

PHOTOCHEMISTRY OF α -HALO-SUBSTITUTED STILBENES*

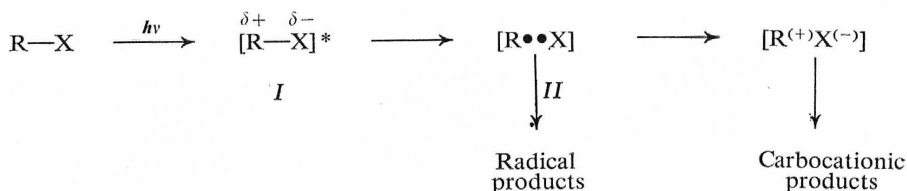
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Competing ionic and radical photobehaviour has been observed for α -halo substituted stilbenes. Irradiation of *cis*- or *trans*- fluorostilbene in cyclohexane or ether afforded only *cis*, *trans* isomerization. Irradiation of chloro or bromo analogues gave a complex mixture up to eight products with three major ones: diphenylacetylene, *cis*- and *trans*-stilbene. Product distribution proved to depend on the halogen and on the solvent.

The photochemistry of alkyl halides has been the object of study over the years^{1,2}. The earlier studies were conducted mainly in the gas phase¹, but some reports of photobehaviour in the liquid or solution state have also appeared. In all these studies the common factor has been the formation of radical products, resulting from initial homolytic cleavage of the carbon-halogen bond. Kroop and coworkers³ have observed competing ionic and radical photobehaviour for a number of alkyl halides. The initially generated radical pair (Scheme 1) can undergo subsequent electron



SCHEME 1

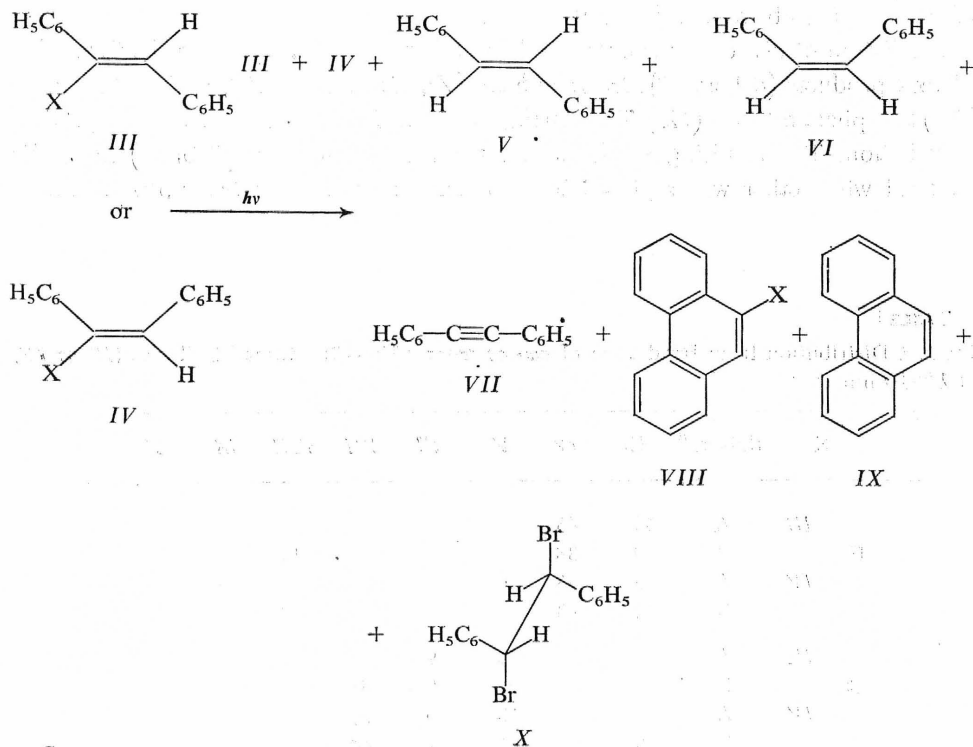
transfer to afford an ion pair and ultimately carbocationic products. They have shown that irradiation of alkyl bromides, and particularly iodides, in solution is a convenient and powerful means for the generation of carbocations, especially those of high energy. We have recently found⁴ that irradiation of 1,1-diphenyl-2-fluoroethylene resulted in the formation of *cis*- and *trans*-fluorostilbene, while the irradiation of chloro, bromo and iodo analogues⁵ gave a mixture of eight products, with the

