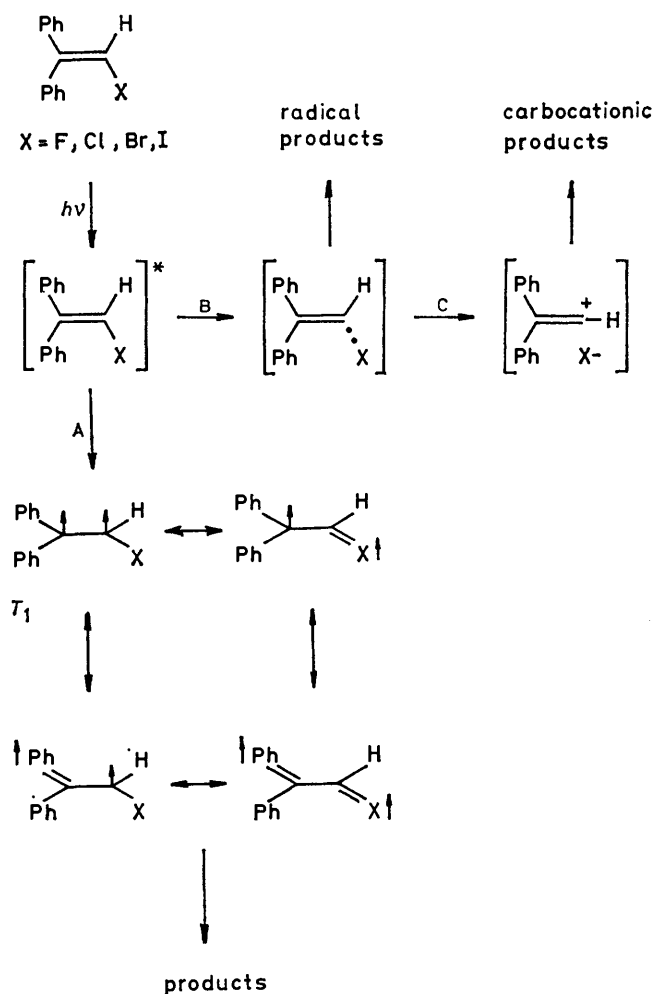


Photochemistry of 2-Halogeno-1,1-diphenylethylenes. The Photo-Fritsch-Buttenberg-Wiechell Rearrangement

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Competing ionic and radical photobehaviour has been observed for 2-halogeno-1,1-diphenylethylenes. Irradiation of 2-fluoro-1,1-diphenylethylene in cyclohexane or ether afforded *cis*- and *trans*-fluorostilbene. Irradiation of the chloro, bromo, or iodo analogues gave a complex mixture of up to eight products, the three major products being diphenylacetylene, 1,1-diphenylethylene, and 1,1,4,4-tetraphenylbutadiene. The product distribution proved to depend on the halogen and on the solvent. Benzophenone or xanthone sensitised irradiation of 2-fluoro-1,1-diphenylethylene in cyclohexane gave 1-cyclohexyl-1-fluoro-2,2-diphenylethane, while irradiation of 2-chloro-1,1-diphenylethylene gave 2-cyclohexyl-1,1-diphenylethylene.

THE photochemistry of alkyl halides has been the subject of extensive study over the years and has been recently reviewed.^{1,2} Earlier studies were conducted mainly in the gas phase,¹ but some reports of the photobehaviour in the liquid or solution state have also appeared.² In



these studies the common theme has been the formation of radical products, resulting from initial homolytic cleavage of the carbon-halogen bond.^{1,2} Kropp³ and his co-workers have observed competing ionic and radical photobehaviour for a number of alkyl halides.

The initially generated radical pair can undergo subsequent electron 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 now report results for 2-halogeno-1,1-diphenylethylenes which after irradiation can undergo either C-X bond cleavage, thus forming a radical pair (path B, Scheme 1), which upon subsequent electron transfer, can afford an ion pair (path C), or alternatively, undergo triplet state stabilisation (path A). The nature of the halogen-olefinic carbon bond (X = F, Cl, Br, or I) has a strong influence on the product distributions observed in photolysis of 2-halogeno-1,1-diphenylethylenes, which means that the proportion of each of the three paths A-C depends on the halogen.

