Photochemistry of Alkyl Halides. 9. Geminal Dihalides[1]

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The photobehavior of the geminal dihalides (diiodomethyl)cyclohexane (7), (bromoiodomethyl)cyclohexane (11), (dibromomethyl)cyclohexane (17), (diiodomethyl)cyclopentane (22), 3,3-dimethyl(diiodomethyl)cyclobutane (27), and 8,8-diiodo-2,6-dimethyl-2-octene (31) has been studied and compared with that previously observed for diiodomethane. In all solvents the corresponding vinyl halides (iodomethylene)cyclohexane (13), (bromomethylene)cyclohexane (21), (iodomethylene)cyclopentane (23), 3,3-dimethyl(iodomethylene)cyclobutane (28), or cis- and trans-3,7-dimethyl-1-iodo-1,6-octadiene (33) were obtained, which are thought to arise from an α-halo cationic intermediate formed via initial light-induced homolytic cleavage of the carbon–iodine bond followed by electron transfer within the resulting caged radical pair, as shown in Schemes II and III. In the case of diiodide 31 competing intramolecular trapping of the α-iodo cation afforded in addition the cyclized isopulegyl iodide (34). In polar solvents the vinyl iodides were accompanied by the nonhalogenated products methylenecyclohexane (15), 1-methylcyclopentene (25), cyclohexene (26), 4,4-dimethylcyclopentene (29), and cis- and trans-carane (35), which are thought also to arise from the α-halo cationic intermediate. 1,1-Diiodo-2,2-dimethylpropane (1b) afforded 2-methyl-2-butene (6b). Except for carane (35) from diiodide 31 there was no detectable formation of cyclopropanes. In methanol the nucleophilic substitution products (dimethoxymethyl)cyclohexane (14), (dimethoxymethyl)cyclopentane (24), and 1,1-dimethoxy-2,2-dimethylpropane (30) were obtained. It is concluded that geminal dihalides undergo predominant, if not exclusive, photoreaction via initial cleavage of a single carbon–halogen bond in analogy with monohalides and that carbene intermediates are not formed. A similar conclusion has been reached previously for diiodomethane in the photocyclopropanation of alkenes.

It has been known for some time that irradiation of polyhalomethanes in the presence of alkenes results in the formation of cyclopropanes.[2-4] Recent studies in these laboratories have shown that photocyclopropanation of alkenes with diiodomethane is a convenient procedure which has synthetic utility, being much less subject to steric inhibition than the traditional Simmons–Smith procedure.[5] Both carbene[2,4] and carbenoid[2,5] intermediates have been suggested for the photocyclopropanation process. In an effort to gain further mechanistic insight, Neuman studied the intramolecular photobehavior of iodides 1a,b in hydrocarbon solvents.[3] It was concluded that the observed products (3a and 5a from iodide 1a; 3b from iodide 1b) arise from an initially formed radical pair 2 (Scheme I); the absence of cyclopropane and 1,1-dimethylcyclopropane was taken to indicate that no carbene intermediates are formed.[6] We report here a more detailed study of the photobehavior of geminal dihalides and relate the insights gained to the photocyclopropanation reaction.[7,8]

(Dihalomethyl)cycloalkanes. The results from irradiation of (diiodomethyl)cyclohexane (7) and its deuterated derivative 7-d are summarized in Scheme II and Table I.

(1) Part 8: Kropp, P. J.; Worsham, P. R.; Davidson, R. I.; Jones, T. H. *J. Am. Chem. Soc.* 1982, *104*, 3972–3980.

(2) Blomstrom, D. C.; Herbig, K.; Simmons, H. E. *J. Org. Chem.* 1965, *30*, 959–964.

(3) Neuman, R. C.; Wolcott, R. G. *Tetrahedron Lett.* 1966, 6267–6272.

(4) (a) Marolewski, T.; Yang, N. C. *J. Chem. Soc., Chem. Commun.* 1967, 1225–1226. (b) Yang, N. C.; Marolewski, T. A. *J. Am. Chem. Soc.* 1968, *90*, 5644–5646.

(5) Kropp, P. J.; Pienta, N. J.; Sawyer, J. A.; Polniaszek, R. P. *Tetrahedron* 1981, *37*, 3229–3236.

(6) Propene (6a) and 2-methyl-2-butene (6b) were also obtained in low yield, but their origin was described as "not clear".

(7) For a preliminary report of a portion of the present study, see: Pienta, N. J.; Kropp, P. J. *J. Am. Chem. Soc.* 1978, *100*, 655–657.

(8) For another recent report see: Moret, E.; Jones, C. R.; Grant, B. *J. Org. Chem.*, this issue. We are indebted to these authors for sharing their results prior to publication.
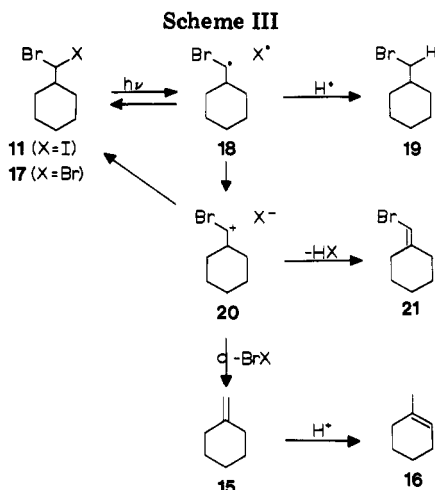
Scheme I

Scheme II
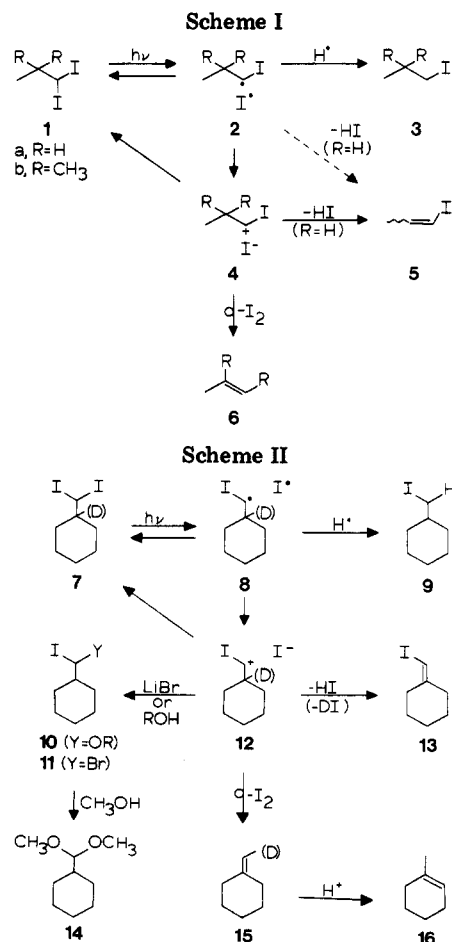
Irradiation of 7 at wavelengths >280 nm in a variety of solvents of low polarity afforded principally the vinyl iodide 13, accompanied by small amounts of the reduction

