Preparation of Some 2-Aryl-1-bromocyclopropanes by Irradiation of the Corresponding *gem*-Dibromocyclopropanes with Pyrex-filtered Light

Leiv K. Sydnes,* Ann V. Nilssen, Evy Jørgensen and Anita Pettersen

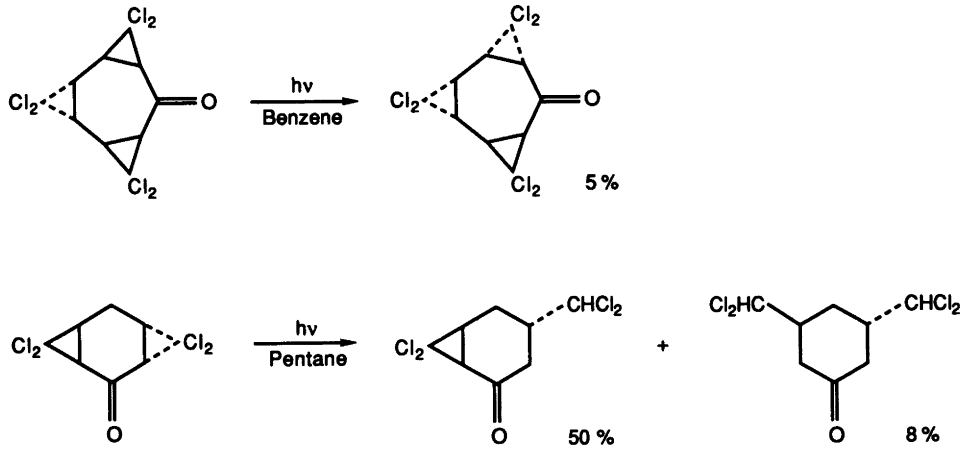
Department of Chemistry, University of Tromsø, N-9000 Tromsø, Norway

Sydnes, L. K., Nilssen, A. V., Jørgensen, E. and Pettersen, A., 1992. Preparation of Some 2-Aryl-1-bromocyclopropanes by Irradiation of the Corresponding *gem*-Dibromocyclopropanes with Pyrex-filtered Light. – Acta Chem. Scand. 46: 661–668.

The title monobromides were obtained by photolysis of ethanol solutions of the corresponding *gem*-dibromocyclopropanes. The reduction proceeds via triplet intermediates as indicated by quenching (isoprene, oxygen) and sensitization (acetone) experiments. Most monobromides are formed in excellent yield when acetone-sensitized reduction is performed. Each monobromide is obtained as an isomeric mixture with a *cis/trans* ratio almost identical with that achieved when the reduction is carried out with tributyltin hydride. The mechanism of the reduction is discussed.

Dedicated to Professor Lars Skattebøl on the occasion of his 65th birthday.

gem-Dihalocyclopropanes can undergo a number of chemical transformations upon irradiation. The course of reaction is rather sensitive to the nature of the substituents attached to the ring as well as to the conditions under which the photolysis is carried out. Thus, irradiation of a benzene solution of (1α,2β,4β,5α,7α,9α)-3,3,6,6,10,10-hexachlorotetracyclo[7.1.0.$0^{2,4}$.$0^{5,7}$]decan-8-one with light from a medium-pressure mercury lamp gave the corresponding (1α,2β,4β,5β,7β,9α) isomer as the only product (Scheme 1, upper reaction),[1] whereas *anti*-4,4,8,8-tetrachlorotricyclo[5.1.0.$0^{3,5}$]octan-2-one under the same conditions suffered ring opening, the result of which was, eventually, the formation of fair amounts of *anti*-7,7-dichloro-4-(dichloromethyl)bicyclo[4.1.0]hexan-2-one and *trans*-3,5-bis(dichloromethyl)cyclohexanone (Scheme 1, lower reaction).[2] Irradiation of solutions of 1,1-dichloro-2-phenylcyclopropane with light of λ ≥ 210 nm, on the other hand, led to extrusion of dichlorocarbene and destruction of the cyclopropane,[3,4] but when the same compound was exposed to Pyrex-filtered light (λ > 270 nm), no reaction took place.[5] Photolysis of 5,5-dichlorocyclopropa[*l*]phenanthrene at 280 nm, however, gives rise to dichlorocarbene in almost quantitative yield.[6] Carbene extrusion also occurred when 10,10-dibromotricyclo[4.3.1.$0^{1,6}$]deca-2,4-diene was irradi-



Scheme 1.

* To whom correspondence should be addressed.

