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PHOTOCHEMISTRY OF ORGANOHALOGENO-COMPOUNDS. PART XIX
THE EFFECT OF FLUORINE ON PHOTOCHEMICAL CARBON-HALOGEN BOND CLEAVAGE*

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SUMMARY

Irradiation of 1,1-diphenyl-2-fluoro-2-haloethenes at λ=253.7 nm gave 1,1-diphenyl-2-fluoroethene and the rearranged product trans-fluorostilbene. The phototransformation depended on the halogen present and the solvent used. Introduction of fluorine on the sp^2-carbon atom increased carbon-halogen bond dissociation compared to the unsubstituted product, and reduced electron transfer from the caged radical pair to cationic intermediates. Increased solvent polarity diminished the photocleavage of the carbon-halogen bond.

INTRODUCTION

The photochemistry of halogen-substituted organic molecules has been the subject of extensive studies and several reviews have appeared [2-5]. There has been great interest in the photobehaviour of halo substituted alkanes and alkenes in the liquid phase and special attention has been paid to the nature of carbon-halogen bond cleavage and both ionic and radical intermediates were suggested. The nature of photochemical carbon-halogen bond

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*See [1] for Part XVIII.

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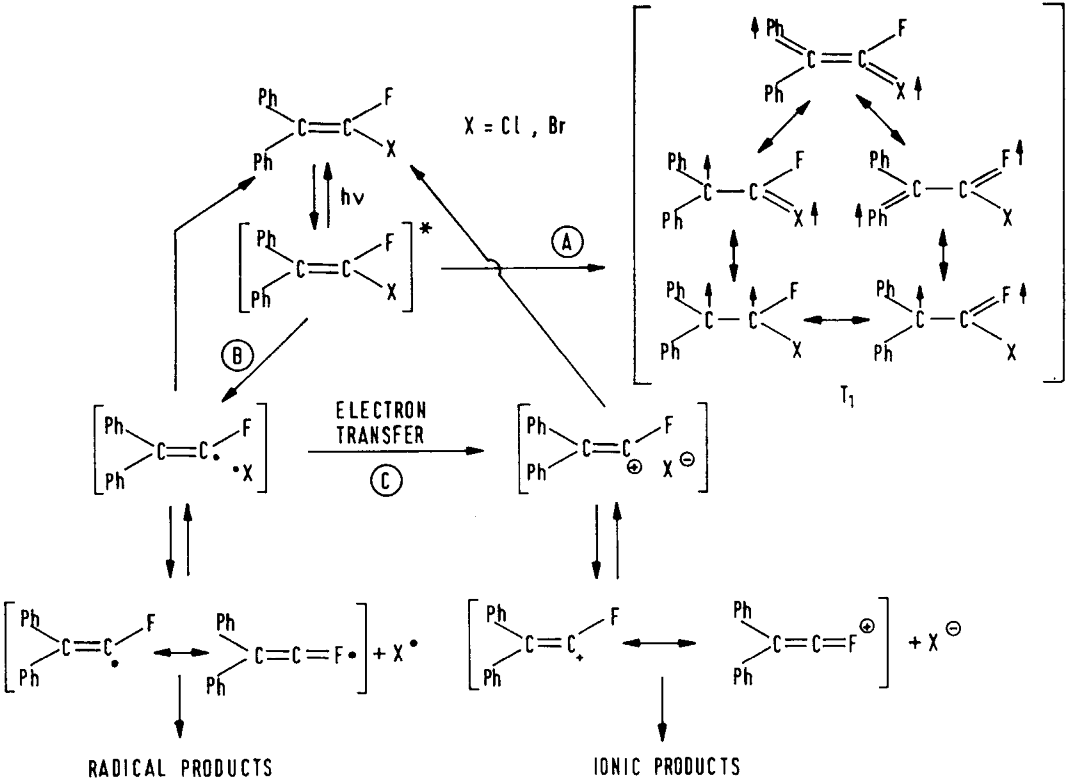
cleavage mainly depends on the hybridization of the carbon atom, on the halogen bonded, on solvent polarity and on the wavelength used. In the irradiation of alkyl halides, it has been generally observed that the ratio of ionic to radical products is substantially larger for iodides than bromides [5], while the tendency becomes the opposite when the halogen atom is bonded to an olefinic carbon [6,7]. Recently, it has been found that by phototransformation of the halo-carbon bond between bromine or iodine and the sp carbon in alkynes, only homolytic bond cleavage occurs in both polar and nonpolar solvents [8].

