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PHOTOCHEMISTRY OF 1,1-DIIODOALKANES[1]

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Photolysis of 1,1-diiodoalkanes could lead to the formation of iodoalkyl radicals and/or carbenes as shown in reactions 1-3.[3]

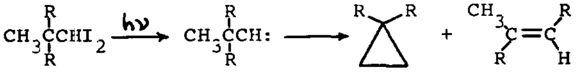
$$RCHI_2 \xrightarrow{h\nu} RCHI + I \qquad (1)$$

$$RCHI_2 \xrightarrow{h\nu} RCH: + I_2 \qquad (2)$$

$$RCHI\cdot^{*} \longrightarrow RCH: + I \qquad (3)$$

Reaction 1 is apparently characteristic of all organic iodides while the possibility of reactions (2) and/or (3) was first suggested by Gregory and Style on the basis of photolysis studies of methylene iodide in the vapor phase at 3100 Å.[4] Later, Style and coworkers concluded from the observation of fluorescence emission of excited I_2 on photolysis of methylene iodide that reaction (2) was important using light of wavelength 1250-2000 Å.[5,6] Most recently, Blomstrom, Herbig and Simmons have observed the characteristic addition and insertion reactions of a divalent carbon intermediate on photolysis of methylene iodide in solution in the presence of olefins.[7] They concluded on the basis of product distributions and stereochemical studies that the main product forming intermediate was probably an excited state of methylene iodide rather than free methylene, but that the latter was also formed.

The similarity in the electronic absorption spectra of 1,1-diiodoalkanes[8] suggested that the primary photolytic processes of methylene iodide could be expected on photolysis of alkyl substituted diiodomethanes, and if free alkylidenes were formed from these diiodides, their facile intramolecular reactions[9] might serve as a diagnostic probe. In particular, if photolysis of 1,1-diiodopropane (1a) or 1,1-diiodo-2,2-dimethylpropane (1b) led to the formation of the corresponding propylidenes (2a and 2b, respectively), propylene (90%) and cyclopropane (10%); and 2-methyl-2-butene (7%) and 1,1-dimethylcyclopropane (92%), respectively, would be expected (reaction 4).[10]



(4)

1a: R=H 2a or b 3a or b 4a or b

1b: $R=CH_3$

We now report that photolysis[11] of 1a or 1b, ($\lambda > 2900$ Å; solvent: cyclohexane or cyclohexene) under the same conditions that methylene iodide acts as a methylene donor towards olefins[12], led to the formation of low yields of propylene (4a) and 2-methyl-2-butene (4b), respectively. However, neither cyclopropane (3a) nor 1,1-dimethylcyclopropane (3b) were detected as reaction products. Although 3a was not checked, low concentrations of 3b were shown to be unchanged under the reaction conditions. The absence of these cyclopropanes implies that neither reactions 2 or 3 are important under these conditions and more specifically seems to rule out the significant intermediacy of free methylene in the reactions of methylene iodide with olefins under these conditions. The results with 1,1-diiodo-2,2-dimethylpropane (1b) seem to be particularly significant since 1,1-dimethylcyclopropane (3b) would have been the major product of 2,2-dimethylpropylidene (2b).[13]

We propose that photolysis of 1a and 1b under these conditions led exclusively to the primary reaction 1. In cyclohexene (N_2) 1b[14] gave an essentially quantitative yield of 1-iodo-2,2-dimethylpropane, while 1a[15] gave 1-iodopropane (18%), *cis*-1-iodopropene (30%), and *trans*-1-iodopropene (38%).[16] The formation of the saturated 1-iodoalkanes is expected if α-iodoalkyl radicals are formed (reaction 1) and abstract an allylic hydrogen atom from cyclohexene. Although a chain reaction (reactions 5 and 6) can be envisioned in cyclohexene, the observation that the rates

$$RCHI\cdot + SH \longrightarrow RCH_2I + S\cdot \qquad (5)$$

$$S\cdot + RCHI_2 \longrightarrow SI + RCHI\cdot \qquad (6)$$

of decomposition of 1,1-diiodopropane in cyclohexene (N_2) and in cyclohexane (N_2) were essentially the same (although no 1-iodopropane was formed in cyclohexane) seems to rule out this possibility: The formation of *cis*- and *trans*-1-iodopropene may also be explained by reaction 1 followed by a cage disproportionation (reaction 7).[17] In cyclohexane (N_2), only *cis*-1-iodopropene (38%) and *trans*-1-iodopropene (47%) were formed which presumably reflects

$$\overline{CH_3CH_2CHI\cdot + I\cdot} \longrightarrow CH_3CH{=}CHI + HI \qquad (7)$$

the lower reactivity of this solvent as a hydrogen donor compared to cyclohexene. Although reaction 7 adequately accounts for iodopropene formation, a molecular elimination (reaction 8)[18] cannot be absolutely discounted at this time.

$$CH_3CH_2CHI_2 \xrightarrow{h\nu} CH_3CH{=}CHI \quad + \quad HI \qquad (8)$$

Neither reactions 7 nor 8 would be expected with 1,1-diiodo-2,2-dimethylpropane (1b), and since cyclohexane appeared to be a very poor hydrogen donor to α-iodoalkyl radicals the observation that photolysis of 1b in cyclohexane (N_2) was 15 times slower than in cyclohexene (N_2) was not surprising. A complete product analysis is not yet available, but of the 17% 1b which decomposed in 28 hours, 1-iodo-2,2-dimethylpropane (20%) and 2-methyl-2-butene (10%) were formed. It is unreasonable that the true quantum efficiencies for the primary reactions of 1b should be significantly different in cyclohexene or cyclohexane. Thus, reaction of the α-iodo-t-butylmethyl radicals with I_2, present in low concentration, to regenerate starting material must represent the major reaction pathway.

