Our observation that 1,4-dibromides may be efficiently converted to cyclobutanes by electrochemical reduction at a relatively negative potential[8,9] provides an attractive alternative to dissolving metal reduction. A potentiostatic electrochemical reduction may be performed at low temperature, and thus increase the lifetime of the unstable propellane.

The reduction of 1,4-dibromobicyclo[2.2.2]octane (II) in *N,N*-dimethylformamide was carried out under a constant stream of nitrogen at a temperature of −15 to −25°, using tetraethylammonium bromide as the supporting electrolyte. A three-electrode configuration was used, with a platinum mesh working electrode, a platinum counter electrode (separated from the cathodic cell by a sintered glass partition), and a mercury pool reference electrode. The current density was 0.12 A. Electrolysis was continued at −2.35 V for 5 hr. Since the propellane, if formed, would be present in dilute solution from which it would be isolated with difficulty at this low temperature, chlorine was added to the reaction solution. By analogy to the known electrophilic additions to the central bond of the [3.2.1] propellane,[7] the chlorine should add across the central bond of this propellane to give 1,4-dichlorobicyclo[2.2.2]octane. This compound could only be formed from propellane I.

The electrolyte solution containing the dissolved chlorine was stored at −15° for 14 hr, allowed to warm to room temperature, and then diluted with cold, saturated aqueous sodium chloride. The suspension was extracted with ether–pentane, the organic phase was washed with water, dried over anhydrous sodium sulfate, and concentrated to give a semicrystalline residue. Vapor-phase chromatography of the residue at 150° on a 19 in. by $^1/_4$ in. column of 30% SE-30 on Anakrom showed there were two main products. The major product was easily identified as the chlorine addition product of 1,4-dimethylenecyclohexane (III). The other product (isolated by column chromatography or preparative gas chromatography) had a uniquely simple nmr spectrum consisting of a singlet at δ 2.2. It was identified as the desired 1,4-dichlorobicyclo[2.2.2]octane. The structure was confirmed by independent synthesis, using a modified Kochi reaction[10] on bicyclo-[2.2.2.]octane-1,4-dicarboxylic acid to give a compound[11] identical with that isolated from the electrolysis.

Thus, the presence of the 1,4-dichlorobicyclo[2.2.2]-octane provides clear evidence for the formation of the [2.2.2]propellane in the electrochemical reduction of 1,4-dibromobicyclo[2.2.2]octane.[12] Although the yield was low (*ca.* 12%), it has not been determined whether this results from the Grob-type fragmentation of a reaction intermediate or rather from the thermal ring opening of the propellane while it is still adjacent to the electrode surface. However, an attempt to improve the yield by running at a lower temperature led instead to a lowered yield of the desired product.

The successful formation of the [2.2.2]propellane illustrates the potential power of low-temperature potentiostatic electrolysis. It may provide a route to the still more interesting [2.2.1]propellane (IV). This would be expected to have a strain energy only slightly greater than that of I and should be formed more readily than I by electrolysis since the carbons bearing the halogens will be closer. If the theoretical treatments[3,4] of the thermal ring opening of I are correct, IV should have a markedly higher thermal stability since the orbitals forming the central bond cannot be moved far enough apart to make the antibonding arrangement of energy comparable to the bonding arrangement. Further efforts are being made to improve the electrochemical synthesis and to use it for the synthesis of IV and related compounds.

Kenneth B. Wiberg,* Gary A. Epling, Mark Jason
Department of Chemistry, Yale University
New Haven, Connecticut 06520

Received September 22, 1973

---

(8) K. B. Wiberg and G. A. Epling, to be submitted for publication.

(9) The electrochemical conversion of 1,4-dibromobutane to cyclobutane also has been noted by M. R. Rifi, *J. Amer. Chem. Soc.*, **89**, 4442 (1967).

(10) H. K. Hall, C. D. Smith, E. P. Blanchard, S. C. Cherkofsky, and J. B. Sieja, *J. Amer. Chem. Soc.*, **93**, 121 (1971).

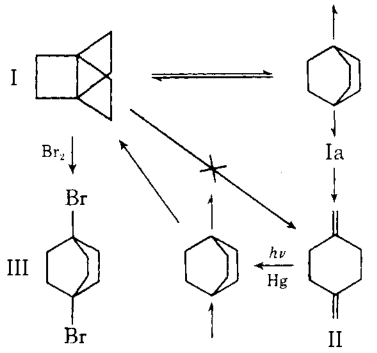
(11) Elemental analysis gave Calcd for $C_8H_{12}Cl_2$: C, 53.7; H, 6.8; Cl, 39.6. Found: C, 53.6; H, 6.8; Cl, 39.7.