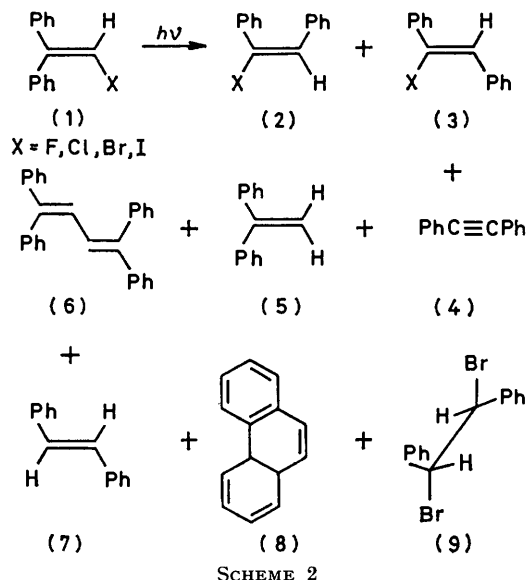
The photochemistry of 1,1-diphenylethylenes has been intensively studied. Rosenberg and Serve⁴ showed that irradiation of 1,1-diphenylethylene in propan-2-ol solution produced 1,1-dimethyl-2,2-diphenylpropyl alcohol, 2,2,3,3-tetraphenylbutane, and 2,3-dimethylbutane-2,3-diol. Irradiation of 2-bromo-1,1-bis-*p*-methoxyphenylethylene with sunlight in acetic acid resulted in the formation of the dimeric product 1,1,4,4-tetrakis-*p*-methoxyphenylbutadiene.⁵ Taniguchi *et al.*⁶ found that irradiation of 2-bromo-1,1-diphenylethylene in benzene resulted in the formation of 9-phenylphenanthrene and 1,1-diphenylethylene, while Zupan *et al.*⁷ observed that reaction in ether resulted in the formation of diphenylacetylene, 1,1-diphenylethylene, and 1,1,4,4-tetraphenylbutadiene. Taniguchi *et al.*⁶ also showed that the structure of the products formed by irradiation of 1,1-diaryl-2-bromoethylenes in benzene was largely independent of the substituents on the phenyl ring.

The dehydrohalogenation of olefins with hydrogen and halogen on the same carbon atom to acetylenes under basic conditions is known as the Fritsch-Buttenberg-Wiechell rearrangement,⁸ and has been studied in detail.⁹

RESULTS AND DISCUSSION

Irradiation for 15 h of 2-halogeno-1,1-diphenylethylene (1) (Scheme 2) in cyclohexane or ether (0.023M) at λ 253.7 nm resulted in a crude mixture. Products were

separated by preparative g.l.c. and identified by their n.m.r., mass, and i.r. spectra. As shown in Table 1, the number of products and their distribution depend on the halogen and also on the solvent used. Irradiation of 2-fluoro-1,1-diphenylethylene (1; X = F) resulted in the formation of only two products, *i.e.* *cis*- (2; X = F) and *trans*-fluorostilbene (3; X = F). The conversion of starting material was higher in cyclohexane than in



ether, the solvent also influencing the ratio of the products (2) : (3) (1.22 and 1.44 for cyclohexane and ether,

TABLE 1

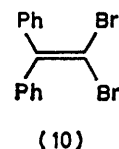
Product distribution from the irradiation of 2-halogeno-1,1-diphenylethylenes at λ 253.7 nm