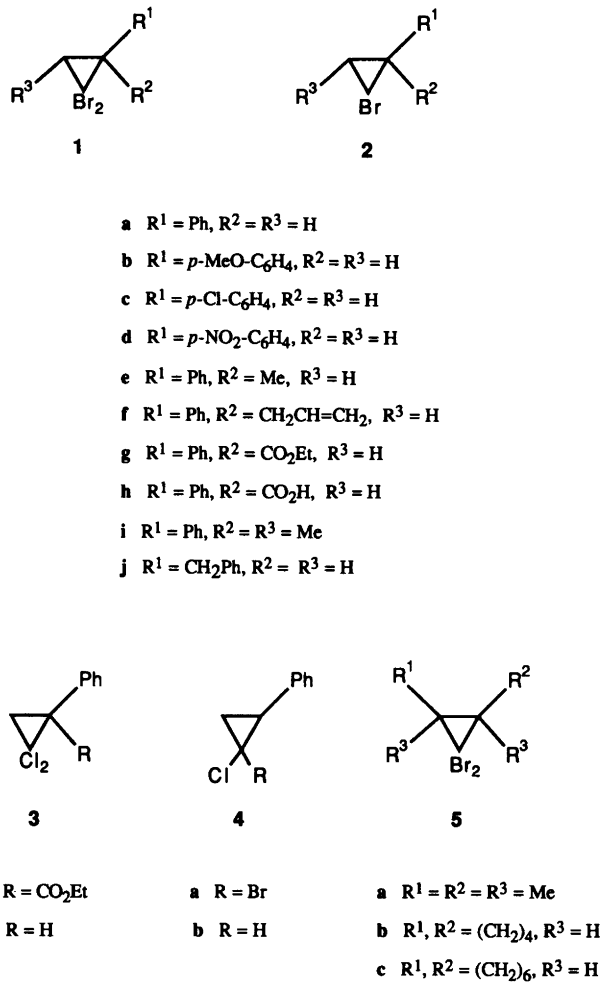
ated, even when Pyrex-filtered light from a medium-pressure mercury arc was employed.[7] This fragmentation process was, however, much less pronounced when other 1,1-dibromocyclopropane derivatives were allowed to react. In fact, when alkyl- and phenyl-substituted *gem*-dibromocyclopropanes, e.g. 7,7-dibromonorcarane and 1,1-dibromo-2-phenylcyclopropane (**1a**), in various solvents were photolyzed through quartz ($\lambda > 210$ nm) isomeric mixtures of the corresponding monobromocyclopropanes were predominantly formed; in addition ring-opened products and fully reduced cyclopropanes were obtained.[8] However, sulfides, selenides and tellurides, and no monobromides, were formed when a liquid-ammonia solution of 7,7-dibromonorcarane was irradiated in the presence of sodium benzenethiolate, sodium benzeneselenide, and sodium benzenetelluride, respectively.[9]

The results presented above indicate that the *gem*-dichlorocyclopropanes are photochemically less labile than the corresponding *gem*-dibromides. It therefore seemed reasonable to try to achieve more selective chemical transformations by irradiating *gem*-dibromocyclopropanes with Pyrex-filtered light. When such reactions had been carried out we were pleased to note that our goal was met; the results of our investigation are reported here.

Results and discussion

A number of alkyl and phenyl substituted *gem*-dibromocyclopropanes, prepared by using well-established literature procedures, were dissolved in an organic solvent and subsequently irradiated under nitrogen at room temperature with light from a medium-pressure mercury lamp. In exploratory experiments glass filters with different cut-off values were used and various solvents were tried, and these irradiations revealed that the reactivity was both solvent-dependent and wavelength-dependent. Thus, no reaction occurred in acetone and benzene, but when ethanol was used as the solvent photochemical transformations took place. Furthermore, when Pyrex-filtered light of $\lambda > 295$ nm was employed alkyl substituted dibromides, e.g. **5a–5c** (Scheme 2), were unreactive, even after days of irradiation, whereas phenyl substituted *gem*-dibromocyclopropanes, e.g. **1a–1c**, were reduced to the corresponding monobromides (**2**). Photolysis through Pyrex of ethanol solutions of selected compounds of the latter group was therefore studied more closely under different conditions.

When ethanol solutions of **1a–1j** (150 ml, approximately 0.005 M) were directly irradiated ($\lambda > 295$ nm) for 22 h most of the substrates were transformed into the corresponding monobromides (**2**) in moderate to good yields (Table 1). Each monobromide was formed as a mixture of the *cis* and *trans* isomers with a *cis*/*trans* ratio almost identical with that obtained when the same reduction was performed with tributyltin hydride (Table 1), an observation which definitely indicates that the photoreduction takes place via an intermediate cyclopropyl radical (*vide infra*).



Scheme 2.

Table 1. The composition of the reaction mixtures obtained by direct irradiation ($\lambda > 295$ nm) of ethanol solutions (150 ml) of *gem*-dibromocyclopropanes (**1**) for 22 h.[a]

Starting material	[1]/10^{-3} M	Yield (%)		*cis*-**2** : *trans*-**2**[b]
		1	**2**	
1a	5.2	56	44	63 : 37 (65 : 35)[c]
1b	5.1	56	44	63 : 37 (70 : 30)
1c	5.3	49	51	64 : 36 (58 : 42)
1d	4.1	0	0	
1e	4.9	63	37	72 : 28 (67 : 33)[d]
1f	4.3	57	43	58 : 42 (69 : 31)
1g	3.9	15	85	56 : 44 (65 : 35)[c]
1h	3.9	37	63	32 : 68 (32 : 68)
1i	4.4	100	0	
1j	5.1	96	4	64 : 36 (58 : 42)[e]

[a]According to calibrated GC analysis. [b]The ratios in parentheses are the isomeric ratios obtained by reduction of **1** using tributyltin hydride. [c]Taken from Ref. 30. [d]Taken from Ref. 38. [e]The stereochemistry is not certain; as a result the ratios may be reversed.

