



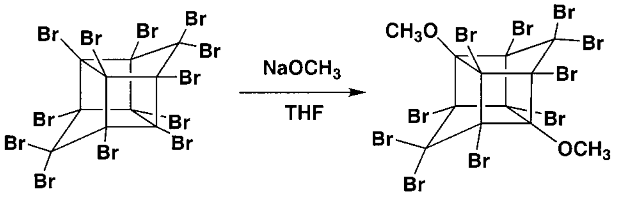
2



3

The proposed conversion is very unusual and is difficult to understand mechanistically. We found it worthy of further attention as hydrolysis of the ether groups would provide a diketone well-suited for double Favorskii contraction into the cubane system.[5]

We repeated the reaction of **1** with sodium methoxide without difficulty and obtained in similar yield a crystalline dimethoxy compound[6] identical (IR and ^{1}H NMR spectra) to that previously reported. However, single-crystal X-ray analysis[7] proved definitively that this product is 2,8-dimethoxydecabromopentacyclo[5.3.0.0.^{2,6}0.^{3,9}0^{4,8}]decane (**4**), rather than the previously proposed 5,10 isomer **3**.



1 **4**

It is no easier to explain mechanistically the formation of **4** than it was the earlier hypothesized formation of **3**.[8] It is clear that backside attack on carbon at any of the cage corners is entirely blocked. S$_N$2-like displacement at either of the dibromomethano bridges is not at all favorable, for the same reason that displacements are very difficult at the 7 position of a norbornane[9]—the enforced C−C−C angle of 90° is far from the 120° preferred by the pentacoordinate intermediate. As halogenated cage systems are inert to silver nitrate, mechanisms involving ionization to a cation are unlikely. We thought that the reaction might be initiated by methoxide ion attack directly on one or another bromine of **1** (Scheme 1) resulting in the formation of methoxyhypobromite, bromide ion, and one or another highly reactive

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[1] (a) Earle, R. H., Jr. Ph.D. Thesis, Purdue University, June 1957. (b) Roberts, C. W; Chenoweth, M. B. U.S. Patent 3,212,973, 1965. (c) Pews, R. G.; Roberts, C. W. *J. Org. Chem.* **1969**, *34*, 2029. (d) West, R.; Kwitowski, P. T. *J. Am. Chem. Soc.* **1968**, *90*, 4697.

[2] No successful X-ray analysis of Mirex has been reported; there is a problem with twinning. Reaction of hexachlorocyclopentadiene with chlorosulfonic acid gives a highly chlorinated D_{2h}-bishomocubane cage whose structure has been determined by X-ray analysis: Okaya, Y.; Bednowitz, A. *Acta Cryst.* **1967**, *22*, 111. Hydrolysis gives a ketone (Kepone) related to Mirex, but the connection is not unambiguous as the PCl$_5$ conversion of one to the other (Gilbert, E. E. U.S. Reissue Patent 24,397, 1957.) might involve a Lewis acid-catalyzed rearrangement (cf.: Griffin, G. W.; Price, A. K. *J. Org. Chem.* **1964**, *29*, 3192.). For other relevant X-ray determinations, see: (a) Gassmann, J.; Voss, J.; Adiwidjaja, G. *Z. Naturforsch., Teil B*, **1995**, *50*, 953. (b) Cordes, A. W.; Eubanks, J. R. I. *Acta Crystallogr.* **1987**, *C43*, 1848.

[3] Crystal data for **1**: C$_{10}$Br$_{12}$, fw = 1079.02, monoclinic space group *C*2/*c*; a = 15.673(3), b = 8.844(2), c = 15.804(3)Å , β = 114.09(1)°, V = 1999.9(6) Å^3, Z = 4, and D (X-ray) = 3.584 mg/mm^3. A total of 2729 data were measured with Cu Kα X-rays (λ = 1.54178 Å) to a 2θ max of 116° at T = 294(2) K. R = 0.0557 for 1217 reflections with [$I > 2\sigma(I)$], and R = 0.0623, wR2 = 0.1516 for *all* 1387 unique reflections.

[4] Ungefug, G. A.; McGregor, S. D.; Roberts, C. W. *J. Org. Chem.* **1971**, *36*, 352.

[5] (a) Eaton, P. E.; Cole, T. W. Jr. *J. Am. Chem. Soc.* **1964**, *86*, 962 and 3157. (b) Barborak, J. C.; Watts, L.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 1328. (c) Scherer, K. V., Jr.; Lunt, R. S., III; Ungefug, G. A. *Tetrahedron Lett.* **1965**, 1199. (d) Griffin G. W., Umrigar, P. P., Lankin, D. C., Stevens, E. D., Majeste, R. J. *Abstracts of Papers*, 189th National Meeting of the American Chemical Society, Miami Beach, FL, April 28−May 3, 1985; ORGN 183.

