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CHEMISTRY OF ORGANO HALOGENIC MOLECULES. PART XCIV. THE EFFECT OF FLUORINE ON PHOTOCHEMICAL CARBON-HALOGEN BOND CLEAVAGE IN Z AND E-1-FLUORO-2-HALO-1,2-DIPHENYLETHYLENES.

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SUMMARY

Irradiation of Z and E-1-fluoro-2-halo-1,2-diphenylethylenes at λ=253.7nm gave Z and E-2-fluoro-1,2-diphenylethylene and 1,2-diphenylacetylene. The phototransformation depended on the geometry of the molecule, the halogen atom present, and the solvent used. Introduction of fluorine on the olefinic carbon atom in the ß-position to a carbon-halogen bond increased the photocleavage compared to the unsubsituted substrate, and reduced the electron transfer from the caged radical-pair to cationic intermediates. Increased solvent polarity resulted in enhanced photocleavage of the carbon-halogen bond.

INTRODUCTION

The phototransformations of organic molecules containing halogen atoms has been the subject of extensive studies [1-4]. The photobehaviour of halo substituted alkanes and alkenes in the gas and liquid phase has been studied and special attention has been paid to the nature of the photocleavage

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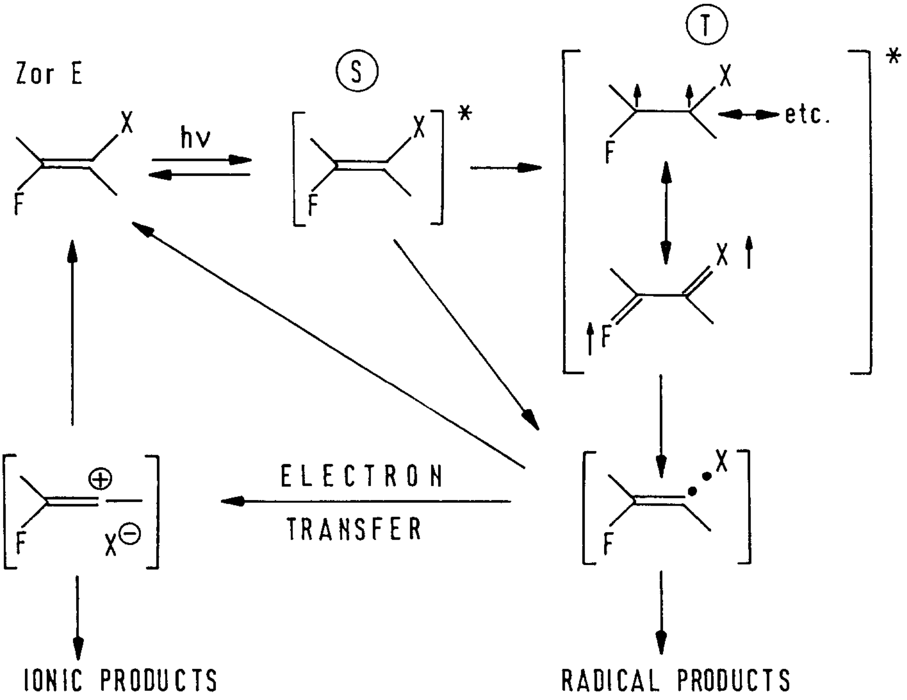
of the carbon-halogen bond, and radical and ionic species were suggested as reaction intermediates. The main factors influencing the mode of photochemical carbon-halogen bond cleavage are hybridization of the carbon atom, the halogen bonded, the solvent polarity, and the wavelength used. The ratio of ionic to radical products on irradiation of alkyl halides is substantially larger for iodides than bromides [4], while the tendency becomes the opposite in the case of olefins [5, 6], and only homolytic bond cleavage was found in bromo- and iodo- substituted alkynes [7].

The advantages of the use of fluorine as a substituent in the studies of phototransformations of organic molecules have been proven several times [8, 9]. Recently we have demonstrated that the introduction of fluorine on the olefinic carbon atom bearing the halogen atom, increased the photochemical carbon-halogen bond cleavage, and reduced the electron transfer from the caged radical pair to cationic intermediates [10]. We now present further investigations of the effect of the fluorine atom on the nature of the photochemical carbon-halogen bond cleavage, with our attention now aimed at its influence when bonded to the olefinic carbon in the ß-position to the carbon bearing the halogen atom.

Irradiation of a substituted Z or E-1-fluoro-2-haloethylene results in a singlet excited state, which can be transformed to the triplet state, undergoing stabilization. However, from both the intermediate states, the carbon-halogen bond cleavage can then lead to a caged radical pair (Scheme 1). Radical intermediates can be either converted to products, to the starting substrate, or undergo electron transfer, resulting in ionic intermediates. All these processes can be influenced by the presence of the fluorine atom, the geometry of the molecule, and the halogen atom bonded.

