

## Thermal and Photochemical Reactions of Tetracyanoethylene with *NN*-Dimethyl-*p*-toluidine in Methanol

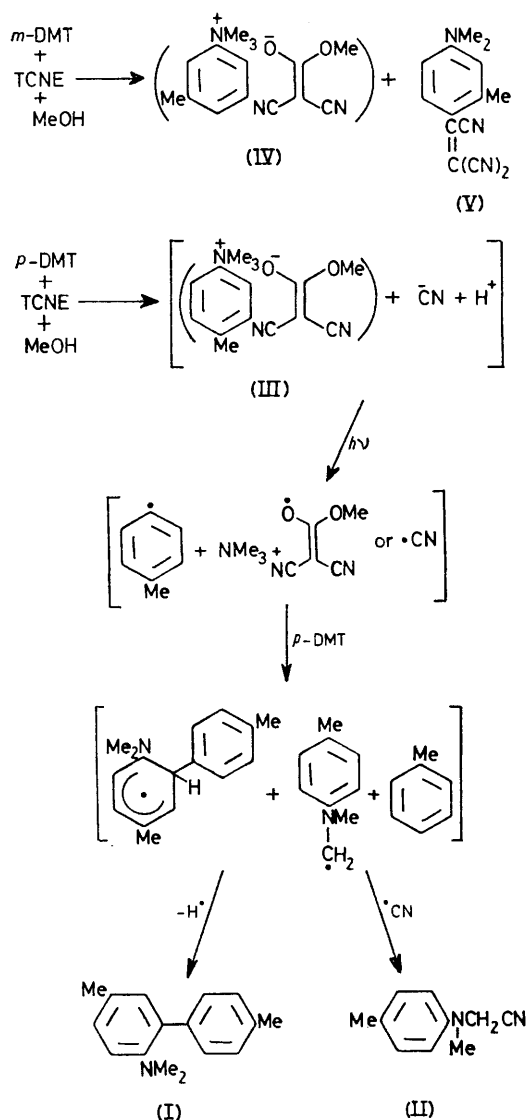
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*Summary* Irradiation of tetracyanoethylene (TCNE) with *NN*-dimethyl-*p*-toluidine in methanol gave a biphenyl derivative together with *N*-cyanomethyl-*N*-methyl-*p*-toluidine through radical reactions of the thermal reaction products, *NNN*-trimethyl-*p*-toluidinium salts.

It is well known that TCNE, a typical electron acceptor, reacts with various electron donors *via* charge-transfer complexes.<sup>1</sup> It has been well established that TCNE

readily reacts with various arylamines, attacking the ring to give 4-tricyanovinylarylamines, but with *NN*-dimethyl-*p*-toluidine (*p*-DMT) no tricyanovinylation was detected.<sup>2</sup> We demonstrated previously that the photochemical reaction of TCNE with toluene in methanol resulted in the 1,2-addition of the methyl group of toluene to TCNE *via* an exciplex with the formation of a tetracarbonitrile derivative.<sup>3</sup> Since *p*-DMT is a more powerful electron donor than toluene, the same type of photoreaction was expected



SCHEME. DMT = *NN*-dimethyltoluidine, TCNE = tetra-cyanoethylene.

† The structure was determined by mass, i.r., and n.m.r. spectroscopy and elemental analysis.

<sup>1</sup> E. Ciganek, W. J. Linn, and O. W. Webster in 'The Chemistry of the Cyano Group,' ed. Z. Rappoport, Interscience, New York, 1973, ch. 9; R. Foster, 'Organic Charge-Transfer Complexes,' Academic Press, London, 1969, ch. 11.

<sup>2</sup> B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *J. Amer. Chem. Soc.*, 1958, **80**, 2806; Z. Rappoport, *J. Chem. Soc.*, 1963, 4493; T. Nogami, Y. Hasegawa, Y. Shiota, and H. Mikawa, *Bull. Chem. Soc. Japan*, 1975, **48**, 3048 and refs. therein.

<sup>3</sup> M. Ohashi, S. Suwa, and K. Tsujimoto, *J.C.S. Chem. Comm.*, 1976, 404.

<sup>4</sup> W. J. Middleton and V. A. Engelhardt, *J. Amer. Chem. Soc.*, 1958, **80**, 2788.

<sup>5</sup> T. D. Walsh and R. C. Long, *J. Amer. Chem. Soc.*, 1967, **89**, 3943.

to proceed in the TCNE-*p*-DMT-methanol system. However, we have now shown that the photochemical reaction of this system proceeds in an entirely different manner.

Irradiation of a mixture of TCNE (300 mg) and *p*-DMT (10 ml) in methanol (350 ml) with a medium-pressure mercury arc (100 W) for 6.5 h gave the biphenyl (I; 118 mg)† and the *N*-cyanomethyl compound (II; 140 mg).† In sharp contrast to the case of TCNE-toluene, no adduct of TCNE and *p*-DMT was detected. To elucidate the difference between these two systems we examined the corresponding thermal reactions.

When a mixture of TCNE (0.10M) and *p*-DMT (0.63M) in methanol was allowed to stand for 7 h at room temperature, the salt (III),† m.p. 93–95 °C, was obtained in 88% yield. Under similar conditions *m*-DMT reacted with TCNE to give the corresponding salt (IV),† m.p. 101–102 °C, and the tricyanovinylated product (V)<sup>2</sup> in 70 and 8% yields, respectively. Middleton and Engelhardt reported that TCNE is easily converted into dicyanoketen dimethyl acetal (VI) in the presence of urea in methanol and that such acetals act as alkylating agents.<sup>4</sup> In view of their observations we conclude that in our case *p*- or *m*-DMT can act as a catalyst as urea does and (VI) must be formed in the reaction mixture, which methylates both *p*- and *m*-DMT, although no example of methylation of tertiary amines with (VI) has been reported. In fact, treatment of *p*-DMT with (VI) also resulted in the formation of (III) in quantitative yield. The formation of (III) and (IV) may be the first example where methylation of tertiary amines with (VI) is characterized.

If the photochemical reaction of *p*-DMT with TCNE is preceded by salt formation, irradiation of the system may produce tolyl radicals as demonstrated by Walsh and Long in the photochemical investigations of quaternary ammonium salts,<sup>5</sup> which then react with *p*-DMT. Thus, irradiation of (III) (0.014M) in the presence of *p*-DMT under similar conditions gave (I) in 41% yield, together with a small amount of toluene but (II) was not detected. This fact suggests that the presence of cyanide anion is essential for the formation of (II). From these observations the formation of (I) and (II) can be rationalised as in the Scheme.

(Received, 28th January 1977; Com. 073.)