(12) The supporting electrolyte, tetraethylammonium bromide, was carefully purified and was chlorine free. 1,4-Dibromobicyclo[2.2.2]-octane does not react with chlorine in dimethylformamide to give 1,4-dichlorobicyclo[2.2.2]octane. Similarly, 1,4-dimethylenecyclohexane gives only the tetrachloride and no 1,4-dichlorobicyclo[2.2.2]octane on treatment with chlorine in dimethylformamide.

Preparation and Trapping of [2.2.2]Propellane

Sir:

There has been considerable recent interest in the synthesis and properties of [2.2.2.$0^{1,4}$]tricyclooctane, commonly known as [2.2.2]propellane[1] (I). Hoffmann and Stohrer[2] suggested that the ground-state potential surface of I should have two minima, I and Ia. Although the orbital symmetry rules forbid a direct decomposition of I to 1,4-dimethylenecyclohexane (II), they offer no impediment to the decomposition Ia to II.[2] Since the barrier between I and Ia is predicted to be only 29 kcal/mol,[3] a facile route from I to II might exist. The problem of synthesizing I, therefore, is complicated by the necessity of entering the energy surface of the product on the correct side of the barrier between I and Ia and preventing the product from decomposing long enough to prove its existence. We have previously reported that INDO calculations predict that the triplet-state energy surface for [2.2.2]-propellane had only one minimum which corresponds to a ground-state geometry that is close to, but on the



---

(1) D. Ginsburg, *Accounts Chem. Res.*, 2, 1216 (1969); **5**, 249 (1972).

(2) R. Hoffmann and W. D. Stohrer, XXIII International Congress of Pure and Applied Chemistry, Special Lectures, Vol. 1, Butterworths, London, 1971, 157; W. D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 779 (1972).

(3) M. D. Newton and J. M. Schulman, *J. Amer. Chem. Soc.*, **94**, 4391 (1972).

desired side of, the barrier between I and Ia.[4] We, therefore, suggested that one might synthesize I by populating the triplet state of II, which lies on the same potential surface as the triplet of I. This approach was made more attractive by the consideration that those triplet states of I which did not decay to ground state I would probably decay to Ia and reopen to II, thus regenerating our starting material. We report the one-step preparation of unsubstituted I *via* the triplet state of II. The product, I, was trapped as the dibromide, III.

Eaton[5] has recently reported the synthesis of a derivative of I, and Wiberg has recently prepared I, itself, by another method.[6]

Solutions of II (0.5–0.74 *M* in ether), to which 0.5 g of Hg was added, were placed in quartz tubes, evacuated and sealed. After irradiation (254 nm) for up to 600 hr at −30°, the tubes were opened and decanted into a flask containing excess Br_2 in ether at 0°. The mixture was slowly (~6 hr) allowed to warm to room temperature. The excess bromine was removed as AgBr. After the inorganic material was removed, a proton nmr spectrum of the organic residue was taken in $CHCl_3$. Most of the peaks in the spectrum could be attributed to bromination products of starting material, II. Indeed, bromination of unreacted II produces a mixture whose proton nmr spectrum contains most of the peaks in that of the irradiated sample. However, a resonance at δ 2.41 appeared in the proton nmr of the irradiated sample that did not appear in that of brominated II. When authentic 1,4-dibromo[2.2.2]bicyclooctane (III), prepared by an established procedure,[7–9] was added to the sample, this peak grew in intensity.

Gas chromatography in a 10% ucon 50 HB 280X column produced a peak with the same retention time as authentic III. Upon addition of III, this peak increased in relative intensity.

Small amounts of the compound corresponding to this peak were trapped using a procedure described elsewhere.[10] The mass spectrum of this compound was shown to be essentially identical with that of authentic III.