Table I. Irradiation of (Diiodomethyl)cyclohexanes 7 and 7-d [a]

iodide	solvent	D	time, h	yield,[b] % 7	9	13	15	16
7	C$_6$H$_{10}$	2.0	2	c	18	78		
7	CCl$_4$	2.2	2	40	c	47		
7	C$_6$H$_6$	2.3	2	20	c	62		
7	(C$_2$H$_5$)$_2$O	4.3	12	28	6	51		
7	CHCl$_3$	4.8	2	66	c	31		
7	CH$_2$Br$_2$	7.5	2	c	c	46		41
7	CH$_2$Cl$_2$	8.9	2	10	c	39		28
7	CH$_2$Cl$_2$ [d,e]		1	5	c	47	14	3
7	CH$_2$Cl$_2$ [f]		1	c	c	82	10	
7	CH$_3$CHCl$_2$	10.1	1	22	c	52		8
7	(CH$_2$Cl)$_2$	10.4	2	4	c	40		33
7	CH$_3$OH [g]	32.7	5	32	3	8		
7	CH$_3$CN [h]	37.5	8	35	c	9		11
7	CH$_3$CN [i,j]		10	40	c	11		10
7-d [k]	CH$_2$Cl$_2$ [f]	8.9	1	5	4	70 [l]	9 [m]	

[a] Conducted as described in the Experimental Section unless otherwise indicated. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. [c] Trace. [d] Conducted in a Pyrex round-bottomed flask equipped with a magnetic stirring bar, condenser, and nitrogen inlet and stirred with 3 mL of an aqueous solution 10% each in sodium thiosulfate and sodium bicarbonate. [e] Cyclohexanecarboxaldehyde obtained in 22% yield. [f] Contained 2 molar equiv of epichlorohydrin. [g] 1-Methoxy(iodomethyl)cyclohexane and acetal 14 obtained in yields of 2% and 45%, respectively. [h] Cyclohexanecarboxaldehyde obtained in 25% yield. [i] Contained 4.5 molar equiv of lithium bromide. [j] Iodobromide 11 and cyclohexanecarboxaldehyde obtained in yields of 15% and 14%, respectively. [k] 94% d_1, 6% d_0. [l] 100% d_0. [m] 89% d_1, 11% d_0.

Scheme III

Table II. Quantum Yields for Disappearance of Diiodode 7 and Diiodomethane[a]

halide	solvent	Φ
7	(C$_2$H$_5$)$_2$O	0.48
7	CH$_2$Cl$_2$	0.35
CH$_2$I$_2$	C$_6$H$_6$	0.55 [b]

[a] Determined at 366 nm as described in the Experimental Section. [b] Reference 10.

Table III. Irradiation of (Bromoiodomethyl)cyclohexane (11) and (Dibromomethyl)cyclohexane (17)[a]

halide	solvent	time, h	yield,[b] % 11/17	19	21	16
11	(C$_2$H$_5$)$_2$O	24	44	c	35	
17	(C$_2$H$_5$)$_2$O	0.5	48	26	c	
11	CH$_3$OH	4.0	67	c	9	
17	CH$_3$OH [d]	0.5	26	31	c	
11	(CH$_2$Cl)$_2$	16	21	c	56	7
17	(CH$_2$Cl)$_2$ [e]	1	56	21	3	

[a] Conducted as described in the Experimental Section. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. [c] Trace. [d] Methylcyclohexane obtained in 12% yield. [e] Methylcyclohexane obtained in 7% yield.

Table IV. Irradiation of (Diiodomethyl)cyclopentane (22)[a]

solvent	time, h	yield,[b] % 22	23	other
(C$_2$H$_5$)$_2$O	12	26	58	
CH$_3$OH	4	34	9	38 (24)
CH$_2$Cl$_2$	1	43	13	12 (25), 11 (26)

[a] Conducted as described in the Experimental Section. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard.

product 9. In solvents of higher polarity these products were accompanied by substantial quantities of 1-methylcyclohexene (16), which is apparently a secondary product arising via acid-catalyzed isomerization of methylenecyclohexane (15) since irradiation of diiodide 7 in dichloromethane in the presence of an acid scavenger afforded 15 instead. Irradiation of diiodide 7-d under these latter conditions afforded 15 with almost total retention of deuterium, which was shown by ^{1}H NMR spectroscopy to be located in the vinyl position; the accompanying vinyl iodide 13 contained no deuterium detectable by mass spectral analysis.

In the nucleophilic solvent methanol the principal product was the acetal 14, accompanied by the usual products 9 and 13. In acetonitrile and in wet dichloromethane substantial quantities of cyclohexanecarboxaldehyde were obtained. In acetonitrile containing lithium bromide the bromo iodide 11 was obtained in addition. Control experiments showed that the monoiodide 9 and the vinyl iodide 13 are photostable under the irradiation conditions in dichloromethane solution.

The quantum yield for disappearance of diiodide 7 is given in Table II. Little difference was observed between the less polar solvent ether and the more polar solvent dichloromethane, in which the dehalogenated product methylenecyclohexane (15) is formed.[9] Both values are

(9) The substantial differences in irradiation times required for extensive conversion of diiodide 7 in ether and dichloromethane despite the similarity of the quantum yields in these two solvents, which were determined at low conversion, is apparently attributable to the differences in absorption properties in these two solvents of the byproduct iodine which accumulates on extended irradiation and competes with diiodide 7 for light.
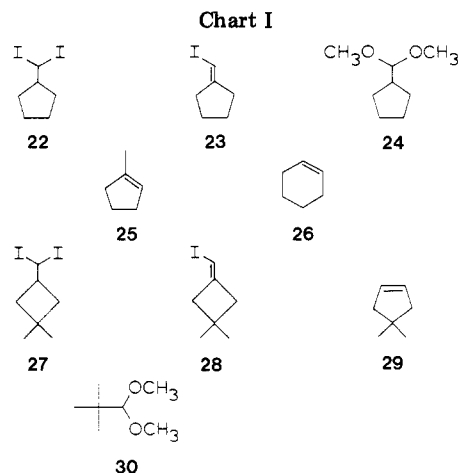
Chart I

Table V. Irradiation of
3,3-Dimethyl-1-(diiodomethyl)cyclobutane (27)[a]

solvent	time, h	yield,[b] %		
		27	28	29
$(C_2H_5)_2O$	25	52	28	8
CH_2Cl_2	1	5	5	69

[a] Conducted as described in the Experimental Section.
[b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard.