Substrate (1)	Solvent	Product (%)							
		(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
X = F	EtOEt	13	9						
	cyclo-C ₆ H ₁₂	28	23						
X = Cl	EtOEt			25	28	10			
	cyclo-C ₆ H ₁₂	4		16					
X = Br	EtOEt			23	34	10			
	MeCOMe			28	37	10			
X = I	cyclo-C ₆ H ₁₂	3	4	3			12	5	12
	EtOEt			19	51	6			
	cyclo-C ₆ H ₁₂			9	51	6			

respectively). Irradiation of 2-fluoro-1,1-diphenylethylene at λ 253.7 nm in the presence of piperylene (triplet quencher^{4,10}) yielded a complex mixture of five products: *cis*- (2; X = F) and *trans*-fluorostilbene (3; X = F) in low yield, two cycloaddition products with piperylene as major products, and unchanged starting olefin (1). On the other hand, no photorearrangement occurred when the solution was irradiated at λ 350 nm.

Irradiation for 15 h of a cyclohexane solution of 2-chloro-1,1-diphenylethylene resulted in the formation of two products, diphenylacetylene (4) and *cis*-chlorostilbene (2; X = Cl), while irradiation in ether give three

products in high yield, diphenylacetylene (4), 1,1-diphenylethylene (5), and 1,1,4,4-tetraphenylbutadiene (6). Irradiation of 2-bromo-1,1-diphenylethylene (1) was carried out in ether, acetone, and cyclohexane. Only three products (4)–(6) (Table 1) were formed in ether or acetone solution, while in the case of cyclohexane six products were isolated: *cis*-bromostilbene, *trans*-bromostilbene, diphenylacetylene, *trans*-stilbene, phenanthrene, and *meso*-1,2-dibromo-1,2-diphenylethane. The solvent (ether or cyclohexane) only slightly affected the product distribution observed for irradiation of 2-iodo-1,1-diphenylethylene at λ 253.7 nm (Table 1); diphenylacetylene, 1,1-diphenylethylene, and 1,1,4,4-tetraphenylbutadiene were isolated.



We also studied the effect of solvent and wavelength on the product distribution for irradiation of 1,1-dibromo-2,2-diphenylethylene (10). Irradiation for 10 h of a cyclohexane solution (0.023M) at λ 253.7 nm resulted in the formation of seven products (Table 2), 2-bromo-1,1-diphenylethylene, *cis*-bromostilbene, *trans*-bromostilbene, diphenylacetylene, *trans*-stilbene, phenanthrene, and *meso*-1,2-dibromo-1,2-diphenylethane. Upon irradiating (10) at λ 300 nm, the quantity of (1) was raised to 25%, while the formation of (7) was diminished to 7% and product (2) was not formed at all (Table 2). Irradiation of (10) in ether at λ 253.7 nm

TABLE 2

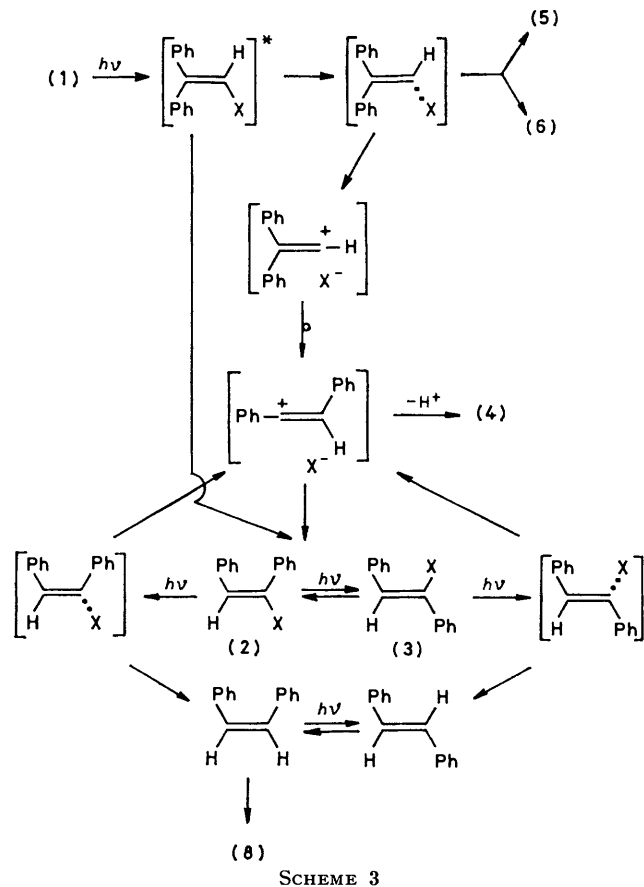
Product distribution from the irradiation of 1,1-dibromo-2,2-diphenylethylene (10)