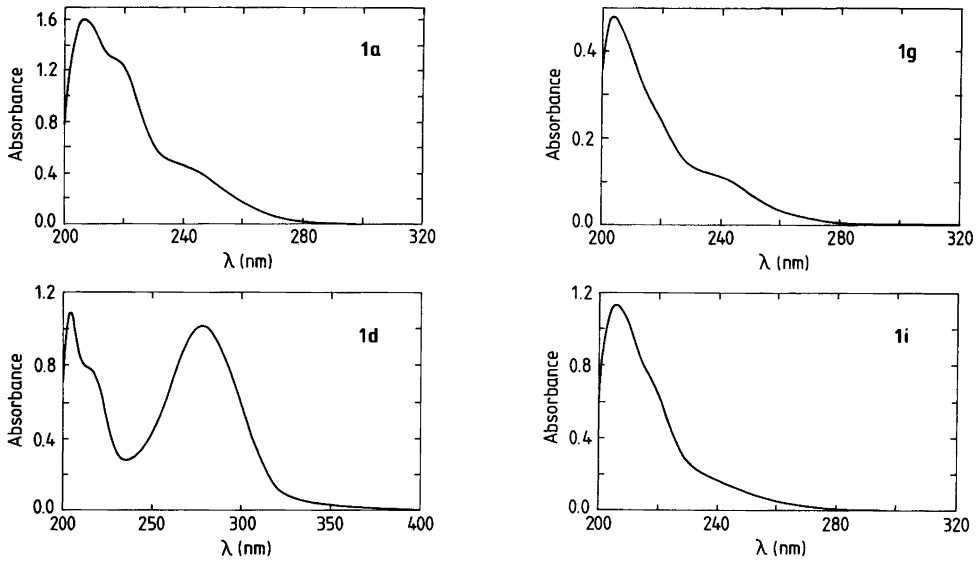


Fig. 1. The UV spectra of solutions of 1,1-dibromo-2-phenylcyclopropane (**1a**) [6.6×10^{-5} M], 1,1-dibromo-2-(*p*-nitrophenyl)cyclopropane (**1d**) [7.3×10^{-5} M], ethyl 2,2-dibromo-1-phenylcyclopropanecarboxylate (**1g**) [5.0×10^{-5} M] and *trans*-1,1-dibromo-2,3-dimethyl-2-phenylcyclopropane (**1i**) [8.2×10^{-5} M] in 96 % ethanol.

However, two of the phenyl-substituted cyclopropanes exhibited different reactivity. The most striking example is 1,1-dibromo-2-(*p*-nitrophenyl)cyclopropane (**1d**); this compound was completely converted into an exceedingly complex mixture of products, none of which is any of the corresponding isomeric monobromides. This reactivity is, conceivably, related to the characteristic and strong absorption bands above 250 nm in the UV spectrum of **1d**, as compared with the UV spectra of the other compounds investigated (Fig. 1, Table 2). The other exception is *trans*-1,1-dibromo-2,3-dimethyl-2-phenylcyclopropane (**1i**), which did not react under our experimental conditions; this is most likely related to its low extinction coefficient at and above 295 nm (Table 2).

Quenching and sensitization experiments revealed that the reaction involves the triplet excited state of the substrates. When ethyl 2,2-dibromo-1-phenylcyclopropanecarboxylate (**1g**), the most reactive of the *gem*-dibromophenylcyclopropanes investigated, was irradiated in the presence of oxygen or isoprene no reduction took place. On the other hand, irradiation of the same compound in the presence of acetone, a triplet sensitizer, increased the reaction rate tremendously. Since acetone has a triplet energy (E_T) of approximately 80 kcal mol^{-1},[10] E_T of **1g** is below 80 kcal mol^{-1}. Acetophenone (E_T = 73.7 kcal mol^{-1} [10]), however, did not act as a sensitizer, which indicates that the triplet energy of **1g** is larger than 74 kcal mol^{-1}. Based on these results acetone-sensitized photolysis of *gem*-dibromocyclopropanes **1a–1j** was carried out on a preparative scale using an immersion-well reactor and Pyrex-filtered light ($\lambda > 295$ nm) from a 125 W mercury lamp. With the exception of **1d** and **1i**, which once again exhibited strange behavior and gave very complex reaction mixtures, most substrates were cleanly and effectively converted into the corresponding monobromides (Table 3). Again each monobromide was formed as an isomeric mixture with a *cis/trans* ratio almost identical with that obtained upon tributyltin hydride reduction of **1** (Table 1).

The results presented above reveal several interesting features about the mechanism for the reduction under con-

Table 2. Characteristic features of the UV spectra of the *gem*-dibromocyclopropanes **1a–1j** dissolved in 96 % aqueous ethanol.

Compound	λ_{max}/nm (ε)	$\lambda_{shoulder}$/nm (ε)	ε at 295 nm
1a	204 (13.100)	220 (8.500), 246 (2.500)	32
1b	206 (7.800), 225 (10.200)	248 (5.100), 274 (2.550)	200
1c	203 (20.450), 225 (13.100)	244 (5.250)	56
1d	204 (13.100), 277 (12.800)	215 (9.500)	10.220
1e	209 (11.100)	240 (2.100), 262 (850)	35
1f	221 (3.800)	258 (660)	40
1g	205 (9.550)	239 (2.350)	64
1h	204 (11.500)	220 (6.100), 240 (2.500)	40
1i	205 (12.300)	219 (8.200)	10
1j	208 (9.900)	253 (550)	172

Table 3. Bromocyclopropanes obtained by irradiation (λ > 295 nm) of *gem*-dibromocyclopropanes (**1**) dissolved in a mixture of acetone and ethanol.