The photobehaviour of substituted 1,1-diphenylethenes has been intensively studied. Tanigushi and coworkers have extensively investigated the photobehaviour of 1,1-diaryl-2-haloalkenes over the last decade [7,9-13]. We have found that 1,1-diphenyl--2-fluoroethene undergoes photochemical rearrangement [14], while chloro, bromo, and iodo derivatives undergo the photo-Fritsch-Buttenberg-Wiechell rearrangement [6,15].

The following benefits can be expected when fluorine is used as a substituent in studies of the phototransformation of organic molecules:

a) greater thermal stabilities of the photo-products primary formed in comparision to those containing hydrogen or other substituents;
b) greater stabilization of intermediates by the fluorine atom;
c) easier determination of the stereochemistry of phototransformation in comparison to systems containing hydrogen or other substituents;
d) no additional steric interactions;
e) the high energy required for C-F bond cleavage means that such reactions can be prevented by using light of λ= 250-400 nm;
f) ^{19}F nmr spectroscopy enables the determination of small amounts of products in crude reaction mixtures.

The above-mentioned advantages have been proven several times [16]. We now wish to present further investigations of the effect of fluorine as a substituent in phototransformations of organic


X = Cl , Br
hν
Ⓐ
Ⓑ
ELECTRON TRANSFER
Ⓒ
T1
RADICAL PRODUCTS
IONIC PRODUCTS

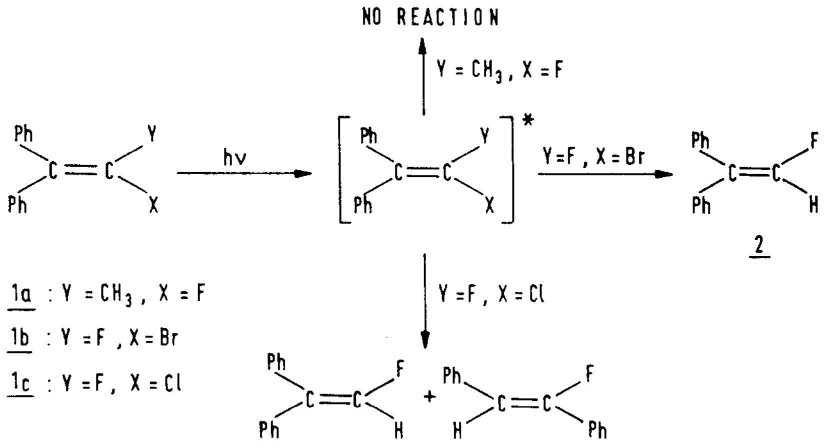
SCHEME 1

molecules and the results of the irradiation of 2-halo-2-fluoro-1,1-diphenylethenes. These were found to undergo either C-X bond cleavage (path B, Scheme 1), which upon subsequent electron transfer can afford an ion pair (path C), or alternatively triplet state stabilization. Concerning how the introduction of fluorine onto an olefinic carbon will affect photochemical carbon-halogen bond cleavage, fluorine can enhance or diminish the rate of phototransformation and the electron transfer from a caged radical pair to cationic intermediates. Other factors will be the influence of the other halogen bonded and the solvent used on the phototransformation.

RESULTS AND DISCUSSION

1,1-Diphenyl-2-fluoro-2-chloroethene (1c) and 1,1-diphenyl-2-fluoro-2-bromoethene (1b) (Scheme 2) were synthesized from 1,1-diphenylethene in the following reaction sequence: fluorination with xenon difluoride, elimination of hydrogen fluoride [17], chlorination or bromination and subsequent elimination under basic conditions.

1,1-Diphenyl-2-fluoro-2-bromoethene (1b) and 1,1-diphenyl-2-fluoro-2-chloroethene (1c) are much more photolabile than the corresponding 1,1-diphenyl-2-haloethenes and for this reason a lower light intensity was used during this study than in an earlier one [6]. In order to compare the photoreactivity, we also irradiated 1,1-diphenyl-2-fluoroethene for 16 hours, but only trace amounts of rearranged products were obtained, while prolongation of irradiation time by a factor of five resulted in 19% conversion, the ratio of cis and transfluorostilbene formed being similar to that observed before [6]. Irradiation for 16 hours of 1,1-diphenyl-2-fluoro-2-bromoethene (1b) in cyclohexane at λ=253,7 nm and at a light intensity of 5.78×10^{16} photons $ml^{-1}s^{-1}$ at $T=22^{\circ}C$ resulted in the formation of only



