(25) (a) Wertz, D. H.; Allinger, N. L. *Tetrahedron* **1974**, *30*, 1579. (b) Allinger, N. L.; Sprague, J. T. *Ibid.* **1974**, *31*, 21. (c) Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1.

(26) For reviews, see: Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978. Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 464. Keese, R. *Ibid.* **1975**, *14*, 528. Buchanan, G. L. *Chem. Soc. Rev.* **1974**, *3*, 41.

(27) Lesko, P. M.; Turner, R. B. *J. Am. Chem. Soc.* **1968**, *90*, 6888. Also see Chiang, Y.; Kresge, A. J.; Wiseman, J. A. *Ibid.* **1976**, *98*, 1564.

(28) Chong, J. A.; Wiseman, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 8627. Dauben, W. G.; Robbins, J. D. *Tetrahedron Lett.* **1975**, 151.

(29) Shea, K. J.; Wise, S. *J. Am. Chem. Soc.* **1978**, *100*, 6519; *Tetrahedron Lett.* **1979**, 1011.

(30) Casanova, J.; Bragin, J.; Cottrell, F. D. *J. Am. Chem. Soc.* **1978**, *100*, 2264, and earlier references cited therein.

(31) Greenhouse, R.; Ravindranathan, T.; Borden, W. T. *J. Am. Chem. Soc.* **1976**, *98*, 6738. Greenhouse, R.; Borden, W. T.; Ravindranathan, T.; Hirotsu, K.; Clardy, J. *Ibid.* **1977**, *99*, 6955.

(32) Greenhouse, R.; Borden, W. T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1977**, *99*, 1664.

(33) Burkert, U. *Chem. Ber.* **1977**, *110*, 773.

(34) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005. Also compare Wertz, D. H.; Allinger, N. L. *Tetrahedron* **1979**, *35*, 3.

(35) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734.

(36) Calculated differences between the heats of formation of alkene and of alkane (corresponding to the heats of olefin hydrogenation) provide an alternative, but equivalent index.

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Adamantene

Sir:

The severely distorted anti-Bredt olefin, adamantene (**1**), has been sought repeatedly.[1-5] So far, the evidence for generation of **1** has been only indirect. For instance, self-trapping produced a mixture of [2 + 2] dimers,[1-3] and trapping with dienes[1,2,4] and methanol[5] produced the expected adducts. We now report a direct spectroscopic observation of **1**.

The method used for the generation of **1** is based on the "sodium flame" technique developed by Polanyi[6] for kinetic studies of gas-phase dehalogenation of organic halides with alkali metal vapors. Our experimental arrangement is different in that the gas-phase products are carried in a stream of argon to a cold (10 K) window where they are trapped in an argon matrix.[7] In this fashion, alkyl halides produce radicals, readily identified by their ESR spectra.[8]

1-Bromoadamantane reacts with either Na or K vapor in this manner to produce the known ESR spectrum of the 1-adamantyl radical.[9] 2-Bromoadamantane and Na or K similarly produce an ESR spectrum which even under optimum conditions (45 K) consists only of a broad doublet ($a_H \simeq 23$ G) with indications of further unresolved splitting. We assign it to the 2-adamantyl radical and the large splitting constant to the α proton. The spectra of both radicals are very intense and disappear in $\sim$1 h upon warming to 50 K under reduced pressure of argon, which prevents rapid sublimation of the matrix.

In organic dihalides, one can expect the initial formation of a monohalo radical, followed either by fragmentation or by further dehalogenation reaction with metal. This has indeed been observed. For instance, 1,3-diiodopropane produces a mixture of cyclopropane and propene[8] and benzylic 1,2- or 1,4-dihalides produce the expected polyolefins.[7] We now find that the use of either 1,2-dibromoadamantane (**2**) and K vapor or 1,2-diiodoadamantane (**3**) and either Na or K vapor produces only very weak ESR signals. The dihalides were prepared by the method of ref 2 and were free of monohalides as judged by gas-liquid chromatography. The ESR signals are identical with those of the 1-adamantyl radical and disappear upon warming in the same fashion. We have found no evidence for the presence of halogen-containing radicals in the spectra. Since so little paramagnetic material is produced from **2** and **3**, which ought to be at least as reactive as the corresponding monohaloadamantanes, the bulk of the reaction products is likely to be diamagnetic, similarly as in the case of other dihalides.