Table VI. Irradiation of
1,1-Diiodo-2,2-dimethylpropane (1b)

solvent	time, h	yield,[b] %		
		1b	3b	6b
C_6H_{10}	4	45	32	
CH_3OH[c]	8	35		
$(CH_2Cl)_2$[d]	6	2	5	60
$(CH_2Cl)_2$[d,e]	20	3	7	61

[a] Conducted as described in the Experimental Section.
[b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. [c] Acetal 30 obtained in 61% yield. [d] Irradiation conducted in a sealed tube.
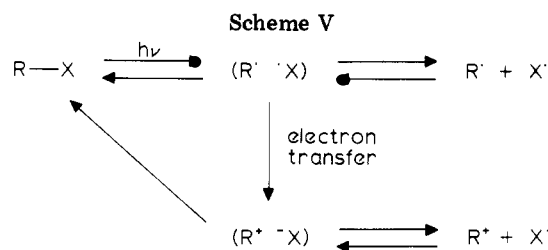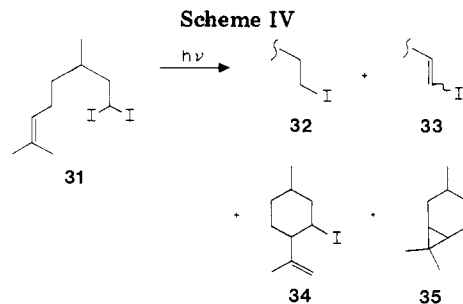[e] Contained 30 molar equiv of cyclohexene.

similar to that reported previously for diiodomethane.[10]

The results from irradiation of the analogous bromo iodide 11 and dibromide 17[11] are summarized in Scheme III and Table III. The behavior of bromo iodide 11 was analogous to that of diiodide 7. The carbon–iodine bond was cleaved selectively to afford the vinyl bromide 21 as the principal product in all solvents; in the more polar 1,2-dichloroethane some 1-methylcyclohexene (16) was obtained as well. By contrast, the dibromide 17 afforded principally the reduction product 19; even in 1,2-dichloroethane no 1-methylcyclohexene (16) was obtained. Some methylcyclohexane was formed, presumably from secondary irradiation of the monobromide 19.

The results from irradiation of the cyclopentyl analogue 22 (Chart I) are summarized in Table IV. In ether the principal product was the vinyl iodide 23 and in methanol the acetal 24. In dichloromethane the vinyl iodide 23 was accompanied by the hydrocarbons 1-methylcyclopentene (25) and cyclohexene (26). By contrast, the cyclobutyl analogue 27 afforded the ring-expanded hydrocarbon product 29 in high yield in dichloromethane and as the minor product in ether (Table V).

Diiodide 1b. In view of these results it was of interest

(10) Gibson, K. E.; Iredale, T. *Trans. Faraday Soc.* **1936**, *32*, 571–576.
(11) Gudkova, A. S.; Uteniyazov, K.; Reutov, O. A. *Dokl. Akad. Nauk SSSR* **1974**, *214*, 572–575; *Dokl. Chem. (Engl. Transl.)* **1974**, *214*, 70–72.

Scheme IV

Scheme V

to reexamine the photobehavior of diiodide 1b. As was found previously,[3] irradiation in cyclohexene afforded the reduction product 3b (Table VI). However, in methanol the acetal 30 was obtained in excellent yield, as was the alkene 6b in 1,2-dichloroethane. There was no detectable formation of 1,1-dimethylcyclopropane when the irradiation was conducted in a sealed tube and monitored by ^{1}H NMR. The yield of 6b was unaffected by the presence of a large excess of cyclohexene, and ^{1}H NMR monitoring showed no detectable formation of cyclopropane adduct.

Diiodide 31. Since the presence of an external alkene had no effect, the photobehavior of diiodide 31 was explored to determine the effect of an intramolecular alkene. As summarized in Scheme IV and Table VI, irradiation of citronellal iodide (31) in either ether or 1,2-dichloroethane afforded not only the reduction product 32 and the vinyl iodide 33 but also the cyclization product 34 and the internal trapping product carane (35).

Discussion

Comparison with Monohalides. Previous studies in these laboratories have shown that alkyl monoiodides and monobromides afford a mixture of radical and carbocationic products on irradiation in solution.[1,12] A mechanism has been suggested involving initial homolytic cleavage of the carbon–halogen bond followed by competing electron transfer within the resulting caged radical pair and diffusion from the cage (Scheme V).[12]

In many respects the photobehavior of geminal dihalides resembles that previously observed for monohalides. Formation of the reduction products 3b, 9, 19, and 32 is consistent with initial homolytic cleavage of one of the carbon–halogen bonds to afford a radical pair followed by abstraction of a hydrogen atom from the solvent. In the case of the bromo iodide 11 the weaker carbon–iodine bond apparently undergoes cleavage exclusively since there was no detectable formation of iodide 9, which is photostable under the conditions used for irradiation of bromo iodide 11.

Accompanying the saturated monohalides 9, 19, and 32 were the vinyl halides 13, 21, and 33. In addition, diiodides 22 and 27, which afforded no detectable amounts of the corresponding monoiodides, gave the vinyl iodides 23 and 28, respectively. Each of these vinyl halides could conceivably arise via disproportionation of the initially formed radical pair, as was proposed for the conversion of diiodide

(12) Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *J. Am. Chem. Soc.* **1976**, *98*, 8135–8144.