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three major products being diphenylacetylene, 1,1-diphenylethylene and 1,1,4,4-tetraphenylbutadiene. The dehydrohalogenation of olefins, bearing hydrogen and halogen on the same carbon, to acetylenes under basic conditions has been known for a long time as the Fritsch–Buttenberg–Wiechell rearrangement⁶ and has been studied in detail⁷.

In order to establish the mechanism of photorearrangement of 1,1-diphenyl-2-haloethylenes to diphenylacetylenes, we found it helpful to irradiate some *cis* and *trans* halogen-substituted stilbenes. The photochemistry of stilbenes and substituted stilbenes has been the subject of extensive studies⁸.

A 15-hour irradiation of *cis* or *trans* halo-substituted stilbene (*III* or *IV*, Scheme 2) in cyclohexane or ether (0.023M) at λ 253.7 nm resulted in a crude reaction mixture.



SCHEME 2

The products were separated by preparative gas-liquid chromatography and identified by their ¹H-NMR, mass and IR spectra. As shown in Table I, the number of products and the product distributions depend on the halogen and also on the solvent used. The irradiation of *cis*- or *trans*-fluorostilbene (*III* or *IV*) in ether resulted only

in *cis-trans* photoisomerization with different ratios, *cis/trans* equal to 1.22 and 0.77, corresponding to the photoisomerization of *cis*-fluorostilbene to *trans*-fluorostilbene and *vice versa*, respectively. On the other hand, irradiation in cyclohexane solution, besides photoisomerization, also resulted in the formation of 9-fluorophenanthrene (VIII). The observed *cis/trans* ratios are very similar to those observed in ether, while 9-fluorophenanthrene was formed in higher amounts when *cis*-fluorostilbene was irradiated. Irradiation of *cis*- or *trans*-fluorostilbene under the conditions mentioned above, and in the presence of iodine, resulted in the formation of 50% of 9-fluorophenanthrene.

Irradiation of *cis*- or *trans*-chlorostilbene in ether (III or IV, Scheme 2) resulted in the formation of three products: *trans*-stilbene (V), *cis*-stilbene (VI) and diphenylacetylene (VII), with very little dependence of product distribution on the starting olefin (Table I). In cyclohexane solution *trans*-chlorostilbene was also isolated in addition to the above mentioned products.

Irradiation of *cis*- or *trans*-bromostilbene ether solution resulted in the formation of four products (Scheme 2): *trans*-stilbene (V), *cis*-stilbene (VI), diphenylacetylene (III) and phenanthrene (IX). The starting olefin had very little influence on product distribution. The resulting products and product distribution (Table I) markedly changed when ether was replaced by cyclohexane as solvent: *trans*-bromostilbene

TABLE I

Product Distribution from Irradiation of *cis*- or *trans*- α -Halo-Substituted Stilbenes (III or IV) at λ 253.7 nm

