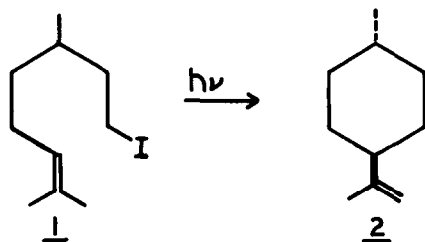


#### 4-PHENYL-1-IODOBUTANE PHOTOCHEMISTRY

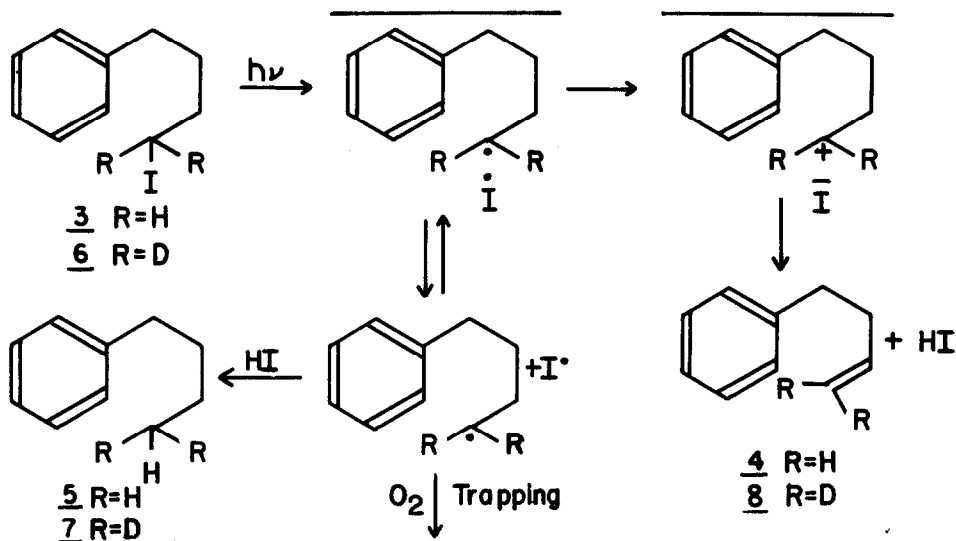
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The recent work of Kropp *et al.*<sup>1</sup> has shown that the photolysis of alkyl iodides can give both free radical and ionic intermediates. The pathway to ions apparently involves the formation of an alkyl radical-iodine atom pair. Since dissociation-reassociation of the radical pair may occur, the possibility exists for a competition between ionic and free radical pathways. The observation of ionic products in any specific case does not preclude the possibility of a principally radical pathway in other cases. Such may be the case for citronellyl-iodide 1. Although Gokhale *et al.*<sup>2</sup> have interpreted the photocyclization to *trans*-p-menth-8-ene 2 as a cationic process, our investigation of 4-phenyl-1-iodobutane 3<sup>3</sup> would indicate that free radical cyclization is more likely.



Irradiations of 3 in dry, thiophene free benzene (ca.  $3 \times 10^{-3}$ M) were carried out: (a) in the presence of oxygen, (b) in the presence of water (1/3 the volume of benzene) and (c) flushed with nitrogen, using a 450 watt medium pressure mercury lamp with a 2mm pyrex filter. The products were analysed on a gas chromatograph (6' by 1/8" column packed with 10% carbowax 20M on acid washed Chromosorb W) interfaced with a Finnigan 1015 mass spectrometer. The major products were the alkene 4 and the alkane 5. Their yields are given in the table below for various sample conditions.



