The Photochemical Debromination of Bromocyclopropane in the Presence of Amine

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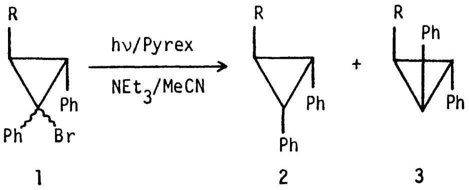
Synopsis. The irradiation of bromoarylcyclopropanes (**1**) in the presence of tertiary amine resulted in the formation of the debrominated cyclopropanes as a mixture of geometrical isomers, whose ratios were essentially similar regardless of the stereochemistry of the bromide. The reactions were not, however, observed in the absence of amine. The results are interpreted as indicating that the reactions proceed through an initial single-electron transfer to the excited **1**, followed by debromination and hydrogen-abstraction.

Since the early 1980s, the scope of cyclopropane photochemistry has been greatly broadened by electron-transfer-sensitized reactions.[1] However, in most of these reactions cyclopropanes have been used as electron donors, which transfer single electrons to the excited-state acceptors (e.g., cyanoaromatics) to generate cyclopropane cation radicals. Recently we found, however, that some cyclopropanes can act as electron acceptors as well in the excited state when irradiated with an appropriate electron donor (e.g., amines). Thus, the irradiation of an arylcyclopropane bearing electron-withdrawing group in the presence of tertiary amine resulted in the regioselective addition of the amine, which can be explained as proceeding through a single-electron transfer mechanism.[2] As an extension of such works, we studied the photochemistry of halocyclopropanes in the presence of amine and found that bromocyclopropanes underwent efficient photodebromination,[3] most probably via single-electron transfer.

The irradiation of *r*-1-bromo-1,*t*-2-diphenylcyclopropane (**1a**) in acetonitrile or cyclohexane with a 300 W Hg lamp through a Pyrex filter did not result in the formation of any appreciable products, more than 95% of the starting compound being recovered unchanged even after a 16 h irradiation. In marked contrast, a similar irradiation of **1a** in the presence of a 5 molar excess of triethylamine led to the rapid disappearance of **1a** and the concurrent formation of the debrominated cyclopropanes (**2** and **3**) as a 6.1 : 1 mixture of geometrical isomers, predominantly **2**. Similarly, the irradiation of *r*-1-bromo-1,*c*-2-diphenylcyclopropane with the amine also afforded the debrominated cyclopropanes (**2** and **3**) in an isomer ratio almost identical with that observed in the irradiation of the trans isomer. 1-Bromo-3-methyl-1,2-diphenylcyclopropanes (**1b**) also underwent smooth photo-debromination in the presence of amine, although the yield and stereoselectivity of the reduction decreased considerably.[4] Control experiments showed that the reduction did not occur in the absence of light and that the product cyclopropanes did not isomerize under these conditions.



1 2 3

a: R=H

b: R=Me

In order to get insight into the mechanism of the present photoreduction, we carried out some additional experiments. First, the reactions were found to be somewhat sensitive to the solvent employed, as is summarized in Table 2. Thus, the photodebromination proceeded quite smoothly in acetonitrile, while the reduction was relatively inefficient in cyclohexane. This is, however, in marked contrast with the situation observed[2] in the photochemical addition of amines to electrophilic cyclopropanes, where the reactions did not proceed in any of those solvents listed in Table 2 except acetonitrile. Second, the bromocyclopropane fluorescence was quenched by the amine, indicating that the excited singlet state is involved in the present photoreduction.

The above findings can be better explained in terms of a mechanism involving electron transfer, as is

Table 1. Photodebromination of Bromocyclopropane (**1**) in the Presence of Amine[a]

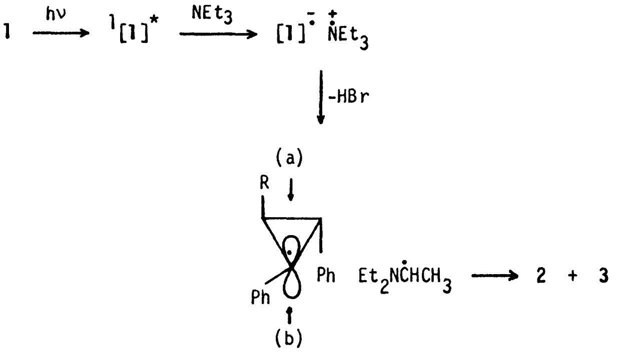
1	R	1-Br/ 2-Ph	Conv/%[b]	Yield/%[b]		2/3
				2	3	
a	H	trans	94.6	46.5	7.6	6.1
	H	cis	85.3	53.1	7.7	6.9
b	Me	trans	100	12.4	5.2	2.4
	Me	cis	97.5	15.2	6.5	2.3

a) Irradiations were carried out on 10-mM degassed solution of **1** in MeCN in the presence of a 5-molar excess of NEt_3 for 2 h through a Pyrex filter with a 300 W high pressure Hg lamp. b) Determined by GC.

Table 2. Effect of Solvent on the Photodebromination of **1a**[a]

Solvent	Conv/%[b]	Yield/%[b]	
		2a	**3a**
MeCN	67.4	44.1	7.8
EtOH	41.9	40.8	14.0
CH_2Cl_2	42.0	36.9	9.7
THF	66.8	53.1	14.1
AcOEt	46.1	51.9	11.5
PhH	46.4	44.6	10.5
c-C_6H_{12}	23.0	32.0	13.5

a) See footnote a) in Table 1. The irradiation time was 1 h. b) See footnote b) in Table 1.