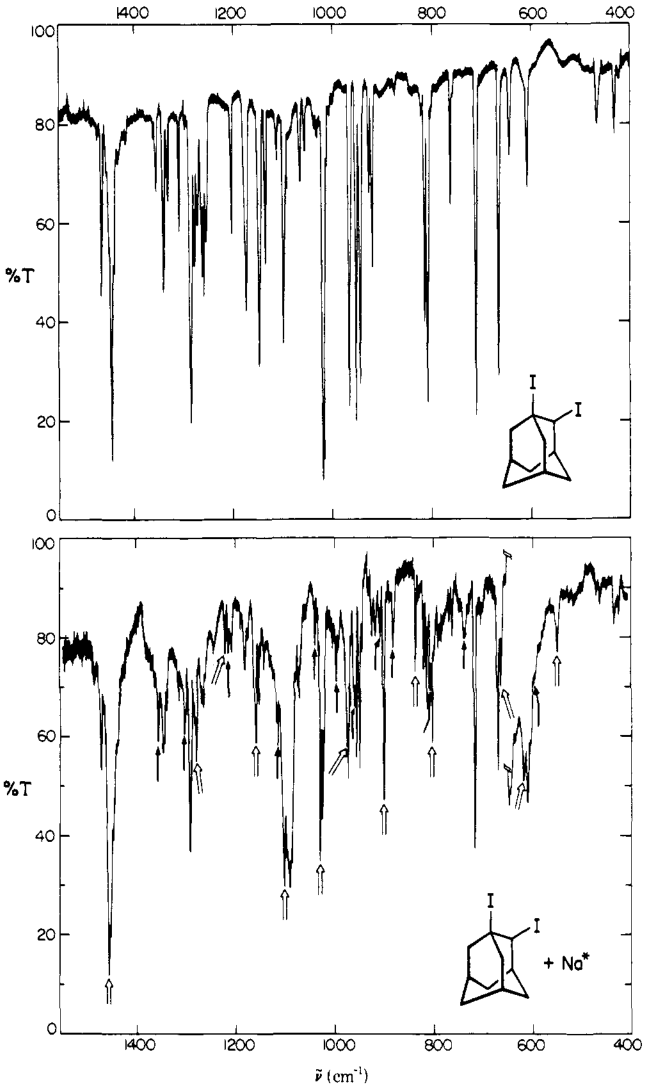

Figure 1. IR spectrum of **3** (top) and of a reaction mixture from **3** and excited Na vapor (bottom), argon 10°. The principal absorptions assigned to **1** are indicated by double arrows. Weaker absorptions probably also associated with **1** are indicated by single arrows.

IR spectra (Figure 1) reveal that about half of **3** is converted into a single new product using either K vapor or microwave-discharged[7] Na vapor. Both reactions produce the same product, characterized by about a dozen strong absorptions. These differ from the known[10] absorptions of adamantene dimers and biadamantyls. The strongest among these are also observed starting with **2**, and we conclude that the product contains neither halogen nor metal atoms. It survives for at least 1 h at 70 K[11] under reduced argon pressure without an appreciable change, proving that it is distinct from the radicals observed in the ESR experiments. The positions of the IR absorptions are compatible with an assignment of the new

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species as **1**. The intense band at 900 cm^{-1} is probably due to an out-of-plane CH bend (848 cm^{-1} in homoadamantene[12]), but a definitive assignment will have to await the results of experiments on deuterated material. A very weak band appears at ~3015 and could be attributed to olefinic C—H stretch. Several very weak bands occur in the 1520-1650-cm^{-1} region where a C=C stretch would be expected; unfortunately this region is obscured in our spectra by absorptions owing to trace amounts of water.