Scheme VI
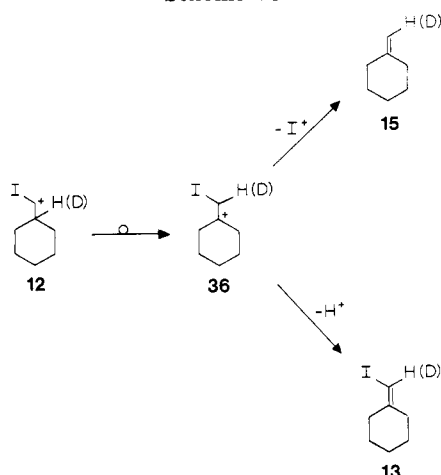
1a to vinyl iodide 5 via the radical pair 2a.[3] However, comparison of the relative amounts of reduction product 19 and vinyl bromide 21 afforded by bromo iodide 11 and dibromide 17 suggests that this is not the principal mode of formation of the vinyl halides. In each of these two cases initial homolytic cleavage affords the same α-bromo radical. However, bromo iodide 11, in which the accompanying halogen atom is iodine (18, X = I), affords predominantly the vinyl bromide 21, whereas dibromide 17, in which the accompanying halogen atom is bromine (18, X = Br), gives principally the reduction product 19. The observed photobehavior is inconsistent with the fact that bromine atoms are usually much better at hydrogen abstraction than iodine atoms.

The observed behavior is, however, consistent with the previous observation that alkyl iodides afford principally ionic products whereas the corresponding bromides give predominantly radical behavior and with the proposal that unsaturated products arise via deprotonation of the alkyl cation resulting from competing electron transfer within the initially formed radical pair (e.g., 12 → 13).[12,13] The observed formation of the nucleophilic substitution product 11 and acetals 14, 24, and 30 confirms the presence of cationic intermediates. Although the cyclized product 34 formed on irradiation of diiodide 31 might conceivably arise via trapping of either the corresponding α-iodo radical or α-iodo cation intermediate, the fact that it is unsaturated suggests that it too is an ionic product.[14]

Nonhalogenated Products. In addition to the above-mentioned products, each of the geminal dihalides studied, except for the dibromide 17, afforded one or more nonhalogenated photoproducts (6b, 15, 25, 26, 29, and 35) in solvents of higher dielectric constant. Control experiments showed that they are not secondary products arising from further irradiation of the monohalogenated products. Do they arise from the α-halo radical or cationic intermediates involved in the formation of the monohalogenated products, or do they arise directly from the geminal dihalides via a carbene intermediate? Formation of carane (35) from diiodide 31 might suggest a carbene intermediate. However, as noted previously, the lack of cyclopropane products from diiodides 1a and 1b indicates that a carbene intermediate is not involved.[3,15] Similarly,

cyclohexyl- and cyclopentylcarbene, the intermediates that would be formed from diiodides 7 and 22, respectively, and cyclobutylcarbene, the unsubstituted analogue of the intermediate from diiodide 27, normally afford 1,3 insertion products in significant amounts.[16]

A conceivable alternative mechanism involving the α-halo cation as an intermediate is illustrated in Scheme VI for the α-iodo cation 12 derived from diiodide 7; rearrangement of 12 to the tertiary cation 36 followed by loss of iodonium ion (or iodine) would afford methylenecyclohexane (15). However, cation 36 would be expected to undergo competing deprotonation to afford vinyl iodide 13, but this latter product was formed with no detectable retention of deuterium when diiodide 7-*d* was irradiated. Moreover, this mechanism would not readily account for the formation of carane (35) from diiodide 31.

More compatible with the available data would be direct conversion of the α-iodo cation 12 to methylenecyclohexane (15) by loss of iodonium ion (or iodine) with an accompanying 1,2 hydride shift (Scheme II). Differing from the previous mechanism in the timing of events, this alternative is analogous to that recently proposed for the photocyclopropanation of alkenes by diiodomethane (cf. 37).[5]
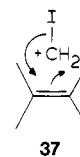
On the basis of the high degree of electrophilic selectivity exhibited by the photocyclopropanation reaction and the lack of C–H insertion products, it was concluded that the α-iodo cationic intermediate, rather than the carbene methylene, is involved. A similar mechanism can be written for the formation of carane (35). In this case the intramolecular availability of an alkene moiety resulted in the cyclopropanation reaction. Interestingly, diiodide 1b underwent loss of iodine and rearrangement to 2-methyl-2-butene (6b) with no detectable intermolecular cyclopropanation when irradiated in the presence of cyclohexene. This implies that the cyclopropanation reaction will be limited to either intramolecular systems or to simple diiodides such as diiodomethane which have no β carbon atom.

The curious solvent effect, with hydrocarbon products formed only in solvents of higher dielectric constant, is apparently related to the effect of solvent polarity on the relative rates of deprotonation or loss of halonium ion from the α-halo cation. This, in turn, may be related to the degree of solvent separation in the ion pair resulting from electron transfer. The one exception is the highly polar solvent methanol, in which little or no hydrocarbon products were formed. In this case, however, competing nucleophilic trapping of the α-halo cation occurred.

We continue to explore both synthetic and mechanistic aspects of the varied photobehavior of alkyl halides.

Experimental Section

General Procedures. Infrared spectra were obtained on carbon tetrachloride solutions with a Beckman 4250 or Perkin-Elmer 421 grating spectrophotometer, and ultraviolet spectra were

(13) Since the reduction products and vinyl halides are formed in unequal amounts, they apparently do not arise via disproportionation of a pair of α-halo radicals.

(14) For analogous behavior by the corresponding monohalide citronellyl iodide, see: Gokhale, P. D.; Joshi, A. P.; Shani, R.; Naik, V. G.; Damodaran, N. P.; Nayak, U. R.; Dev, S. *Tetrahedron* **1976** *32*, 1391–1393.

(15) For a recent report of the formation of *tert*-butylcarbene by passing diiodide 1b through a hot tube containing methyllithium-coated Pyrex chips, see: Fukushima, M.; Jones, M., Jr.; Brinker, U. H. *Tetrahedron Lett.* **1982**, *23*, 3211–3214.

(16) Paskovich, D. H.; Kwok, P. W. N. *Tetrahedron Lett.* **1967**, 2227–2231. See also: Richey, H. G., Jr.; Hill, E. A. *J. Org. Chem.* **1964**, *29*, 421–423.

obtained with a Cary 14 or 17 spectrophotometer. Melting points were determined by using a Thomas-Hoover apparatus and are uncorrected and uncalibrated. Mass spectra were obtained with an AEI MS-902 or a Du Pont 21-490B spectrometer; m/e values reported include the parent ion peak and other significantly large peaks appearing above m/e 55. Gas chromatographic analyses were performed on a Hewlett-Packard 5750 instrument by using 300 cm × 0.3 cm stainless steel columns packed with either (A) 20% SF-96 or (B) 20% Carbowax 20M on 60–80-mesh Chromosorb W. Peak areas were obtained by the cut-and-weight method and corrected for experimentally determined response factors. Preparative gas chromatography was carried out on a Varian-Aerograph 90P or 920 instrument by using 300 cm × 0.65 cm or 150 cm × 0.65 cm stainless steel or nickel columns packed with the materials described above. ^{1}H NMR spectra were obtained on chloroform-d solutions with a Varian XL-100 spectrometer; data are reported in the following manner: chemical shift (multiplicity, integration, coupling constant, and assignment). Multiplicity is indicated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = unresolved multiplet, and br = broadened.

