

# PHOTOCHEMISTRY OF ALKYL HALIDES—VII

## CYCLOPROPANATION OF ALKENES<sup>1</sup>

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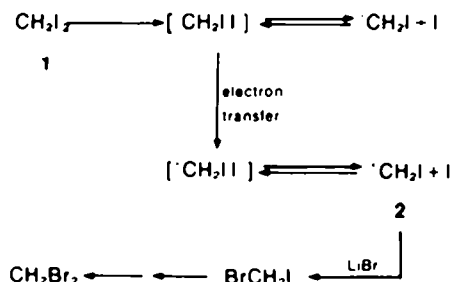
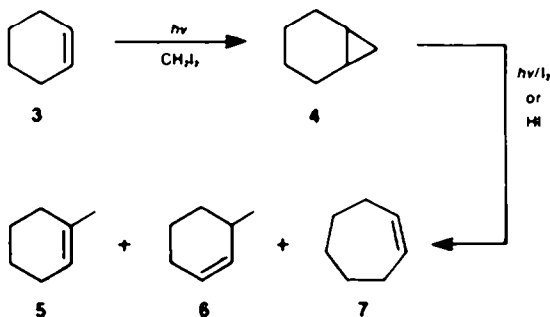
**Abstract**—The previously observed cyclopropanation of alkenes by irradiation of diiodomethane (1) in their presence has been studied in more detail and found to be a synthetically useful procedure which is significantly less subject to steric effects than the traditional Simmons-Smith method. The results from photocyclopropanation of a variety of alkenes are summarized in Tables 1 and 3–4. In a number of cases the photochemical procedure afforded improved results over the Simmons-Smith method, particularly with sterically congested alkenes. Cycloalkenes showed relative rates of photocyclopropanation as a function of ring size similar to those of the Simmons-Smith method (Table 5). However, the photocyclopropanation reaction exhibited steadily increasing relative rates with increasing substitution about the double bond—in contrast with the Simmons-Smith method (Table 6), in which steric effects offset increasing nucleophilicity of the alkene with increasing substitution. The  $\alpha$ -iodocation 2 is suggested as the methylene transfer species. In the presence of lithium bromide cation 2 was trapped to afford bromiodomethane.

Previous studies in these laboratories have shown that irradiation of alkyl monoiodides in solution is a convenient and powerful method for the generation of carbocations, via a process thought to involve initial light-induced homolytic cleavage of the C–I bond followed by electron transfer within the resulting caged radical pair.<sup>2</sup> If the geminally disubstituted analog diiodomethane (1) were to exhibit analogous behavior, the  $\alpha$ -iodocation 2 would result (Scheme 1). However, irradiation of dibromo- and diiodomethane in the presence of alkenes is reported to result in methylene transfer to afford cyclopropane adducts,<sup>3–5</sup> via a mechanism proposed to involve the intermediacy of either methylene<sup>3,5</sup> or an excited state of the dihalide<sup>3</sup> as the methylene transfer agent. We wish to report here a more detailed study of this reaction for diiodomethane (1) which shows that it is a convenient and useful method for the cyclopropanation of alkenes which has some distinct advantages over the traditional Simmons-Smith procedure. The  $\alpha$ -iodocation 2 is suggested as the methylene transfer species.

### RESULTS

The results from irradiation of diiodomethane (1) in the presence of cyclohexene (3) under a variety of conditions are summarized in Table 1. As noted previously, norcaradiene (4) is the principal product but is usually accompanied by a mixture of 1- and 3-methylcyclo-

hexene (5 and 6) and cycloheptene (7)—a result attributed to the involvement of methylene, which undergoes competing cyclopropanation and C–H insertion.<sup>3</sup> However, control studies have now revealed that norcaradiene (4) is converted to a similar mixture of these same alkenes on either irradiation in the presence of iodine or treatment with HI in the dark (Table 2). It was subsequently found that irradiation of diiodomethane (1) in the presence of cyclohexene (3) afforded norcaradiene (4) as the exclusive product when the irradiation mixture was stirred with a scavenger solution of aqueous sodium thiosulfate and sodium bicarbonate (Table 1). Several different light sources were found to be effective. A preparative scale run using a sun lamp and 0.1 mol of cyclohexene (3) in the presence of scavenger afforded norcaradiene (4) in greater than 70% isolated yield.