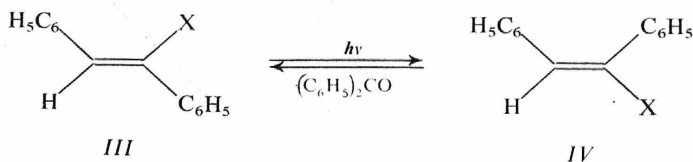
	X	Solvent ^a	III	IV	V	VI	VII	VIII	IX	X
F	III	A	55	45	—	—	—	—	—	—
		B	49	38	—	—	—	13	—	—
	IV	A	45	55	—	—	—	—	—	—
		B	34	43	—	—	—	23	—	—
Cl	III	A	—	—	16	9	63	—	—	—
		B	9	—	26	9.5	43	—	—	—
	IV	A	—	—	18	10	57	—	—	—
		B	5	—	23	7	44	—	—	—
Br	III	A	—	—	13	18	30	—	10	—
		B	6.5	3	18.5	—	2	—	2	25
	IV	A	—	—	14	19	25	—	8	—
		B	6	3	14	—	3	—	5	20

^a A diethyl ether, B cyclohexane.

(III), *cis*-bromostilbene (IV), *trans*-stilbene (V), diphenylacetylene (VII), phenanthrene (IX) and *meso*-1,2-dibromo-1,2-diphenylethane (X). The starting olefin again had very little influence on product distribution.

The explanation of all the above-mentioned phototransformations of *cis*- or *trans*-halostilbenes (III or IV) is presented in Scheme 3. In the first step, the stilbene molecule is converted to an excited state with the further possibility of isomerization, followed by photocyclization, thus forming 9-halophenanthrene. The excited molecule can, on the other hand, undergo C—X bond dissociation. The isomerisation and cyclisation to the phenanthrene ring is operating in the case of *cis*- or *trans*-fluorostilbene, where no C—F bond dissociation is possible, while C—X bond dissociation in the case of other halogens (X = Cl or Br) becomes more important, if not the exclusively proceeding process. The formation of *cis* or *trans*-stilbene (V or VI) by irradiation of *cis*- or *trans*-chloro or bromostilbene could be ascribed to the formation of free radical intermediates, arising from homolytic C—X bond cleavage. However, the initially generated radical pair can undergo subsequent electron transfer forming diphenylacetylene (VII) after proton loss. *cis*- and *trans*-Stilbene can photoisomerise and *cis*-stilbene can undergo photocyclisation to phenanthrene.

We have found⁴ that the triplet state of 1,1-diphenyl-2-fluoroethylene, formed by benzophenone sensitized photoirradiation in cyclohexane solution, gave 1,1-diphenyl-2-fluoro-2-cyclohexylethane, while direct irradiation of 1,1-diphenyl-2-fluoroethylene resulted in *cis*- and *trans*-fluorostilbene. The formation of the adduct has been explained by strongly induced electron delocalization in the 1,1-diphenyl-2-fluoroethylene triplet state, so that reaction sites in this biradical species resemble free radicals⁹. Now it is interesting to compare the benzophenone sensitized reactions of *cis*- and *trans*- α -halostilbenes, with those observed by 1,1-diphenyl-2-fluoroethylene. By irradiation of a cyclohexane solution of *cis*- and *trans*-fluoro and chlorostilbenes at $\lambda = 350$ nm, the starting olefins remained unchanged, while *cis*- or *trans*-bromostilbene gave small amounts of *meso*-1,2-dibromo-1,2-diphenylethane (X) (4.5% in the case of *cis*-bromostilbene and 8% in the case of *trans*-bromostilbene) and *trans*-stilbene (5% and 6% in the case of *cis*- and *trans*-bromostilbene, respectively). The benzophenone sensitized reaction of *cis*- or *trans*-fluoro and chlorostilbenes resulted only in *cis*-*trans* photoisomerization of the starting olefins (Scheme 4).



X = F, Cl

SCHEME 4

The ratios *cis/trans* were: 1.13, 0.79, 1.41 and 0.85 in the case of *cis*-fluorostilbene, *trans*-fluorostilbene, *cis*-chlorostilbene and *trans*-chlorostilbene, respectively. The observed results clearly show that the 1,1-diphenyl-2-fluoroethylene triplet state has a different reactivity from the fluorostilbene triplet state formed by benzophenone sensitized irradiation. The absence of the formation of 9-fluorophenanthrene, which was formed by irradiation at λ 253.7 nm, could be ascribed to the fact that photocyclisation occurs only from singlet state of *cis*-fluorostilbene.