Carbene formation (reactions 2 or 3) could be considerably less efficient than reaction 1 and would be obscured under conditions in which the α-iodoalkyl radicals were rapidly converted to products. However, the complete absence of 1,1-dimethylcyclopropane on photolysis of 1b in cyclohexane, where the occurrence of reaction 1 does not lead to rapid consumption of starting material, seems to be particularly strong evidence that reactions 2 and 3 do not occur at $\lambda > 2900$ Å.[11]

Preliminary experiments have shown, however, that photolysis of 1a and 1b in the vapor phase at shorter wavelengths ($\lambda < 2400$ Å) does lead to the formation of cyclopropane and 1,1-dimethylcyclopropane respectively. This implies that alkylidenes can be formed from 1,1-diiodoalkanes under the appropriate conditions and further studies are in progress.[19]

References

(1) Photochemistry of Organic Iodides. II. Paper I in this series was R. C. Neuman, Jr., J. Org. Chem., 31, 1852 (1966). b) Support by the National Science Foundation through grant GP 4287 is gratefully acknowledged. c) Presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept. 11-16, 1966.

(2) National Science Foundation Undergraduate Research Participant.

(3) J. R. Majer and J. P. Simons, Adv. Photochem., 2, 137 (1964).

(4) R. A. Gregory and D. W. G. Style, Trans. Faraday Soc., 32, 724 (1936).

(5) a) P. J. Dyne and D. W. G. Style, J. Chem. Soc., 2122 (1952); b) D. W. G. Style and J. C. Ward, ibid, 2125 (1952).

(6) However see K. E. Gibson and T. Iredale, Trans. Faraday Soc., 32, 571 (1936).

(7) D. C. Blomstrom, K. Herbig and H. E. Simmons, J. Org. Chem., 30, 959 (1965).

(8) Diiodomethane: λ max (hexane) mμ(ε); 214(1550), 250 (600), 286(900), 312(800, Sh). 1,1-Diiodopropane: λ max (ether) mμ(ε); 210(2300), 250(650), 290(1180), 320(750, Sh). 1,1-Diiodo-2,2-dimethylpropane: λ max (ether) mμ(ε); 210(1650), 250(590), 290(1100), 320 (870, Sh).

(9) See W. Kirmse, "Carbene Chemistry", Academic Press, Inc., New York, N. Y., 1964, pp 52-53.

(10) L. Friedman and H. Shecter, J. Am. Chem. Soc., 81, 5512 (1959).

(11) Reactions were run in a *pyrex vessel* using the filtered (Vycor-Corning #7910 and a mercury filter) irradiation of a medium pressure Hanovia mercury arc (Type SH). Vapor phase photolysis was avoided by covering that portion of the cell. The organic phase (diiodide concentration 0.08-0.10M) was stirred over a dilute aqueous solution of sodium hydroxide to remove hydrogen iodide and iodine. Control experiments showed that this did not complicate the photochemistry and dark reactions did not occur. Samples were vacuum degassed and run under nitrogen. Analyses were performed by vapor phase chromatography and products were identified by comparison with authentic samples.

(12) Methylene iodide (0.10M) in cyclohexene underwent 50% decomposition in 10 hours giving 50% norcarane.[11]

(13) The question of the spin-states of the alkylidenes has not been mentioned and one might expect different intramolecular product distributions from singlet and triplet alkylidenes. Professor L. Friedman has informed us that sensitized and unsensitized decomposition of diazoneopentane lead to different olefin/cyclopropane ratios, however this ratio is also strongly solvent dependent. In no case, however, has carbenoid decomposition of this diazo compound ever been observed to give less than 50% 1,1-dimethylcyclopropane.

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(15) R. C. Neuman, Jr. and M. L. Rahm, *J. Org. Chem.*, **31**, 1857 (1966).

(16) See R. C. Neuman, Jr., *ibid*, **31**, 1852 (1966).

(17) See H. A. Gillis, R. R. Williams, Jr. and W. H. Hamill, *J. Am. Chem. Soc.*, **83**, 17 (1961).

(18) See R. H. Luebbe, Jr. and J. E. Willard, *ibid*, 81, 761 (1959).

(19) The origin of propylene and 2-methyl-2-butene from 1a and 1b is not clear. The former could have arisen from photolysis of the iodopropenes,[16] but the latter is not so simply explained. It is possible that they are formed by rearrangement and subsequent loss of I• from the initial α-iodoalkyl radicals. However, they may also arise from excited states of the diiodoalkanes. Further work on these questions is in progress.