Photochemical Formation of an Anthracene from 4,4′-Diethoxycarbonylstilbene

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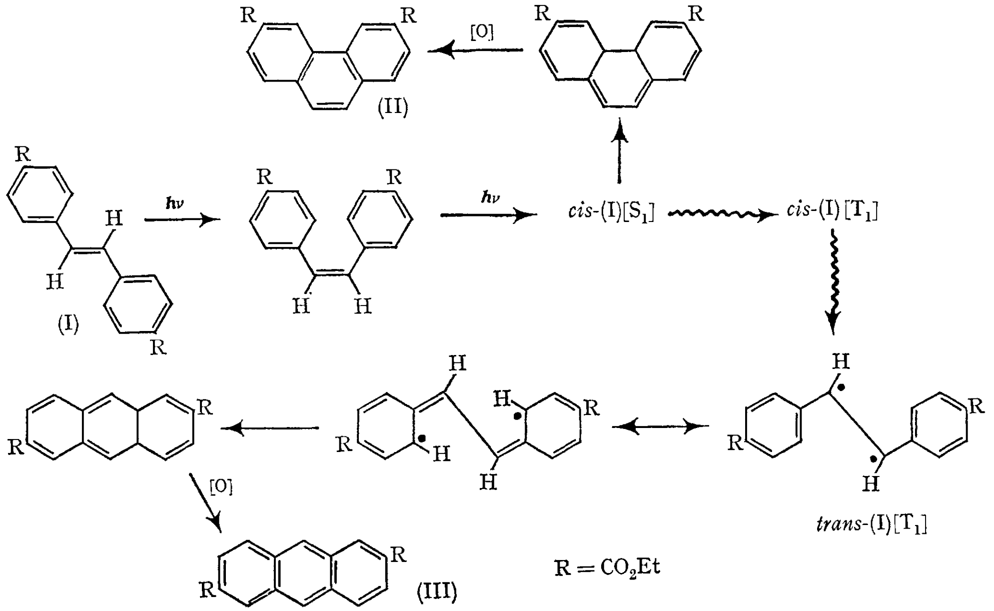
THE irradiation of stilbenes by u.v. light,[1] has been found to lead to either isomerization, the formation of phenanthrenes, or, at sufficiently high concentrations, dimerization to cyclobutane derivatives. We now report the photo-formation of a substituted anthracene from a stilbene.

A solution of 4,4′-diethoxycarbonylstilbene (I) (1·6 g.) in AnalaR n-butanol (1 l.) was irradiated in a falling-film apparatus[2] with a 20w fluorescent u.v. lamp. This source has an emission which is approximately Gaussian ($\lambda_{max} = 350$ nm.).[3] The reaction was followed spectrophotometrically and irradiation was terminated when no further significant change was observed (18 hr.).

The photolysis products were separated by column chromatography and were identified as 3,6-diethoxycarbonylphenanthrene (II) and as 2,6-diethoxycarbonylanthracene (III). The ratio of phenanthrene (II) to anthracene (III) was approximately 4 : 1. The u.v. absorption spectrum of compound (II) $C_{20}H_{18}O_4$ (m.p. 159—161°) was consistent with that of a substituted phenanthrene and the u.v. absorption spectrum of compound (III) $C_{20}H_{18}O_4$ (m.p. 199—200°) consistent with that of a substituted anthracene. The n.m.r. spectra determined at 100 MHz in trifluoroacetic acid were in both cases consistent with symmetrical structures having two 1,2,4-trisubstituted benzene rings and a third ring carrying two equivalent protons. For compound (II) the chemical shifts (relative to Me_4Si) of the aromatic protons were 7·92, 8·22, and 9·42 p.p.m. for the protons on the 1,2,4-trisubstituted rings, and 7·84 p.p.m. for the two remaining protons. For compound (III) the spectrum showed that two protons on the trisubstituted rings were equivalent (8·03 p.p.m.) and the other proton gave a signal at 8·54 p.p.m. The two protons on the third ring resonated at 8·82 p.p.m.

The oxidation of compound (III) gave a quinone $C_{20}H_{16}O_6$ (IV) which had u.v. and i.r. absorption spectra and melting point identical with those obtained from 2,6-diethoxycarbonylanthraquinone (m.p. 218—220°).[4] A mixed melting point of (IV) with an authentic sample of 2,6-diethoxycarbonylanthraquinone gave no depression.

It would seem that the anthracene is formed from an excited *trans*-stilbene, since it is highly unlikely that C–C bond-fission of the ethylenic bond has occurred as a result of irradiation at the wavelengths employed. The following reaction mechanism is tentatively proposed (Figure). Irradiation of the starting material of predominantly *trans*-configuration yields *cis*-stilbene in a fast isomerization reaction. A second photon promotes the *cis*-isomer to a singlet excited state which can either close the rings to yield a dihydrophenanthrene or cross over to the triplet excited



$R = CO_2Et$

state. In the triplet state the ethylenic double bond is opened and the molecule can revert to a *transoid* conformation.

The anthracene structure can then be formed by a double ring-closure with subsequent loss of two hydrogen atoms. The possibility of the formation of a Dewar anthracene derivative as intermediate cannot be excluded.

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[2] S. D. Cohen, M. V. Mijovic, G. A. Newman, and E. Pitts, *Chem. and Ind.*, 1967, 1079.

[3] Philips Electrical Ltd. Data Sheet "Black Light" Lamps.

[4] Ch. Seer, *Monatsh.*, 1911, **32**, 163.