Photolysis of 4,5-Diphenyl-oxazoles, -thiazoles, and -imidazoles. Formation of Phenanthro[9,10-*d*]-heterocyclic Systems

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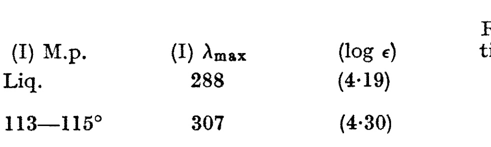
THE photocyclization of *cis*-stilbenes to give phenanthrene derivatives is widely used.[1–3] We report an extension of this reaction which provides a convenient preparation of heterocyclic systems incorporating the phenanthrene component. During photo-oxidation studies we found that u.v. irradiation of (I) gives (II) in good yield with no side products.



a, X=O, R=Me; b, X=O, R=Ph
c, X=S, R=Me; d, X=NH, R=H
e, X=NH, R=Ph; f, X=NPh, RPh

The photolyses were carried out in ethanol (1 g./150 ml.) open to the air, in the presence of iodine, and with a Rayonet photoreactor (RS, 3000 Å, 85 w.) as irradiation source.[1,†] The u.v. spectra of the mixtures show the gradual disappearance of absorption at λ_{max} (EtOH) 285—288 mμ (log ε 4·09—4·20) due to the *cis*-stilbene chromophore and the appearance of characteristic phenanthrene absorption

TABLE

	(I) M.p.	(I) λ_{max}	(log ε)	Reaction time (hr.)	Yield (%)	(II) M.p. found (lit.)	(II) λ_{max}	(log ε)
a:	Liq.	288	(4·19)	12·5	55	147—148° (145°[a])	255 302	(4·71) (3·93)
b:	113—115°	307	(4·30)	†	47	203—204 (204°[b])	260 302	(4·69) (4·12)
c:	51—52	288	(4·04)	6·25	87	144—145 (145°[c])	254 304	(4·69) (3·90)
d:	231—233	285	(4·06)	12	75	302° subl. (292°[d])	255 301	(4·92) (3·89)
e:	274—278	308	(4·34)	55	40	320—321 (314°[d])	261 310	(4·75) (4·27)
f:	215—218	285	(4·20)	3	90	198—201	260 306	(4·83) (4·20)

All products are known compounds except (IIf) [Found: C, 87·25, H, 5·0, N, 7·3%; *M* (mass spec.) 370]. [a] A. Schönberg and W. I. Awad, *J. Chem. Soc.*, 1947, **651**; [b] A. Schönberg, N. Latif, R. Monbasher, and W. I. Awad, *J. Chem. Soc.*, 1950, 374; [c] ref. 5; [d] E.A. Streck and A. R. Day, *J. Amer. Chem. Soc.*, 1943, **65**, 452.

[†] As observed by D. W. Kurtz and H. Schecter, *Chem. Comm.*, 1966, 689, the photolysis of (Ib) in the presence of oxygen leads to photo-oxidation. Thus, under the conditions described above, *NN*-dibenzoylbenzamide was the isolated product. However, by degassing the reaction mixture (10^{-6} mm.) and increasing the reaction time (12 days) the phenanthrene (IIb) was isolated in 46% yield.

at λ_{max} (EtOH) 245—260 mμ (log ε 4·69—4·83). Chromatography of the product on deactivated silica gel ($CHCl_3$) with ether–hexane as eluant gave the compounds listed in the Table. In addition to the u.v. spectral changes noted above, the n.m.r. spectra of the products exhibit characteristic low field (τ 1—2) peaks for phenanthrenes.[4] As expected, i.r. absorption (1600 and 700 cm.$^{-1}$, monosubst. Ph) disappears in the conversion of (Ia,c,d) into (IIa,c,d). Mass spectra show the expected parent peaks and correct molecular masses for (II).

Previous syntheses of (II), based on phenanthrene derivatives or phenanthrenequinone, gave poor overall yields;[5] the possibility of obtaining unsymmetrically substituted phenanthrene rings was also limited. Our method provides a route from the appropriately substituted benzoins.[1]

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