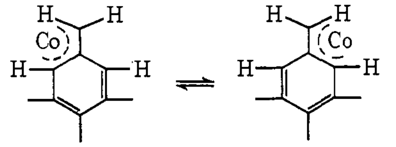
mers in five coordination. (In this context, there is no distinction between bond rotation and a polytopal rearrangement.)

The benzyl compound must undergo an additional fast rearrangement because there is no detectable inequivalence of ortho (and of meta) carbon atoms by ^{13}C nmr even at −130°. It is proposed that the bond shift (eq 1) is rapid on the nmr time scale at



(1)

−130°.[12] Although slow with respect to the nmr time scale, a $\pi \rightleftharpoons \sigma$ process[13] may be less activated in the benzyl than in the allyl derivatives because the former has a qualitatively higher reactivity toward CO displacement of one $P(OCH_3)_3$ group.[14,15]

---

(12) This is also necessary to account for the low-temperature AB_2 (rather than ABC) ^{31}P spectrum.

(13) For discussion of fluxionality in a far more rigid class of *trihapto*-benzyl complexes, $(h^3\text{-}C_6H_5CH_2)(h^5\text{-}C_5H_5)Mo(CO)_2$, see discussion by F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 1339 (1969). In their carefully designed experiments, rearrangement mechanism was not established, but they suggested that a $\pi \rightleftharpoons \sigma$ process might be dominant.

(14) This research was supported by National Science Foundation Research Grant GP-9562.

(15) We are indebted to Messrs. G. Watunya and J. White for the low-temperature ^{31}P and ^{13}C spectra and Dr. P. Meakin for simulation of the ^{31}P spectra.

(16) Address correspondence to this author at the Department of Chemistry, Cornell University, Ithaca, N. Y. 14850.

(17) National Science Foundation predoctoral trainee.

E. L. Muetterties,*[16] F. J. Hirsekorn[17]
Department of Chemistry, University of Pennsylvania
Philadelphia, Pennsylvania 19104

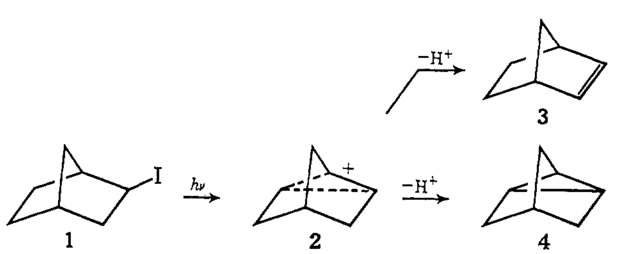
Received April 23, 1973

Photochemistry of Alkyl Halides. I. Ionic *vs.* Radical Behavior

Sir:

The photochemistry of alkyl iodides has been the subject of extensive study.[1] Except for the possibility of "molar elimination" of hydrogen iodide under certain conditions,[2] it is generally thought that absorption of light by the C–I chromophore results invariably in homolytic cleavage of the C–I bond and the subsequent generation of radical-derived products.[1] We wish to report the results of preliminary studies which show that the photochemical behavior of alkyl iodides in solution is richly varied and does not uniformly lead, at least ultimately, to free-radical-type products. Moreover, there is a marked contrast in behavior between alkyl iodides and the corresponding bromides.

For example, irradiation[3] of 2-*exo*-iodonorbornane (**1**),[4,5] bp 87° (16 mm), in ether solution afforded a mixture of 2-norbornene (**3**) and nortricyclene (**4**) in yields of 81 and 19%, respectively; in methanol the hydrocarbons **3** and **4** were again formed (77 and 12.5%).[6]



Additional insight was obtained by irradiation of the iodo ether **5** (X = I; Y = H_2),[7] bp 105° (4 mm), in ether solution to give a mixture of the products **9–12**[8] (Table I). Analogous behavior was exhibited by the corresponding lactone **5** (X = I; Y = O),[9] which again afforded products **9–12**.[10] A marked solvent effect was observed for both iodides; in methanol only a single principal photoproduct was formed, the ring-opened system **12**. In contrast to the iodides, the corresponding bromides **5** (X = Br; Y = H_2 and O)[7,9] afforded only the reduction products **9** (Y = H_2 and O). Similarly, 2-*exo*-bromonorbornane gave norbornane (92%) on irradiation in either ether or methanol.

