Tetrahedron Letters No. 11, pp 943 - 946, 1975. Pergamon Press. Printed in Great Britain.

PHOTOCHEMICAL SUBSTITUTION REACTIONS OF ADAMANTYL HALIDES

Robert R. Perkins and Richard E. Pincock*

Department of Chemistry, University of British Columbia, Vancouver, Canada, V6T 1W5

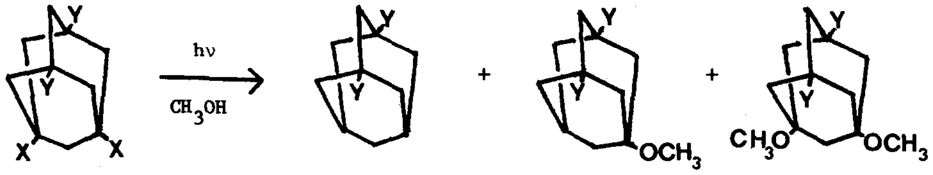
(Received in USA 30 December 1974; received in UK for publication 10 February 1975)

Recent reports concerning the photochemistry of alkyl halides have given evidence of competing free radical and ionic reaction pathways.[1,2] The irradiation of 1-bromonorbornane in methanol yields 30% of the corresponding 1-methyl ether accompanied by hydrogen transfer to give 55% of norbornane; with 1-iodonorbornane a greater cationic contribution occurs and the yields are 72 and 15% respectively.[2]

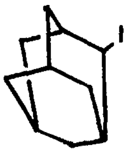
During investigations to determine alternate means of generating 1,3-dehydroadamantanes[3] we have examined the photochemistry of several bromides and iodides of adamantane; the results illustrate competing pathways in this ring system and the reactions involved may have some synthetic utility.

Irradiation[4] of either 1-bromo- or 1-iodoadamantane (I-Br or -I) in methanol leads to adamantane (II) (28 and 5%, respectively) and 1-methoxyadamantane (III) (72 and 95%, respectively). Nearly quantatative yields of the corresponding ethers[5] are readily obtained by irradiation of 1-iodoadamantane in ethanol, isopropanol, or 2-methoxyethanol. In methanol 2-iodoadamantane (IV) produces 2-methoxyadamantane without rearrangement to any 1-substituted product.

A considerable difference between reactions of iodides and bromides is shown with the dihalides V and VI (see table). The distribution of products is consistent with independent and successive reactions of each halide in a dihaloadamantane; no concerted nor interrelated loss of both halogens (which would give rise to the strained propellane system of 1,3-dehydroadamantane VII) was noted.[6] Thus if the reaction of the dibromide Va is monitored by gas liquid chromatography, and stopped before replacement of all bromides occurs, the products are 2% II, 25% III, 18% I-Br, 33% VIII, 18% XII, and 4% Va. Dibromide VIa gave a similar distribution of products when incompletely photolyzed. In a related manner, the photolysis of 1,3,5 -tribromoadamantane in methanol results in considerable hydrogen transfer from solvent and the final product is partitioned between 1-methoxy-, 1,3-dimethoxy-, and 1,3,5-trimethoxyadamantane in 30, 50, and 11% yields, respectively. The relative amount of substitution by solvent anion (cationic path) and replacement by hydrogen (free radical or anionic path) is greater with iodides than with bromides but the distribution between reaction paths is completely unaffected by the presence of the two methyl groups at the other bridgehead positions of adamantane (compare Va with VIa above). In contrast to solvolytic formation of adamantyl ions[7] the decomposition of the photoactivated carbonium ion percursor is apparently insensitive to electronic properties of methyl substitutents.