$\underline{1a}$: Y = CH$_3$, X = F

$\underline{1b}$: Y = F , X = Br

$\underline{1c}$: Y = F , X = Cl

SCHEME 2

TABLE 1

$\underline{2}$ $\underline{3}$

PRODUCT DISTRIBUTION FROM IRRADIATION OF 2-HALO-2-FLUORO-1.1-DIPHENYLETHYLENES AT λ = 253,7 nm[a]

SUBSTRATE (1)	SOLVENT	CONVERSION OF (1) [%]	PRODUCTS $\underline{2}$ [%]	$\underline{3}$ [%]	$\underline{4}$ [%][c]
Y = H , X = F[b]	c C$_6$H$_{12}$	19	81	8	11
Y = F , X = Br	c C$_6$H$_{12}$	87	87		
Y = F , X = Cl	c C$_6$H$_{12}$	58	50	8	
Y = F , X = Cl	Et O Et	43	43		
Y = F , X = Cl	CH$_3$OH	21	21		

[a] IRRADIATION TIME 16h,

[b] IRRADIATION TIME 89h,

[c] Cis FLUOROSTILBENE

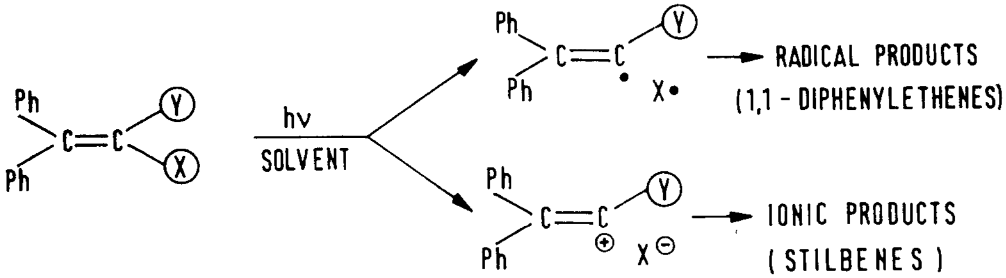
1,1-diphenyl-2-fluoroethene (Table 1). Similar irradiation of the chloro derivative 1c led to diminished conversion as compared to that observed with the bromo derivative, but besides 1,1-diphenyl-2-fluoroethene, the rearranged product trans-fluorostilbene also appeared. The change of solvent from cyclohexane to ether or methanol enhanced the photostability of 1c and suppressed the photorearrangements (Table 1). 1,1-Diphenyl-2-fluoropropene also proved to be photostable under the above mentioned reaction conditions.

The sensitized irradiation of 1,1-diphenyl-2-fluoro-2-chloroethene (1c) was carried out in cyclohexane by using benzophenone as a triplet sensitizer at λ=350 nm. Surprisingly both compounds were found to be photostable, which is in contrast to our observations on the similar reaction of 1,1-diphenyl--2-fluoroethene, where 1,1-diphenyl-2-fluoro-2-cyclohexylethane was formed [6]. However, similar photostability under sensitized conditions was also observed on irradiation of 2-bromo-1,1-diphenylprop-1-ene [7].

From these results, it is evident that introduction of fluorine at an olefinic double bond enhanced the photolability of the C-X bond, but the electron transfer process from a caged radical pair was completely suppressed in the case of the bromo derivative, while it occured only slightly in the case of the chloro compound. Variation of solvent showed that the change from non-polar solvent, *i.e.* cyclohexane, to polar, *i.e.* methanol, increased the photostability and suppressed the photorearrangement. The formation of trans-fluorostilbene could be explained by the formation of an ionic intermediate or by photoreaction of Z- or E-1-fluoro-2-chlorostilbene, which can be formed in a similar way to that suggested for rearrangement of 1,1-diphenyl-2-fluoroethene [6]. However, the second possibility is much less probable because in the crude reaction mixture we did not detect

TABLE 2

THE EFFECT OF STRUCTURE VARIATION ON PHOTOTRANSFORMATIONS OF SUBSTITUTED 1,1-DIPHENYLETHENES



COMPOUND Ⓨ	Ⓧ	SOLVENT	IONIC PRODUCTS / IONIC + RADICAL PROD.	REF.
Ph	Br	CH_3OH	0.94	14
CH_3	I	CH_3OH	0.38	13
	Br	CH_3OH	0.52	13
	Cl	CH_3OH	0.80	13
H	I	c C_6H_{12}	0.14	6
	I	EtOEt	0.25	6
	Br	EtOEt	0.34	6
	Cl	EtOEt	0.40	6
F	Br	c C_6H_{12}	0	
	Cl	c C_6H_{12}	0.14	

the presence of Z- or E-1-chloro-2-fluorostilbene. In Table 2 the effects of structure variation on the phototransformations of substituted 1,1-diphenylethenes are presented.