RESULTS AND DISCUSSION

1-Fluoro-2-halo-1,2-diphenylethylenes are much more photolabile than the corresponding 1-halo-1,2-diphenylethylenes and for this reason a lower light intensity was used during this study than in an earlier one [11, 12]. Irradiation of E-1-fluoro-2-chloro-1,2-diphenylethylene (1a), Z-1-fluoro-2-chloro-1,2-diphenylethylene (2a), E-1-fluoro-2-bromo-1,2-diphenylethylene (1b), and Z-1-fluoro-2-bromo-1,2-diphenylethylene (2b) in diethylether at λ=253.7nm and at a light intensity of 5.78 x 10^{16} photons $ml^{-1}s^{-1}$ at T=22 °C resulted in the formation of a crude reaction mixture containing up to five compounds in each case. The crude reaction mixtures were analyzed by ^1H and ^{19}F nmr spectroscopy, the products were isolated by preparative glc and the structures of the products were determined on the basis of their



SCHEME 1

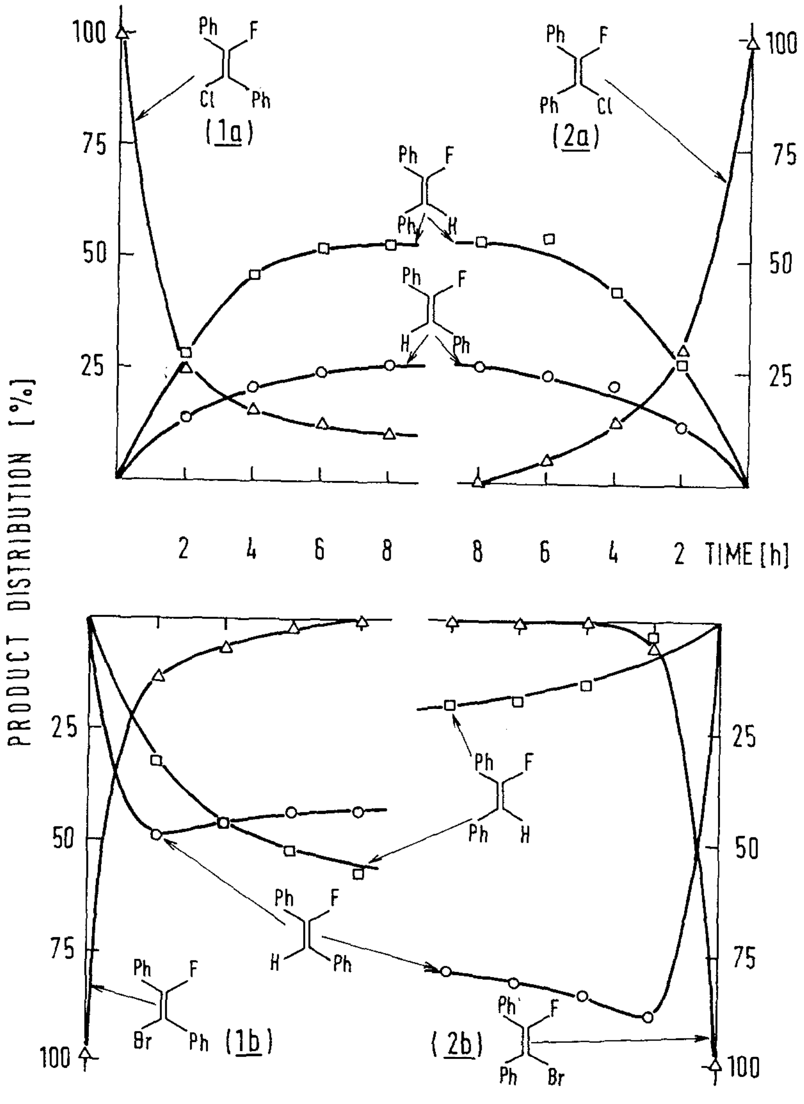
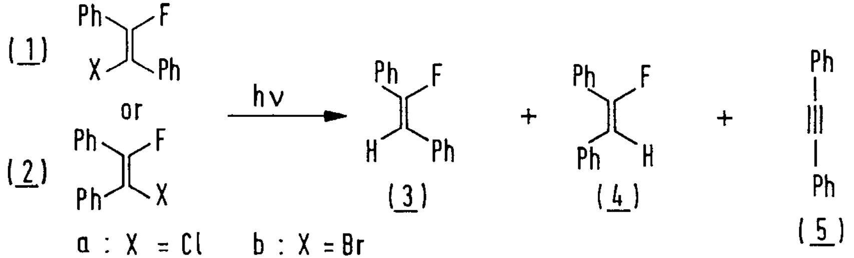