Scheme 1.

The results from the photocyclopropanation of a number of alkenes in the presence of the scavenger system are summarized in Tables 3 and 4. Also included are the results from treatment of these same alkenes in the dark with diiodomethane (1) and Zn–Cu couple, the traditional Simmons-Smith method for the cyclopropanation of alkenes.<sup>7</sup> Photocyclopropanation occurred readily with a wide variety of alkenes, including the sterically congested t-Bu-substituted alkenes 28, 30, 32, and 34. By contrast 32 afforded no adduct using two different procedures for the Simmons-Smith method.<sup>8,9</sup>

Table 1. Irradiation of diiodomethane (1) in the presence of cyclohexene (3)<sup>a</sup>

[1], M	[3], M	time, h	yield, % <sup>b</sup>			
			1	3	4	5-7
0.05 <sup>c</sup>	0.18	2	45	<i>d</i>	16	9
0.05 <sup>c</sup>	1.8	2	14	<i>d</i>	66	8
0.05 <sup>c,e</sup>	10	2	19	<i>d</i>	80	<i>f</i>
0.13 <sup>g,h</sup>	0.05	11	<i>d</i>	13	70	<i>i</i>
0.16 <sup>h,j</sup>	0.06	16	<i>d</i>	<i>f</i>	50	<i>i</i>

<sup>a</sup> In 1,2-dichloromethane solution. <sup>b</sup> Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. <sup>c</sup> Irradiation conducted on a 5-ml solution contained in a Pyrex tube suspended in a Rayonet RPR-100 photochemical reactor equipped with a circular array of 16 F8T5 BL lamps. <sup>d</sup> Not determined. <sup>e</sup> Irradiation run in neat cyclohexene. <sup>f</sup> Trace. <sup>g</sup> Irradiation conducted on a 10-ml solution contained in a Pyrex round-bottomed flask equipped with a magnetic stirring bar, condenser, and nitrogen inlet and suspended 6 cm from a Hanovia 450-W mercury arc equipped with a reflector. <sup>h</sup> Stirred with 3 ml of an aqueous solution 10% each in sodium thiosulfate and sodium bicarbonate. <sup>i</sup> None detectable. <sup>j</sup> Irradiation conducted on a 10-ml solution contained in a Pyrex round-bottomed flask equipped with a magnetic stirring bar, condenser, and nitrogen inlet and suspended in a rayonet RPR-100 photochemical reactor equipped with a circular array of 16 P8T5 BL lamps.

Table 2. Rearrangement of norcaradiene (4)<sup>a</sup>

conditions	time, h	yield			
		4	5	6	7
$h\nu^b/I_2^c$	8	<i>d</i>	7	39	0.2
dark/HI <sup>c</sup>	2.5	<i>d</i>	2	28	0.5

<sup>a</sup> Conducted on 10-ml dichloromethane solutions 0.05 M in norcaradiene (4) and contained in a Pyrex round-bottomed flask. <sup>b</sup> Flask suspended 6 cm from a Hanovia 450-W mercury arc equipped with a reflector. <sup>c</sup> One mol equiv. <sup>d</sup> Trace.

Reaction was usually quite clean, with no detectable formation of either C-H insertion or secondary products. *cis*- and *trans*-3-Hexene (16 and 18) underwent stereospecific reaction with no detectable formation of the isomeric cyclopropane. The more highly strained *cis*-di-*t*-Bu and diisopropyl analogs 30 and 36, however,

underwent some competing isomerization to the *trans*-alkenes 32 and 38, respectively, and subsequent cyclopropanation.<sup>10</sup> Bicyclohexylidene (40) afforded some of the homologous cyclopropane 47, presumably via isomerization of the initial adduct 41 to alkene 46 followed by recyclopropanation.

