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Registry No. Hg⁺, 22542-11-6; KH₂PO₄, 7778-77-0; NH₄H₂PO₄, 7722-76-1.

(8) We thank a referee for suggesting this point.

[2.2.1]Propellane

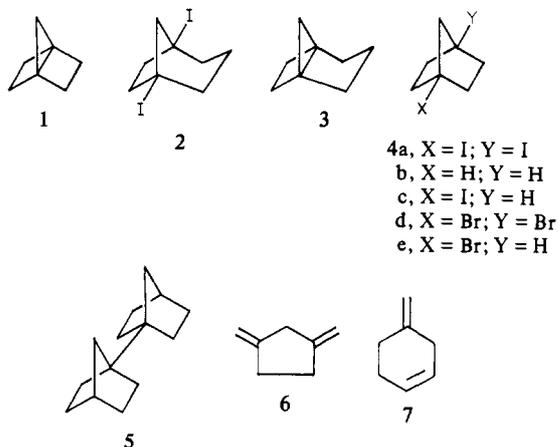
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Because of an inverted geometry at the bridgehead carbons^{1,2} and a consequent unusual degree of reactivity, small strained-ring propellanes have generated considerable recent interest both from theoretical and synthetic points of view.³⁻¹⁰ Much evidence for the transient existence of [2.2.1]propellane¹¹ (**1**) has been amassed



from both chemical and electrochemical reduction of 1,4-dihalonorbornanes,^{4c,5,10} but attempts to isolate this compound have failed so far. We now report the preparation of matrix-isolated

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(11) An alternative name for **1** is tricyclo[2.2.1.0^{1,4}]heptane.

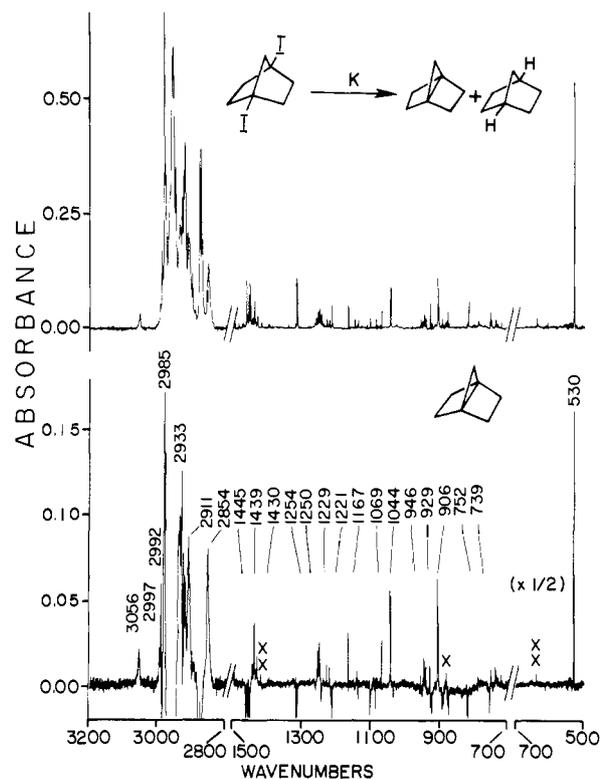


Figure 1. (Top) Matrix IR absorption spectrum (29 K) of the reaction products of **1** with potassium at 120 °C in nitrogen. (Bottom) Matrix IR absorption spectrum of [2.2.1]propellane (29 K) with norbornane computer subtracted. More norbornane is subtracted than is actually present so the norbornane bands are now negative. The band marked X probably belongs to **6**. Those marked XX are unidentified. Note change of vertical scale below 700 cm⁻¹.

1 by the method of gas-phase dehalogenation with metal atoms^{12,13} and its characterization by chemical and low-temperature spectroscopic means.

In the present version of the method,^{12b} which developed from that described in ref 13, the vapor of the dihalide precursor in a sonicated stream of excess matrix gas is allowed to react with alkali metal vapor in a reaction cell (12 cm), whose extension reaches into an ultrasound cleaning bath, and is subsequently deposited on a cold CsI window. In this fashion, 1,3-diiodopropane yields cyclopropane and propene and 1,5-diiodobicyclo[3.2.1]octane^{4f} (**2**) yields the known⁴ [3.2.1]propellane (**3**).

