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PHOTO-DEHALOGANATION OF VICINAL DIHALIDE TO OLEFIN

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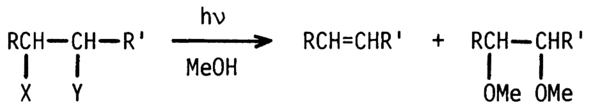
Irradiation of vicinal dihalides in the presence of methanol or triethylamine resulted in an efficient dehalogenation to regenerate olefins.

There has been an increasing interest paid recently to photolysis of organic halides,1) since it becomes clear that cationic, as well as free radical, intermediates play an important role in the solution-phase photochemistry of these halides. During an effort to generate α-ketocarbonium ion in the photolysis of α-haloketone,2-5) we found that α,β-dihalocarbonyl compounds underwent an efficient dehalogenation upon uv irradiation in the presence of nucleophiles, e.g., methanol or amine, to regenerate α,β-unsaturated carbonyl compounds. The reaction was found to be applicable to other simpler vicinal dibromide. Since carbon-carbon double bonds are commonly protected as dihalides through reaction sequences involving oxidizing, reducing and electrophilic agents,6) the present photo-dehalogenation would be a useful method for regeneration of the double bond under very mild conditions.

Irradiation of a methanol solution of erythro-4-phenyl-3,4-dibromobutan-2-one (**1a**) in a Pyrex tube resulted in disappearance of the starting bromide and concurrent appearance of two products, which were isolated by column chromatography and identified as trans-4-phenyl-3-buten-2-one (**2a**, 30%) and 4-phenyl-3,4-dimethoxybutan-2-one (**3a**, 45%). Similar irradiation of other α,β-dibromocarbonyl compounds (**1b**∿**f**) in methanol also gave unsaturated carbonyl compounds (**2b**∿**f**) and methoxy-substituted products (Table 1), but the product distributions as well as stereoselectivity of debromination were dependent upon the structure of the starting bromide. Thus, photodebromination of 4-phenyl-3,4-dibromoketone derivatives (**1a**∿**c**) was highly stereospecific and accompanied by the substitution, whereas the corresponding esters (**1e**∿**f**) exclusively underwent non-stereospecific photodebromination. Generally, threo-derivatives were less susceptible to photodebromination than the erythro. Irradiation of 3,4-dibromobutyrophenone (**1d**), on the other hand, afforded the products resulting from the cleavage of one of two C-Br bonds.



$$\underset{X}{RCH}-\underset{Y}{CH}-R' \xrightarrow[\text{MeOH}]{h\nu} RCH{=}CHR' + \underset{OMe}{RCH}-\underset{OMe}{CHR'}$$

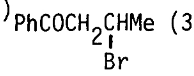
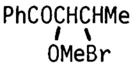
1 **2** **3**

Table 1. Photomethanolysis of α,β-Dibromocarbonyl Compounds[a)]

1 (X=Y=Br)	R	R'	Yield/%[b)] **2** (trans:cis)	**3**
1a(erythro)	Ph	COMe	33.2(99: 1)	49.6
1b(threo)	Ph	COMe	1	36.7
1c(erythro)	Ph	COPh	59.9(99: 1)	30.1
1d(erythro)	Me	COPh	1	c)
1e(erythro)	Ph	CO_2Et	90.0(60:40)	d)
1f(threo)	Ph	CO_2Et	45.5(61:39)	d)

a) Irradiations were performed using 300 W high-pressure Hg lamp on a 40 mM solution of 1 in Pyrex tubes for 6 h at 10°C.

b) Determined by GC. The ratio of olefin was not extrapolated to zero conversion.

c) 
$PhCOCH_2\underset{Br}{C}HMe$ (38.0%) and 
$PhCO\underset{OMe}{C}H\underset{Br}{C}HMe$ (47.0%). d) Not isolated.

Irradiation of these halides either in benzene or in cyclohexane did not afford appreciable amount of olefins (**2**). More than 80% of the starting material was recovered even after 6 h irradiation. When the irradiation of **1a** in benzene was carried out in the presence of 3-molar equivalent triethylamine, however, the dibromide was rapidly consumed (in 1.5 h) to regenerate the keto-olefin (**2a**) in almost quantitative yield along with triethylamine hydrogenbromide (Table 2). Similar reaction was found to occur with other dihalocarbonyl compounds, but the stereochemistry of photodebromination with the amine was somewhat different with that observed in methanol especially in the case of dibromoketone (**1a**∿**d**). Thus, the photodebromination of dibromoketone (**1a**, **c**) was almost completely stereospecific in methanol but nonstereospecific with the amine. Dihaloketones which were less susceptible to photodehalogenation in methanol, e.g., **1b** and **d**, underwent relatively smooth dehalogenation upon irradiation in NEt_3-PhH. More importantly, the photodebromination in the presence of NEt_3 was observed for other simpler vicinal dibromides, e.g., **1j**∿**l**.

$$\mathbf{1} \xrightarrow[NEt_3/PhH]{h\nu} \mathbf{2} + NEt_3{\cdot}HX$$

There are several a priori mechanisms for the photodehalogenation. A radical mechanism was eliminated for the reaction in methanol and triethylamine since the photodebromination was not observed in benzene or cyclohexane. The fact that the photodebromination in methanol was accompanied by nucleophilic substitution (e.g., **3**), but not by hydrogen abstraction (e.g., $PhCH_2CH_2COR$), suggests that α-ketocarbonium ion, presumably generated via initial homolysis of C-X bond followed by electron transfer,[2)] would be involved as a common intermediate, which either undergoes nucleophilic trapping by methanol or releases Br^+ from the vicinal C-Br bond. We do not know exactly which one of two C-Br bonds is cleaved initially upon irradiation at present. But since, in the photolysis of **1d** which did not undergo debromination, the C-Br bond adjacent to methyl group