Solvent	λ /nm	Product (%)							
		(1)	(2)	(3)	(4)	(5)	(7)	(8)	(9)
cyclo-C ₆ H ₁₂	253.7	4	2	7	6		14	2	15
	300	25		8	3		7		15
EtOEt	253.7	8			8	25			11

gave four products, 2-bromo-1,1-diphenylethylene, diphenylacetylene, 1,1-diphenylethylene, and phenanthrene. No phototransformation was observed when the solution was irradiated at λ 350 nm. In all irradiations some polymeric materials were formed.

An explanation for these phototransformations of 2-halogeno-1,1-diphenylethylenes (1) is presented in Scheme 3. In the first step the diphenylethylene molecule is converted into the singlet excited state (S_1), which can be further converted to the triplet state (T_1). The excited molecule can directly rearrange to *cis*- (2) or *trans*-halogenostilbene (3) or undergo C-X bond dissociation. The first type of transformation, *i.e.* direct rearrangement, operates in the case of 2-fluoro-1,1-diphenylethylene, where no C-F bond dissociation is possible, the dissociation energy for the C-F bond (520 kJ mol⁻¹) being considerably higher than the energy of

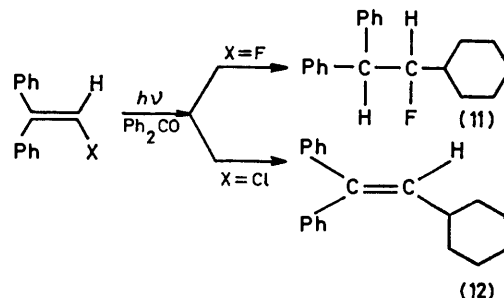
the exciting radiation (254 nm; 468 kJ mol⁻¹), while in the case of other halogens (X = Cl, Br, or I) C-X bond dissociation becomes a more important, if not the exclusive process. The formation of 1,1-diphenylethylene and 1,1,4,4-tetraphenylbutadiene by irradiation of the chloro, bromo, and iodo derivatives in ether solution (Table 1), could be ascribed to formation of free radical intermediates arising from homolytic C-X bond cleavage. However, the initially generated radical pair can undergo subsequent electron transfer to afford an ion pair, which can further undergo phenyl group migration, forming diphenylacetylene after proton loss,



while reaction with halide ion resulted in *cis*- or *trans*-halogenostilbene. *cis*- and *trans*-halogenostilbene can photoisomerise and undergo further homolytic C-X bond dissociation (X = Cl or Br), forming radical intermediates, which can be transformed into *cis*- or *trans*-stilbene or undergo subsequent electron transfer, thus affording an ion pair. *cis*- and *trans*-stilbene can photoisomerise and *cis*-stilbene can undergo cyclisation to phenanthrene (8). The absence of isolated *cis*-stilbene can be ascribed to photocyclisation to phenanthrene in the presence of halogens.