Starting material	[**1**]/10^{-3} M	[Acetone]/M	Yield of **2** (%)[a]	*cis*-**2** : *trans*-**2**
1a	5.0	6.0	100	67 : 33
1b	0.8	12.6	29	68 : 32
1c	4.0	11.7	57	62 : 38
1e	5.0	3.0	94	63 : 37
1f	5.0	3.1	100	55 : 45
1g	5.0	6.3	100	58 : 42
1h	5.0	4.7	100	32 : 68
1j	5.7	3.8	95	62 : 38

[a]Determined by a combination of ^{1}H NMR spectroscopy and calibrated GC analysis.

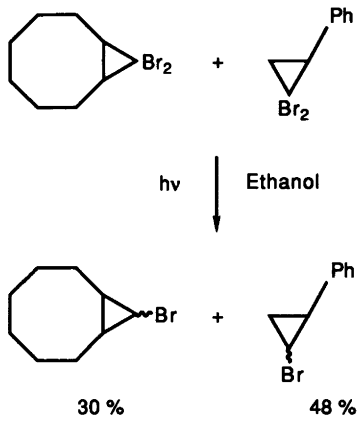
sideration. First of all, the reduction is considerably more efficient during sensitization than during direct photolysis, which indicates that the reaction mechanism depends on the reaction conditions. Furthermore, the fact that alkyl-substituted *gem*-dibromocyclopropanes do not react upon direct irradiation whereas the phenyl substituted ones do, clearly emphasizes the important role played by the phenyl group in the photophysical steps involved in the reduction process. The nature of this role remains to be examined, but Hixson[11–14] and Tomioka[15–17] have shown that aryl groups attached to a cyclopropane ring often participate in primary and secondary absorption processes and subsequently induce opening of the cyclopropane ring. None of our cyclopropanes suffered ring opening and this might indicate that possible ring cleavage reactions are prevented by energy transfer from the excited phenyl group to the *gem*-dibromo moiety because of heavy-atom spin–orbital coupling.[18–20] In principle an excited *gem*-dibromo moiety can form radical, carbocation, and carbene intermediates.[21] Formation of a carbene is out of question since such an intermediate should give an allene,[22,23] which was not observed in any reaction. A carbocation can also be ruled out because cyclopropyl cations would undergo ring opening and subsequent secondary reactions under our experimental conditions.[24] The remaining alternative, a cyclopropyl radical, is, however, likely. Such an intermediate does not undergo ring cleavage, but will abstract hydrogen from an available source such as ethanol. The isomer composition of the monobromides should therefore be comparable to that obtained when tributyltin hydride is used,[25] and this was indeed the case (Tables 1 and 3).

The fact that *gem*-dichlorocyclopropanes **3a** and **3b** remain unchanged whereas the corresponding dibromides **1a** and **1g** react upon direct and sensitized irradiation may be explained in various ways. One probable interpretation is that the *gem*-dichloro moiety is not involved in spin–orbital coupling owing to the low atomic number of chlorine.[19] Another possible explanation is that such coupling does occur, but the energy is dissipated as heat and/or radiation prior to any chemical transformations because of the strength of the C–Cl bond. In order to look into this problem a 42:58 isomeric mixture of 1-bromo-1-chloro-2-phenylcyclopropane (**4a**) (it is not known which is the predominant isomer) was excited by direct and sensitized photolysis. Analyses of the resulting reaction mixtures revealed that under both conditions **4a** reacted essentially as fast as **1a**, but one of the isomers was consumed faster than the other (Table 4). Furthermore, even though the conversion is different under the different conditions (58 and 92 %), the *cis*/*trans* ratio of the only product formed, 1-chloro-2-phenylcyclopropane (**4b**), was almost the same. This might indicate that *cis*-**4a** and *trans*-**4a** are converted into a common intermediate, the 1-chloro-2-phenylcyclopropyl radical, but that the rate of formation of this radical is different for the two isomers. This rate difference may reflect the different positions of the chlorine and bromine atoms relative to the aryl group in the two isomers, a fact which is in accordance with the observation that the spin–orbital coupling is sensitive to the orientation of the orbitals involved in the coupling process. In this connection it is relevant to note that the efficiency of the photoreduction drops significantly when the distance from the phenyl group to the *gem*-dibromo moiety increases; the yield of monobromide drops from 44 % to 4 % when the phenyl group in **1a** is replaced by a benzyl group (**1j**) (Table 1).

Table 4. The composition of solutions of 1-bromo-1-chloro-2-phenylcyclopropane (**4a**) before and after irradiation.[a]

Irradiation	Conversion (%)	Isomer ratio	
		4a-I : **4a**-II[b]	*cis*-**4b** : *trans*-**4b**
None	0	42 : 58	–
Direct, 22 h	59	48 : 52	68 : 32
Sensitized,[c] 1.5 h	92	93 : 7	62 : 38

[a]The composition as determined by GC analysis using 1,1-dichloro-2-phenylcyclopropane (**3b**) as an internal standard. [b]**4a**-I is the isomer with the shorter retention time and **4a**-II is the isomer with the longer retention time (see the Experimental for the conditions). [c]Acetone used as sensitizer.



Scheme 3.

However, the results in Table 4 can be explained in a different way. When **4a** absorbs light, excitation of the *gem*-dihalo moiety and subsequent formation of the 1-chloro-2-phenylcyclopropyl radical takes place *only with the isomer that is consumed the faster* whereas the other isomer relaxes to the ground state. A fraction of this radical is converted into **4b** through hydrogen abstraction whereas the rest abstracts a bromine atom from *both* isomers of **4a**. The net result of the latter process is consumption of the less reactive isomer of **4a**. Experiments aiming to prove or disprove that such a step is involved in the reduction of **4a** are currently under way. In this context it is encouraging to observe that when an ethanol solution of a 1:1 mixture of 9,9-dibromobicyclo[6.1.0]nonane (**5c**), which is unreactive toward light of $\lambda > 295$ nm, and **1a** is irradiated through Pyrex ($\lambda > 295$ nm), both *gem*-dibromocyclopropanes are converted into the corresponding monobromides (Scheme 3).