Using 1,4-diiodobicyclo[2.2.1]heptane (**4a**)^{10a,14} purified by preparative VPC (mp 103-104 °C), sonicated nitrogen carrier gas, and potassium vapor at 120 °C and trapping at 29 K, we obtained the FT IR matrix spectrum shown in Figure 1 (top). Comparison with authentic samples shows the presence of norbornane (**4b**) and another major component and the absence of significant amounts of 1-iodobicyclo[2.2.1]heptane¹⁵ (**4c**), 1,1'-binorbornyl¹⁶ (**5**), 1,3-dimethylenecyclopentane^{10a,17} (**6**), and 4-methylenecyclohexene^{18,19} (**7**).

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(17) The strongest band in **6** occurs at 883 cm⁻¹, and the small band at 881 cm⁻¹ may be due to traces of this material.

Computer subtraction of the spectrum of **4b** isolates the spectrum of the second major reaction product (Figure 1, bottom). We assign its structure as **1** on the basis of the following evidence: (i) the relative intensities of peaks in the IR spectrum remain the same in a series of experiments under varying conditions, indicating that only one species is involved; (ii) the IR spectrum remains unchanged when the matrix is annealed at 45 K for 3 h,²⁰ indicating that none of the major peaks belong to radicals;²¹ (iii) the use of cesium in argon²² at 115 °C in place of potassium and the use of 1,4-dibromobicyclo[2.2.1]heptane (**4d**)²³ at 150 °C in place of the diiodo precursor **4a** still lead to spectra containing the bands assigned to **1** and **4b**, although the degree of conversion is lower, demonstrating that neither the metal nor the halogen are present in the molecule;²⁴ (iv) the spectrum is compatible with the structure and quite similar to that of **3**, with characteristic cyclopropane CH₂ stretches at 3056 and 2997 cm⁻¹ (3065 and 2989 cm⁻¹ in **3**), CH₂ bends at 1445, 1439, and 1430 cm⁻¹ (1454 and 1438 cm⁻¹ in **3**), and intense peaks at 1044 and 906 cm⁻¹ (1030 and 955 cm⁻¹ in **3**) in regions characteristic for cyclopropanes and cyclobutanes, respectively;²⁵ both spectra exhibit a very intense peak at low frequencies (**1**, 530 cm⁻¹, **3**, 515 cm⁻¹); (v) heavy doping of the matrix with bromine during the course of the deposition,²⁶ isolation of warmup products by pumping into a trap and working up rapidly with pentane and aqueous bisulfite, followed by comparison of GC retention times and mass spectra (EI and CI), show the presence of 12% **4b**, 11% **5**, and 77% **4d** as the only major products.^{27,28}

The importance of ultrasound mixing to the success of the experiments should be noted. Without sonication, higher reaction temperatures were necessary and the reaction was still incomplete. The trapping with bromine then produced 12% **4a**, 52% **4c**, 23% **4d**, and 8% 1-bromobicyclo[2.2.1]heptane (**4e**) as the major products.

The very high intensity of the peak at 530 cm⁻¹, located in a region characteristic for skeletal deformation vibrations, which are usually of negligible intensity, is quite striking and may reflect an unusual charge distribution in small-ring propellanes.

All attempts to isolate or chemically trap **1** by distilling the matrix into a cold vessel met with failure. We hypothesize that **1** oligomerizes or polymerizes with extreme ease. This is perhaps not surprising in view of the expected extreme weakness of the central bond. Taking 27 and 28 kcal/mol as the strain energy of cyclobutane and cyclopropane, respectively, 17 kcal/mol as the strain energy of norbornane, and an estimate of 10 kcal/mol for the bridgehead distortion energy of **1**, one finds that approximately 75 kcal/mol of strain energy is relieved in breaking the bridgehead-bridgehead bond. Even if the bridgehead distortion energy were zero and the strength of a C-C bond were taken as 85

kcal/mol, the energy of this bond can be no more than 20 kcal/mol. This indicates that **1**, along with [2.2.2]propellane,^{8,29} may contain the most highly strained C-C bond yet synthesized. A more detailed discussion of this point is not warranted at this time, but it is interesting to note that barring a dramatic increase in the bridgehead distortion energy, the bridgehead-bridgehead bonds of both [2.1.1]- and [1.1.1]propellanes will actually be stronger than that in [2.2.1]propellane due to the larger residual strain left in the resultant biradical.