EXPERIMENTAL

Irradiation was carried out with a Rayonet Model RMR 400 with RPR 253.7 nm and 350 nm lamps at a light intensity of 5.78 x 10^{16} photons $ml^{-1}s^{-1}$. Ir spectra were recorded using a Perkin Elmer 727 B spectrometer and ^1H and ^{19}F nmr spectra by a Jeol JNM-PS-100 spectrometer using $CDCl_3$ or CCl_4 solutions with $Si(CH_3)_4$ or CCl_3F as internal references. Mass spectra and high resolution measurements were taken on a CEC 21-110 spectrometer. Tlc was carried out on Merck PSC Fertigplatten F 254, and glc on a Varian Aerograph, Model 1800.

1,1-Diphenyl-2-Fluoro-2-Chloroethene (1c, NC)

1 mmol of 1,1-diphenyl-2-fluoroethene was dissolved in 4 ml of CCl_4 and under stirring at 0°C 1 ml stock solution of chlorine in CCl_4 (2 mmols of Cl_2) was added. The reaction mixture was stirred for 1 hour at 0°C and for 2 hours at room temperature, the solvent was evaporated in vacuo and 96% of crude product was obtained, which was used without purification for further elimination. The crude reaction mixture was mixed with 2 ml of a 1 M solution of $KOC(CH_3)_3$ in $C(CH_3)_3OH$ and heated at 60°C for five hours. The reaction mixture was then poured into water and the product extracted with CH_2Cl_2. The organic layer was washed with water, dried over anhydrous Na_2SO_4, the solvent evaporated in vacuo and 85% of the crude product was obtained. The product was purified by preparative tlc (SiO_2, petrolether: $CHCl_3$=8:2) and 74% of pure product mp=36-37°C was isolated. NMR: δF = -78.4 ppm(s), δPh = 7.2 ppm (m), mass spectrum calcd. for $C_{14}H_{10}FCl$ m/e 232.0455, found m/e 232.0458, m/e 234(M^+ +2, 36), 233(M^+ +1, 18) 232(M^+,100), 197(41), 196(78), 165(9), 98(28), 85(13), 51(10).

1,1-Diphenyl-2-Fluoro-2-Bromoethene (1b, NC)

1 mmol of 1,1-diphenyl-2-fluoroethene was dissolved in 4 ml of $CHCl_3$ and under stirring at 0°C, 1.6 ml of bromine solution in $CHCl_3$ (1 g Br_2 in 10 ml of $CHCl_3$) was added, the reaction mixture stirred for 1 hour at 0°C and 2 hours at room temperature. The solvent was evaporated in vacuo and the crude product was used without purification for further reaction. The crude reaction mixture was mixed with 2 ml of 1M $KOC(CH_3)_3$ in $C(CH_3)_3OH$ and heated for 5 hours at 60°C. The reaction mixture was then poured in water, the product extracted with CH_2Cl_2, the organic layer washed with water, dried over anhydrous Na_2SO_4 and the solvent evaporated in vacuo. The product was purified by preparative tlc (SiO_2, petrolether: $CHCl_3$= 8:2) and 47% of pure product, mp = 59-60°C, was isolated. NMR: δF = -71.7 ppm (s), δPh= 7.2 ppm (m), mass spectrum calcd. for $C_{14}H_{10}FBr$ m/e 275.9950, found m/e 275.9953, m/e 279 (M^+ +3, 10) 278(M^+ + 1, 10), 276(M^+, 68), 197(39), 196(100), 194(12), 177(11), 176(12), 170(11), 99(10), 98(28), 85(14), 51(16), 50(10), 40(33).

Irradiation of 2-Halo-2-Fluoro-1,1-Diphenylethenes

2-Chloro and 2-bromo-2-fluoro-1,1-diphenylethene (0.34 mmol) was dissolved in 15 ml of solvent (cyclohexane, diethylether, or methanol), and the solution was irradiated for 16 hours at λ=253.7 nm with a light intensity of 5.78 x 10^{16} photons $ml^{-1}s^{-1}$ at 22°C. The solvent was evaporated in vacuo and the reaction mixture was analyzed by ^1H and ^{19}F nmr and glc. Product distributions are presented in Table 1 and were calculated from ^{19}F nmr spectra. Products were isolated by preparative glc and were identified by comparison of their ir, nmr, and mass spectra with those of authentic samples.

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