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PHOTOCHEMICAL REDUCTION OF gem-DIBROMOCYCLOPROPANES

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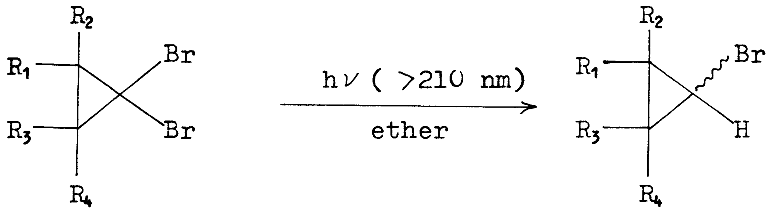
Photo-irradiation of nine gem-dibromocyclopropanes in ether solution leads to the corresponding monobromocyclopropanes in moderate to good yields. The stereochemical observation indicates that the partial reduction proceeds <u>via</u> an α-bromocyclopropyl radical.

Thermally gem-dihalocyclopropanes are known to undergo the skeltal rearrangement to 1,2-dihaloprop-2-ene derivatives.[1] In contrast, 1,1-dichloro-2-phenylcyclopropane produces a dichlorocarbene on irradiation of uv light.[2] Little is known, however, on the photochemical behavior of other gem-dihalocyclopropanes. The photochemistry of organic halides has been the subject of current interests,[3] and we wish to report here the result that the gem-dibromocyclopropanes **1** were easily converted to the corresponding monobromocyclopropanes **2** when irradiated in ether solution, indicating that this photochemical partial reduction may provide a useful alternative of transforming gem-dibromocyclopropanes to bromocyclopropanes to the chemical methods with R_3SnH,[4] $LiAlH_4$,[5] $NaBH_4$,[6] and methylmagnesium bromide.[7]

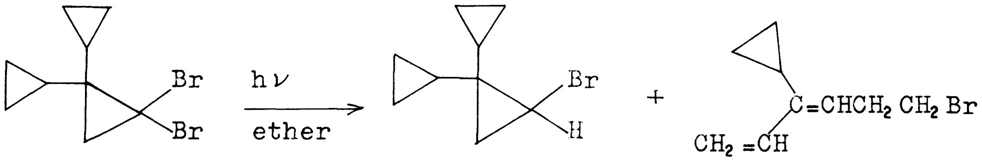


1 **2**

a; $R_1 = R_2 = R_3 = R_4 = CH_3$
b; $R_1 = R_2 = R_3 = CH_3$, $R_4 = H$
c; $R_1 = R_2 =$ cyclo-C_3H_5, $R_3 = R_4 = H$
d; $R_1 =$ cyclo-C_3H_5, $R_2 = CH_3$, $R_3 = R_4 = H$
e; $R_1 = R_3 = -(CH_2)_4-$, $R_2 = R_4 = H$
f; $R_1 = R_3 = -(CH_2)_6-$, $R_2 = R_4 = H$
g; $R_1 = Ph$, $R_2 = R_3 = R_4 = H$
h; $R_1 = t\text{-}C_4H_9$, $R_2 = R_3 = R_4 = H$
i; $R_1 = n\text{-}C_6H_{13}$, $R_2 = R_3 = R_4 = H$

Thus an ethereal solution (ca. 0.02 M, 200 ml) of 1,1-dibromo-2,2,3,3-tetramethylcyclopropane 1a was irradiated (> 210 nm) in a quartz reaction vessel with a low-pressure mercury lamp at ca. 5° for 3 hr under nitrogen atmosphere. The mixture was concentrated, and the residue was passed through a short alumina column eluting with a small amount of pentane to remove a colored material and distilled to give 1-bromo-2,2,3,3-tetramethylcyclopropane 2a in 75% yield along with a small amount of the unchanged 1a (15%).

In a similar procedure various dibromocyclopropanes 1 were irradiated in ether solution for 3 hr.[8] In all cases, partial reduction occurred smoothly giving the monobromides 2, as shown in Table. The monobromide 2 also absorbs some light under the present conditions, but owing to a low extinction coefficient relative to 1 in a region of the wavelength above 210 nm the dibromide can be selectively reduced to the monobromide.[9] Two cases should be commented: In the case of 1g, a small amount of the completely reduced product, phenylcyclopropane, was also isolated (11%) besides 2g (80%).[10] A ring-cleaved product 3 and 2c were isolated from the photolysate of 1c. However, the former was found to be a rearranged product derived from 2c during the isolation process.[11]



1c 2c, 69% 3 (E/Z=1.5), 21%

The photoreduction occurred also in other solvents such as pentane, methylene chloride or methanol, however, the best yield was obtained in ether solution.