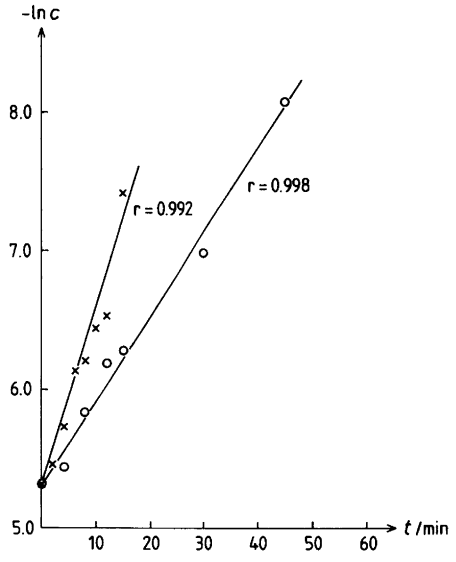


Fig. 2. The variation of the concentration of 1,1-dibromo-2-phenylcyclopropane (**1a**) (○) and ethyl 2,2-dibromo-1-phenylcyclopropanecarboxylate (**1g**) (×) with time during acetone-sensitized irradiation.

Finally it should be mentioned that although several *gem*-dibromophenylcyclopropanes are converted into the corresponding monobromides in quantitative yield the rate of disappearance differs. Thus, acetone-sensitized reduction of 1,1-dibromo-2-phenylcyclopropane (**1a**) proceeds more slowly than the reduction of ethyl 2,2-dibromo-1-phenylcyclopropanecarboxylate (**1g**) under the same conditions (Fig. 2), the rate constants being 1.0×10^{-3} s^{-1} and 2.3×10^{-3} s^{-1}, respectively. This may this reflect an electronic influence on the C–Br bond strength and on the stability of the intermediate cyclopropyl radical.

Experimental

General. UV spectra were obtained on a Shimadzu UV-160 spectrophotometer. IR spectra were recorded on a Shimadzu IR-435 spectrophotometer with the compounds as liquid films unless stated otherwise. ^{1}H NMR spectra were obtained on Jeol PMX 60 SI (60 MHz) and Jeol FX 90Q (89.55 MHz) spectrometers and ^{13}C NMR spectra on a Jeol FX 90Q (22.50 MHz) instrument. $CDCl_3$ was used as the solvent unless stated otherwise and tetramethylsilane (TMS) was added as an internal reference. Chemical shifts are reported in ppm downfield from TMS. GC analyses were performed either on a Carlo Erba HRGC 5300 Mega Series gas chromatograph, which was equipped with FID and a Chrompack CP-Sil 5CB fused silica column (26 m × 0.32 mm i.d.) and connected to an LDC/Milton Roy CI-10B integrator, or on a Varian 3700 gas chromatograph equipped with a TCD and a Carbowax 20M or an OV-17 column and attached to a Varian 9176 recorder. No corrections were made for response ratios. Mass spectra were obtained on a VG 7070H Micromass spectrometer or a VG Tribid mass spectrometer, both operated in the EI mode at 70 eV. The spectra are reported as *m/z* (% rel. int.). Photolyses were carried out with 125 W and 400 W medium-pressure mercury lamps from Applied Photophysics (model 3010 and 3040, respectively).

Reagents and solvents. Tributyltin hydride was prepared according to Kuivila.[26] Isoprene (*purum*, Fluka) and acetophenone (*puriss*, Fluka) were used without further purification as was absolute ethanol. Benzene was purified by distillation. Acetone was dried with $CaCl_2$ and subsequently distilled from P_2O_5.

Starting materials. The *gem*-dihalocyclopropanes previously reported in the literature were prepared as follows. 1,1-Dibromo-2-phenylcyclopropane (**1a**),[23] 1,1-dibromo-2-(*p*-methoxyphenyl)cyclopropane (**1b**),[27] 1,1-bibromo-2-(*p*-chlorophenyl)cyclopropane (**1c**),[27] 1,1-dibromo-2-methyl-2-phenylcyclopropane (**1e**),[28] 1,1-dibromo-2-phenyl-2-(2-propenyl)cyclopropane (**1f**),[29] ethyl 2,2-dibromo-1-phenylcyclopropanecarboxylate (**1g**),[30] *trans*-1,1-dibromo-2,3-dimethyl-2-phenylcyclopropane (**1i**),[31] ethyl 2,2-dichloro-1-

phenylcyclopropanecarboxylate (**3a**),[32] 1,1-dichloro-2-phenylcyclopropane (**3b**),[33] 1,1-dibromo-2,2,3,3-tetramethylcyclopropane (**5a**),[23] 7,7-dibromobicyclo[4.1.0]heptane (**5b**)[28] and 9,9-dibromobicyclo[6.1.0]nonane (**5c**)[23] were synthesized from haloform and the corresponding olefins using Makosza's method.[33] 1-Bromo-1-chloro-2-phenylcyclopropane (**4a**), prepared as described by Dehmlow,[34] was obtained as a 42 : 58 mixture of isomers (the predominant isomer had the longer retention time on a Chrompack CP-Sil 5CB fused silica column; the structure of the predominant isomer is unknown). 1,1-Dibromo-2-(*p*-nitrophenyl)cyclopropane (**1d**) was obtained by nitration of **1a** as described in the literature.[35] Saponification of **1g** gave 2,2-dibromo-1-phenylcyclopropanecarboxylic acid (**1h**)[36] in 85 % yield.