EXPERIMENTAL

IR spectra were recorded with a Perkin-Elmer 137 spectrometer and ^1H - and ^{19}F -NMR spectra with a Jeol-JNM-PS-100 instrument for solutions in CCl_4 or CDCl_3 with $(\text{CH}_3)_4\text{Si}$ or CCl_3F as internal reference. Mass spectra (including high resolution) were taken with CEC-21-110. Gas-liquid chromatography (GLC) was carried out on a Varian Aerograph 1800 instrument. Melting points were determined on a Koffler microscope and are uncorrected. Irradiation was carried out in a Rayonet Photochemical Chamber Reactor, Model RPR-100, with RPR-253.7 nm, RPR-300 nm and RPR-350 nm lamps.

Materials

The starting olefins *cis*- and *trans*-fluorostilbene¹⁰, *cis*- and *trans*-chlorostilbene¹¹ and *cis*- and *trans*-bromostilbene¹² were synthesised according to the literature and purified by GLC before use. Solvents were purified¹³.

Irradiation of *cis*- or *trans*-Fluorostilbene

820 mg of *cis*-fluorostilbene was dissolved in 180 ml of cyclohexane and the solution irradiated for 15 h at λ 253.7 nm at room temperature. The solvent was evaporated *in vacuo* and the residue analyzed by NMR spectroscopy, 43% of *cis*-fluorostilbene, 34% of *trans*-fluorostilbene and 23% of 9-fluorophenanthrene were present. In the case of *trans*-fluorostilbene, 38% of *cis*-fluorostilbene, 49% of *trans*-fluorostilbene and 13% of 9-fluorophenanthrene were formed.

By irradiation of *cis*-fluorostilbene in ether under the conditions mentioned above, only 55% of *cis*-fluorostilbene and 45% of *trans*-fluorostilbene were formed, while the irradiation of *trans*-fluorostilbene in ether resulted in the formation of 45% of *cis*-fluorostilbene and 55% of *trans*-fluorostilbene. The crude reaction mixtures were separated by preparative GLC (Carbowax 20 M, Varaport 30 70/80 10%, T 240°C). The structures of the products were determined on the basis of comparison of IR, NMR and mass spectra.

Irradiation of *cis*- or *trans*-Chlorostilbene

800 mg of *cis*-chlorostilbene was dissolved in 180 ml of cyclohexane and irradiated with λ 253.7 nm for 15 h at room temperature. The solvent was evaporated *in vacuo* and the residue was separated by preparative GLC (Carbowax 20 M, Varaport 30 (70/80 10%, T 240°C). The following products were isolated: 44 mg (5%) of *trans*-chlorostilbene, 170 mg (23%) of *trans*-stilbene, 52 mg (7%) of *cis*-stilbene and 322 mg (44%) of diphenylacetylene. Products were identified by comparison of IR, NMR and mass spectra with the authentic compounds.

The irradiation of *trans*-chlorostilbene under the conditions mentioned above, and separation by preparative GLC, gave the following products: 79 mg (9%) of *trans*-chlorostilbene, 192 mg (26%) of *trans*-stilbene, 70 mg (95%) of *cis*-stilbene and 315 mg (43%) of diphenylacetylene.

The irradiation of *cis*-chlorostilbene under the conditions mentioned above resulted in 133 mg (18%) of *trans*-stilbene, 74 mg (10%) of *cis*-stilbene and 417 mg (57%) of diphenylacetylene, while the irradiation of an ethereal solution of *trans*-chlorostilbene gave 118 mg (17%) of *trans*-stilbene, 67 mg (9%) of *cis*-stilbene and 461 mg (63%) of diphenylacetylene.