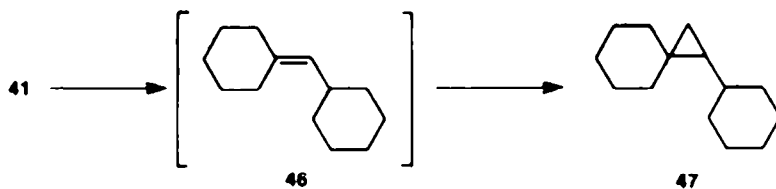


Table 3.


































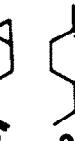
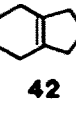
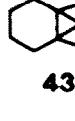
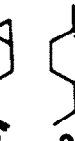


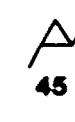
alkene	cyclopropane	alkene	cyclopropane
			
<b>5</b>	<b>8</b>	<b>26</b>	<b>27</b>
			
<b>9</b>	<b>10</b>	<b>28</b>	<b>29</b>
			
<b>11</b>	<b>12</b>	<b>30</b>	<b>31</b>
			
<b>7</b>	<b>13</b>	<b>32</b>	<b>33</b>
			
<b>14</b>	<b>15</b>	<b>34</b>	<b>35</b>
			
<b>16</b>	<b>17</b>	<b>36</b>	<b>37</b>
			
<b>18</b>	<b>19</b>	<b>38</b>	<b>39</b>
			
<b>20</b>	<b>21</b>	<b>40</b>	<b>41</b>
			
<b>22</b>	<b>23</b>	<b>42</b>	<b>43</b>
			
	<b>24</b>		
			
	<b>25</b>	<b>44</b>	<b>45</b>

Table 4. Photocyclopropanation of various alkenes<sup>a</sup>

alkene	time, h	solvent	yield, % <sup>b</sup>	
			alkene	cyclopropane
5	4.5	d	14	8, 68 (33)
9	12	d	10	10, 65
11	10	e	10	12, 64 (53)
7	6	d	6	13, 60 (48 <sup>f</sup> )
14	6	d	21	15, 60 (47)
16	12	d	10	17, 75 (36)
18	10	d	16	19, 76 (16)
20	8	e	9	21, 83 (42)
22	3	d	10	23, 47 <sup>h</sup>
				24, 7 <sup>h</sup> (50)
				25, 14 <sup>h</sup>
26	12	e	9	27, 80 (39)
28	12	d	53	29, 40 (22 <sup>i</sup> )
30	16	e	15	31, 15 <sup>k</sup>
32	36	d	69	33, 30 <sup>j</sup> (0, <sup>f</sup> <sup>g</sup> )
34	120	e	46	35, 15
36	20	e	55	37, 31 <sup>m</sup> (5, <sup>f</sup> 10 <sup>j</sup> )
38	48	e	43	39, 43 (19, <sup>f</sup> 11 <sup>j</sup> )
40	4	e	7	41, 86 <sup>n</sup> (87)
42	2	d	13	43, 47 (9- <sup>j</sup> )
44	24	d	49	45, 36 <sup>o</sup> (9)

<sup>a</sup> Irradiations were conducted on 10-ml solutions in a Pyrex round-bottomed flask equipped with a magnetic stirring bar, condenser, and nitrogen inlet tube and suspended 6 cm from a Hanovia 450-W mercury arc equipped with a reflector. The solutions were stirred with 3 ml of an aqueous solution containing 10% sodium thiosulfate and 10% sodium bicarbonate, which was changed every 4 h.

<sup>b</sup> Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. Numbers in parentheses are for the Simmons-Smith method; for the original literature citations see ref 7. <sup>c</sup> Solution contained 0.5 mmol of alkene and 1.5 mmol of diiodomethane. <sup>d</sup> 1,2-Dichloroethane. <sup>e</sup> Dichloromethane. <sup>f</sup> The procedure of ref 8 was followed. <sup>g</sup> Trace. <sup>h</sup> After 8 h: 22, <sup>g</sup>; 23, 12; 24, <sup>g</sup>; 25, 40. <sup>i</sup> Solution contained 1.0 mmol of alkene and 2.0 mmol of diiodomethane. <sup>j</sup> The procedure of ref 9 was followed. <sup>k</sup> Competing formation of *trans*-alkene 32 and -cyclopropane 33 observed in 69% total yield. <sup>l</sup> Two additional unidentified products formed in trace quantities. <sup>m</sup> Competing formation of *trans*-alkene 38 and -cyclopropane 39 observed in 10% total yield. <sup>n</sup> Cyclopropane 47 obtained in 6% yield. <sup>o</sup> One additional unidentified product observed in <5% yield.