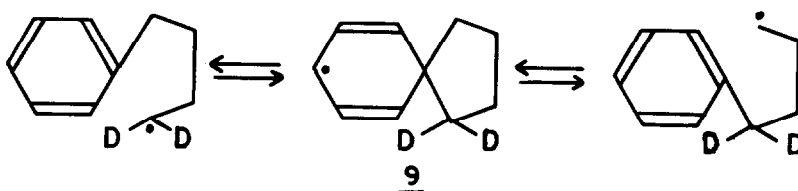
Irradiation in presence of	<u>4</u>	<u>5</u>
N <sub>2</sub>	61%	27%
O <sub>2</sub>	51%	<1%
N <sub>2</sub> /H <sub>2</sub> O	88%	<1%

Yields were determined at 50-90% conversion using naphthalene as internal standard and correcting for unreacted starting material. The yield of tetralin was determined to be less than 1%. The only other significant product in nitrogen flushed solution was 1,4-diphenylbutane in approximately 2% yield.

The above product distribution indicates that about 50% of the initially formed radical pairs give alkene, presumably through a "hot cation" although a direct collapse of the radical pair is not excluded.<sup>5</sup> In the absence of oxygen the alkane 5 becomes a major product and at low conversions its rate of formation increases with percent conversion. Since hydrogen iodide is a byproduct of alkene formation its participation would explain both the presence and rate of formation of alkane. On addition of water, HI is apparently removed and most of the radicals that escape the primary cage re-encounter and proceed to alkene. It is also possible that water could increase the proportion of primary radical pairs that proceed to alkene versus

dissociation to free radicals. No evidence for the cation entering into a cyclization reaction (leading to tetralin) could be found.

Since such a large proportion of the 4-phenylbutyl radicals do become kinetically free of the initial solvent cage, the reversible closure of the 1,1-dideutero-4-phenylbutyl radical to the spirocyclohexadienyl radical 9 was investigated.



Careful mass spectral analysis of the dideutero-4-phenyl-1-butene 8 and butane 7, from irradiation of 1,1-dideutero-4-phenyl-1-iodobutane 6<sup>4</sup> in nitrogen flushed benzene solution, showed less than 2% deuterium at the benzylic positions. Hence we conclude that closure to the spiro radical is very slow as it does not compete with trapping by the low concentration of HI present. This low rate of equilibration is in contrast to earlier predictions by Julia<sup>6</sup> who first investigated this reaction.

Chain decomposition of alkyl iodides to alkenes has also been proposed<sup>7</sup> involving  $I^\circ$  as a propagating radical, therefore,  $I_2$  was irradiated in the presence of 3 with an appropriate filter to prevent excitation of the iodide. No reaction could be detected.

Our observation that approximately 50% of the initially formed radical pairs dissociate to give free radicals would indicate that the same might occur in similar systems. In the absence of HI and  $O_2$  the reencounter of alkyl radicals and iodine atoms may lead to electron transfer and ionic reactions but in the absence of specific evidence some caution should be exercised in assigning the nature of intermediates.<sup>2</sup>

## References and Notes

1. P. J. Kropp, T. H. Jones and G. S. Poindexter, J. Am. Chem. Soc., 95, 5420 (1973); G. S. Poindexter and P. J. Kropp, ibid., 96, 7142 (1974); P. J. Kropp, G. S. Poindexter, N. J. Pienta and D. C. Hamilton, ibid., 98, 8135 (1976).
2. P. D. Gokhale, A. P. Joshi, R. Sahni, V. G. Naik, N. P. Damodaran, U. R. Nayak and S. Dev, Tetrahedron, 32, 1391 (1976).
3. 4-phenyl-1-iodobutane was prepared from 4-phenyl-1-butanoic acid<sup>4a</sup> by reduction with lithium aluminum hydride<sup>4b</sup> followed by treatment with iodine and phosphorous.<sup>4c</sup>
4. (a) A. I. Vogel, "Practical Organic Chemistry," third edition, Longmans, Green and Co. Ltd., London, England, 1964, pp 737-738; (b) ibid., pp 887-891; (c) ibid., pp 285-287. LiAlD<sub>4</sub> was used for preparation of 6.
5. Thermal reaction of 3 with HI was excluded in a separate experiment in which the solution was saturated with HI in the dark.
6. M. Julia, Pure Appl. Chem., 40, 553 (1974).
7. J. R. Majer and J. P. Simons, "Advances in Photochemistry," Vol. 2, Interscience, New York, N.Y., 1964, p 146.