Characteristic features of the UV spectra of compounds **1a–1j** dissolved in 96 % aqueous ethanol are summarized in Table 2. For almost all the compounds the extinction coefficient proved to be sensitive to the concentration of the cyclopropanes. Maxima and shoulders are determined from spectra of $(4–8)\times10^{-5}$ M solutions whereas ε at 295 nm was calculated from spectra of solutions that were close to 1×10^{-3} M in **1**.

1,1-Dibromo-2-(phenylmethyl)cyclopropane (**1j**) was prepared from allylbenzene (10.0 g, 85 mmol) using Makosza's method.[33] The product was isolated in 34 % yield (8.4 g) by column chromatography (SiO_2, hexane). IR (film): 3050 (m), 3020 (m),2800 (m), 1603 (m), 1584 (w), 1495 (s), 1450 (s), 1425 (s), 1220 (m), 1040 (s), 730 (s), 695 (s), 675 (s) cm^{-1}; ^1H NMR (89.55 MHz): δ 1.2–1.5 (1 H, m), 1.7–2.1 (2 H, m), 2.6–3.2 (2 H, m), 7.3 (5 H, m); ^{13}C NMR: δ 28.5, 28.9, 31.9, 38.2, 126.4, 128.3, 128.6, 139.2; MS: 290 (1, M^+), 211 (5), 209 (5), 130 (6), 129 (21), 128 (13), 127 (5), 115 (7), 105 (17), 104 (100), 103 (14). Mol. wt.: calc. for $C_{10}H_{10}Br_2$ 291.91083; found 291.90152.

Direct irradiation of **1**: *general procedure.* A solution of **1** (see Table 1 for concentrations) in ethanol (150 ml), kept under nitrogen in an immersion-well reactor, was irradiated with light from a 125 W medium-pressure mercury lamp. The lamp was kept in a water-cooled Pyrex well (cut-off 295 nm), which was immersed in the solution. The irradiation was stopped after 22 h, the solvent was removed, and the reaction mixture was analyzed by GC. The results are shown in Table 1.

gem-Dihalocyclopropanes **3** and **5** were photolyzed under the same conditions, but no products were formed.

Quenching and sensitization experiments. These photolyses were conducted in the same way as the direct irradiations. In the quenching experiments ethyl 2,2-dibromo-1-phenylcyclopropanecarboxylate (**1g**) (3.9×10^{-3} M) was used as the substrate, oxygen (bubbled through prior to and during the irradiation) and isoprene (3.9×10^{-3} M) were used as quenchers, and the time of irradiation was 22 h. No reaction occurred. In the sensitization experiments **1a–1j** were used as substrates, acetone (see Table 3 for concentrations), acetophenone (0.06 M), and benzene (0.42 M) were employed as sensitizers, and the time of irradiation was 1.5 h. The results from the acetone-sensitized experiments are compiled in Table 3.

Irradiation of 1-bromo-1-chloro-2-phenylcyclopropane (**4a**). Both direct (22 h) and sensitized (1.5 h) photolyses were carried out according to the general procedures with the exception that Pyrex tubes (cut-off 295 nm) containing 8 ml of solution were used. The solutions were thoroughly degassed with nitrogen and the tubes were thoroughly closed before the irradiation started. 1,1-Dichloro-2-phenylcyclopropane (**3b**) was used as an internal standard during the photolysis as well as during the analysis of the photolysates, which was carried out by GC. The results are compiled in Table 4.

Direct irradiation of a mixture of 1,1-dibromo-2-phenylcyclopropane (**1a**) *and 9,9-dibromobicyclo[6.1.0]nonane* (**5c**). An ethanol solution (30 ml) containing **1a** (0.0425 g, 5.1×10^{-3} M) and **5c** (0.0425 g, 5.0×10^{-3} M) was irradiated directly for 22 h following the general procedure. The reaction mixture consisted of **1b** (48 %, *cis:trans* ratio = 69:31) and 9-bromobicyclo[6.1.0]nonane (30 %, *cis:trans* ratio = 71:29) on the basis of GC analaysis.

Determination of reaction rates. Experiments were carried out with 2,2-dibromo-1-phenylcyclopropane (**1a**) and ethyl 2,2-dibromo-1-phenylcyclopropanecarboxylate (**1g**) in order to determine reduction rates upon acetone-sensitized irradiation. Both experiments were performed as follows. The *gem*-dibromocyclopropane was dissolved to a concentration of 5.0×10^{-3} M in an acetone/ethanol mixture (6 M solution of acetone in absolute ethanol). Samples of this solution was added to nine Pyrex test-tubes (cut-off 295 nm, 8 ml in each tube), which were degassed with nitrogen and subsequently fastened side by side at the same level along the wall of a water-cooled glass well containing a 125 W medium-pressure mercury lamp. Samples were removed at intervals and the amount of unchanged *gem*-dibromocyclopropane was determined by GC analysis. The results are plotted in Fig. 2.

