

PHOTOREARRANGEMENT OF 1,1-DIPHENYL-2-FLUOROETHYLENE TO  
CIS- AND TRANS-FLUOROSTILBENE

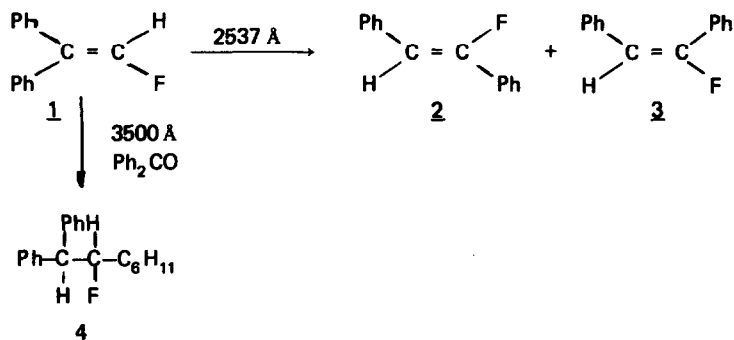
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(Received in UK 2 November 1976; accepted for publication 6 December 1976)

Several authors have shown that the excited triplet state of 1,1-diphenyl-ethylene has the ability to abstract hydrogen, similar to that of the lowest triplet of benzophenone<sup>1,2,3</sup>. On the other hand, some (2+2) cycloaddition reactions were observed with various olefins, which proceed via the excited triplet<sup>3</sup>. The study of the photochemical migration reactions of  $\beta$ -substituted styrenes and 1,1-diphenyl-ethylenes has proved to be interesting area for research<sup>5</sup>. In such systems, the most commonly observed photochemical process is the 1,2 migration of a  $\gamma$ -substituent to form a cyclopropane, though other migration processes have been noted<sup>6</sup>. S.S. Hixson<sup>7</sup> found that irradiation of  $\beta$ -tert-butyl-1,1-diphenylethylene produced 1-benzhydryl-2,2-dimethylcyclopropane and 9-tert-butylphenanthrene. He explained the unusual reactivity by the excited singlet state of olefin, which undergoes a 1,2-shift of its vinyl hydrogen to form carbene.

We now report results of irradiation of 1,1-diphenyl-2-fluoroethylene (**1**) in cyclohexane and of irradiation in the presence of benzophenone. A 15-hr. irradiation of (**1**) (0.023 M) at 2537 Å in cyclohexane resulted in a crude reaction

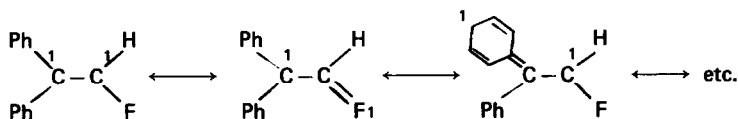


mixture of three compounds, i.e.: 49 % of starting material (**1**), 28 % of cis-fluorostilbene (**3**) and 23 % of trans-fluorostilbene (**2**) (calculated from <sup>19</sup>F integrals), which could be separated by preparative GLC and identified by their n.m.r. and mass spectra. Irradiation of **1** at 2537 Å in the presence of piperylene (triplet quencher<sup>2,3,4</sup>) yielded a complex reaction mixture of five products: cis (**3**)–

and trans (2) – fluorostilbene in low yield, two cycloaddition products with piperylene as major product and unreacted starting olefin (1). On the other hand, no photorearrangement occurred when irradiated at 3500 Å.

Furthermore, 1,1-diphenyl-2-fluoropropene remained unchanged when irradiated 15-hr. at 2537 Å. Benzophenone ( $E_t = 68$  kcal/mol) sensitized photolysis of 1 at 3500 Å, thus resulting in formation by one hydrogen abstraction of an oily product, 1,1-diphenyl-2-fluoro-2-cyclohexylethane (4), which could be purified by preparative t.l.c. and isolated in a 50% yield. Compound 4 was identified by n.m.r. ( $\delta F-213$  (ddd, J 51 Hz, 24 Hz, 18 Hz),  $\delta -CFH-$  4.66 (ddd, 1H, 51, 6, 25 Hz),  $\delta -C\Phi_2H-$  4.04 (dd, 1H, 24, 6 Hz),  $\delta \Phi$  7.12 (m, 10 H),  $\delta C_6H_{11}-$  2.0 – 0.8 (m, 11 H)) and mass spectral data (calcd. for  $C_{20}H_{23}F = 282.1784$ , found m/e 282.1772, m/e: 282 ( $M^+$ , 5%), 262 ( $M^+ - HF$ , 100%), 261 (80), 248 (47), 205 (53), 180 (90), 167 (73), 165 (43), 83 (57)).

The product formed in this sensitized photolysis indicates a different reaction pathway from that in the case of unsubstituted diphenylethylene, where group R enters at position 1, thus forming 1,1-diphenyl-1-R-substituted ethanes. Formation of (4) could be explained by strongly induced electron delocalization, so that the reaction sites in this biradical species resemble free radicals.



A similar explanation was suggested for diphenylethenes and benzophenone<sup>23</sup>. However, the investigation of the mechanism of photorearrangement of 1,1-diphenylethylene to cis- and trans-fluorostilbene with possible formation of carbene intermediate observed earlier<sup>7</sup> is in progress.

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