Tetrahedron Letters No. 3, pp 207 - 210, 1978. Pergamon Press. Printed in Great Britain.

PHOTOCHEMISTRY OF ALKYL HALIDES, 5. 2,4-DEHYDROADAMANTANE AND PROTOADAMANTENE FROM 2-BROMO- AND 2-IODOADAMANTANE[1]

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(Received in USA 22 September 1977; received in UK for publication 21 November 1977)

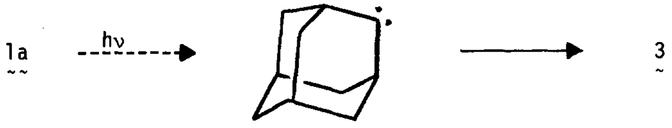
Recent studies from these laboratories have shown that alkyl bromides and iodides afford ionic, as well as radical, intermediates on irradiation--by a process thought to involve initial light-induced homolytic cleavage of the carbon-halogen bond, followed by electron transfer within the resulting radical pair cage (eq 1).[1] Thus the observations that irradiation of 2-iodoadamantane (1a) in ether[1] or methanol[1,2] affords the 2-alkoxy derivative 5a or 5b appeared to be readily explained via simple nucleophilic trapping of the 2-adamantyl cation generated in the electron transfer process. We wish now to report that a primary fate of the 2-adamantyl cation is instead deprotonation to afford a mixture of 2,4-dehydroadamantane (3)[3] and protoadamantene (4)[4] which on reprotonation afford the alkoxy derivative 5.

$$\text{R-X} \xrightarrow{h\nu} [\text{R}^\cdot\ \text{X}^\cdot] \xrightarrow[\text{transfer}]{\text{electron}} [\text{R}^+\ \text{X}^-] \qquad (1)$$

As can be seen in Table I, gas chromatographic monitoring of an irradiation of iodide 1a in ether revealed the transient presence of small quantities of 3 and 4 in addition to the reduction product 2 and ether 5a, the principal product. Irradiation in the presence of 1 mol equiv of triethylamine (as an acid quencher) resulted instead in the formation of 3 as the principal product, accompanied by a smaller amount of 4. Under these conditions the rate of conversion of iodide 1a was greatly accelerated and only trace amounts of the ether 5a were formed. These results indicate that 3 and 4 are primary photoproducts, along with the reduction product 2. In the absence of a quencher 3 and 4 undergo reaction with accumulated hydrogen iodide to afford a mixture of starting iodide 1a and ether 5a. The decreasing ratio of 3:4 with increasing reaction time is attributable to a faster rate of acid-catalyzed reaction by the highly strained 3. As expected, treatment of 3 in the dark with ether containing hydrogen iodide afforded a 1.6:1 mixture of iodide 1a and ether 5a.

By contrast, irradiation of iodide 1a in methanol afforded no detectable amounts of 3 or 4, even at short reaction time; the principal product in high yield was ether 5b.[5] In the presence of triethylamine small amounts of 3 and 4 were detected, but the major product was still ether 5b.[6] However, when the irradiation was carried out in methanol-*O*-*d*, the resulting ether 5b was formed with 25% incorporation of deuterium. These results indicate that the photochemically generated 2-adamantyl cation is more efficiently trapped in the more nucleophilic solvent methanol, but that some competing deprotonation to 3 and 4 still occurs. Bromide 1b displayed analogous behavior except for an enhanced amount of photoreduction, which is characteristic of bromides.[1]

The alternative possibility that 2,4-dehydroadamantane (3) arises via initial photoconversion of 1a to 2-adamantyl carbene (eq 2), a photoprocess which has been proposed for alkyl iodides,[7] was tested by irradiation of 1a-2-d (95% D_1). The resulting 3 was formed with substantial retention of deuterium (95% D), which is incompatible with the carbene route.