There is thus a significant difference in photochemical behavior between alkyl iodides and their corresponding bromides. The photoproducts from the bromides are typical of radical-derived products.[11] However, the occurrence of Wagner–Meerwein shifts, 1,3 elimination,

Table I. Irradiation of Halides **5**

Halide **5**	Solvent	Time, hr	Yield, % **5**	**9**	**10**	**11**	**12**
X = I; Y = H_2	$(C_2H_5)O$	12	11	33	23	28	2
		2[a,b]	8	9	21	30	*c*
	CH_3OH	1	3	*c*	*c*	*c*	93
X = I; Y = O	$(C_2H_5)_2O$	12	2	36	18	18	24
	CH_3OH	2	*c*	*c*	*c*	*c*	90[d]
X = Br; Y = H_2	$(C_2H_5)_2O$	8[a]	18	78	*e*	*e*	*e*
	CH_3OH	8[a]	*e*	83	*e*	*e*	*e*
X = Br; Y = O	$(C_2H_5)_2O$	20[a,f]	6	87	*e*	*e*	*g*

[a] The broad spectrum of a 450-W mercury arc was used. [b] An additional product was obtained in 26% yield. [c] Trace. [d] Isolated yield. [e] None detectable. [f] Vycor filter used. [g] Not analyzed.

---

(1) For a recent review, see J. R. Majer and J. P. Simons, *Advan. Photochem.*, 2, 137 (1964).

(2) R. Schindler and M. H. J. Wijnen, *Z. Phys. Chem.* (*Frankfurt am Main*), 34, 109 (1962).

(3) Irradiations were conducted at 253.7 nm in a quartz vessel using 50-ml solutions containing 1.0 g of halide. Mossy zinc was normally used as an anhydrous means for scavenging liberated iodine and hydrogen iodide, but similar results were obtained in the absence of zinc. Yields were determined by gas chromatographic analysis relative to a hydrocarbon standard. Except where indicated, control studies showed that no reaction occurred in the absence of light, even in the presence of added iodine or zinc iodide.

(4) Prepared by the general procedure of H. Stone and H. Shechter, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 543.

(5) Proper spectral and analytical data were obtained for all novel compounds. Novel photoproducts were further characterized by conversion to compounds of known structure.

(6) Methyl 2-*exo*-norbornyl ether was also obtained in 10% yield. However, control runs afforded this product, *but not* 3 *or* 4, in similar yields in the dark.

(7) Prepared by treatment of 5-norbornene-2-*endo*-methanol (12, Y = H_2) with an excess of iodine or bromine and 1 equiv of triethylamine in methanolic solution.

(8) H. A. Bruson and T. W. Riener, U. S. Patent 2,440,220 (1948); *Chem. Abstr.*, 42, 5471 (1948); T. Shono, A. Ikeda, and Y. Kimura, *Tetrahedron Lett.*, 3599 (1971).

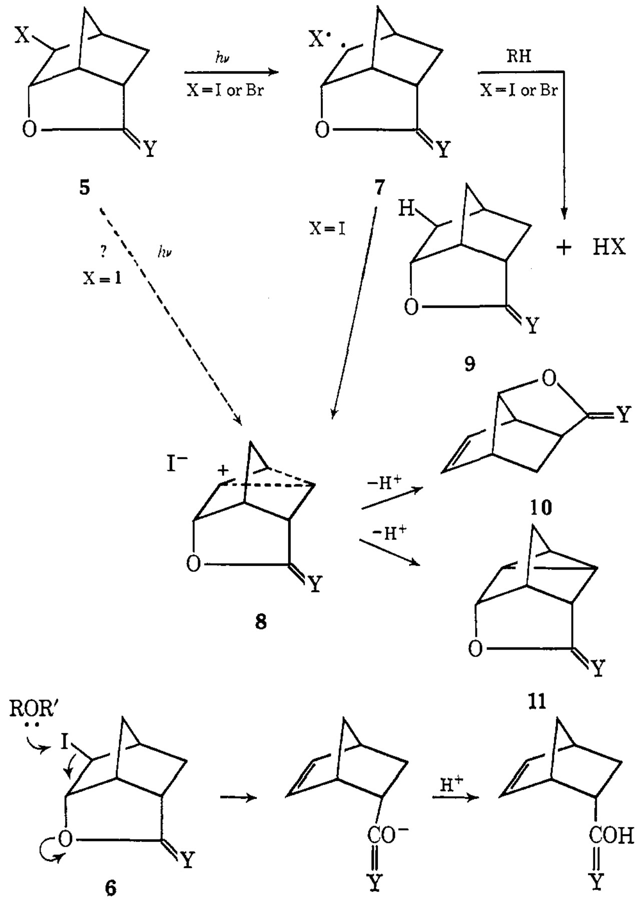
(9) C. D. Ver Nooy and C. S. Rondestvedt, Jr., *J. Amer. Chem. Soc.*, 77, 3583 (1955).

(10) K. Alder and G. Stein, *Justus Liebigs Ann. Chem.*, **514**, 197 (1934); K. Alder and O. Diels, *ibid.*, **460**, 117 (1928).