Further comparison of the photocyclopropanation and Simmons-Smith methods is seen in Tables 5 and 6. With cycloalkenes the two methods displayed similar relative rates as a function of ring size (Table 5). On the other hand, photocyclopropanation exhibited increasing rates on going from cyclohexene (3) to 1-methylcyclohexene (5) and then 1,2-dimethylcyclohexene (9), whereas the Simmons-Smith procedure shows a smaller increase on going to 1-methylcyclohexene (5)<sup>11</sup> and a decrease on going to the dimethyl derivative 9 (Table 6).<sup>11,12</sup> The relative rates in the case of the Simmons-Smith reaction apparently arise from increasing steric effects offsetting increasing nucleophilicity of the alkene with increasing substitution. This is also seen in the case of limonene (22), which undergoes preferential reaction at the less highly substituted, but also less hindered, isopropenyl double bond under the Simmons-Smith conditions to afford cyclopropane 24.<sup>7</sup> By contrast, photocyclopropanation occurred preferentially at the more highly substituted cyclohexenyl double bond to afford adduct 23 as the principal product.

As seen in Table 7, the quantum yield for formation of

norcaradiene (4) in several solvents was approximately 0.2, whereas the quantum yield for disappearance of diiodomethane (1) was approximately twice as large. In neat cyclohexene (3) the quantum yield for norcaradiene (4) formation was substantially larger and more closely equal to that for disappearance of diiodomethane (1). Finally, it was observed that irradiation of diiodomethane (1) in the presence of lithium bromide afforded bromiodomethane (53%) and dibromoethane (19%).

#### DISCUSSION

From the preceding results it is clear that the photocyclopropanation of alkenes is a synthetically useful reaction which is frequently superior to the Simmons-Smith method, particularly for sterically congested alkenes. Its principal drawback, competing rearrangement of the starting alkene or the cyclopropane adduct if it is particularly sensitive, can often be minimized by efficient scavenging of the iodine and HI by-products. The methylene transfer species involved is electrophilic, highly selective, and relatively insensitive to steric

Table 5. Relative rates of cyclopropanation as a function of cycloalkene ring size

method	alkene		
	3	7	11
CH <sub>2</sub> I <sub>2</sub> , hν <sup>a</sup>	1.0	1.4	1.7
CH <sub>2</sub> I <sub>2</sub> , Zn(Cu)	1.0	1.18 <sup>b</sup>	1.60 <sup>b</sup>

<sup>a</sup> Irradiations were conducted on 10-ml 1,2-dichloroethane solutions, 0.15 M in diiodomethane and 0.05 M in each of two alkenes, contained in a round-bottomed flask suspended 6 cm from a Hanovia 450-W mercury arc equipped with a reflector. The solutions were stirred with a 3-ml aqueous solution containing 10% sodium thiosulfate and 10% sodium bicarbonate. The irradiations were conducted for 2 h, to approximately 10% consumption of the more reactive alkene. <sup>b</sup> Ref 11.

Table 6. Relative rates of cyclopropanation as a function of the degree of substitution of the alkene

method	alkene		
	3	5	9
CH <sub>2</sub> I <sub>2</sub> , hν <sup>a</sup>	1.0	3.6	8.7
CH <sub>2</sub> I <sub>2</sub> , Zn(Cu)	1.0	2.14 <sup>b</sup>	0.58, <sup>c</sup> 0.94 <sup>b</sup>

<sup>a</sup> Irradiations were conducted on 10-ml 1,2-dichloroethane solutions, 0.15 M in diiodomethane and 0.05 M in each of two alkenes, contained in a round-bottomed flask suspended 6 cm from a Hanovia 450-W mercury arc equipped with a reflector. The solutions were stirred with a 3-ml aqueous solution containing 10% sodium thiosulfate and 10% sodium bicarbonate. The irradiations were conducted for 1 h, to approximately 10% consumption of the more reactive alkene. <sup>b</sup> Ref 11. <sup>c</sup> Ref 12.