Scheme 1.

summarized in Scheme 1, rather than in terms of simple free-radical mechanism. Thus, **1** is first excited to its singlet state, which accepts an electron from the ground state amine to generate a cyclopropane-anion radical and an amine-cation radical. The cyclopropane anion radical, which had no bromine substituent, underwent efficient protonation by the amine cation radical, resulting in the ring cleavage.[2] The absence of any appreciable formation of such ring-opened products in the present photoreaction implies that the bromocyclopropane anion radical releases bromide, leaving the cyclopropyl radical, before it undergoes protonation. The solvent effects are worthy of comment in this connection. The effects of solvents in the electron-transfer reactions are usually explained in terms of the dissociation of the primary geminate-ion-radical pair, leading to a separated radical ion.[1a] Thus, a high polarity of the medium is usually required to solvate the separated radical ions. The moderate effect of solvents on the present photoreduction is in marked contrast with the fatal effects of solvent on the photoaddition[2] of amine to cyclopropane: this would indicate that the elimination of bromide ion is so efficient as to occur within the primary geminate pair. The abstraction of hydrogen from the resulting α-aminoalkyl radical by the cyclopropyl radical then affords the final products.

The fact that essentially similar isomer ratios are observed, regardless of the stereochemistry of the starting bromide, indicates that the geometry of the radical is planar rather than pyramidal. Apparently the attack of the hydrogen atom from a side (a) opposite to the 2-phenyl group leading to **2** is favored over that from the other side (b) giving **3**, since there is interference between the attacking hydrogen and the 2-phenyl group in the latter case. Obviously, the preference for the formation of **2** will be decreased by the introduction of the 3-methyl group since side (a)-attack is also subjected to steric hindrance by the methyl group, as was observed.

Experimental

Instrumentation. The UV and fluorescence spectra were recorded on a Hitachi 220-S spectrophotometer and a Hitachi MPF-2A spectrofluorometer respectively. The IR spectra were determined with a JASCO A-100 spectrometer, while the ^1H NMR spectra were measured on a JEOL JNM-MH-100 NMR spectrometer in CCl_4 with Me_4Si, as the internal reference. The mass spectra were recorded on a Shimadzu QP-1000 mass spectrometer (70 eV). The GC analyses were performed on a Yanagimoto instrument, Model G-80. The GC column A was prepared from 10% SE-30 on Diasolid L (5.0 mm×2.0 m); column B consisted of 5% PEG-20M on Diasolid L (5.0 mm×1.0 m).

Materials. The bromocyclopropanes (**1a** and **b**) were prepared by refluxing phenylbromodiazirine with alkenes (styrene and *trans*-β-methylstyrene respectively) in benzene according to the method of Padwa.[5] Geometrical isomers were separated by column chromatography (silica gel) eluted with ether. The data are show below.

trans-**1a**: Yield, 37%; yellow oil; ^1H NMR δ=7.5—6.6 (10H, m), 2.78 (1H, dd), 1.90 (1H, dd), 1.23 (1H, dd).

cis-**1a**: Yield, 42%; yellow oil; ^1H NMR δ=7.6—6.9 (10H, m), 2.42 (1H, dd), 1.93 (1H, dd), 1.83 (1H, dd).

trans-**1b**: Yield, 35%; yellowish semisolid; ^1H NMR δ=7.1—6.9 (10H, m), 2.46 (1H, bd), 1.69 (1H, d), 1.66 (3H, bs).

cis-**1b**: Yield, 27%; yellow oil; ^1H NMR δ=7.5—7.0 (10H, m), 2.11 (1H, d), 2.08 (1H, dq), 1.07 (3H, d).

The debrominated cyclopropanes **2a**[6] and **2b**[7] were prepared according to the reported procedures.

Irradiation for Product Identification. In a typical run, a solution of **1** (1 mmol) and triethylamine (5 mmol) in MeCN (50 cm^3) was placed in a quartz tube and irradiated using a high pressure, 300 W, Hg lamp with a water-cooled quartz jacket. The progress of the reaction was monitored by means of TLC. After irradiation for 5 h, the irradiation mixtures were concentrated on a rotary evaporator, chromatographed on preparative TLC (silica gel), and eluted with chloroform–hexane. The fast-moving fraction was found to contain the debrominated cyclopropanes as a mixture of geometrical isomers.

Irradiation for Analysis Purposes. All the irradiations outlined in the tables were carried out on 10 mM (1 M= 1 mol dm^{-3}) solutions of **1** in a quartz tube with a capacity of 5 cm^3 at 15 °C. The yields were conveniently determined by standard GC techniques, and the identity of the products was confirmed by GC using both A and B columns as well as GC-MS comparison with authentic samples prepared as above.

References

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3) The direct irradiation of *gem*-dibromocyclopropanes in ether has been reported to yield the corresponding monobromocyclopropanes. The photoreduction has, however, been explained in terms of the initial homolytic cleavage of the C-Br bond in the excited cyclopropanes to give the α-bromocyclopropyl radical, followed by hydrogen abstraction; N. Shimidzu and S. Nishida, *Chem. Lett.*, **1979**, 839.

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