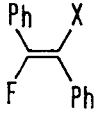
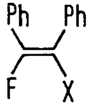
Fig. 1. The effect of the halogen atom and the structure of the molecule on phototransformation of 1-fluoro--2-halo-1,2-diphenylethylenes in Et_2O at λ=253.7 nm.

spectroscopic data and their comparison to authentic samples. Besides the cis-trans photoisomerisation of the starting substrate, the main products present in all the reaction mixtures were Z-1-fluoro-1,2-diphenylethylene (3), E-1-fluoro-1,2-diphenylethylene (4), and diphenylacetylene (5) as a minor product accompanying the olefins in Et_2O. In Fig. 1, the effect of the halogen atom and the geometry of the molecule on the phototransformation of Z and E-1-fluoro-2-halo- 1,2-diphenylethylenes in Et_2O to Z or E-1-fluoro-1,2-diphenylethylenes is presented (in order to obtain a clearer presentation in the figure, the cis-trans isomerisation of the starting olefin and the formation of the minor product diphenylacetylene are omitted; product distribution was determined by glc). In order to compare the effect of the structure of stilbenes (1 and 2) on the photoconversion, product distributions observed after 2 and 6 hours irradiation at a light intensity of 5.78×10^{16} photons $ml^{-1}s^{-1}$ with λ=253.7nm are presented in Scheme 2. It is evident that bromo derivatives are more photolabile than the chloro ones, and Z-isomers are also more readily converted. It is interesting that after 2 hours in the reaction mixtures resulting from irradiation of both isomers of the chloro derivative, predominantly Z-1-fluoro-2 -chloroethylene was present; i.e. the cis-trans isomerisation took place, while bromo derivatives undergo rapid carbon-bromine bond photodissociation. It is also evident that the amount of diphenylacetylene formed by irradiation in Et_2O is larger from Z-1-fluoro-2-halo-1,2 -diphenylethylene and for this reason irradiation was also carried out in the less polar solvent cyclohexane. Diminished solvent polarity increased the photostability of the olefin, which is opposite to the observation found by irradiation of 1,1-diphenyl-2-fluoro-2-haloethylene [10]. Surprisingly, phototransformation of 2b is mainly directed to the elimination process, resulting in diphenylacetylene formation, the time dependent product distribution being presented in Fig. 2.



a : X = Cl   b : X = Br

PRODUCT DISTRIBUTION FROM IRRADITION OF 1-FLUORO-2-HALO-1,2-DIPHENYLETHYLENES AT $\lambda = 253.7$ nm

SUBSTRATE	X	SOLVENT	IRRADITION TIME [h]	CONVERSION OF (1) OR (2)	PRODUCT DISTRIBUTION (1)	(2)	(3)	(4)	(5)
 (1)	Cl	Et_2O	2	75	25	33	14	28	—
	Cl	Et_2O	6	87	13	9	24	52	2
	Br	Et_2O	2	87	13	5	49	32	1
	Br	Et_2O	6	98	2	2	43	52	1
 (2)	Cl	Et_2O	2	70	24	30	13	27	6
	Cl	Et_2O	6	95	8	5	24	55	8
	Br	Et_2O	2	95	1	5	89	3	2
	Br	Et_2O	6	100	—	—	81	18	1
	Br	$c\,C_6H_{12}$	2	36	11	64	16	—	9
	Br	$c\,C_6H_{12}$	6	81	10	19	8	—	63