Table 7. Quantum yields for the irradiation of diiodomethane (1) in the presence of cyclohexene (3)<sup>a</sup>

solvent	Φ	
	-1	+4
Cyclohexene	0.78	0.70
CH <sub>2</sub> Cl <sub>2</sub> <sup>b</sup>	0.36	0.14
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O <sup>b</sup>	0.54	0.15
C <sub>6</sub> H <sub>6</sub> <sup>b</sup>	0.43	0.20

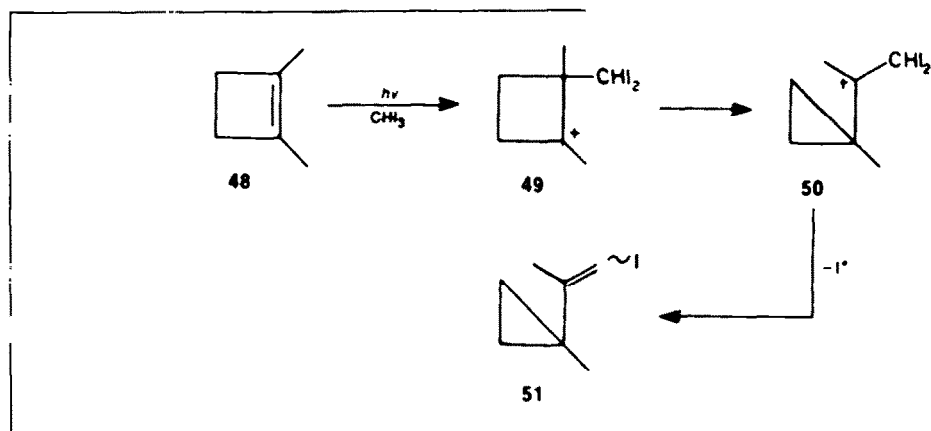
<sup>a</sup> Determined as described in the Experimental Section on solutions 0.07 M in 1. <sup>b</sup> [3] = 0.07 M.

effects. The high selectivity, both for  $\pi$  over C-H insertion and for reaction with a more highly substituted double bond, are inconsistent with the intermediacy of methylene as proposed previously.<sup>3,5</sup>

In analogy with monohalides, independent photobehavior by the two halogen substituents of diiodomethane (1) should afford the  $\alpha$ -iodocation 2 (Scheme 1).<sup>2</sup> Indeed, the presence of this intermediate was confirmed by its trapping with lithium bromide to afford in high yield bromoiodomethane, some of which underwent further conversion to dibromomethane. It is not unreasonable to assign to this same intermediate the role of methylene transfer agent, as shown in A. This species would be highly electrophilic and substantially less subject to steric effects than the organozinc intermediate (ICH<sub>2</sub>ZnI) thought to be involved in the Simmons-Smith reaction.<sup>7</sup> The effects of cyclohexene concentration on quantum

The alternative possibility of stepwise addition to the alkene as depicted in B seems less likely in view of the stereoselectivity of the reaction and the lack of rearranged products in the t-Bu systems 28, 30, 32, and 34—which are highly prone toward cationic rearrangements. On the otherhand, stepwise addition by the analogous intermediate +CH<sub>2</sub> derived from irradiation of iodoform in the presence of 1,2-dimethylcyclobutene (48) would account for the observed rearranged products 51.<sup>5,6</sup> Cyclobutenes readily undergo electrophilic addition whereas cyclopropanation would require the formation of a highly strained product.

It is clear that irradiation of geminal diiodides in the presence of unsaturated substrates holds promise as a broadly useful cyclopropanation procedure. Studies continue on both the synthetic and mechanistic aspects of this interesting reaction.



yield displayed in Table 6 are readily explained in terms of competing trapping of the  $\alpha$ -iodocation 2 by alkene to afford the cyclopropane adduct and by iodide ion to regenerate the starting diiodide.