Irradiations. Unless otherwise indicated irradiations were conducted on 5-mL solutions containing 50 mg of diiodide or bromo iodide in Pyrex vessels suspended in a Rayonet RPR-100 photochemical reactor equipped with a circular array of 16 G8T5 BL lamps or containing 60 mg of dibromide in quartz vessels with G8T5 lamps. Solutions were degassed with bubbling nitrogen for 15 min prior to irradiation. Diethyl ether used for irradiations was distilled from lithium aluminum hydride; benzene was stirred over concentrated sulfuric acid and distilled; cyclohexene, 1-chlorobutane, and dibromomethane were fractionated and stored under nitrogen; chloroform was passed through a column of alumina, which had been activated at 400 °C for 24 h, and stored in the dark under nitrogen; methanol was dried over 3A molecular sieves; acetonitrile was passed through a column of alumina, which had been activated at 400 °C for 24 h, and stored over 3A molecular sieves; dichloromethane, 1,1-dichloroethane, and 1,2-dichloroethane were washed with concentrated sulfuric acid followed by 10% sodium carbonate, dried over calcium chloride, and distilled from phosphorous pentoxide.

(Diiodomethyl)cyclohexane (7). (A) Preparation. The general procedure of Pross and Sternhell was employed.[17] Into a 100-mL round-bottomed flask equipped with a magnetic stirring bar, condenser, and additional funnel was placed 20.0 g (400 mmol) of hydrazine hydrate (64% in water). A solution of 10.0 g (90.0 mmol) of cyclohexanecarboxaldehyde in 25 mL of ethanol was added very slowly (less than 5 drops/min) to the hydrazine hydrate with vigorous stirring. After the addition was complete, the contents of the flask were heated to reflux for 1 h, and then cooled to room temperature. The reaction mixture was poured into 200 mL of cold water and then extracted with two 100-mL portions of chloroform. The combined chloroform extracts were washed successively with two 50-mL portions of a saturated sodium chloride solution. The chloroform extracts were dried over anhydrous sodium sulfate, filtered, and concentrated by rotary evaporation to yield 10.1 g (81.0 mmol, 90%) of cyclohexanecarboxaldehyde hydrazone.

A solution of this crude hydrazone in 30 mL of tetrahydrofuran and 70 mL of triethylamine was placed into a 200-mL round-bottomed flask equipped with an addition funnel and magnetic stirring bar. The flask was cooled to 0 °C, and a saturated solution of iodine in 25 mL of tetrahydrofuran was added with vigorous stirring until the evolution of nitrogen ceased and the color of the reaction mixture changed from yellow to brown. The reaction mixture was stirred at room temperature for 1 h and then poured into 400 mL of a mixture of ice and water. The aqueous layer was extracted with three 100-mL portions of pentane, and the combined pentane extracts were washed with 100-mL portions of 1 N hydrochloric acid until the aqueous layer became slightly acidic. The pentane layer was then washed with one 50-mL portion each of saturated sodium bicarbonate and saturated sodium chloride solution, dried over anhydrous sodium sulfate, and filtered. Removal of the pentane under reduced pressure yielded

13.4 g of a yellow oil, which on distillation afforded 760 mg (3.4 mmol) of (iodomethylene)cyclohexane (13)[18] and 4.92 g (14.1 mmol, 16% based on starting aldehyde) of diiodide 7 as a pale yellow oil: bp 95–98 °C (0.5 mm); UV (EtOH) λ_{max} 253 nm (ϵ 740), 292 (1260); UV (CH$_2$Cl$_2$) λ_{max} 248 nm (ϵ 785), 291 (1310); IR ν_{max} 2937, 2862, 1449, 1349, 1304, 1291, 1237, 1211, 1153, 1131, 1090, 1074 cm^{-1}; ^{1}H NMR δ 5.25 (d, 1, J = 2.1 Hz, CHI$_2$), 1.38 (m, 11); mass spectrum, m/e (relative intensity) 349.9030 (calcd for C$_7$H$_{12}$I$_2$, m/e 349.9032), 350 (19), 223 (42), 128 (4), 127 (5), 97 (10), 96 (16), 95 (100), 81 (16), 68 (11), 67 (38), 55 (41). Anal. Calcd for C$_7$H$_{12}$I$_2$: C, 24.02; H, 3.46; I, 72.52. Found: C, 24.32; H, 3.26; I, 72.20.

(Diiodomethyl)cyclohexane-1-d (7-d) was prepared in an analogous manner. According to the general procedure,[19] 10.0 g (89.0 mmol) of cyclohexanecarboxaldehyde, 16.0 g (800 mmol) of deuterium oxide, and 60 mg of potassium carbonate were vigorously stirred in a 50-mL round-bottomed flask. The contents of the flask were heated to 75 °C and maintained at that temperature for 10 h. The mixture was cooled to room temperature and then poured into a separatory funnel containing a 100-mL portion of pentane. The aqueous layer was saturated with sodium chloride and extracted with an additional 50-mL portion of pentane. The combined pentane extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to yield 9.22 g (80.9 mmol, 92%) of 1-deuteriocyclohexanecarboxaldehyde.

According to the general procedure of Pross and Sternhell,[17] a solution of 8.00 g (71.00 mmol) of deuterated aldehyde in 40 mL of absolute ethanol was added dropwise to 20 g of 99% hydrazine hydrate. Isolation as described above afforded 13.2 g of crude hydrazone. Oxidation of the deuterated hydrazone with iodine as described above yielded 15.1 g of a dark reddish oil. Distillation afforded 1.50 g (6.75 mmol) vinyl iodide 13 and 6.86 g (19.5 mmol, 22% based on starting aldehyde) of diiodide 7-d as a pale yellow oil: bp 113–116 °C (0.80 mm); IR ν_{max} 2923, 2848, 1446, 1341, 1332, 1275, 1089 cm^{-1}; ^{1}H NMR δ 5.24 (s, 1, CHI$_2$), 1.46 (m, 10). Mass spectral analysis afforded the composition 94% d_1 and 6% d_0.