Further investigations of **1** and of the reaction of 1,4-diiodobicyclo[2.1.1]hexane with alkali metal vapors are currently under way.

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Registry No. **1**, 36120-90-8; **4a**, 40950-21-8; **4b**, 279-23-2; **4c**, 930-80-3; **4d**, 40950-22-9; **4e**, 13474-70-9; **5**, 18313-42-3; **6**, 59219-48-6.

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Triplet ESR Spectrum of the Copper Porphyrin Cation Radical

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It is well recognized that metalloporphyrin cation radicals play a key role as reaction intermediates in photosynthetic and metabolic processes.¹ They are also an interesting group of compounds insofar as metal ion is surrounded by a conjugated π radical. For these reasons, they have been attracting the increasing attention of chemists in diverse fields. Cation radicals with different central metal ions have been generated chemically, electrochemically, and photochemically, and their electronic structures have been extensively investigated by optical absorption and ESR spectroscopy.²⁻⁵ The central metal ions studied so far are mostly diamagnetic. It is expected that ESR spectra of the cation radicals with paramagnetic metal ions, if observed, will provide valuable information about the electronic structure of the systems. Copper porphyrin cation radicals belong to such species. They are the systems with one odd electron on the central metal ion and the other on the porphyrin ring. Therefore, their spin state is either singlet or triplet depending on which is lower in energy. No triplet ESR spectrum, however, has been detected for any of them. This has been speculated as being due to a singlet ground state or to line broadening of triplet spectra.

We report the first detection of a triplet ESR spectrum of a copper porphyrin cation radical produced in tetrachloroethane matrix at 77 K by γ radiolysis. Figure 1 shows the X-band ESR spectra at 77 K of a degassed tetrachloroethane solution of 10⁻³ M copper octaethylporphyrin (Cu^{II}OEP) before and after γ irradiation. The solution was irradiated with a 3.2 Mrd dose of γ rays from a ⁶⁰Co source. Since little information was available in the region around $g = 2$ owing to the strong signal of solvent radicals, the spectra taken with high gain are presented showing clear signals in the other region. The irradiated sample shows a pair of signals on both sides of the solvent radical signal with

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(19) In the pyrolysis of [3.2.1]propellane, D. H. Aue and collaborators detected small amounts of 4-methylenecycloheptene in addition to 1,3-dimethylenecyclohexane (personal communication).

(20) The optical quality of the matrix deteriorates in the process such that small peaks are no longer visible.

(21) Attempts to anneal to higher temperatures resulted in a loss of the matrix.

(22) The spectrum also contains **6** and large amounts of **4a**.

(23) The spectrum also contains **4e** and **6**, as well as large amounts of **4d**.

(24) Reaction of **4a** with sodium vapor required temperatures of 190 °C and gave only **4b** and **6**.

(25) Bellamy, L. J. "The Vibrational Spectra of Complex Molecules"; Chapman and Hall: London, 1975; Vol. I, pp 18, 32, 33; Vol. II, pp 8, 18.

(26) Sublimed at -78 °C through a tube held ~1 cm from the cold window.

(27) Control experiments gave complete recovery of starting material in the absence of metal vapor. Bromine will react with **4a** under more vigorous conditions. In CH₂Cl₂ at 41 °C with excess Br₂ the rate constant is 1.8 × 10⁻⁴ s⁻¹. In less polar solvents such as C₆H₁₂, no reaction occurs even at 80 °C: Pratt, W. E., Ph.D. Thesis, Yale University, New Haven, Conn., 1978.

(28) Controls showed that substantial amounts (about 70%) of **4b** are lost in workup. Also, some of **1** is sprayed onto the radiation shield and other parts of the cryostat, preventing its reaction with bromine, and we have no means of measuring the efficiency of reaction of bromine with **1**. These factors undoubtedly exaggerate the amount of **5** obtained. Percentages are corrected for detector response factors.

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