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[2.2.1]PROPELLANE. GENERATION UPON ELECTROLYTIC REDUCTION OF 1,4-DIHALONORBORNANES

William F. Carroll, Jr. and Dennis G. Peters*

Department of Chemistry, Indiana University
Bloomington, Indiana 47401

Synthesis of [2.2.1]propellane (tricyclo[2.2.1.0]heptane) has been attempted by both electrochemical[1] and chemical[2] means. Although never isolated, it was apparently trapped in the aforementioned chemical study.[2] In the present communication, we wish to report evidence, including the detection of oligomers seemingly derived from the propellane, for the electrolytic generation and reduction of this species at a mercury cathode in dimethylformamide.

In the earlier investigation by Wiberg, Bailey, and Jason,[1] electrolytic reduction of 1,4-dibromonorbornane at a platinum electrode in dimethylformamide at -20°C was found to yield norbornane, 1,1'-binorbornyl, and a norbornyl adduct of dimethylformamide; radical-coupling reactions were invoked to explain the formation of the latter two products. However, no coulometric $\underline{n}$-values (the number of electrons transferred per molecule of starting material) or absolute yields of products were reported, and the intermediacy of the propellane was neither confirmed nor denied.

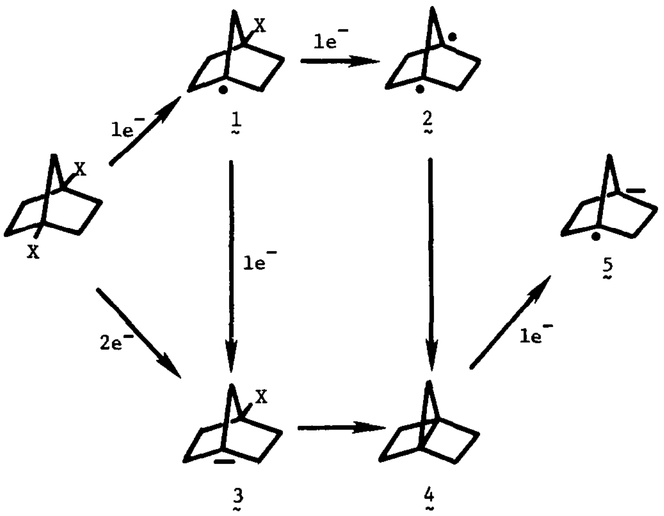
We have observed that polarograms for the reduction of 1,4-diiodonorbornane in dimethylformamide containing 0.1 $\underline{F}$ tetramethylammonium perchlorate exhibit two waves with diffusion currents in an approximate 2:1 ratio, the larger wave appearing at a more positive potential; in addition, the polarograms show a large current maximum similar to that previously described for 1-iododecane.[3] Half-wave potentials[4] are -1.05 and -1.38 V at 25°C and are -1.12 and -1.45 V at -36°C. Under similar conditions, 1,4-dibromonorbornane shows only a single polarographic wave with a much less pronounced maximum; the diffusion current is comparable to the total diffusion current for 1,4-diiodonorbornane and the half-wave potential is -1.35 V at 25°C and -1.40 V at -36°C. For both compounds a severe polarographic current minimum is seen at temperatures below -28°C.[5]

At a temperature of -33°C, controlled-potential electrolyses of 1,4-diiodonorbornane at mercury pool cathodes in dimethylformamide containing 0.1 $\underline{F}$ tetramethylammonium perchlorate result in an $\underline{n}$-value of 1.6 at potentials corresponding to the rising portion of the first polarographic wave; a 30% yield of 1-iodonorbornane and less than 10% yields of both norbornane and 1,1'-binorbornyl are obtained.[6] 1-Iodonorbornane, an intermediate in the reduction of 1,4-diiodonorbornane, is produced by transfer of one electron to the diiodide; other experiments have demonstrated that 1-iodonorbornane is reduced virtually quantitatively to norbornane in a two-electron step.[7] For potentials on the plateau of the first polarographic wave for 1,4-diiodonorbornane, the major electrolysis products are norbornane (15%) and bis(1-norbornyl)mercury (15%) and the $\underline{n}$-value is 2.2. For potentials on the plateau of the second wave, norbornane

(47%), bis(1-norbornyl)mercury (45%), and 1,1'-binorbornyl (2%) are produced; the *n*-value is 3.0. In low-temperature controlled-potential electrolyses of 1,4-dibromonorbornane, the *n*-value ranges from 2.5 to 3.0; electrolysis products include bis(1-norbornyl)mercury (up to 70%), norbornane (25 to 45%), and 1,1'-binorbornyl (up to 10%). No 1-bromonorbornane is formed upon reduction of the dibromide, even at potentials for which the monobromide is electroinactive and should be isolable. For both 1,4-diiodonorbornane and 1,4-dibromonorbornane, the *n*-values and product yields decrease at potentials corresponding to the polarographic minimum.

Coulometric reduction of either 1,4-diiodonorbornane or 1,4-dibromonorbornane at potentials for which the sum of the yields of norbornane and bis(1-norbornyl)mercury is greater than 90% has substantiated that each of the latter two compounds arises from transfer of three electrons to the starting material. By combining the absolute yield of each product with the number of electrons transferred to a molecule of starting material to form a particular product, we have performed a simple calculation which suggests that any molecule of starting material not transformed into and recovered as one of the various previously identified products undergoes a two-electron reduction and ultimately results in a nominally intractable material. Thus, three compelling features of the electrochemical reduction of 1,4-dihalonorbornanes have emerged: (a) norbornane is obtained from 1,4-dibromonorbornane by an alternate three-electron process which cannot involve 1-bromonorbornane as an intermediate; (b) although bis(1-norbornyl)mercury is a major product of the electrolysis of 1,4-dihalonorbornanes, little or no diorganomercury compound results from the reduction of 1-halonorbornanes;[7] and (c) a species is produced by the two-electron reduction of 1,4-dihalonorbornanes that is capable of undergoing polymerization.

