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PHOTODEHYDROCYCLIZATIONS OF STILBENES AND STILBENE-LIKE COMPOUNDS IN THE PRESENCE OF π-ACCEPTORS

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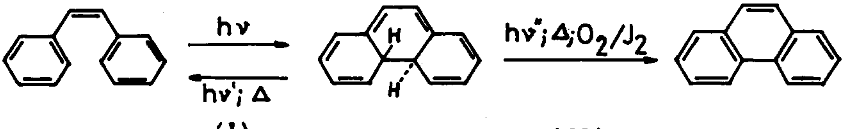
The oxidative photodehydrocyclization of stilbenes[1], substituted stilbenes[2], other 1,2-diaryl-substituted ethylenes[3] and further stilbene-like compounds[4] generally proceeds by the partial steps (I) and (II)[5].



(I) (II)

This elegant and widely used method for the preparation of various condensed aromatic hydrocarbons and their derivatives has the drawback, depending on the substrates and conditions of hydrogen abstraction employed (II), of giving less or more low yields and forming by-products (e. g. photooxides etc.) that are often difficult to separate.

Investigating substituted stilbenes and other 1,2-diaryl-substituted ethylenes in the presence of π-acceptors[6] we observed an extremely rapid formation of condensed aromatic hydrocarbons which are derived from the stilbenes (Table 1 lists several of the polycyclic aromatic hydrocarbons prepared by this procedure). When using equimolar amounts of the given trans-stilbene as the donor and an appropriate π-acceptor (Table 2) in methylene chloride ($c = 1 \cdot 10^{-2}$ M/l), a practically complete conversion takes place according to (I) and (II) through irradiation into the longest-wave absorption band of the respective stilbene, the aromatic hydrocarbon precipitating in excellent purity.

Under anaerobic conditions and, if required, at low temperature, irradiation in the absence of a π-acceptor causes, aside from the cis-forms of stilbenes, a spectroscopically detectable enrichment of the dihydro-cyclization products which are being oxidized instantaneously to give the corresponding aromatic systems on addition of the π-acceptor. As a result, the latter are converted into the hydrogenated derivatives listed in Table 2. Most advantageous proved the use of tetracyanoethylene as the hydrogen abstractor because its intrinsic absorption which is below 280 nm ensures, on irradiation into the donor, excitation of the latter only, thus entirely avoiding the usual photoreactions between olefinic double bonds and the π-acceptor employed.

By-products, such as photooxides etc., resulting from the photoreaction were not observed in any appreciable amounts. The identification of the photolytic products was done by comparing their melting points, UV, IR and NMR spectra with the relevant literature data.

Table 1.

π-Donors	Photodehydro-cyclization Products
Stilbene	Phenanthrene
4,4'-Dimethoxy-stilbene	3,6-Dimethoxy-phenanthrene
1-(1-Naphthyl)-2-phenyl-ethylene	Chrysene
1-(2-Naphthyl)-2-phenyl-ethylene	Benzo[c]phenanthrene
1,2-Bis-(1-naphthyl)-ethylene	Picene
1,2-Bis-(2-naphthyl)-ethylene	Dibenzo[b,h]phenanthrene

Table 2.

π-Acceptors	Dihydro-products
Tetracyanoethylene	1,1,2,2-Tetracyanoethane
Tetracyanoquinodimethane	1,4-Bis-(dicyanomethyl)-benzene
Chloranil	Tetrachloro-p-hydroquinone
Bromanil	Tetrabromo-p-hydroquinone

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