When the argon matrix is warmed and the residue subjected to GC-MS analysis, only two major peaks appear. By comparison with authentic samples, the first is identified as due to the starting dihalide, the second as due to the [2 + 2] dimers of adamantene. The two peaks have comparable areas. In addition, several much smaller GC peaks are present. One of the larger of these has the mass spectrum expected for a biadamantyl. These results agree exactly with expectations based on previous reports[1-3] and leave little doubt that the new product whose IR spectrum is observed at 10 K indeed is **1**.

We can now interpret the ESR results obtained with **2** and **3**. We propose that the small amounts of the 1-adamantyl radical formed originate in a gas-phase reaction in which **1** abstracts a hydrogen from **2** or **3**. This process will also account for the formation of biadamantyls (1,1-biadamantyl is the dominant isomer[1]). A close analogy is found in the gas-phase dehalogenation reactions of iodinated benzenes, run under similar conditions, in which benzene is one of the main products.[8]

From the properties of **1** observed so far, we conclude that its severely distorted double bond still is best viewed as a double bond rather than a biradical: the dimerization of **1** is not diffusion controlled at 70 K, monohaloadamantyl radicals apparently fragment readily at 120 °C, and the CH out-of-plane bend region in the IR spectrum resembles that of trisubstituted olefins more than that of the isopropyl radical (out-of-plane CH bend at 375 cm^{-1}).[13] However, the double bond undoubtedly has a partial biradicaloid character: after all, ordinary olefins do not dimerize nor do they abstract hydrogen atoms, even from good donors.[14]

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References and Notes

(1) D. J. Martella, M. Jones, Jr., and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **100**, 2896–2897 (1978).
(2) W. Burns, D. Grant, M. A. McKervey, and G. Step, *J. Chem. Soc., Perkin Trans. 1*, 234–238 (1976), and references therein.
(3) D. Lenoir, *Tetrahedron Lett.*, 4049–4052 (1972); D. Lenior and J. Firl, *Justus Liebigs Ann. Chem.*, 1467–1473 (1974).
(4) A. H. Alberts, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 3047–3049 (1973).
(5) J. E. Gano and L. Eizenberg, *J. Am. Chem. Soc.*, **95**, 972–974 (1973).
(6) For a review, see B. G. Gowenlook, C. A. F. Johnson, and J. E. Parker, in "Comprehensive Chemical Kinetics", Vol. 18, C. H. Bamford and C. F. G. Tipper, Eds., Elsevier, New York, 1976, Chapter 4 ("Selected Elementary Reactions"). For a survey of preparative applications, see M. J. McGlinchey and P. S. Skell in "Cryochemistry", M. Moskovits and G. A. Ozin, Eds., Wiley, New York, 1976, Chapter 4.
(7) K. L. Tseng and J. Michl, *J. Am. Chem. Soc.*, **99**, 4840–4842 (1977).
(8) D. Otteson, R. Sustmann, F. H. Walker, K. B. Wiberg, and J. Michl, unpublished results. Similar dehalogenation reactions occur in the surface on cold matrices (see, e.g., J. E. Bennett, B. Mile, and A. Thomas, *Proc. R. Soc. London, Ser. A*, **293**, 246–258 (1966)) and with photoactivation, in the bulk (P. H. Kasai, *Acc. Chem. Res.*, **4**, 329 (1971)).
(9) At low temperatures, the ESR spectrum is very poorly resolved, but at ~45 K and above, we observe ~60 of the lines reported: P. J. Krusic, T. A. Rettig, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 995–997 (1972).
(10) D. J. Martella and M. Jones, Jr., private communication.
(11) The temperature readings in our ESR and IR experiments are only approximate since they were taken at the cold heads of an Air Products Displex cryostat rather than in the matrices themselves. The differential error between the ESR and the IR cryostat is <10° as judged by events such as disappearance of hydrogen gas from an argon matrix or of the argon matrix itself.
(12) D. J. Martella, M. Jones, Jr., P. v. R. Schleyer, and W. F. Maier, *J. Am. Chem. Soc.*, preceding paper in this issue.
(13) J. Pacansky, D. E. Horne, G. P. Gardini, and J. Bargon, *J. Phys. Chem.*, **81**, 2149–2154 (1977).
(14) *trans*-Cyclohexene appears to abstract hydrogen atoms from ether solvent: P. J. Kropp, H. G. Fravel, Jr., and T. R. Fields, *J. Am. Chem. Soc.*, **98**, 840 (1976).
(15) University of Utah.
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Mechanism of the Formation of Dihydrogen from the Photoinduced Reactions of Tris(bipyridine)ruthenium(II) with Tris(bipyridine)rhodium(III)