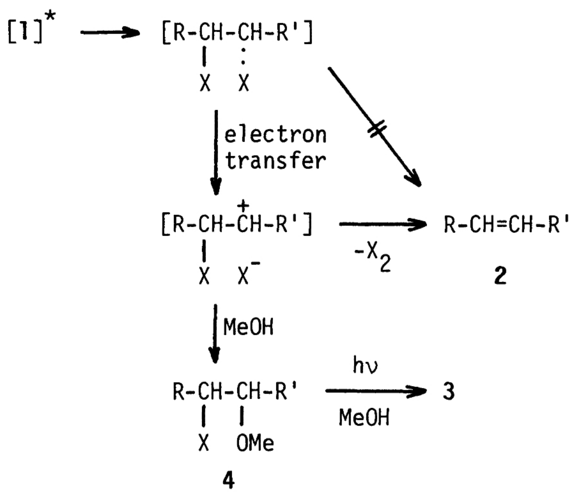
Table 2. Photodehalogenation of Vicinal Dihalides in NEt_3/PhH[a]

1	R	R'	X	Y	Time/h	Yield/% of **2**[b] (trans:cis)
1a(erythro)	Ph	COMe	Br	Br	1.5	92.1(44:56)
1b(threo)	Ph	COMe	Br	Br	1.5	59.9(37:63)
1c(erythro)	Ph	COPh	Br	Br	3.0	99.5(40:60)
1d(erythro)	Me	COPh	Br	Br	0.5	48.8(56:44)
1e(erythro)	Ph	CO_2Et	Br	Br	1.0	$\sim$100 (62:38)
1f(threo)	Ph	CO_2Et	Br	Br	2.0	75.4(51:49)
1g(erythro)	Ph	CO_2Et	Cl	Cl	6.0	35.7(41:59)
1h(erythro)	Ph	CO_2Et	Cl	Br	1.5	89.5(55:45)
1i(erythro)	Ph	CO_2Et	I	Cl	2.5	95.6(42:58)
1j(meso)	Ph	Ph	Br	Br	3.0	78.0(21:79)
1k(dl)	Ph	Ph	Br	Br	3.0	67.1(20:80)
1l(erythro)	Me	^{i}Pr	Br	Br	3.0	76.4(85:15)

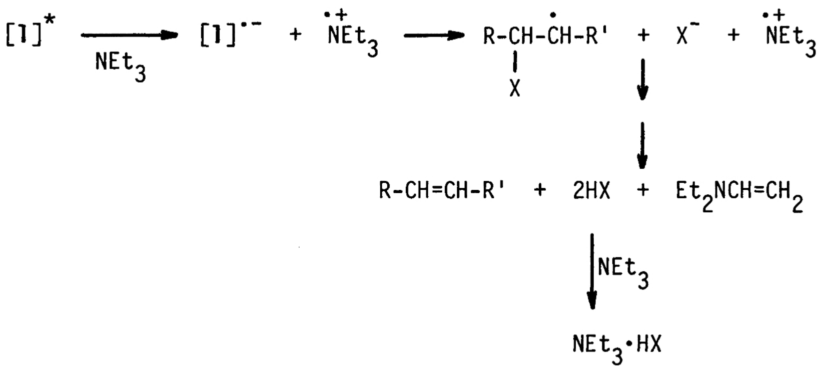
[a] Benzene solutions of **1** (40 mM) and NEt_3 (120 mM) were irradiated in Pyrex tubes at 10°C.

[b] Determined by GC. The ratio of olefin was not extrapolated to zero conversion.

remained unchanged, it is tempting to assume that the phenyl group at β-carbon would facilitate the release of Br^+ from initially formed ketocarbonium ion[7] presumably by delocalizing the partially formed π-bond in the transition state.[8]



The photodehalogenation with NEt_3 must proceed by a mechanism different from that in methanol since the stereochemistry as well as the reactivity of the dihalides are quite different from one another. Presumably, the reaction would involve initial electron transfer from NEt_3 to dihalide in its excited states to give dihalide radical anion. Such an electron transfer has been well-documented[9] in the photochemistry of polyhalo compounds with amine and has been recently demonstrated[10] by laser-flash photolytic techniques. Support is lent to the assumption by the findings that the uv absorption spectra of **1a** in the presence of NEt_3 shows a contact charge transfer spectrum at around 310 nm. Presumably, X^- would be released from the radical anion to lead to the corresponding monohalide radical as proposed[9,11,12] for the other photochemical reactions between amines and halides. The monohalide radical would then lose the remaining halide either spontaneously or via interaction with NEt_3 (and/or with species derived from NEt_3) to regenerate olefin (**2**).



$$[\mathbf{1}]^* \xrightarrow[NEt_3]{} [\mathbf{1}]^{\bullet -} + \overset{\bullet +}{NEt_3} \longrightarrow R\text{-}\underset{X}{CH}\text{-}\overset{\bullet}{C}H\text{-}R' + X^- + \overset{\bullet +}{NEt_3}$$

$$\downarrow$$

$$R\text{-}CH\text{=}CH\text{-}R' + 2HX + Et_2NCH\text{=}CH_2$$

$$\big\downarrow NEt_3$$

$$NEt_3 \cdot HX$$

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8) Irradiations were generally conducted until all of the bromide was consumed since any remaining bromide tends to interfere the analytical procedures due to its decomposition in GC and column chromatograph. Thus, attempt to isolate methoxy bromoketone was not made.

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