A Convenient Synthesis of 1,4-Dinitriles from Furazans by Ultraviolet Irradiation

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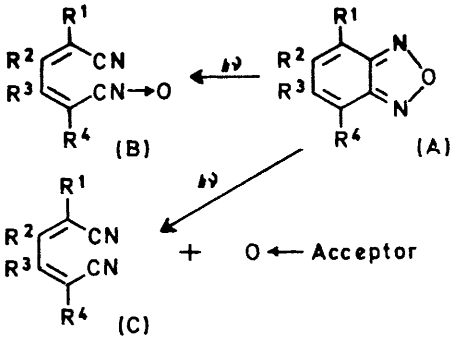
Summary In the presence of triethyl phosphite, irradiation of the furazan derivatives (A) afforded 1,4-dinitrile derivatives (C) in very good yields.

THE photoreaction of oximes,[1] including α-dioximes,[2] has been studied in several laboratories.† In connection with α-dioximes we have investigated the photoreaction of 3,4-diphenyl-1,2,5-oxadiazole, from which products resulting from fragmentation[3] of the furazan ring and from recombination[4] of the fragments were obtained. However, we have also found that some oxadiazoles (A) such as benzo- (I), naphtho- (II), and phenanthro-furazans (III), upon irradiation, afford a very complex mixture of photoproducts. Such behaviour can be explained by the formation of a reactive intermediate of the type (B), possessing a nitrile oxide group. In order to obtain a clean reaction, the irradiation of (I), (II), or (III) was carried out in the presence of a reagent capable of reducing the nitrile oxide group to the nitrile group. As we expected, the photoreaction afforded the corresponding 1,4-dinitriles of the type (C), in high yield.



When a solution of (I) (600 mg, 5 mmole) dissolved in benzene (500 ml) was externally irradiated in the presence of triethyl phosphite (1·245 g, 7·5 mmole) in a Pyrex vessel using a high-pressure mercury lamp (Toshiba H 400-p); *cis-cis*-1,4-dicyanobuta-1,3-diene (IV), m.p. 128°,[5] was obtained in 80% yield accompanied by the *cis,trans*-isomer, m.p. 72°,[6] and the *trans,trans*-isomer, m.p. 160°,[5,6] in 2 and 3·5% yields, respectively. Preferential formation of (IV) is ascribed to an internal filtering effect of benzene, because (IV) has u.v. absorption bands in the same region as benzene. Application of the same method to naphthofurazan (II) resulted in the formation of *cis-o*-cyanocinnamonitrile (V), m.p. 70°,[5] and the *trans*-isomer (VI), m.p. 111°,[7] in 45 and 35% yields. A photodimer (VII), m.p. 309°,‡ was isolated in about 1% yield. In this case, triphenylphosphine could also be used as a reducing agent. Phenanthrofurazan (III), upon irradiation in the same manner, produced 2,2′-dicyanobiphenyl (VIII), m.p. 175°,[8] in 70% yield. Since preparation of furazans (I) and (II) is quite simple, the method described here is very convenient for the preparation of dinitriles such as (IV), (V), and (VI).

The formation of (IV) by irradiation of (I) was not retarded in the presence of ferrocene as a triplet quencher. Furthermore, no sensitizing effect for the formation of (IV) was observed when (I) was irradiated by light of 365 nm in the presence of benzophenone, xanthone, or phenanthrene. In the photoreaction of (II), neither ferrocene nor piperylene quenched the formation of (V) and (VI). The formation of (VII) was not retarded when oxygen was bubbled into the irradiated solution of (II). These facts may suggest that the photo-cleavage reaction of the furazan ring, as well as the formation of the photodimer (VII), proceeds *via* the singlet state of the furazans.§ Recently it was pointed out that trimethyl phosphite or triphenylphosphine acts as the quencher for n–π^* singlet, n–π^* triplet, and π–π^* singlet states.[9] This fact, however, would not necessarily be incompatible with our finding that the photoreactions occur *via* the singlet state even in the presence of such phosphorus compounds, probably because of the low efficiency of their quenching effect or of the short life-time of the singlet state concerned.

(*Received, July 7th,* 1970; *Com.* 1087.)

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† It was found in our laboratory that irradiation of phenanthraquinone dioxime in methanol afforded phenanthrofurazan in 34% yield.[2]

‡ All new compounds reported gave satisfactory elemental analyses.

§ On the other hand, the formation of benzonitrile was accelerated by the addition of benzophenone as the sensitizer, when 3,4-diphenyl-1,2,5-oxadiazole was irradiated in the presence of triethyl phosphite (*cf.* ref. 5).

[1] H. Izawa, P. de Mayo, and T. Tabata, *Canad. J. Chem.*, 1969, **47**, 51; G. Just and L. S. Ng, *ibid.*, 1968, **46**, 3381; T. Oine and T. Mukai, *Tetrahedron Letters*, 1969, 157; B. L. Fox and H. M. Rosenberg, *Chem. Comm.*, 1969, 1115.

[2] K. H. Grellamann and E. Taner, *Tetrahedron Letters.*, 1967, 1901.

[3] T. S. Cantrell and W. S. Haller, *Chem. Comm.*, 1968, 977.

[4] T. Mukai, T. Oine, and A. Matsubara, *Bull. Chem. Soc. Japan*, 1969, **42**, 581.

[5] C. D. Campbell and C. W. Rees, *Chem. Comm.*, 1965, 192; J. H. Hall, *J. Amer. Chem. Soc.*, 1965, **87**, 1147; K. Nakagawa and H. Onoue, *Tetrahedron Letters*, 1965, 1433.

[6] H. F. Piepenbrick, *Annalen*, 1951, **572**, 83.

[7] R. P. Linstead and E. G. Noble, *J. Chem. Soc.*, 1937, 933.

[8] H. W. Underwood, jun., and L. A. Clough, *J. Amer. Chem. Soc.*, 1924, **51**, 584.

[9] R. S. Davidson and P. E. Lambeth, *Chem. Comm.*, 1969, 1098.