(Bromoiodomethyl)cyclohexane (11) was prepared according to the general method of Fry and Cawse.[20] To 20.0 g (256 mmol) of pyridine in 100 mL of dichloromethane that was cooled with an ice bath was added a solution of 26.4 g (128 mmol) of iodine bromide in 100 mL of dichloromethane over a period of 15 min. To this stirred, ice-cooled solution was added 4.0 g (31.7 mmol) of cyclohexanecarboxaldehyde hydrazone, and the stirring continued overnight as the solution warmed to room temperature. The mixture was then washed with three, ice-cold 50-mL portions each of saturated sodium sulfite, 0.1 N hydrochloric acid, and water. The solvent layer was dried over saturated sodium chloride solution followed by anhydrous sodium sulfate and concentrated on a rotary evaporator. Short-path distillation afforded 1.50 g (4.95 mmol, 16%) of bromo iodide 11 as a clear oil: bp 75–77 °C (0.5 mm); UV (EtOH) λ_{max} 220 nm (ϵ 1380), 276 (403); IR ν_{max} (CCl$_4$) 2915, 2856, 1451, 1363, 1350, 1334, 1308, 1294, 1257, 1242, 1219, 1182, 1168, 1145, 1121, 1093, 1003, 979, 968, 893, 881 cm^{-1}; ^{1}H NMR δ 5.60 (d, 1, J = 2.90 Hz, CHIBr), 1.48 (m, 11); mass spectrum, m/e (relative intensity) 301.9168 (calcd for C$_7$H$_{12}$BrI, m/e 301.9169), 350 (3), 223 (7), 222 (11), 177 (19), 175 (21), 128 (8), 127 (7), 97 (13), 96 (17), 95 (100), 82 (12), 80 (9), 78 (6), 67 (33), 55 (41). Anal. Calcd for C$_7$H$_{12}$BrI: C, 27.82; H, 4.01; Br, 26.14; I, 42.03. Found: C, 27.91; H, 3.91; Br, 25.97; I, 41.76.

(Dibromomethyl)cyclohexane (17) was prepared according to the general method of Roberts et al.[21] To 20.0 g (146 mmol) of phosphorus trichloride which had been cooled to 0 °C was added dropwise with stirring 16.0 g (100 mmol) of bromine followed by 9.65 g (86.2 mmol) of cyclohexanecarboxaldehyde. The resulting mixture was allowed to warm to room temperature, was hydrolyzed by careful dropwise addition of about 100 mL of water, and was extracted with two 100-mL portions of ether. The combined

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ethereal extracts were washed with one 100-mL portion each of water, saturated sodium bicarbonate solution, and again with water, dried over saturated sodium chloride solution followed by anhydrous sodium sulfate, filtered, and concentrated under aspirator pressure. Distillation afforded 13.7 g (53.5 mmol, 62%) of a colorless liquid: bp 60–61 °C (0.3 mm); UV (EtOH) λ_{max} 224 nm (ϵ 369); IR ν_{max} (CCl$_4$) 2939, 2908, 2861, 1447, 1363, 1348, 1305, 1294, 1241, 1222, 1183, 1167, 1156, 1116, 957 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.72 (d, 1, J = 4.0 Hz, CHBr$_2$), 1.70 (m, 11) (lit.,[10] no spectral data).

(B) Photoproducts. From the irradiations described in Tables I and III the following products were isolated as colorless liquids by preparative gas chromatography. (Iodomethyl)cyclohexane (9) and (dimethoxymethyl)cyclohexane (14) were identified by comparison of their spectral properties with those of specimens prepared independently as described below, and methylenecyclohexane (15), 1-methylcyclohexene (16), methylcyclohexane, and cyclohexanecarboxaldehyde were identified by similar comparison with commercial specimens. 1-Methoxy(iodomethyl)-cyclohexane,[22] (bromomethyl)cyclohexane (19),[23] and (bromomethylene)cyclohexane (21)[18] were identified by comparison of their spectral properties with those previously reported. (Iodomethylene)cyclohexane (13)[18] had spectral properties in agreement with those previously reported and with those of material obtained during the preparation of diiodide 7.

Independent Synthesis of Iodide 9. A solution of 5.3 g (2.0 mmol) of cyclohexylmethyl tosylate[24] and 6.0 g (4.0 mmol) of sodium iodide in 75 mL of anhydrous acetone was heated under reflux for 12 h. The salt that formed was removed by filtration, the filtrate was poured into 200 mL of water, and this mixture was extracted with two 50-mL portions of pentane. The combined pentane extracts were dried over anhydrous sodium sulfate, filtered, and concentrated by rotary evaporation to yield 3.4 g (15 mmol, 76%) of iodide 9. Distillation in a Kugelrohr apparatus yielded 2.3 g (10 mmol, 52%) of a colorless liquid: bp 48–52 °C (0.35 mm) [lit.[23] bp 60 °C (1.0 mm)]; IR ν_{max} 2933, 2866, 1450, 1427, 1305, 1295, 1240, 1210, 1190, 1175, 964, 899 cm^{-1}; ^{1}H NMR δ 3.12 (d, 2, J = 6.2 Hz, CH$_2$I), 1.40 (m, 11).

Independent Synthesis of Acetal 14. To a solution of 123 mg (1.02 mmol) of cyclohexanecarboxaldehyde in 10 mL of anhydrous methanol were added 136 mg (1.28 mmol) of trimethyl orthoformate and a trace of p-toluenesulfonic acid. The resulting solution was stirred at room temperature for 6 h, poured into a 25-mL portion of water, and extracted with two 20-mL portions of pentane. The combined pentane extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to yield 145 mg (0.92 mmol, 94%) of acetal 14. Final purification by preparative gas chromatography afforded a colorless liquid: IR ν_{max} 2994, 2931, 2863, 2832, 1451, 1195, 1148, 1125, 1080, 1049, 977, 966, 885 cm^{-1}; ^{1}H NMR δ 3.99 (d, 1, J = 6.8 Hz, CH-1), 3.35 (s, 6, OCH$_3$), 1.30 (m, 11) (lit.,[25] no spectral data).

(C) Quantum Yields. The quantum yields shown in Table II were determined by using a merry-go-round apparatus, equipped with a Honovia 450-W mercury arc and Corning 0-52 and 7-37 filters, the benzophenone–benzhydrol actinometry system,[26] and solutions 0.07 M in diiodide 7. Conversions were 2–3% for diiodide 7 and 5–7% for actinometry solutions.