Reduction of **1** *with tributyltin hydride (BTH).* The reaction was carried out as described in the literature.[29] Isomeric mixtures of the corresponding monobromides were generally formed in good yields. The isomeric composition was determined from GC analysis and proton NMR spectra. The structure elucidation was based on authentic samples and their spectral properties, which have been reported in the literature for **2a**,[30,37] **2e**,[38] **2g**[30] and *trans*-**2h**,[36] and by comparing the NMR data with those of the corresponding chlorides.[39]

1-Bromo-2-(*p*-methoxyphenyl)cyclopropane (**2b**) was obtained as a 42:58 mixture (GC) of isomers in 80 % yield when **1b** (2.4 g, 7.8 mmol) was treated with BTH; b.p.

79–81°C/0.1 mmHg. IR (CCl_4): 3050 (w), 3020 (m), 1605 (s), 1580 (w), 1505 (s), 1460 (s), 1435 (s), 1360 (w), 1300 (s), 1240 (s), 1170 (s), 1105 (m), 1035 (s), 1000 (w), 670 (m), 595 (w) cm^{-1}. ^1H NMR (60 MHz): δ 1.1–2.3 (3 H, m), 2.85–3.10 and 3.10–3.35 (1 H, 2 m in a ratio of 2:3, respectively), 4.75 (1 H, br s), 6.6–7.15 (4 H, m). Anal. $C_{10}H_{11}BrO$: C, H.

1-Bromo-2-(*p*-chlorophenyl)cyclopropane (**2c**) was obtained from **1c** (2.07 g, 7.1 mmol) as a mixture of isomers in 84 % yield, b.p. 80–82°C/0.5 mmHg. IR: 3040 (w), 3005 (w), 2910 (m), 2820 (w), 1580 (w), 1493 (s), 1435 (m), 1255 (s), 1230 (m), 1090 (s), 1012 (s), 815 (s), 755 (w) cm^{-1}; ^1H NMR (89.55 MHz): δ 1.05–1.75 (2 H, m), 2.1–2.50 (1 H, m), 2.82–3.08 and 3.15–3.45 (1 H, m and dt, respectively, in a ratio of 42:58, *J* 4.5 and 7.6 Hz in the dt), 6.88–7.40 (4 H, m).

1-Bromo-2-phenyl-2-(2-propenyl)cyclopropane (**2f**) was obtained from **1f** (6.3 g, 20 mmol) as a 69:31 mixture of isomers in 43 % yield, b.p. 82–86°C/0.1 mmHg. The isomers were separated by column chromatography (SiO_2, pentane). The *major* isomer (eluted first; the *trans* isomer on the basis of comparison with the NMR spectra of both isomers of **2a**, **2b**, and **2c**): IR: 3055 (m), 3010 (m), 2960 (m), 2900 (w), 1640 (m), 1600 (w), 1580 (w), 1493 (s), 1445 (s), 1430 (s), 1235 (s), 1035 (m), 990 (m), 925 (s), 750 (s), 695 (s), 605 (m) cm^{-1}; ^1H NMR (89.55 MHz): δ 1.05 (1 H, dd, *J* 4.7 and 6.4 Hz), 1.47–1.64 (1 H, m), 2.37–2.69 (2 H, m), 3.21 (1 H, dd, *J* 4.7 and 7.9 Hz), 4.81–5.03 (2 H, m), 5.54–5.92 (1 H, m), 7.2–7.3 (5 H, m); ^{13}C NMR: δ 21.6 (CH_2), 29.5 (CH), 30.3 (C), 41.8 (CH_2), 116.8 (CH_2), 126.6 (CH), 128.2 (CH), 128.4 (CH), 134.9 (CH), 143.2 (C); MS: 158 (10), 157 (83), 155 (10), 142 (17), 141 (20), 130 (9), 129 (60), 128 (31), 127 (11), 117 (5), 116 (32), 115 (100), 91 (74), 77 (23). The *minor* isomer: IR: 3055 (s), 3010 (s), 2960 (m), 2900 (s), 1640 (m), 1600 (m), 1580 (w), 1493 (s), 1445 (s), 1430 (s, sh), 1275 (s), 1190 (m), 1040 (s), 1025 (s), 1000 (s), 910 (s), 760 (s), 695 (s), 645 (m), 605 (m) cm^{-1}; ^1H NMR (89.55 MHz): δ 1.26–1.52 (2 H, m), 1.95–2.19 (1 H, m), 3.14 (1 H, dd, *J* 4.7 and 7.3 Hz), 4.81–5.02 (2 H, m), 5.49–5.87 (1 H, m), 7.2–7.5 (5 H, m); ^{13}C NMR: δ 20.5 (CH_2), 26.7 (CH), 31.9 (C), 44.3 (CH_2), 117.4 (CH_2), 127.0 (CH), 128.0 (CH), 130.4 (CH), 134.2 (CH), 140.6 (C); MS: Essentially identical with that of the major isomer. Anal. $C_{12}H_{13}Br$ (isomer mixture): C, H.

1-Bromo-2-(phenylmethyl)cyclopropane (**2j**) was obtained in quantitative yield as a 42:58 isomeric mxture when **1j** (2.0 g, 8.6 mmol) was treated with BTH (2.76 g, 9.5 mmol) at room temperature; b.p. 103–108°C/3.0 mmHg. IR: 3050 (w), 3020 (w), 2950 (m), 2900 (m), 2850 (m), 1600 (w), 1490 (m), 1255 (s), 1025 (s), 725 (s), 695 (s) cm^{-1}; ^1H NMR (89.55 MHz): δ 0.6–1.7 (3 H, m), 2.5–3.2 (3 H, m), 7.1–7.4 (5 H, m); MS (essentially identical for the two isomers): 212 (4, M^+), 210 (4, M^+), 171 (2), 169 (2), 132 (35), 131 (100), 130 (17), 129 (27), 128 (23), 127 (9), 116 (24), 115 (28), 105 (18), 104 (87), 103 (30), 92 (22), 91 (92), 78 (26), 77 (23). Mol. wt.: calc. for $C_{10}H_{11}Br$ 212.01778; found 212.02006 (essentially identical for the two isomers).