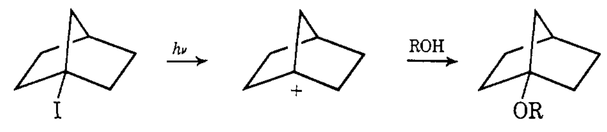
(11) For a recently reported exception to this general behavior shown by a benzylic bromide, see S. J. Cristol and G. C. Schloemer, *J. Amer. Chem. Soc.*, **94**, 5916 (1972).

and nucleophilic substitution in the case of iodides strongly implies the involvement of cationic intermediates. It is not clear from the preliminary data whether these arise directly from excitation of the C–I chromophore or whether, as shown in Scheme I, excitation leads first to homolytic cleavage followed by an electron-transfer process. However, the concurrent formation of the reduction product **9** and the ionic products **10** and **11** makes the latter a tentatively attractive proposal. The difference in behavior between bromides and iodides is perhaps attributable to the difference in reactivity of Br· and I·. The former is a "hot" radical which probably undergoes rapid hydrogen abstraction from the solvent cage, leading to radical-type products, whereas the latter is incapable of abstracting hydrogen atoms from most solvents; in the absence of an efficient competing process in the latter case, the radical pair has sufficient lifetime for electron transfer to occur.

Scheme I



The powerfulness of the photochemistry of alkyl iodides for the facile generation of cations is seen by the rapid conversion of 1-iodonorborane (**13**)[12] to the ether **14a** (79%) and norbornane (8%) on irradiation in methanol (2 hr). Under aqueous conditions the corresponding alcohol **14b**[13] is formed; presumably both products arise *via* generation and nucleophilic trapping of the 1-norbornyl cation.



13

14a, R = CH_3
b, R = H

The ring opening process leading to **12** (Y = H_2 or O) apparently proceeds *via* yet another mechanistic pathway, perhaps involving a nucleophilic attack by solvent on the excited state at iodine prior to homolytic dissociation, as indicated by **6**.[14] In view of the cleaness and rapidity of this photoreaction, it is a desirable alternative to the traditional zinc–acetic acid procedure for the opening of iodo lactones and ethers.[15]

It is clear that alkyl iodides display a rich array of photochemical behavior, much of it having synthetic as well as mechanistic interest. Continued studies are in progress to delineate further both aspects of the photobehavior of a wide variety of organic iodides.

Acknowledgment. Partial support of this work by the Research Corporation is gratefully acknowledged, as is the assistance of T. Randall Fields with some of the initial experiments.

[12] P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. B. Bieber, *J. Amer. Chem. Soc.*, **88**, 78 (1966).

[13] D. B. Denney and R. R. DiLeone, *ibid.*, 84, 4737 (1962).

[14] A free-radical fragmentation process does not seem likely, at least for the lactone **5** (X = I; Y = O), in view of the well-known propensity of the carboxyl radical for undergoing decarboxylation.

[15] C. S. Rondestvedt, Jr., and C. D. Ver Nooy, *J. Amer. Chem. Soc.*, 77, 4878 (1955).

[16] Alfred P. Sloan Research Fellow.

Paul J. Kropp,*[16] Tappey H. Jones, Graham S. Poindexter
Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

Received September 30, 1972

Three-Electron Oxidations. IV. Chromic Acid Cooxidation of Tertiary Hydroxy Acids and Alcohols[1,2]

Sir:

We have recently reported[3] a dramatic rate acceleration of two to three orders of magnitude observed in the chromic acid oxidation of a two-substrate system of isopropyl alcohol and oxalic acid. The results lead us to propose a mechanism consisting of the formation of a termolecular complex and its decomposition in a single-step three-electron oxidation reaction.

We have now obtained evidence showing that the ability to undergo rapid cooxidation in the presence of alcohols is not restricted to oxalic acid, but is shared by numerous other compounds, most notably by hydroxy acids.[4]

The pseudo-first-order rate constant for the chromic acid oxidation in aqueous perchloric acid (0.628 *M*) at 60° is 1.16×10^{-4} sec^{-1} for α-hydroxyisobutyric acid (0.156 *M*) and 1.65×10^{-4} sec^{-1} for 2-hydroxy-2-methylbutyric acid (0.170 *M*). Under the same conditions, the pseudo-first-order rate constant for a 0.039 *M* solution of isopropyl alcohol is 1.16×10^{-3} sec^{-1}. However, a mixture containing isopropyl alcohol and either of the hydroxy acids, all in the concentrations given above, reacts considerably faster: $k = 5.78 \times$

---

[1] Part III: F. Hasan and J. Roček, *J. Amer. Chem. Soc.*, **94**, 8946 (1972).

[2] This investigation was supported by the National Science Foundation.

[3] F. Hasan and J. Roček, *J. Amer. Chem. Soc.*, **94**, 3181 (1972).

[4] F. Hasan and J. Roček, unpublished results.