SCHEME 2

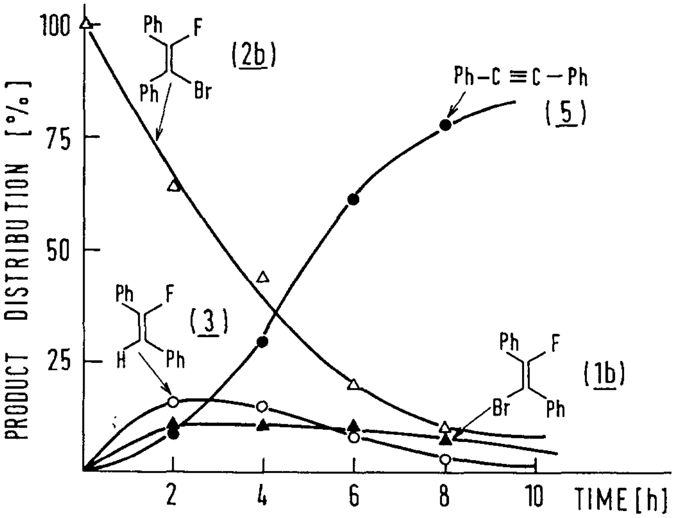
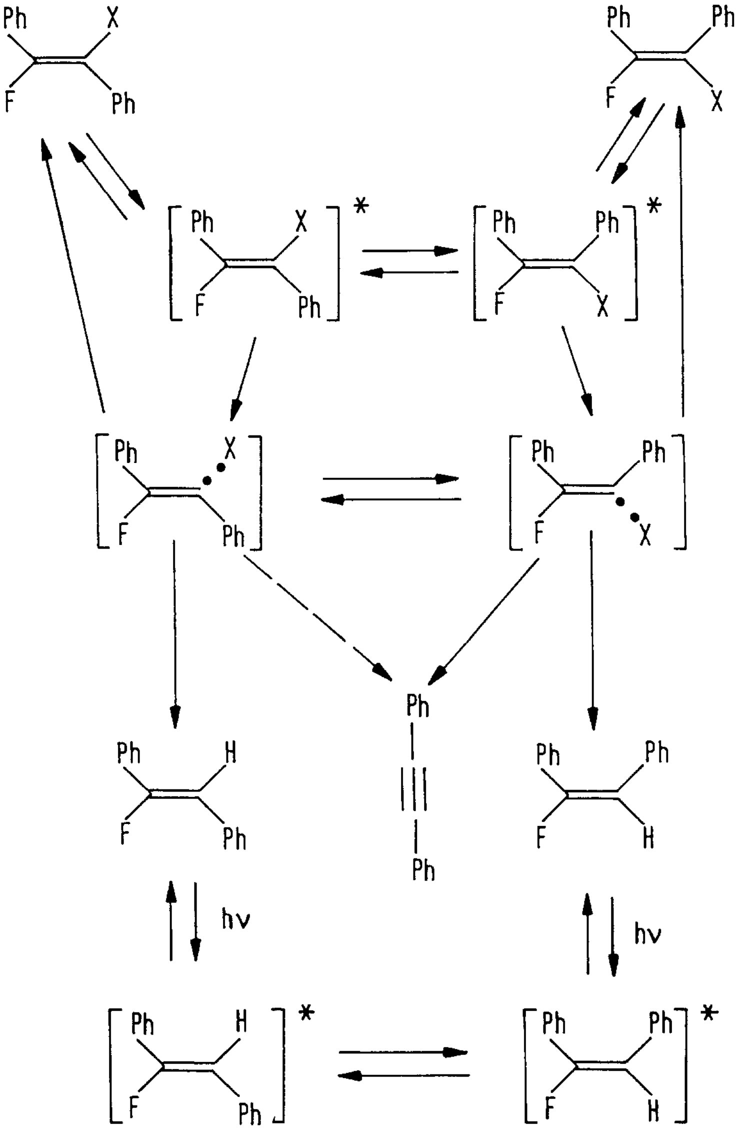


Fig. 2. Time dependence for phototransformation of Z-1-fluoro--2-bromo-1,2-diphenyl=ethylene in cyclohexane at λ=253.7 nm.

From the above results it is evident that introduction of fluorine into the olefinic double bond enhances the photostability of the carbon-halogen bond, but the electron transfer process from the caged radical pair was completely supressed. A possible explanation for the formation of the observed products is presented in Scheme 3.

EXPERIMENTAL SECTION

Irradiation was carried out with a Rayonet Model RMR 400 with RPR 253.7nm and 350.0nm 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 ^{1}H 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



SCHEME 3

was carried out on Merck PSC Fertigplatten F 254, and glc on a Varian Aerograph, Model 1800. E-1-fluoro-2-chloro-1,2-diphenylethylene (1a), E-1-fluoro-2-bromo-1,2-diphenylethylene(1b), Z-1-fluoro-2-chloro-1,2-diphenylethylene (2a) and Z-1-fluoro-2-bromo-1,2-dipnenylethylene (2b) were synthesized [13]. Diethylether and cyclohexane were purified [14].

Irradiation of Z or E-1-Fluoro-2-Halo-1,2-Diphenylethylenes.

2-Chloro or 2-bromo -1-fluoro-1,2-diphenylethylene (0.34mmol) was dissolved in 15ml of solvent (Et_2O, cyclohexane), and the solution was irradiated for various times (2-8 hours) at λ =253.7nm with a light intensity of 5.78 x 10^{16} photons $ml^{-1}s^{-1}$ at 22 °C. The solvent was evaporated in a vacuum and the reaction mixture was analyzed by ^1H and ^{19}F nmr and glc: reaction mixtures from chloro substituted olefins using OV 101 (10%) - Chromosorb W/AW 80/100, T=150 °C, while reaction mixtures resulting from bromo substituted olefins were analysed on SE-30 (10%) - Chromosorb W/AW 80/100, T=180°C. Product distributions are presented in Fig. 1, Fig. 2. and Scheme 2. Products were isolated by preparative glc and were identified by comparison of their ir, nmr, and mass spectra to those of authentic samples.

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