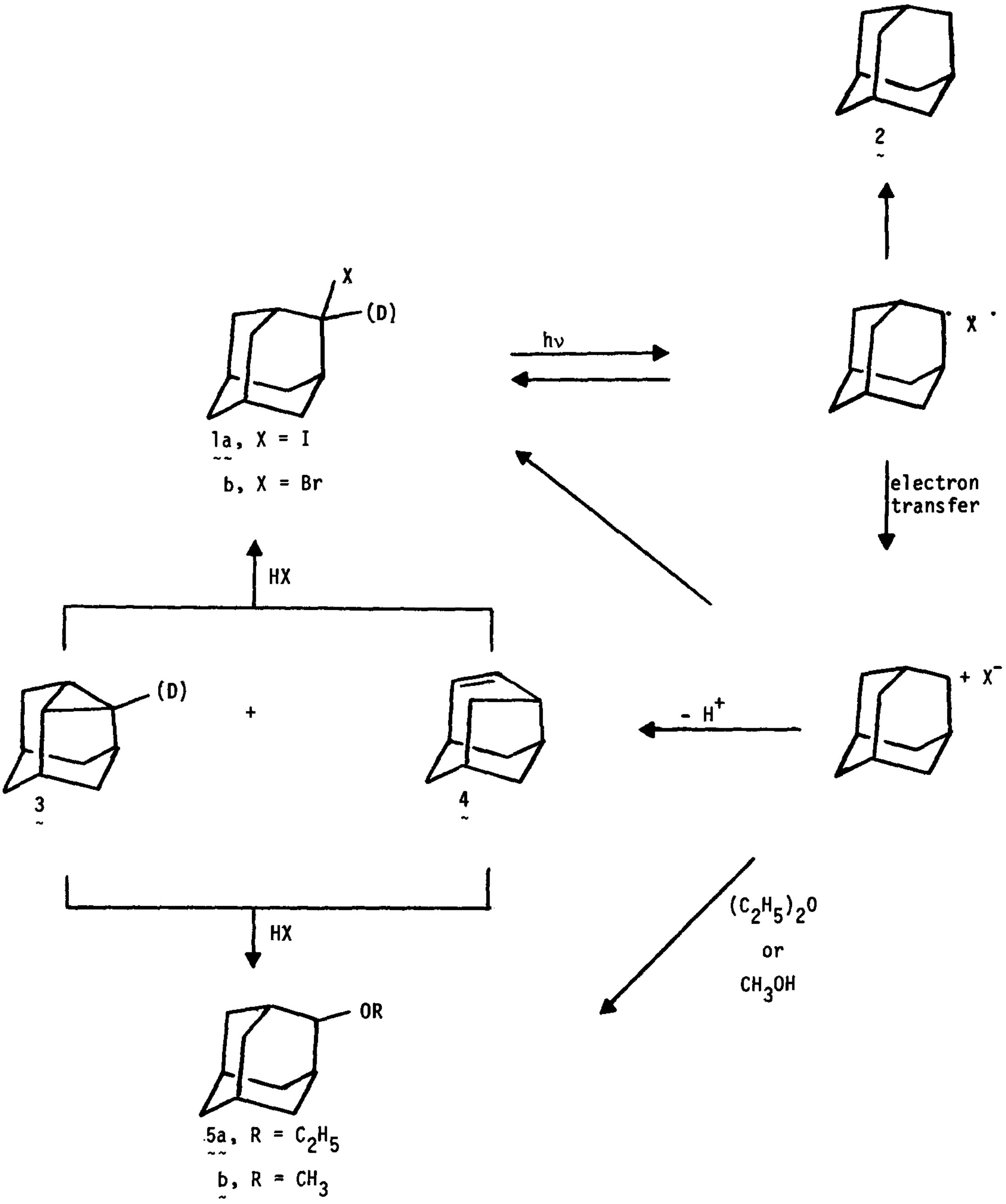
(2)

No evidence could be found for involvement of the analogous 1,3-dehydro intermediate 8 in the photochemistry of the 1-adamantyl isomer 6. Irradiation of 6 in ether or methanol in the presence or absence of triethylamine afforded adamantane (2) and the 1-adamantyl ether 7a or b as the only observable photoproducts. Moreover, irradiation of 6 in methanol-O-d afforded ether 7b with no detectable incorporation of deuterium.

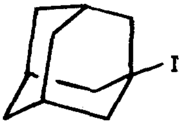
Table I. Irradiation of 2-Iodo- (1a) and 2-Bromoadamantane (1b)[a]

Halide	Solvent	Time, h	Yield, %[b] 1	2	3	4	5	R
1a	$(C_2H_5)_2O$	1	50	10	14	4	7	C_2H_5
		22	2	18	2	7	53	C_2H_5
1a	$(C_2H_5)_2O$[c]	2	d	18	55	8	4	C_2H_5
1a-d	$(C_2H_5)_2O$[c]	3	d	10	73	12	4	C_2H_5
1b	$(C_2H_5)_2O$[c]	8	3	47	12	1	d	C_2H_5
1a	CH_3OH	4	d	d	e	e	99	CH_3
1a	CH_3OH[c]	2	e	30	7	15	38	CH_3
1b	CH_3OH[c]	8	d	38	10	e	25	CH_3

[a] Irradiations were conducted under a nitrogen atmosphere using 0.05M solutions of halide and a 450-W medium-pressure arc (bromide 1b) or a Rayonet RPR-100 Photochemical Reactor equipped with a circular array of 16 G8T5 lamps (254 nm, iodide 1a). [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. [c] Triethylamine (1 mol equiv) added. [d] Trace. [e] None detectable.


2
X
(D)
hν
X·
1a, X = I
b, X = Br
electron transfer
HX
(D)
+
3
4
- H^+
$+ X^-$
HX
$(C_2H_5)_2O$
or
CH_3OH
OR
5a, R = C_2H_5
b, R = CH_3

In addition to affording a convenient alternative route for the synthesis of **3**, the observed formation of **3** and **4** underscores the previously observed propensity of alkyl halides to afford photoelimination products,[1] even when the product is at least moderately strained. On the other hand, the failure to afford the more highly strained **8** places a limit on the ability to form elimination products. Work continues on delineating the usefulness of the photochemical behavior of alkyl halides in the synthesis of strained elimination products.



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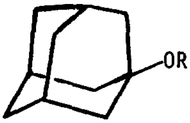
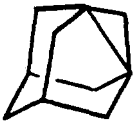


7a, R = C_2H_5

b, R = CH_3



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Acknowledgment. Generous financial support by the National Science Foundation is gratefully acknowledged.

References and Footnotes

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(5) Two additional products tentatively assigned as protoadamantyl methyl ethers were also obtained in trace amounts. The possible formation of small amounts of protoadamantyl iodide cannot be excluded.

(6) The addition of triethylamine resulted in an enhanced yield of the reduction product 2. The tendency of amines to facilitate photoreduction of alkyl iodides in polar solvents has been previously discussed (ref 1).

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