Sir:

The properties of the metal to ligand charge-transfer excited state of tris(2,2′-bipyridine)ruthenium(II) ($^*Ru(bpy)_3^{2+}$) have been extensively studied[1] and the use of $Ru(bpy)_3^{2+}$ in various solar energy conversion schemes has been proposed.[2-5] Recently $Ru(bpy)_3^{2+}$ has been employed successfully as a mediator in the photoreduction of water to dihydrogen in both heterogeneous[6-9] and homogeneous systems.[10] The report of Lehn and Sauvage[6] concerning hydrogen production from aqueous solutions containing $Ru(bpy)_3^{2+}$, triethanolamine (TEOA), $RhCl_3$, K_2PtCl_6, and 2,2′-bipyridine (bpy) evoked our interest and led us to a detailed study of a closely related system. We find that visible light irradiation of aqueous solutions of $Ru(bpy)_3^{2+}$, $Rh(bpy)_3^{3+}$, TEOA/TEOAH$^+$ (pH 8.1), and K_2PtCl_4 (or K_2PtCl_6) yields dihydrogen with a quantum yield of up to 0.11 ± 0.01 mol einstein^{-1} depending on the conditions used.[11] The dihydrogen is the end product of a sequence of electron-transfer reactions: $^*Ru(bpy)_3^{2+}$ formed by visible light absorption is oxidized by $Rh(bpy)_3^{3+}$ to produce $Rh(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$. The latter is rapidly reduced by TEOA. In the absence of platinum the rhodium(II) disproportionates to give rhodium(III) and rhodium(I); in the presence of platinum the rhodium(II) may either disproportionate or yield dihydrogen. Here we report our observations on the photochemical and dark reactions in this system.

Continuous photolysis (450-W xenon lamp, λ 450 ± 20 nm, $I_0 = 2 \times 10^{-8}$ einstein s^{-1}) of solutions containing 0.005-3.0 $\times 10^{-4}$ M $Ru(bpy)_3^{2+}$, 2-5 $\times 10^{-3}$ M $Rh(bpy)_3^{3+}$,[12] and 0.2 M TEOA at pH 8.1 (μ = 0.5 M, Na_2SO_4), but no $PtCl_6^{2-}$ or $PtCl_4^{2-}$, gives no dihydrogen; instead a pink species is formed. The pink species is identified as a Rh(I) complex containing two bpy ligands[13] from the following experiments. An aqueous solution of $Rh(bpy)_2(OH_2)_2^{3+}$ [14] was reduced with amalgamated zinc to give a pink-brown stock solution A. The spectra observed when this solution is diluted in various media are similar to those produced in photolysis experiments under the same conditions (see Figure 1).[15] Solution A was treated with excess $Os(bpy)_3^{3+}$ and the $Os(bpy)_3^{2+}$ produced was calculated from the absorbance increase at 480 nm to be (2.0 ± 0.2)Os(II) per $Rh(bpy)_2(OH_2)_2^{3+}$ present in the solution before reduction.[16] Thus the rhodium species in solution A is Rh(I). Since no bpy could be extracted into chloroform from solution A, two bpy groups must be attached to Rh(I). From the $Rh(bpy)_2^+$ molar absorptivity[15] the quantum yield for Rh(I) formation (conditions as above) is 0.11 ± 0.01 mol einstein^{-1} and the ratio of Rh(I) to bpy produced in the photoinduced reduction of $Rh(bpy)_3^{3+}$ is 1.1 ± 0.1 (eq 1).

$$Rh(bpy)_3^{3+} + 2e \rightarrow Rh(bpy)_2^{+} + bpy \qquad (1)$$

Since TEOA and $Rh(bpy)_3^{3+}$ do not absorb light in the visible region, the primary product of irradiation of the

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