(Diiodomethyl)cyclopentane (22). (A) Preparation. The general method of Pross and Sternhell was followed.[17] The hydrazone of cyclopentanecarboxaldehyde was prepared by a procedure identical with that described above. A solution of 11.0 g (102 mmol) of the hydrazone in 70 mL of triethylamine and 30 mL of tetrahydrofuran was treated with iodine; isolation as described above yielded 13.0 g of a brown oil, which upon distillation afforded 1.53 g (7.40 mmol) of (iodomethylene)cyclopentane (23)

as an early fraction. Continued distillation afforded 3.55 g (10.5 mmol, 10% based on starting aldehyde) of diiodide 22 as a pale yellow oil: bp 87–88 °C (0.35 mm); IR ν_{max} 2964, 2873, 1456, 1334, 1305, 1241, 1142, 1082 cm^{-1}; ^{1}H NMR δ 5.21 (d, 1, J = 5.4 Hz, CHI$_2$), 2.27 (m, 1, CH-1), 1.79 (m, 8); mass spectrum, m/e (relative intensity) 335.8873 (calcd for C$_6$H$_{10}$I$_2$, m/e 335.8876), 336 (17), 209 (43), 205 (12), 167 (8), 128 (4), 127 (6), 82 (23), 81 (100), 79 (21), 67 (36), 55 (8). Anal. Calcd for C$_6$H$_{10}$I$_2$: C, 21.45; H, 3.00; I, 75.55. Found: C, 21.05; H, 3.21; I, 75.46.

(B) Photoproducts. From the irradiations described in Table IV were isolated the following products as colorless liquids by preparative gas chromatography. Vinyl iodide 23 was identified by comparison of its spectral properties with those previously reported[18] and with those of material obtained during the preparation of diiodide 22. (Dimethoxymethyl)cyclopentane (24) had spectral properties similar to those previously reported.[27] 1-Methylcyclopentane (25) and cyclohexene (26) were identified by comparison with commercial specimens.

3,3-Dimethyl(diiodomethyl)cyclobutane (27). (A) Preparation. Treatment of 3.2 g (28 mmol) of 3,3-dimethylcyclobutanecarboxaldehyde according to the general method of Pross and Sternhell[17] afforded 7 g of a red oil. Distillation yielded 2.21 g (9.95 mmol) of 3,3-dimethyl(iodomethylene)cyclobutane (28)[18] and 1.52 g (4.34 mmol, 7% based on starting aldehyde) of the desired diiodide 27 as a greenish yellow oil: bp 76–78 °C (0.45 mm); IR ν_{max} 2957, 2928, 2868, 1457, 1449, 1364, 1280, 1211, 1080 cm^{-1}; ^{1}H NMR δ 4.93 (d, 1, J = 10.0 Hz, CHI$_2$), 2.88 (m, 1, CH-1), 1.90 (m, 2), 1.37 (m, 2), 1.15 (s, 3, CH$_3$), 10.9 (s, 3, CH$_3$); mass spectrum, m/e (relative intensity) 349.9030 (calcd for C$_7$H$_{12}$I$_2$, m/e 349.9032), 350 (4), 340 (3), 223 (7), 221 (4), 211 (5), 167 (33), 96 (30), 95 (100), 81 (39), 79 (16), 67 (17), 56 (29), 55 (36). Anal. Calcd for C, 24.02; H, 3.46; I, 72.52. Found: C, 24.40; H, 3.26; I, 72.58.

(B) Photoproducts. From the irradiations described in Table V were isolated vinyl iodide 28 and 4,4-dimethylcyclopentene (29) by preparative gas chromatography as colorless liquids having spectral properties in agreement with those previously reported.[18,28]

Irradiation of 1,1-Diiodo-2,2-dimethylpropane (1b). From the irradiations of diiodide 1b[17] outlined in Table VI were isolated the following products as colorless liquids by preparative gas chromatography.

2,2-Dimethyl-1-iodopropane (3b): IR ν_{max} 2969, 2934, 2873, 2844, 1471, 1462, 1390, 1365, 1248, 1229, 1160, 901 cm^{-1}; ^{1}H NMR δ 3.16 (s, 2, CH$_2$I), 1.06 (s, 9); lit.[29] bp 54–55 °C (55 mm).

2-Methyl-2-butene (6b) was identified by direct comparison with a commercial specimen.

1,1-Dimethoxy-2,2-dimethylpropane (30) was identified by comparison with a specimen prepared independently by the general method described above for acetal 14. Thus, 100 mg (1.16 mmol) of pivaldehyde afforded 138 mg (1.05 mmol, 90%) of acetal 30 as a colorless liquid: IR ν_{max} 2988, 2966, 2876, 2836, 1482, 1463, 1397, 1364, 1189, 1116, 1081, 967 cm^{-1}; ^{1}H NMR δ 4.78 (s, 1, CH-1), 4.50 (s, 6, OCH$_3$), 1.89 (s, 9) (lit.[30] no spectral data).

8,8-Diiodo-2,6-dimethyl-2-octene (Citronellal Iodide, 31). (A) Preparation. According to the general procedure of Pross and Sternhell,[17] a solution of 7.90 g (52.0 mmol) of citronellal in 50 mL of ethanol was added slowly to 20 g of hydrazine hydrate (64% in water) and heated at reflux for 1 h. Isolation in the usual manner afforded a product that contained no starting aldehyde as determined spectrally. Oxidation with iodine gave 15.8 g of a dark brown oil. Isolation of a fraction boiling at 105–107 °C (0.65 mm) and further purification by medium-pressure liquid chromatography with pentane as the column eluent yielded 2.3 g (5.9 mmol, 9%) of diiodide 31 as a pale yellow oil: IR ν_{max} 2962, 2924, 2808, 2871, 2853, 1460, 1443, 1381, 1095, 889 cm^{-1}; ^{1}H NMR δ 5.07 (m, 2, CHI$_2$ and C=CH), 1.69 (br s, 3, CH$_3$), 1.61 (s, 3, CH$_3$), 0.86 (d, 3, J = 6.4 Hz, CH$_3$-6); mass spectrum, m/e (relative intensity) 391.9505 (calcd for C$_{10}$H$_{18}$I$_2$, m/e 391.9502), 392 (5), 265 (4), 137 (100), 95 (78), 93 (28), 91 (15), 83 (38), 82 (28), 81

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Table VII. Irradiation of Diiodide 31[a]

			yield,[b] %			
solvent	31	32	(Z)-33	(E)-33	34	35
$(C_2H_5)_2O$	19	12	14	26	20	6
$(CH_2Cl)_2$	19	3	14	28	22	8

[a] Irradiations were conducted for 2 h as described in the Experimental Section. [b] Determined by gas chromatographic analysis relative to a hydrocarbon standard.