Apparently photoreduction seems to be a common behavior of the gem-dibromocyclopropanes even in the case where an aromatic chromophore is present. This is interesting because the irradiation of such a compound would involve the excitation of the aromatic chromophore leading to fragmentation of the cyclopropane ring.[2,12] The remarkable difference in the photochemical behavior between 1,1-dichloro-2-phenyl- and 1,1-dibromo-2-phenylcyclopropane presumably arises from the weak C-Br bond relative to the C-Cl bond.[13] The fact that the photoexcitation of 1 yielded 2 without accompanying the skeltal rearrangement is in contrast with the thermal behavior of 1,[1,11] and the present photoreduction may involve the excitation of the C-Br bond resulting in the homolytic cleavage to give an α-bromocyclopropyl radical which undergoes hydrogen abstraction from the solvent yielding the observed product. The stereochemical observation that the photoreduction of 1 gave predominantly a thermodynamically less favorable isomer seems to support this mechanism. Although it is not clear whether photoexcitation of the dibromide 1 results in the selective cleavage of the less hindered C-Br bond, the present stereochemistry may be rationalized in terms of the steric requirement that the hydrogen

Table 1. Photochemical Reduction of gem-Dibromocyclopropanes[1]

substrate	% conversion	% yield of **2**[2]	rel. rate[3]	isomer ratio (E/Z)[4,5]
1a	85	88	1.1	
1b	75	88	1.1	4.65 (4.0)
1c	43	69[6]		
1d	36	74	1.3	1.20[7]
1e	32	75	(1.0)	2.87 (2.5)
1e	12[8,9]	67[8,9]		4.35[8,9]
1e	22[9,10]	44[9,10]		3.27[9,10]
1e	31[9,11]	50[9,11]		2.75[9,11]
1e	85[9,12]	18[9,12]		3.63[9,12]
1e	58[9,13]	22[9,13]		4.89[9,13]
1f	79	76	1.1	all endo (all endo)
1g	52	80[14]	2.4	3.16
1h	85	80	1.1	4.3
1i	70	79	0.6	2.04
1i	28[8,9]	45[8,9]		2.72[8,9]

1. Irradiation was carried out in ether solution (0.02—0.04 M) with a 100W low-pressure mercury lamp at ca. 5° for 3 hr under nitrogen atmosphere except otherwise noted. 2. Isolated yield based on the converted dibromide. 3. Relative rate of disappearance of **1** determined by competition experiments. 4. Determined by glc analysis (4 mm x 2 M glass column packed with 12% Apiezon grease L on Celite 545). 5. Figures in parentheses are the ratio obtained in the reduction of **1** with tributyltin hydride; D. Seyferth, H. Yamazaki, and D. L. Allestone, J. Org. Chem., 28, 703 (1963). 6. The second product **3** (21%) was accompanied. 7. The stereochemical assignments are tentative. 8. At -70°. 9. A 500W medium-pressure mercury lamp was used. 10. In n-pentane. 11. In methylene chloride. 12. In methanol. 13. In acetone. 14. Phenylcyclopropane was also isolated in 11% yield.

abstraction of the equilibrated α-bromocyclopropyl radicals occurs predominantly at the less hindered site. Similar stereochemical results have been observed also in the chemical reductions of **1** with trialkyltin hydride and other metal hydrides where a free radical mechanism has been postulated.[4—7] The small substituent effect on the photochemical reactivity of **1**, which is parallel to the fact that all the dibromides **1** except **1g** showed a quite similar uv absorption pattern,[9] seems to indicate that the rates of the processes involving in the present photoreduction, excitation, dissociation of the C-Br bond, recombination, and hydrogen abstraction, are not affected significantly by the change of substituent groups at the C-2 and C-3 carbons. The enhanced reactivity of the aromatic bromides **1g** and **2g**[10] as compared to the aliphatic bromides may suggest the participation of the excitation of the aromatic chromophore in the present photoreduction, particularly in the case of the monobromide **2g**.

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8) Conversion was not improved by the longer irradiation in some cases owing to the formation of a polymeric material on the surface of the lamp.

9) Except **1g**, the dibromides showed a single uv absorption (λ_{max} in hexane ranging from 199 nm ($\varepsilon = 2500$) for **1i** to 207 nm ($\varepsilon = 4130$) for **1a**) with end absorptions up to about 280 nm. The extinction coefficients at 254 nm were in the region 340 (for **1c**)—130 (for **1i**), whereas those of the monobromides **2** were less than 15 at 254 nm: The partial reduction of **1e** (0.005 *M*) completed in 3 hr, whereas only 9% of the monobromide **2e** was reduced under an identical condition.

10) Irradiation of an ethereal solution (0.005 *M*) of **2g** (*cis*/*trans* = 1.8) for 3 hr gave phenylcyclopropane in 40% yield besides the uncharged **2g** (*cis*/*trans* = 3.4, 45%).

11) Similar thermal rearrangements were also observed in **1c** and **1d**: They underwent a facile skeltal rearrangement affording 2,6-dibromo-3-cyclopropylhexa-1,3-diene and 2,6-dibromo-3-methylhexa-1,3-diene, respectively when heated above 130°.

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