Irradiation of *cis*- or *trans*-Bromostilbene

1.08 g of *cis*-bromostilbene in 180 ml of cyclohexane was irradiated for 15 h with λ 253.7 nm at room temperature. The solvent was evaporated *in vacuo* and the residue was dissolved in 5 ml of *n*-hexane and crystalline *meso*-1,2-dibromo-1,2-diphenylethane (286 mg, 20%) was filtered off and the filtrate was separated by preparative GLC (OV 1, Varaport 30 70/80 10%, T 235°C). The following products were isolated: 32 mg (3%) of *cis*-bromostilbene, 65 mg (6%) of *trans*-bromostilbene, 22 mg (3%) of diphenylacetylene, 105 mg (14%) of *trans*-stilbene and 37 mg (5%) of phenanthrene. The structures of the product were determined on the basis of a comparison of their IR, NMR and mass spectra with the authentic compounds.

The irradiation of *trans*-bromostilbene in cyclohexane gave the following products: 354 mg (25%) of 1,2-dibromo-1,2-diphenylethane, 32 mg (3%) of *cis*-bromostilbene, 70 mg (6%) of *trans*-bromostilbene, 15 mg (2%) of diphenylacetylene, 139 (18.5%) of *trans*-stilbene and 15 mg (2%) of phenanthrene.

Irradiation of an ethereal solution of *cis*-bromostilbene under the conditions mentioned above gave the following products: 105 mg (14%) of *trans*-stilbene, 143 mg (19%) of *cis*-stilbene, 60 mg (8%) of phenanthrene and 186 mg (25%) of diphenylacetylene, while in the case of *trans*-bromostilbene 98 mg (13%) of *trans*-stilbene 135 mg (18%) of *cis*-stilbene, 75 mg (10%) of phenanthrene, 227 mg (30%) of diphenylacetylene.

Irradiation of *cis*- and *trans*-Fluorostilbene in the Presence of Benzophenone

82 mg of *cis*-fluorostilbene and 750 mg of benzophenone were dissolved in 18 ml of cyclohexane and the solution was irradiated for 15 h at λ 350 nm. The solvent was evaporated *in vacuo* and the residue was analyzed by ^{19}F -NMR spectroscopy. By irradiation in the presence of benzophenone, 53% of *cis*-fluorostilbene and 47% of *trans*-fluorostilbene were formed, while irradiation of *trans*-fluorostilbene under conditions mentioned above gave 44% of *cis*-fluorostilbene and 56% of *trans*-fluorostilbene.

REFERENCES

1. Majer J. R., Simons J. P.: *Advan. Photochem.* 2, 137 (1964).
2. Sammes P. G. in the book: *Chemistry of the Carbon-Halogen Bond* (S. Patai, Ed.), Chapter 11. Wiley, New York 1973.
3. Kropp P. J., Poindexter G. S., Pienta N. J., Hamilton D. C.: *J. Amer. Chem. Soc.* 98, 8135 (1976).
4. Šket B., Zupan M.: *Tetrahedron Lett.* 1977, 257.
5. Šket B., Zupan M., Pollak A.: *Tetrahedron Lett.* 1976, 783.
6. Fritsch P.: *Justus Liebig's Ann. Chem.* 279, 319 (1894).

7. Viehe H. G.: *Chemistry of Acetylenes*, p. 117. Dekker, New York 1969.
8. Photochemistry, Vol.-1-7, Specialist Periodical Reports. The Chemical Society, London, 1970—1976.
9. Rosenberg H. M., Serve P.: *J. Chem. Soc.* 92, 4746 (1970).
10. Zupan M., Pollak A.: *J. Org. Chem.* 42, 1559 (1977).
11. Cristol S. J., Bly R. S.: *J. Amer. Chem. Soc.* 82, 142 (1960).
12. Wislicenus J., Seelers F.: *Chem. Ber.* 28, 2693 (1895).
13. *Technique of Organic Chemistry*, Vol. VII., *Organic Solvents* (A. Weissberger, Ed.). Interscience, New York, 1955.