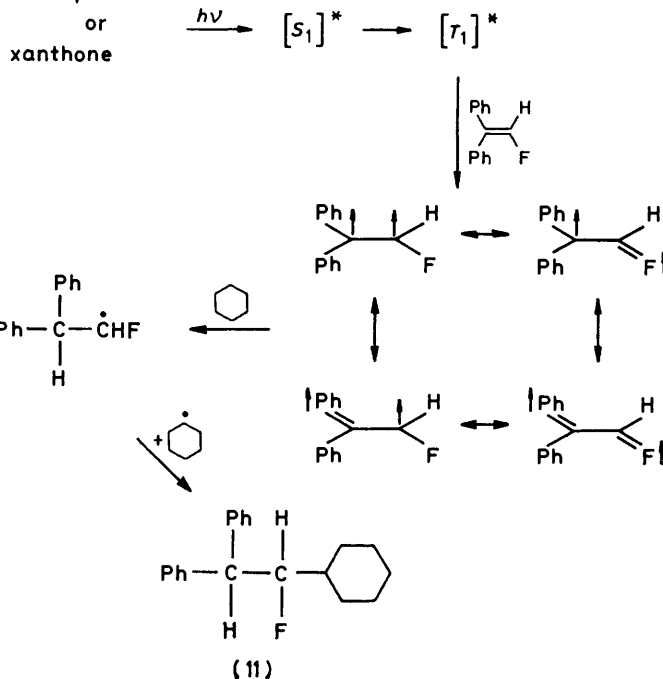
The fact that photorearrangement of 2-fluoro-1,1-diphenylethylene to *cis* and *trans*-fluorostilbene was quenched with piperylene (triplet quencher) suggested that triplet or long lived singlet states were involved and

stimulated us to study the photosensitized reactions. Irradiation of a cyclohexane solution of 2-fluoro-1,1-diphenylethylene of λ 350 nm in the presence of benzophenone or xanthone as sensitizer¹¹ resulted in the



formation of only one product, while irradiation in the presence of benzil as sensitizer did not lead to reaction. The product was isolated by preparative t.l.c. and showed in its ¹⁹F n.m.r. one signal at δ -213 p.p.m. (ddd, 51, 24, and 18 Hz). On the basis of n.m.r., i.r., and mass spectral data we have established that 1-cyclohexyl-1-fluoro-2,2-diphenylethane (11) (Scheme 4) was formed. Irradiation of a cyclohexane solution of 2-chloro-1,1-diphenylethylene in the presence of benzophenone resulted in the formation of one product, which was isolated by preparative g.l.c. and on the basis of i.r., n.m.r., and mass spectral data we have established that 2-cyclohexyl-1,1-diphenylethylene (12) was formed.

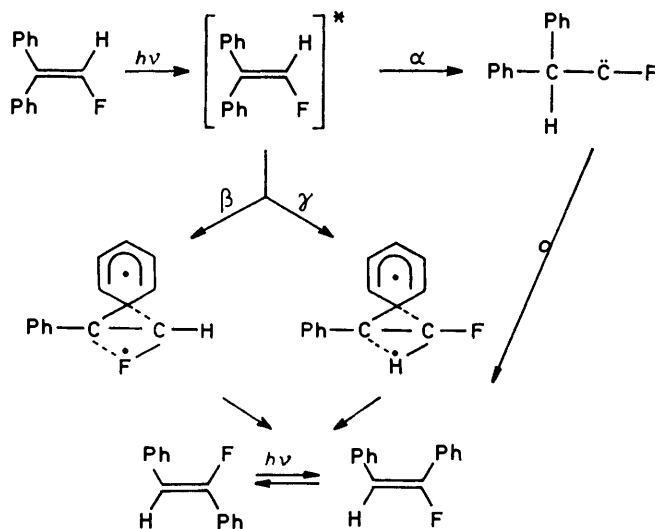
benzophenone



Irradiation of a cyclohexane solution of 2-bromo-1,1-diphenylethylene in the presence of benzophenone resulted in a complex mixture. Analysis by g.l.c.

showed that the reaction resulted in similar products to those observed for irradiation at λ 253.7 nm.