Carbon-13 nmr spectra of authentic III showed resonances at −61.5 and −36.5 ppm from TMS. The first of these peaks was also present in the brominated reaction mixture and grew in intensity when authentic II was added, but the second peak was obscured by other stronger resonances. These resonances agree with published spectra of similar compounds.[11]

Mercury sensitization under our conditions is not a very efficient process. The overall yield of I, trapped as III, was only 2–3% after 120 hr and 4–5% after 600 hr irradiation time (as determined by integration of proton nmr spectra). The yield increased with increasing length of irradiation, indicating that the species brominated must have a considerable half-life at −30°. Even after 600 hr of irradiation, the solution remained clear and colorless and no evidence of polymerization was evident. It is, therefore, unlikely that III could be the result of bromination of a diradical such as Ia.

As a control, unirradiated starting material, II, was brominated using the same procedure used for the irradiated reaction mixture (both in the presence and absence of mercury). The peak corresponding to III was absent both from the proton nmr spectrum and the gas chromatogram, indicating that III is not a side product of the bromination of II.

Acknowledgment. The authors gratefully acknowledge the aid of Professor R. Breslow in obtaining mass spectra and of Drs. L. Sheer and J. Herz in obtaining the ^{13}C nmr spectra. This project was supported, in part, by Grant No. 1614 from the Research Foundation of the City University of New York.

J. J. Dannenberg,* T. M. Prociv, C. Hutt
Department of Chemistry
Hunter College of the City University of New York
New York, New York 10021
Received October 15, 1973

---

[4] J. J. Dannenberg and T. M. Prociv, *J. Chem. Soc., Chem. Commun.*, 291 (1973).

[5] P. E. Eaton and G. H. Temme, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Tex., Apr 1973, No. ORGN-58; *J. Amer. Chem. Soc.*, **95**, 1508 (1973).

[6] K. B. Wiberg, and G. A. Epling, private communication.

[7] M. J. S. Dewar and R. S. Goldberg, *J. Amer. Chem. Soc.*, **92**, 1582 (1970).

[8] J. D. Roberts, W. T. Moreland, Jr., and W. Frazier, *J. Amer. Chem. Soc.*, **75**, 673 (1953).

[9] H. D. Holtz and L. M. Stock, *J. Amer. Chem. Soc.*, **86**, 5183 (1964).

[10] B. J. Bulkin, K. Dill, and J. J. Dannenberg, *Anal. Chem.*, **43**, 974 (1971).

[11] G. E. Maciel and H. C. Dorn, *J. Amer. Chem. Soc.*, **93**, 1268 (1971).

α-Deuterium Isotope Effect for Displacement of the Nitrate Group

Sir:

The relationship between mechanism and the values of associated α-deuterium effects on the rates of nucleophilic displacement of halides and tosylates is supported by numerous investigations.[1] Maximum values corresponding to limiting mechanisms have been established for the above groups, the relative magnitudes having the order $OTs^- > Cl^- > Br^- > I^-$.[2–5] Fluoride is expected to give a value close to that for the tosylate,[6] but experimental data on these leaving groups are lacking. With one exception[7] no corresponding data giving an estimate of the α-deuterium effect for NO_3^- as a leaving group in solvolytic reactions were available prior to this report. In the course of our investigation of the mechanism of the hydrolysis of certain nitrate esters in water,[8] we have determined the kinetic α-deuterium effects associated with the solvolytic displacement of the nitrate group for a series of benzyl nitrates and isopropyl and cylopentyl nitrates in water. These data are summarized in Table I.

The values of the α-deuterium effects on the rates of the hydrolysis of the corresponding chlorides are included, where available. The α-deuterated nitrate

---

[1] V. J. Shiner, Jr., *Amer. Chem. Soc. Monogr.*, No. **157**, 104 (1971).

[2] V. J. Shiner, Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Amer. Chem. Soc.*, **90**, 418 (1968).

[3] V. J. Shiner, Jr., and W. Dowd, *J. Amer. Chem. Soc.*, **93**, 1029 (1971).

[4] V. J. Shiner, Jr., and R. D. Fisher, *J. Amer. Chem. Soc.*, **93**, 2533 (1971).

[5] J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 2551 (1971).

[6] V. J. Shiner, Jr., M. W. Rapp, E. A. Halevi, and M. Wolfsberg, *J. Amer. Chem. Soc.*, **90**, 7171 (1968).

[7] J. A. Llewellyn, R. E. Robertson, and J. M. W. Scott, *Can. J. Chem.*, **38**, 222 (1960).

[8] K. M. Koshy and R. E. Robertson, *Can. J. Chem.*, in press.