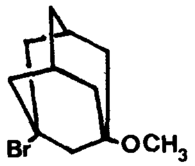


V	II Y=H	III Y=H	VIII Y=H
a; X=Br, Y=H	11%	50%	39%
b; X=I, Y=H	4%	0	96%
VI	IX Y=CH_3	X Y=CH_3	XI Y=CH_3
a; X=Br, Y=CH_3	9%	53%	38%
b; X=I, Y=CH_3	5%	0	95%



IV

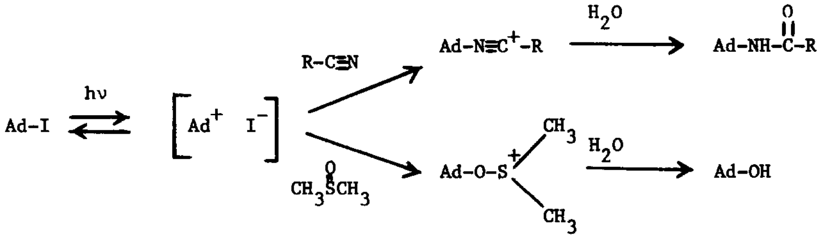
VII



XII

Compared to photolysis of 1-halonorbornanes[2] the greater stability of the bridgehead carbonium ion in the adamantane ring structure results in a greater ionic contribution to the overall reaction from either iodides or bromides. When this is coupled with the greater tendency for iodides to produce the product from cationic reaction, the photolysis of iodoadamantanes should be a good method of producing intermediate adamantyl cations or associated ion pairs. Certainly the mono- or di-iodoadamantanes (see table) produce essentially only the products expected from carbonium ion (rather than free radical, "dehydro", or anionic) intermediates.

Interestingly, attempts to trap out carbonium ion intermediates with nucleophiles such as sodium cyanide in methanol led instead only to relatively more adamantane (56% and 20% from photolysis of 1-adamantyl bromide and iodide, respectively, compared to 28% and 5% without cyanide present). Only traces of 1-cyanoadamantane were produced along with the major product 1-methoxyadamantane. An electron transfer from cyanide or methoxide similar to that suggested[2] may be responsible for this. Photolysis of iodoadamantane in dimethylsulfoxide gives 90% yields of 1-adamantanol; when the solvent is saturated with sodium cyanide only 8% of 1-cyanoadamantane is produced. However, photolysis of iodides in alkyl nitrile solvents containing traces of water[8] readily gave 90% yields of amides through trapping of nitrilium ions with water[9]. Extensions which would allow production of other adamantane derivatives by reaction of adamantyl ions under the mild and neutral conditions of photolysis are being investigated.



Acknowledgement: This work was supported by grants from the National Research Council and from the University Committee on Research, University of British Columbia.

References and Footnotes:

1. P. J. Kropp, T. H. Jones, and G. S. Poindexter, *J. Amer. Chem. Soc.*, **95**, 5420 (1973).
2. G. S. Poindexter and P. J. Kropp, *ibid.*, **96**, 7142 (1974).
3. W. B. Scott and R. E. Pincock, *ibid.*, **95**, 2040 (1973).
4. All reactions were run in degassed solutions(*ca.* 10^{-2} M in halogen compound) in quartz vessels using a General Electric UA-3 360 watt high pressure mercury lamp. Irradiation times varied from 3 hours (usual for iodides) to 20 hours (for bromides). Chlorides were inert. Control experiments in the dark showed solvolytic reaction of only *ca.* 20% for iodoadamantane and *ca.* 0% for bromoadamantane in methanol over a three week period at room temperature.
5. All new compounds gave satisfactory spectral data and analytical results.
6. Electrochemical generation of highly strained [2.2.2]propellane from 1,4-dibromobicyclo [2.2.2]octane has been accomplished by K. B. Wiberg, G. A. Epling, and M. Jason, *ibid.*, **96**, 912 (1974).
7. *Cf.*, R. C. Bingham and P. v. R. Schleyer, *Fortschritte der chemischen Forschung*, **18**, 74 (1971).
8. Although some amide could be detected even when especially dried acetonitrile was used the reaction was very slow and incomplete.
9. For reaction of adamantyl ions (generated from a variety of sources) with acetonitrile to produce 1-adamantylacetamide see V. R. Koch and L. L. Miller, *J. Amer. Chem. Soc.*, **95**, 8631 (1973); D. N. Kevill and F. L. Weitl, *J. Org. Chem.*, **35**, 2526 (1970).