Acknowledgements. Financial support from the Norwegian Research Council for Science and the Humanities (NAVF) is gratefully acknowledged.

References

1. Hashem, M. A., Hülskämper, L. and Weyerstahl, P. *Chem. Ber. 118* (1985) 840.
2. Weyerstahl, P. and Hashem, M. A. *Chem. Ber. 120* (1987) 449.
3. Jones, M., Jr., Sachs, W. H., Kulczycki, A., Jr. and Waller, F. J. *J. Am. Chem. Soc. 88* (1966) 3167.
4. Griffin, G. W. *Angew. Chem. 83* (1971) 604.
5. Cristol, S. J. and Micheli, R. P. *J. Org. Chem. 40* (1975) 667.
6. Chateauneuf, J. E., Johnson, R. P. and Kirchhoff, M. M. *J. Am. Chem. Soc. 112* (1990) 3217.
7. Le, N. A., Jones, M., Jr., Bickelhaupt, F. and de Wolf, W. H. *J. Am. Chem. Soc. 111* (1989) 8491.
8. Shimizu, N. and Nishida, S. *Chem. Lett.* (1977) 839.
9. Rossi, R. A. and Santiago, A. N. *J. Chem. Res. (S)* (1988) 172.
10. Murov, S. L. *Handbook of Photochemistry,* Marcel Dekker, New York 1973, p. 3.
11. Hixson, S. S. *J. Am. Chem. Soc. 93* (1971) 5293.
12. Hixson, S. S., Franke, L. A., Gere, J. A. and Xing, Y. *J. Am. Chem. Soc. 110* (1988) 3601.
13. Hixson, S. S. and Franke, L. A. *J. Org. Chem. 53* (1988) 2706.
14. Hixson, S. S. and Galluci, C. R. *J. Org. Chem. 53* (1988) 2711.
15. Tomioka, H. and Inoue, O. *Bull. Chem. Soc. Jpn. 61* (1988) 1404.
16. Tomioka, H. and Inoue, O. *Bull. Chem. Soc. Jpn. 61* (1988) 3725.
17. Tomioka, H. and Miyagawa, H. *J. Chem. Soc., Chem. Commun.* (1988) 1183.
18. Robinson, G. W. *J. Chem. Phys. 46* (1967) 572.
19. Kavarnos, G., Cole, T., Scribe, P., Dalton, J. C. and Turro, N. J. *J. Am. Chem. Soc. 93* (1971) 1032.
20. Turro, N. J. *Modern Molecular Photochemistry,* Benjamin/Cummings, Menlo Park 1978.
21. Kropp, P. J. *Acc. Chem. Res. 17* (1984) 131.
22. Doering, W. von E. and LaFlamme, P. M. *Tetrahedron 2* (1958) 75.
23. Skattebøl, L. *Acta Chem. Scand. 17* (1963) 1683.
24. Duffey, D. C., Gueldner, R. C., Layton, B. R. and Minyard, J. P., Jr. *J. Org. Chem. 42* (1977) 1082.
25. Seyferth, D., Yamazaki, H. and Alleston, D. L. *J. Org. Chem. 28* (1963) 703.
26. Kuivila, H. G. and Beumel, O. F., Jr. *J. Am. Chem. Soc. 83* (1961) 1246.
27. Kostikov, R. R., Molchanov, A. P., Golovanova, G. V. and Zenkevich, I. G. *Zh. Org. Khim. 13* (1977) 1846.
28. Makosza, M. and Fedorynski, M. *Synth. Commun. 3* (1973) 305.
29. Kocharian, A. K., Nilssen, A. V., Pettersen, A., Rømming, C. and Sydnes, L. K. *Acta Chem. Scand., Ser. A 42* (1988) 463.
30. Sydnes, L. K. *Acta Chem. Scand., Ser. B 32* (1978) 47.
31. Kostikov, R. R. and Molchanov, A. P. *Zh. Org. Khim. 14* (1978) 355.
32. Sydnes, L. K. *Acta Chem. Scand., Ser. B 31* (1977) 823.
33. Makosza, M. and Wawrzyniewics, M. *Tetrahedron Lett.* (1969) 4659.

34. Dehmlow, E. V., Lissel, M. and Heider, J. *Tetrahedron 33* (1977) 363.
35. Novokreshchennykh, V. D., Mochalov, S. S. and Shabarov, Y. S. *Zh. Org. Khim. 15* (1979) 430.
36. Sydnes, L. K. and Skare, S. *Can. J. Chem. 62* (1984) 2073.
37. Sydnes, L. K. and Skattebøl, L. *Acta Chem. Scand., Ser. B 32* (1978) 632.
38. Yakushkina, N. I., Zakharova, G. A., Surmina, L. S. and Bolesov, I. G. *J. Org. Chem. USSR 19* (1980) 1553.
39. Kusuyama, Y., Kagosaku, T. and Hasegawa, T. *Bull. Chem. Soc. Jpn. 63* (1990) 2836.

Received November 14, 1991.