## EXPERIMENTAL

**General methods.** Gas chromatographic analyses were performed on a Hewlett-Packard 5750 instrument using 10 ft  $\times$  1/8 in. stainless steel columns packed with either (A) 20% Carbowax 20 M or (B) 20% SF-96 on 60-80 mesh chromosorb W. Preparative gas chromatography was carried out on either a Varian-Aerograph 90 P or 920 instrument using 10 ft  $\times$  1/4 in. or 5 ft  $\times$  1/4 in. columns packed with the materials described above. IR spectra were obtained with a Perkin-Elmer 421 or Beckman 4250 grating spectrophotometer on CCl<sub>4</sub> solns. Proton NMR spectra were obtained on chloroform-*d* solutions with a Varian XL-100 spectrometer; data are reported in the following manner: multiplicity (s = singlet, m = unresolved multiplet, and br s = broadened singlet), integration, coupling constant, and assign-

ment. Mass spectra were obtained with an AEI MS-902 spectrometer.

**Irradiations.** These were conducted as indicated in Tables 1, 2 and 4-6. Alkenes were obtained commercially and distilled before use, except for 28,<sup>13</sup> (Z)-30,<sup>14</sup> 34,<sup>15</sup> 40,<sup>16</sup> and 42,<sup>17</sup> which were prepared as previously described.

At the end of the irradiation the organic layer was decanted, the aqueous phase was back-extracted with 50 mL diethyl ether, and the combined organic phases were dried over sat NaClq followed by anhyd Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated by distillation of the solvent through a Vigreux column. Preparative gas chromatography afforded the following products as colorless liquids:

1-Methylcyclohexene (5), 3-methylcyclohexene (6), cycloheptene (7), and dibromomethane had spectral data identical with those of commercial specimens. Bromiodomethane had spectral properties identical with those previously reported.<sup>18</sup> Bicyclo[4.1.0]heptane (norcarane, 4),<sup>19,20</sup> 1-methylbicyclo[4.1.0]heptane (8),<sup>11,20</sup> 1,6-dimethylbicyclo[4.1.0]heptane (10),<sup>11</sup> bicyclo[3.1.0]hexane (12),<sup>20,21</sup> bicyclo[5.1.0]octane (13),<sup>20</sup> tricyclo[3.2.1.0<sup>2,4</sup>]octane (15),<sup>20</sup> cis-1,2-diethylcyclopropane (17),<sup>20,21</sup> trans-1,2-diethylcyclopropane (19),<sup>20,21</sup> 1,1,2,2-tetramethylcyclopropane (21),<sup>20,21</sup> 1-methyl-4-(2-propenyl)bicyclo[4.1.0]heptane (23),<sup>20</sup> 1-methyl-4-(1-methylcyclopropyl)-1-cyclohexene (24),<sup>20</sup> 1,1-dimethylcyclopropane (27),<sup>20</sup> dispiro[5.1.5.0]tridecane (41),<sup>22</sup> tricyclo[4.3.1.4<sup>0</sup>]decane (43),<sup>23</sup> and methyl trans-2-methylcyclopropanecarboxylate (45)<sup>24</sup> had spectral properties in agreement with those previously reported and were identical in every respect with specimens prepared independently.<sup>9,9</sup>

1-Methyl-4-(1-methylcyclopropyl)bicyclo[4.1.0]heptane (25) was isolated as a 1:1 mixture of *syn* and *anti* isomers (as determined by <sup>1</sup>H NMR):  $\nu_{\max}$  3072, 3060, 2994, 2956, 2923, 2862, 2738, 1450, 1429, 1381, 1310, 1298, 1269, 1188, 1120, 1072, 1042, 1032, 1011, 971, 958, 932, 904, 877, 864, 853, 673 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  0.99 (br s, 3, CH<sub>3</sub>), 0.85 (s, 1.5, CH<sub>2</sub>), 0.80 (s, 1.5, CH<sub>3</sub>), and 0.13 (m, 6); *m/e* 164.1563 (calcd for C<sub>17</sub>H<sub>26</sub>, 164.1565), 164 (29), 135 (13), 121 (13), 109 (8), 108 (8), 107 (11), 106 (14), 105 (8), 97 (11), 96 (16), 95 (20), 91 (18), 83 (30), 82 (100), 81 (41), 80 (15), 79 (24), 68 (18), 67 (80), 55 (19).

