A Novel 1,2-Photoaddition of Toluene to Tetracyanoethylene

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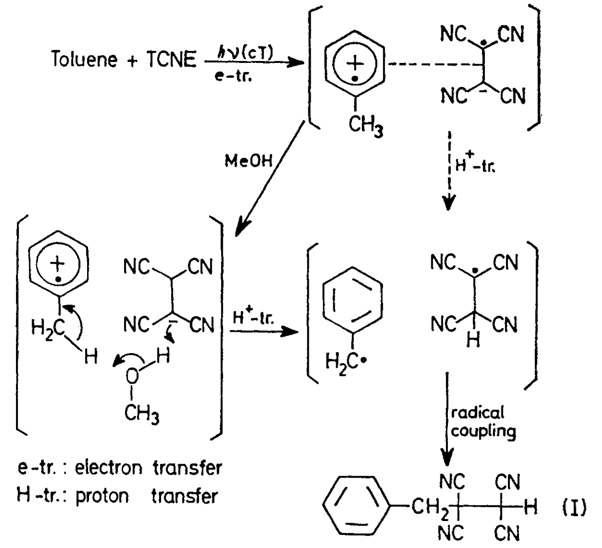
Summary The irradiation of tetracyanoethylene in a mixture of toluene and methanol gave 3-phenylpropane-1,1,2,2-tetracarbonitrile through charge-transfer excitation.

Reactions of tetracyanoethylene (TCNE) with aromatic compounds activated by electron-donating substituents have been studied extensively.[1] *E.g.* the tricyanovinylation of aromatic amines with TCNE occurred with *para* substitution *via* a charge-transfer complex.[2] Henderson and Sheppard reported that the tricyanovinylation of toluene with TCNE in the presence of $AlCl_3$ took place at the *para* position of the benzene ring.[3] We now report that photochemical reactions of TCNE with toluene in the presence of MeOH resulted in the 1,2-addition of the methyl group of toluene to TCNE with the formation of the tetracarbonitrile (I) together with tricyanovinyl methyl ether (II).

Irradiation of a solution of TCNE (0·03M) in toluene with a Pyrex-filtered medium pressure mercury arc for 30 h gave trace amounts of compound (I) and malononitrile, which were identified by g.l.c.–mass spectrometry. However, the reaction rate greatly increased in the presence of MeOH; *e.g.*, when a solution of TCNE (0·11M) in a mixture of toluene (35 ml) and MeOH (40 ml) was irradiated for 3 h (I) (m.p. 110—113 °C) and (II) were isolated in 10 and 30% yields, respectively. Their structures are based on analytical and spectroscopic data. As byproducts small amounts of *o*- and *p*-methoxytoluene and *o*-, *m*-, and *p*-

tricyanovinyltoluene were identified by g.l.c.–mass spectrometry and n.m.r. spectroscopy. The photo-induced 1,2-addition of toluene to TCNE is different from the ground-state reaction, but is somewhat similar to the 1,6-photoaddition of 7,7,8,8-tetracyanoquinodimethane (TCNQ)–toluene systems.[4] Since the charge-transfer absorption of the TCNE–toluene complex is at *ca.* 410 nm,[5] the reaction must be caused by electron transfer from toluene to TCNE. Furthermore, the increase in reaction rate in the presence of a proton donor suggests the involvement of a proton-transfer step.[6]



SCHEME

The formation of (II) was also observed in a thermal reaction; *e.g.* when a similar mixture (TCNE, 0·11M; MeOH, 15 ml; and toluene, 15 ml) was allowed to stand for 3 h at room temperature, (II) was obtained in 20% yield. Therefore, the formation of (II) in the photochemical reaction is independent of the excited-state reaction. Dickinson *et al.* reported that the thermal reaction of TCNE with EtOH gave only tar-like products, but in the presence of a catalyst such as urea, a clean reaction occurred and tricyanovinyl ethyl ether was produced.[7] The replacement of one cyano-group of TCNE by the methoxy-group in the presence of toluene must be a similar reaction. On the basis of these results the mechanism in the Scheme is proposed for the formation of (I).

(*Received*, 29*th March* 1976; *Com.* 326.)

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