An explanation of the photorearrangement of 2-fluoro-1,1-diphenylethylene (1) without C-F bond cleavage is presented in Scheme 6. At least three different possibilities can be taken into account (α, β, δ , Scheme 6). The first possibility (α) is a 1,2-migration of the hydrogen atom, thus forming a carbene intermediate, which can further rearrange to *cis*- or *trans*-fluorostilbene. A carbene intermediate has already been suggested by Hixson¹² for the formation of 2-diphenylmethyl-1,1-dimethylcyclopropane and 9-*t*-butylphenanthrene by irradiation of 1,1-diphenyl-2-*t*-butylethylene. These products may also be formed *via* the excited singlet of the olefin which undergoes a 1,2-hydride shift. However, there are two possibilities for synchronous



SCHEME 6

shifts, *i.e.* the fluorine atom and a phenyl group (β), or a phenyl group and the hydrogen atom (γ). The fact that 2-fluoro-1,1-diphenylprop-1-ene remained unchanged when irradiated for 15 h at λ 253.7 nm reduced the possibility of phenyl group and fluorine atom migration.

However, one fact which supports a synchronous phenyl group and hydrogen atom shift, resulting in the formation of *cis*-fluorostilbene, is that the ratio of *cis*-: *trans*-fluorostilbene observed by photoisomerization of *cis*-fluorostilbene (*cis*:*trans* 1.22) is very similar to the ratio of *cis*- and *trans*-fluorostilbene (1.44) observed for photorearrangement of 2-fluoro-1,1-diphenylethylene, while the corresponding ratio for photoisomerization of *trans*-fluorostilbene is 0.77 (all data for irradiation for 15 h in ether). The fact that photorearrangement of 2-fluoro-1,1-diphenylethylene was quenched by piperylene initially suggested that the reaction proceeded *via* a triplet excited state.^{4,10} On the other hand the sensitized reactions (benzophenone, xanthone) showed that the triplet state of 2-fluoro-1,1-diphenylethylene readily reacted with cyclohexane forming 1-cyclohexyl-1-fluoro-2,2-diphenylethane. The photorearrangement probably occurred therefore *via* a singlet excited state

which was sufficiently long lived to be quenched by piperylene.

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 137 spectrometer, and ¹H and ¹⁹F n.m.r. spectra with a JEOL-JMN-PS-100 instrument for solutions in CCl₄ or CDCl₃ with Me₄Si or CCl₃F as internal reference. Mass spectra (including high resolution) were taken with CED-21-110 instrument. G.l.c. was carried out on a Varian Aerograph 1800 instrument and preparative t.l.c. on Merck-DC-Fertigplatten Kieselgel F 254 (2 mm). M.p.s were determined on a Kofler 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 2-fluoro-1,1-diphenylethylene,¹³ 2-chloro-1,1-diphenylethylene,⁸ 2-bromo-1,1-diphenylethylene,¹⁴ and 2-iodo-1,1-diphenylethylene¹⁵ were synthesized and purified by g.l.c. before use. Solvents were purified.¹⁶

Irradiation of 2-Halogeno-1,1-diphenylethylenes.—2-Halogeno-1,1-diphenylethylene (4.1 mmol) was dissolved in cyclohexane (180 ml) and the solution was irradiated for 15 h at λ 253.7 nm at room temperature. The solvent was evaporated *in vacuo* and the crude mixture was analysed.

2-Fluoro-1,1-diphenylethylene. The reaction mixture contained three products, 2-fluoro-1,1-diphenylethylene (49%) *cis*-fluorostilbene (28%), and *trans*-fluorostilbene (23%). The products were separated by preparative g.l.c. (Carbowax 20 M; 30% Varaport 30 70—80 mesh; 240 °C).

2-Chloro-1,1-diphenylethylene. Products were isolated by preparative g.l.c. (OV 1; 10% Varaport 30 70—80 mesh; 240 °C). Besides unchanged 2-chloro-1,1-diphenylethylene, *cis*-chlorostilbene (4%) and diphenylacetylene (16%) were isolated.

2-Bromo-1,1-diphenylethylene. The solvent was evaporated *in vacuo*, the residue was dissolved in *n*-hexane (10 ml) and crystalline *meso*-1,2-dibromo-1,2-diphenylethane (12%) was filtered off and the filtrate separated by preparative g.l.c. (OV 1; Varaport 30 70—80 mesh; 240 °C); 2-bromo-1,1-diphenylethylene (6.5%), *cis*-bromostilbene (3%), *trans*-bromostilbene (4%), *trans*-stilbene (12%), phenanthrene (5%), and diphenylacetylene (3%) were isolated.