1,1-Di(1,1-dimethylethyl)cyclopropane (29):  $\nu_{\max}$  3090, 3011, 2997, 2949, 2904, 2865, 1480, 1471, 1442, 1421, 1389, 1363, 1267, 1206, 1178, 1130, 1049, 1011, 916, 893, 549 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  1.00 (s, 18, 2 × C(CH<sub>3</sub>)<sub>2</sub>) and 0.38 (s, 4, CH<sub>2</sub>CH<sub>3</sub>); *m/e* 126.1411 (calcd for C<sub>11</sub>H<sub>22</sub>, 126.1408), 154 (trace), 126 (43), 112 (8), 111 (78), 98 (19), 97 (11), 83 (43), 70 (14), 69 (19), 57 (100), 55 (38).

cis-1,2-Di(1,1-dimethylethyl)cyclopropane (31):  $\nu_{\max}$  3057, 2952, 2905, 2878, 1469, 1395, 1358, 1193, 1107, 1031, 857, 570; <sup>1</sup>H NMR  $\delta$  1.02 (s, 2 × C(CH<sub>3</sub>)<sub>2</sub>), 0.6 (m, 2, CH<sub>2</sub>); *m/e* 126.1411 (calcd for C<sub>11</sub>H<sub>22</sub>, 126.1408), 154 (trace), 126 (2), 98 (5), 97 (4), 86 (14), 84 (21), 83 (19), 71 (17), 70 (100), 69 (45), 56 (47), 55 (8), 54 (66).

trans-1,2-Di(1,1-dimethylethyl)cyclopropane (33):  $\nu_{\max}$  3065, 2990, 2955, 2905, 2867, 1475, 1367, 1318, 1265, 1215, 1195, 1122, 1111, 1101, 1040, 1030, 985, 923, 915, 888; <sup>1</sup>H NMR  $\delta$  1.01 (s, 18.2 × C(CH<sub>3</sub>)<sub>2</sub>), 0.5 (m, 2, CH-1 and -2), 0.1 (m, 2, CH<sub>2</sub>); *m/e* 154.1724 (calcd for C<sub>11</sub>H<sub>22</sub>, 154.1721), 154 (2), 98 (6), 97 (6), 85 (16), 83 (26), 71 (18), 70 (100), 69 (65), 67 (7), 57 (33), 55 (55).

1,1,2-Tri(1,1-dimethylethyl)cyclopropane (35):  $\nu_{\max}$  3065, 3015, 2962, 2908, 2867, 1470, 1390, 1364, 1252, 1223, 1183, 1142, 1089; <sup>1</sup>H NMR  $\delta$  1.11 (s, 18, 2 × C(CH<sub>3</sub>)<sub>2</sub>), 1.02 (s, 9, C(CH<sub>3</sub>)<sub>3</sub>), 0.7 (m, 3, CH-2 and CH-3); *m/e* 154.1724 (calcd for C<sub>11</sub>H<sub>22</sub>, 154.1721), 210 (trace), 154 (6), 153 (4), 139 (5), 126 (9), 112 (6), 111 (27), 98 (12), 97 (25), 96 (5), 95 (6), 84 (18), 83 (77), 81 (8), 70 (15), 69 (23), 67 (8), 57 (100), 56 (8), 55 (26).

cis-1,2-Di(1-methylethyl)cyclopropane (37):  $\nu_{\max}$  3054, 2953, 2923, 2897, 2867, 1467, 1457, 1384, 1365, 1278, 1193, 1156, 1040, 1025, 988, 957, 873, 840 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  1.24 (m, 2, 2 × CH), 1.01 (m, 14), 0.49 (m, 2, CH<sub>2</sub>); *m/e* 126.1409 (Calc. for C<sub>9</sub>H<sub>18</sub>, 126.1408), 103 (65), 75 (21), 73 (100), 72 (24).

