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# DEMETHYLATION DURING OXIDATIVE PHOTOCYCLIZATION OF AN ORTHO-METHYLSTILBENE

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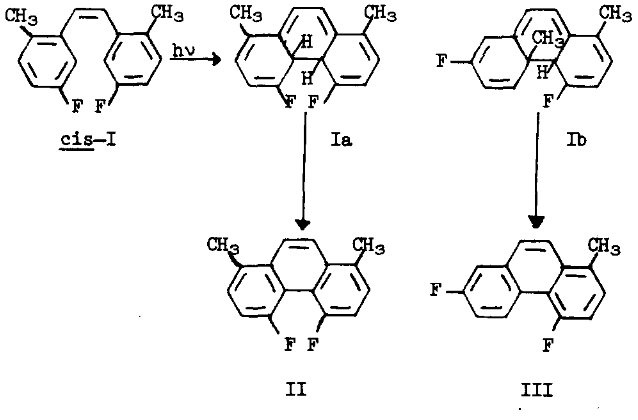
The photoconversion of trienes to aromatic systems is one of the most extensively studied photochemical oxidations (1). A prime example of such a reaction is the oxidative cyclization of cis-stilbene to phenanthrene (2). Stilbenes bearing a variety of substituents (F, Cl, Br, $CH_3$, $CH_3O$, $CF_3$, $C_6H_5$, $CO_2H$) have been found to undergo this photochemical conversion to the corresponding phenanthrene (3). In these reactions, oxidative loss of H–H from the detectable dihydrophenanthrene intermediate leads to the phenanthrene product (4). Formal loss of the elements of H–$CH_3$ (instead of H–H) from an o-methyl stilbene has not previously been observed (5). We have found that the photolytic cyclooxidation of 2,2'-dimethyl-5,5'-difluorostilbene (I) occurs, in part, by loss of H–$CH_3$ to give 1-methyl-4,7-difluorophenanthrene (III) as well as the expected 1,8-dimethyl-4,5-difluorophenanthrene (II).



Diethyl 2-methyl-5-fluorobenzyl phosphonate, prepared from triethyl phosphite and 2-methyl-5-fluorobenzyl chloride, gave upon treatment with sodium hydride in the presence of 2-methyl-5-fluorobenzaldehyde a 70% yield of 2,2'-dimethyl-5,5-difluoro-*trans*-stilbene (I), m.p. 117°. The structure of I was established by its method of synthesis and elemental analysis in conjunction with its infrared, ultraviolet and nmr spectral properties. Alumina chromatography of the product mixture resulting from the photolysis of I by the Mallory procedure gave, after recrystallisation, a 49% yield of II, m.p. 103.5°, and a 13% yield of III, m.p. 56-57°.

The structure of II was established on the basis of its elemental analysis together with its infrared, ultraviolet, and nmr spectral properties. It exhibits a typical phenanthrene ultraviolet absorption,[$\nu_{max}^{C_6H_{12}}$ 248 mμ (log ε 4.9)] infrared absorption, ($\nu_{max}^{CS_2}$ 1250, 818, 735, 703 $cm^{-1}$) characteristic of a fluoro phenanthrene with this symmetry, and the expected $^1H$ nmr absorptions (δ ppm) 2.58 (singlet - 6H), 6.90 - 7.30 (multiplet - 4H), 7.65 (triplet - 2H) and a single $^1F$ absorption 59.2 ppm downfield from hexafluorobenzene.

The structure of III was also established on the basis of its elemental analysis together with its spectral properties. It exhibits a typical phenanthrene ultraviolet absorption ($\nu_{max}^{cyclohexane}$ 249 mμ (log ε 5.0)) and infrared absorptions ($\nu_{max}^{CS_2}$ 1250, 1210, 1158, 1130, 1071, 950, 863, 826, 815, 775, 735, 700, 602 and 591 $cm^{-1}$) indicative of a fluoro-phenanthrene with very low symmetry. In the $^1H$ nmr spectrum resonance characteristic of a single methyl group at 2.42 ppm, six aromatic protons at 6.88 - 7.65 ppm and a single 4-phenanthryl proton at 8.91 ppm were observed; in addition, two $^{19}F$ resonances of equal intensity were observed at 49.0 and 50.5 ppm downfield from $C_6F_6$.

The presence of adjacent hydrogen atoms at the 5 and 6 positions in III is established by the $^1H$ nmr spectrum. The resonance at 8.90 ppm is characteristic of hydrogens in the 4 or 5 position of phenanthrene (7). The location of the F nucleus at position 7 (as opposed to 6 or 8) is not definitely established but is reasonable based on the proposed mechanism of formation of III. No rearrangements of substituents have been observed in the stilbene to phenanthrene photolysis (1,8). Infrared studies of the initial photolysis solution verify that the formation of III is an initial process and not a subsequent reaction. Both II and III were found to be stable under the photolytic conditions.

The intermediate dihydrophenanthrene formed in these solutions is thought to have trans-substituents which are lost in a two–step process (2).

Hydrogen atom abstraction from the corresponding dihydro–derivative, Ib, formed from I followed by loss of a methyl radical could account for the formation of III (9). No evidence bearing on the eventual fate of the eliminated methyl group is yet available.

## References

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4. W. M. Moore, D. D. Morgan, F. R. Stermitz, J.Am.Chem.Soc., 85, 829 (1963).
5. a) Spectroscopic evidence for the loss of H–$OCH_3$ during the photolysis of o–methoxy stilbene has been reported (3). 2,3–Dimethylphenanthrene has been found to be one of the products of photocyclization of 2–methoxy–4,5–dimethyl stilbene (6). o–Chlorostilbene and o–methylstilbene were shown not to be photoconverted to phenanthrene (3).
6. Reference 3, footnote 6.
7. N. Jonathan, S. Gordon, and B. P. Dailey, J.Chem.Phys., 36, 2443 (1962);
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