2-Iodo-1,1-diphenylethylene. The reaction mixture was separated by preparative t.l.c. (SiO₂; cyclohexane—methylene chloride—triethylamine 95:4:1). The mixture of products with higher *R_F* values was again separated by preparative g.l.c. (OV 1; 10% Varaport 30 70—80 mesh; 140 °C) and diphenylacetylene (19%), and 1,1-diphenylethylene (51%) were isolated. The fluorescent product with the lowest *R_F* value proved to be 1,1,4,4-tetraphenylbutadiene (6%).

Products were identified by comparison of their i.r., n.m.r., and mass spectra with those of authentic samples.¹⁷

2-Halogeno-1,1-diphenylethylenes were also irradiated in ether. The product distributions are stated in Table 1.

Irradiation of 1,1-Dibromo-2,2-diphenylethylene.—1,1-Dibromo-2,2-diphenylethylene (0.338 g) was dissolved in cyclohexane (60 ml) and the solution was irradiated for 15 h at λ 253.7 nm at room temperature. The solvent was evaporated *in vacuo* and the crude mixture was separated by preparative t.l.c. (SiO₂; cyclohexane—methylene chloride

95:5). The mixture of products was again separated by preparative t.l.c. (OV 1, 10% Varaport 30 70–80 mesh; 240 °C) and 2-bromo-1,1-diphenylethylene (11.6 g, 4%), *cis*-bromostilbene (5.8 mg, 2%), *trans*-bromostilbene (18 mg, 7%), diphenylacetylene (10.7 mg, 6%), *trans*-stilbene (25.4 mg, 14%), phenanthrene (3, 5 mg, 2%), and *meso*-1,2-dibromo-1,2-diphenylethane (51 mg, 15%) were isolated. Products were identified by comparison of their i.r., n.m.r., and mass spectra with those of authentic samples.

1,1-Dibromo-2,2-diphenylethylene was also irradiated in ether and in cyclohexane at λ 300 nm. Product distributions are stated in Table 2.

Irradiation of 2-Fluoro-1,1-diphenylethylene in the Presence of Benzophenone or Xanthone.—2-Fluoro-1,1-diphenylethylene (82 mg) and benzophenone (750 mg) were dissolved in cyclohexane (18 ml) and the solution was irradiated for 15 h at λ 350 nm. The solvent was evaporated *in vacuo* and the crude mixture was separated by preparative t.l.c. (SiO₂; cyclohexane–methylene chloride–triethylamine 95:4:1) and 1-cyclohexyl-1-fluoro-1,1-diphenylethane (60 mg, 52%), liquid product, was isolated, δ_F –213 p.p.m. (ddd, *J* 51, 24, and 18 Hz), δ_H 7.12 (10 H, m), 4.66 (1 H, ddd, *J* 51 Hz, 6, and 6 Hz), 4.04 (1 H, dd, *J* 24 and 6 Hz), and 2.0–0.8 (11 H, m) (Found: M^+ , 282.1772. Calc. for C₂₀H₂₃F: M , 282.1784), *m/e* 282 (M^+ , 50), 162 (M^+ – HF, 100), 261 (80), 248 (47), 205 (53), 180 (90), 167 (73), 165 (43), and 83 (57).

Irradiation of 2-Chloro-1,1-diphenylethylene in the Presence of Benzophenone.—2-Chloro-1,1-diphenylethylene (88 mg) and benzophenone (750 mg) were dissolved in cyclohexane (18 ml) and the solution was irradiated for 15 h at λ 350 nm at room temperature. The solvent was evaporated *in vacuo* and the crude mixture was separated by preparative t.l.c. (SiO₂; cyclohexane–chloroform 9:1). 2-Cyclohexyl-

1,1-diphenylethylene (56 mg, 52%), was isolated. The product was identified by comparison of its n.m.r., i.r., and mass spectral data with those of an independently prepared sample.¹⁸

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