[6] ^{1}H NMR (400 MHz, CDCl$_3$) 4.068 (s); ^{1}H NMR (400 MHz, benzene-d_6) 3.694 (s); ^{13}C NMR (100 MHz, benzene-d_6) 87.06, 77.16, 72.01, 69.97, 58.64.

[7] Crystal data for **4**: C$_{12}$H$_6$Br$_{10}$O$_2$, fw = 981.27, orthorhombic space group *Pbca*; a = 12.5823(3), b = 11.7851(5), c = 13.6700(8) Å, V = 2027.0(2) Å^3, Z = 4, and D (X-ray) = 3.215 mg/mm^3. A total of 2647 data were measured with Cu Kα X-rays (λ = 1.54178 Å) to a 2θ max of 116° at T = 294(2)K. R = 0.0242 for 1290 reflections with [$I > 2\sigma(I)$], and R = 0.0280, wR2 = 0.0593 for *all* 1407 unique reflections.

[8] Ref 4, footnote 5.

[9] Roberts, J. D.; Johnson, F. O.; Carboni, R. A. *J. Am. Chem. Soc.* **1954**, *76*, 5692.

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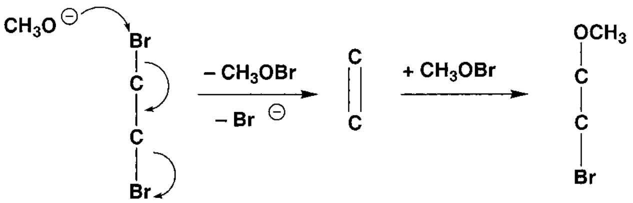
bishomocubene[10] which could then subsequently add the elements of CH_3OBr.

Scheme 1

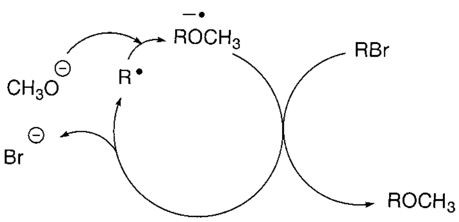


However, all attempts failed to intercept the methoxyhypobromite or trap the bishomocubene with excesses of highly reactive dienes such as 2,3-dimethylbutadiene or furan.

There is the possibility that the conversion of **1** to **4** proceeds by several single electron-transfer $S_{RN}1$ reactions perhaps of the type illustrated (Scheme 2).[11]

However, the observed conversion needs no photochemical or thermal stimulation, is not oxygen sensitive, and is not repressed by radical traps. Nor are we aware of any examples in which sodium methoxide participates so readily in $S_{RN}1$ reactions. Nonetheless, we are unable to exclude the possibility unambiguously.

Scheme 2



Sodium ethoxide, sodium *tert*-butoxide and sodium thiomethoxide in THF react much more rapidly than the less soluble sodium methoxide, but give complex mixtures. Remarkably, sodium methoxide in methanol does not react with **1**, and small quantities of methanol added to THF/NaOMe diminish the rate of conversion of **1** to **4** significantly. Common nucleophiles such as lithium iodide, lithium fluoride, or lithium phenoxide in THF do not react with **1**. This appears to eliminate any mechanism which depends on equilibration of the cage with some reactive open form. Clearly, the mechanistic problem is ripe for further investigation.

Acknowledgment. We are grateful for support from the Office of Naval Research and the U. S. Army Armament Research and Development Center.

Supporting Information Available: ORTEP drawings and tables of crystal data, bond lengths and angles, atomic coordinates, and anisotropic thermal parameters for compounds **1** and **4**. This information is available free of charge via the Internet at http://pubs.acs.org.

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[10] (a) Eaton, P. E.; Maggini, M. *J. Am. Chem. Soc.* **1988**, *110*, 7230. (b) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 7229. (c) Borden, W. T. *Chem. Rev.* **1989**, *89,* 1095.

[11] (a) Costentin, C.; Hapiot, P.; Médebielle, M.; Saveant, J.-M. *J. Am. Chem. Soc.* **1999**, *121*, 4451. (b) For a review see: Rossi, R. A.; Pierini, A. B.; Peñéñory, A. B. *The Chemistry of Functional Groups*; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1995; Supplement D2, Chapter 24, p 1395.