The Photolysis of 1,2,5-Oxadiazoles, 1,2,5-Thiadiazoles, and 2*H*-1,2,3-Triazoles

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THE photochemical behaviour of five-membered ring aromatic heterocycles is of considerable interest. Thiophens,[1] isoxazoles,[2,3] and certain pyrazoles and imidazoles[4] undergo a transposition of ring atoms reminiscent of the behaviour of benzene derivatives on photolysis and which proceeds in at least one case by a ring contraction–ring expansion sequence. By contrast, 1*H*-1,2,3-triazoles[5] and 1,2,4-oxadiazoles[6] undergo cleavages and rearrangements unique to those heterocyclic systems.

We report here a new photolytic cleavage which we have observed in 1,2,5-oxadiazoles, 1,2,5-thiadiazoles, and 2*H*-1,2,3-triazoles, in which two the ring bonds are broken. Irradiation† of 3,4-diphenyl-1,2,5-oxadiazole (Ia) in ether (0·5%) through a Corex filter until all starting material was consumed (4 hr.) gave benzonitrile (82%) and phenyl isocyanate (48% by g.l.c.; 53% as *NN'*-diphenylurea).‡ Irradiation in methanol gave the same products in comparable yield when rapid workup was employed, but delay caused conversion of the phenyl isocyanate into methyl *N*-phenylcarbamate. Similarly, after irradiation of a 1% solution of 3,4-dimethyl-1,2,5-oxadiazole (Ib) in ether through a Vycor filter for 36 hours, there was isolated, in addition to 30% of unchanged (Ib), acetonitrile (41%) and an intractable tar. No methyl isocyanate or its expected hydrolysis products were observed. However, the photolysis of (Ib), when conducted in the presence of a ten-fold excess of cyclopentene, produced, besides acetonitrile, an adduct of cyclopentene and the expected acetonitrile oxide, the isoxazoline (IV) (23%); b.p. 52—55°/0·5 mm.; $\nu_{\max}$ (film) 879 cm.$^{-1}$; τ 5·03 (1 H, pair of multiplets, Hα to oxygen); 6·5/(1 H, m, allylic methine H); 8·09 (3 H, d, *J* 0·8, methyl on C=N); 8·2—8·6 (6 H, multiplets, methylene H's). Irradiation of (Ia) in the presence of cyclopentene gave only benzonitrile and phenyl isocyanate in yields similar to those obtained in its absence. One report has appeared on the photochemical rearrangement of an aryl nitrile oxide to the corresponding isocyanate, possibly *via* an oxirene intermediate. The failure to trap benzonitrile oxide by 1,3-dipolar addition during the photolysis of (Ia) suggests that the rearrangement is faster for benzonitrile oxide than the ground state 1,3-dipolar addition to cyclopentene. Alternatively, an excited benzonitrile oxide fragment rearranges directly to the isocyanate. However, the latter possibility is militated against by the failure to observe methyl isocyanate or its hydrolysis products in the photolysis of (Ib).

Irradiation of 3,4-diphenyl-1,2,5-thiadiazole (IIa) in ether (0·5%) through Corex gave benzonitrile (12%) and elemental sulphur (21%). Similarly, 3·4-dimethyl-1,2,5-thiadiazole (IIb) in ether (1%) gave, after 96 hr. irradiation through Vycor, acetonitrile (35%) and sulphur (32%). Attempts to trap intermediate nitrile sulphides from (IIa) and (IIb) failed.

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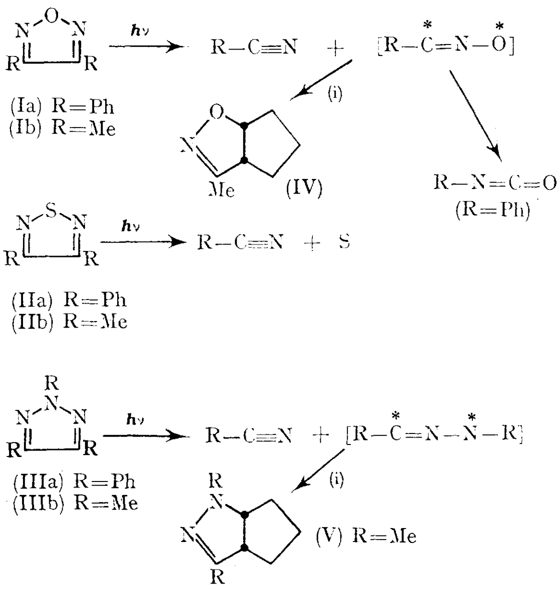
† The light source was a 450 w Hanovia medium-pressure mercury arc surrounded by the filters noted.

‡ This reaction was first performed by Mr. W. C. Timmins in these laboratories.

Irradiation of 2,4,5-triphenyl-2*H*-1,2,3-triazole (IIIa) in several solvents with light of various wavelengths gave no reaction. However, 2,4,5-di-2*H*-methyl-1,2,3-triazole (IIIb) when irradiated through Vycor as a 1% ether solution, gave acetonitrile (22%) and an oil, b.p. 58—63°/0·5 mm. which gas chromatography indicated was composed of at least ten components. When the irradiation of (IIIb) was conducted in the presence of an excess of cyclopentene there was isolated the pyrazoline derivatives (V) [(25%; b.p./0·5 mm.; ν_{max} (film) 1597 cm.$^{-1}$; 6·56 (1 H, m, H_α to nitrogen); 7·38 (3 H, s, *N*-methyl); 7·79 (1 H, pair of doublets, *J* 8·2, *J'* 2·7, H on C=N), 8·20 (3 H, s, *C*-methyl); 8·25—8·50 (6 H, methylenes)].



(i) cyclopentene

In experiments on (Ia) using xanthone as a triplet sensitizer under conditions such that the xanthone absorbed 99% of the incident light, benzonitrile was produced at a rate *ca.* 12% of that in the direct irradiation; (Ia) disappeared at a similar rate. It thus appears that the cleavage of (Ia), and probably that of the other heterocycles studied, occurs predominantly in a singlet excited state. These double fragmentations are in interesting contrast to the one-bond cleavage observed in the photolysis of 3,5-diphenyl-1,2,4-oxadiazole and are reminiscent of the thermal splitting of (Ia) to give benzonitrile and phenyl isocyanate.[7,8] Further studies in this area are in progress and will be the subject of a future report.

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