(84), 79 (35), 77 (20), 69 (83), 68 (24), 67 (54), 55 (99). Anal. Calcd for $C_{10}H_{18}I_2$: C, 30.64; H, 4.63; I, 64.74. Found: C, 30.72; H, 4.58; I, 64.34.

(B) Photoproducts. The following were isolated by preparative gas chromatography from the irradiations described in Table VII.

2,6-Dimethyl-8-iodo-2-octene (citronellyl iodide) (32) had spectral properties in agreement with those previously published.[14]

cis-**3,7-Dimethyl-1-iodo-1,6-octadiene (33c)** was obtained as a colorless liquid: IR ν_{max} 3063, 2962, 2923, 2864, 2845, 1610, 1452, 1377, 1338, 1312, 1292, 1271, 703 cm^{-1}; ^{1}H NMR δ 6.14 (d, 1, J = 7.4 Hz, CH-1), 5.94 (dd, 1, J = 7.4, 8.4 Hz, CH-2), 1.66 (br s, 3, CH$_3$), 1.56 (s, 3, CH$_3$), 0.96 (d, 3, J = 6.8 Hz, CH$_3$-3); mass spectrum, m/e (relative intensity) 264.0375 (calcd for $C_{10}H_{17}I$, m/e 264.0377), 264 (1), 262 (22), 194 (52), 181 (25), 137 (100), 119 (57), 107 (27), 95 (99), 93 (47), 91 (44), 81 (93), 69 (84), 67 (98).

trans-**3,7-Dimethyl-1-iodo-1,6-octadiene (33t)** was isolated as a clear oil: IR ν_{max} 3044, 2964, 2923, 2918, 2871, 2855, 1608, 1454, 1441, 1378, 1196, 949 cm^{-1}; ^{1}H NMR δ 6.42 (dd, 1, J = 14.4, 8.0 Hz, CH-2), 5.96 (dd, 1, J = 14.4, 1.0 Hz, CH-1), 5.02 (m, 1, CH-6), 1.65 (br s, 3, CH$_3$), 1.56 (s, 3, CH$_3$), 0.96 (d, 3, J = 6.6 Hz,

CH$_3$-3); mass spectrum, m/e (relative intensity) 264.0375 (calcd for $C_{10}H_{17}I$, m/e 264.0377), 264 (1), 262 (23), 194 (54), 181 (29), 137 (100), 119 (55), 107 (27), 95 (99), 93 (45), 91 (40), 81 (98), 69 (84), 67 (39).

1-Iodo-2-(2-propenyl)-5-methylcyclohexane (isopulegyl iodide, 34) was obtained as a colorless oil: IR ν_{max} 3079, 2958, 2925, 2871, 1651, 1458, 1449, 1379, 1154, 1090, 939, 896 cm^{-1}; ^{1}H NMR 4.78 (m, 2, C=CH$_2$), 4.11 (ddd, 1, J = 11.8, 11.5, 4.1 Hz, CHI), 1.66 (br s, 3, CH$_3$C=C), and 0.92 (d, 3, J = 6.0 Hz, CH$_3$); mass spectrum, m/e (relative intensity) 264.0375 (calcd for $C_{10}H_{17}I$, m/e 264.0377), 264 (1), 262 (14), 194 (33), 181 (16), 161 (8), 137 (100), 119 (34), 95 (60), 93 (26), 91 (24), 81 (84), 79 (27), 77 (18), 69 (96), 67 (57), 55 (99).

A mixture of *cis*- and *trans*-carane (35) had spectral properties consistent with those expected from the pure cis[31] and trans[32] isomers.

Registry No. 1b, 2443-89-2; 3b, 15501-33-4; 7, 65826-85-9; 7-*d*, 85390-83-6; 9, 5469-33-0; 11, 65826-86-0; 13, 23904-33-8; 14, 18231-08-8; 17, 52470-92-5; 22, 85390-84-7; 27, 85390-85-8; 30, 62617-39-4; 31, 85390-86-9; 33c, 85390-87-0; 33t, 85390-88-1; 34, 85390-89-2; cyclohexanecarboxaldehyde, 2043-61-0; cyclohexanecarboxaldehyde hydrazone, 85390-90-5; 1-deuteriocyclohexanecarboxaldehyde, 85390-91-6.

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Notes

Photochemistry of Organic Geminal Diiodides

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It has been previously reported that irradiation of methylene iodide in the presence of olefins results in cyclopropane products leading to speculations of a carbene or carbenoid intermediate in this photochemistry.[2,3] However, other geminal diiodes when irradiated in the presence of olefins have not yielded cyclopropanes but rather have exhibited chemistry which is dependent upon both their structure and the solvent in which they were irradiated.[3,4] In the present study, we undertook to clarify under what conditions, if any, a carbene is formed.

After the initial reports of cyclopropanation of olefins by photolysis of methylene iodide,[2] Neuman and Wolcott examined the photolysis of 2,2-dimethyl-1,1-diiodopropane (1) in nonpolar solvents such as cyclohexane and cyclohexene.[4] They did not observe formation of 1,1-dimethylcyclopropane (2), which had been shown in previous
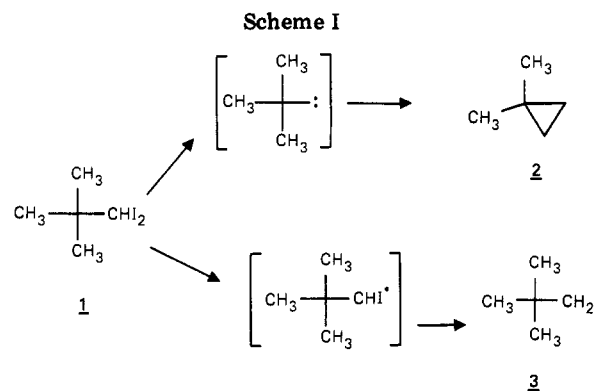
Scheme I

studies to be the major product from neopentylcarbene.[5] Instead, the appearance of the monoiodo product 3 as the major product provided evidence for a predominant radical pathway (Scheme I).

Subsequently, Kropp and co-workers examined the photochemistry of methylene iodide and 1,1-diiodomethylcyclohexane (4) in more polar media and suggested that a carbene or carbenoid intermediate could be consistent with their observations, i.e., cyclopropane products from CH_2I_2 and insertion products from 4.[3] They proposed that the formation of a carbene(oid) is preceded by initial

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