trans-1,2-Di(1-methylethyl)cyclopropane (39):  $\nu_{\max}$  3057, 2953, 2923, 2865, 1462, 1457, 1380, 1363, 1327, 1291, 1253, 1232, 1196, 1182, 1155, 1117, 1025, 993, 917, 907, 893, 865 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  1.2 (m, 2, (CH<sub>3</sub>)<sub>2</sub>CH), 0.93 (m, 12, (CH<sub>3</sub>)<sub>2</sub>CH), 0.17 (m, 4, CH-1 and -2,

CH<sub>2</sub>); *m/e* 126.1406 (Calc. for C<sub>9</sub>H<sub>18</sub>, 126.1408), 126 (24), 83 (14), 70 (58), 69 (60), 57 (34), 56 (100), 55 (95).

6-Cyclohexylspiro[5.2]octane (47):  $\nu_{\max}$  3049, 2987, 2925, 2851, 2662, 1467, 1344, 1019, 889, 878, 692 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  1.41 (m, 21), 0.59 (m, 1, CH-6), 0.19 (m, 2, CH<sub>2</sub>-7); *m/e* 178.1723 (calcd for C<sub>13</sub>H<sub>22</sub>, 178.1721), 192 (trace), 178 (87), 163 (63), 149 (24), 136 (17), 135 (61), 122 (26), 121 (27), 109 (20), 107 (55), 87 (61), 86 (100), 85 (68), 84 (26), 83 (42), 82 (23), 72 (30), 71 (91), 69 (49), 67 (20), 57 (46).

**Preparative run.** A soln containing 8.2 g (0.10 mol) of 3 and 27 g (0.10 mol) of 1 in 300 mL CH<sub>2</sub>Cl<sub>2</sub> was placed in a 1-L 3-necked round-bottomed flask equipped with a condenser, N<sub>2</sub> inlet, and mechanical stirrer and cooled with an ice bath. A 1-L aqueous soln 10% each in sodium thiosulfate and sodium bicarbonate was prepared, and approximately one-third of it was introduced into the flask. The soln was irradiated with a General Electric model RS sun lamp placed directly next to the flask. Vigorous stirring was maintained during irradiation, and ice was added as needed to keep the solvent from boiling too vigorously. When approximately one-third of the original diodomethane (1) remained, as determined by gas chromatographic monitoring (column B), the aqueous layer was decanted from the flask and replaced with about 300 mL of the scavenger soln. Another 26.8 g (0.10 mol) of 1 was added and irradiation was resumed. This procedure was repeated and irradiation was continued until all of 1 had been consumed (72 hr total). The aqueous layer was decanted, the organic layer dried over sat NaClq followed by anhyd Na<sub>2</sub>SO<sub>4</sub>, and the solvent removed by distillation through a Vigreux column. Gas chromatographic analysis showed the presence of 3 (18%) and 4 (82%). The latter was isolated by distillation.

**Quantum yields.** Determinations were made on 5-mL solns, 0.07 M each in 1 and 3, which had been degassed by bubbling of N<sub>2</sub> for 15 min prior to being sealed in Pyrex tubes and placed in a merry-go-round apparatus equipped with a Hanovia 450-W mercury arc and 0-52 and 7-37 glass filters. For actinometry 5-mL benzene solns 0.05 M in benzophenone and 0.10 M in benzyl alcohol were prepared in a similar fashion.<sup>25</sup> Diiodide solns were irradiated to 2-3% conversion and actinometry solns to 5-7% conversion. Reactions were monitored gas chromatographically for the disappearance of 1 and the appearance of 4. Changes were linear to at least 6% conversion. The results are summarized in Table 7.

**Irradiation of diodomethane (1) in the presence of lithium bromide.** A soln containing 134 mg (0.500 mmol) of 1 and 174 mg (2.00 mmol) LiBr in 10 mL acetonitrile was placed in a Pyrex vessel and irradiated for 6 hr in a Rayonet RPR-100 photochemical reactor equipped with a circular array of 16 PFT5 BL lamps. Gas chromatographic analysis revealed the continued presence of 1 (18%) and the formation of bromiodomethane (53%) and dibromomethane (19%).

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