Intermediacy of [2.2.1]propellane satisfactorily accounts for the facts summarized in the preceding paragraph. In the following mechanistic scheme are shown pathways by which transfer of a pair of electrons to 1,4-dihalonorbornanes can lead to generation of the propellane.[8]



Both the diradical (**2**)[9] and the halo-anion (**3**)[2] can give rise to the propellane (**4**). Propellane is known to react with anionic species at the bridgehead position;[2] linkage of two or more propellanes would generate oligomers difficult to detect by means of gas chromatography.

To establish the existence of propellane-derived oligomers, an electrolysis of 1,4-diiodonorbornane was performed under conditions designed to maximize the yield of high-molecular-weight products; the experiment was done at room temperature in dimethylformamide containing 0.1 *F* tetramethylammonium perchlorate at a potential (-1.4 V) corresponding to the rising portion of the second polarographic wave. Subjecting the mixture of products to vacuum removed all low-molecular-weight species; the semi-solid mass that remained showed infrared absorption bands characteristic of the norbornyl system and the carbonyl group of an amide, but no band attributable to the stretching mode of an alkene.[10] Mass spectrometric analysis revealed molecular ions and fragments formed from $H(C_7H_{10})_xC_3H_6NO$, where x is 1, 2, or 3. These compounds apparently arise from addition of a radical or anion derived from the solvent to molecules of the propellane. In the mass spectrum, the base peak (*m/e* = 95) corresponds to the 1-norbornyl moiety; species of mass 94 corresponding to the propellane are lost during the fragmentation process.[11]

One-electron reduction of the propellane completes the alternate three-electron pathway to norbornane. Radical-anion **5**, the product of this one-electron process, can gain a hydrogen atom and a proton to give norbornane or can adsorb upon the mercury surface and accept a proton to eventually yield bis(1-norbornyl)mercury.[12] Electrolytic reduction of the propellane is prevented by adsorption of a complex ionic species consisting of tetramethylammonium and halide ions onto the mercury cathode at potentials corresponding to the polarographic minimum;[5] if the propellane is not reduced, it reacts to form oligomers.

Further work concerning the electrochemistry, product yields, and mechanisms for the reduction of 1-halonorbornanes and 1,4-dihalonorbornanes, the characterization of the propellane-dimethylformamide oligomers, and the adsorption phenomena responsible for the polarographic minimum is in progress.

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References and Notes

1. K. B. Wiberg, W. F. Bailey, and M. E. Jason, *J. Org. Chem.*, **41**, 2711 (1976).
2. K. B. Wiberg, W. E. Pratt, and W. F. Bailey, *J. Am. Chem. Soc.*, **99**, 2297 (1977).
3. G. M. McNamee, B. C. Willett, D. M. La Perriere, and D. G. Peters, *J. Am. Chem. Soc.*, **99**, 1831 (1977).
4. All potentials are quoted with respect to a reference electrode consisting of a saturated cadmium amalgam in contact with dimethylformamide saturated with both cadmium chloride and sodium chloride [L. W. Marple, *Anal. Chem.*, **39**, 844 (1967); J. L. Hall and P. W. Jennings, *Anal. Chem.*, **48**, 2026 (1976)]; this electrode has a potential of -0.750 V *vs.* the aqueous saturated calomel electrode.

5. W. F. Carroll, Jr., D. M. La Perriere, E. C. Torp, and D. G. Peters, Abstracts, 175th National Meeting of the American Chemical Society, Anaheim, CA, March, 1978, ANAL 56.

6. Yields were determined by means of gas chromatographic analysis of the mixture of products (along with phenylcyclohexane, added as an electroinactive internal standard at the start of each electrolysis). Gas chromatographic response factors were measured for each compound, and all yields correspond to the absolute percentage of starting material incorporated into a particular product.

7. Electrolytic reduction of 1-iodonorbornane (as well as 1-bromonorbornane) leads to no more than a 5% yield of bis(1-norbornyl)mercury; W. F. Carroll, Jr., and D. G. Peters, Abstracts, 174th National Meeting of the American Chemical Society, Chicago, IL, August, 1977, ORGN 183. A report of this work has been submitted for publication.

8. An alternate mechanism for formation of the propellane involves intramolecular cyclization of the 4-halo-1-norbornyl radical (**1**) in a manner similar to that of the 3-iodopropyl radical; however, the free halogen atom liberated by the process would be electroactive, so that this alternate mechanism would be indistinguishable from formation of the propellane (**4**) via the diradical (**2**).

9. W-D. Stohrer and R. Hoffmann, J. Am. Chem. Soc., **94**, 779 (1972).

10. It is conceivable that 1,3-dimethylenecyclopentane, the product of rearrangement of the [2.2.1]propellane, might be the source of the polymeric material,[1,9] but the absence of an infrared absorption band corresponding to the stretching mode of an alkene eliminates this possibility.

11. It seems unlikely that oligomers should arise from coupling of 4-halo-1-norbornyl radicals (**1**), because radical-coupling reactions have not been observed under the experimental conditions utilized in this investigation.[3] Moreover, the solvent (dimethylformamide) would act as an efficient hydrogen atom donor for such radicals. Finally, an oligomeric chain would have to be terminated by a solvent-derived radical, and such multiple radical-coupling reactions seem even less probable.

12. J. L. Webb, C. K. Mann, and H. M. Walborsky, J. Am. Chem. Soc., **92**, 2042 (1970).

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