

1,6-Photoaddition of Toluene to 7,7,8,8-Tetracyanoquinodimethane

By K. YAMASAKI, A. YOSHINO, and T. YONEZAWA

(Department of Hydrocarbon Chemistry, Kyoto University, Kyoto, Japan)

and M. OHASHI*

(Department of Materials Science, The University of Electro-communications, Chofu-shi, Tokyo, Japan)

Summary 1,6-Photoinduced addition of toluene to 7,7,8,8-tetracyanoquinodimethane (TCNQ) proceeds via a proton-transfer step in the charge-transfer complex; the reaction is accelerated in the presence of trifluoroacetic acid.

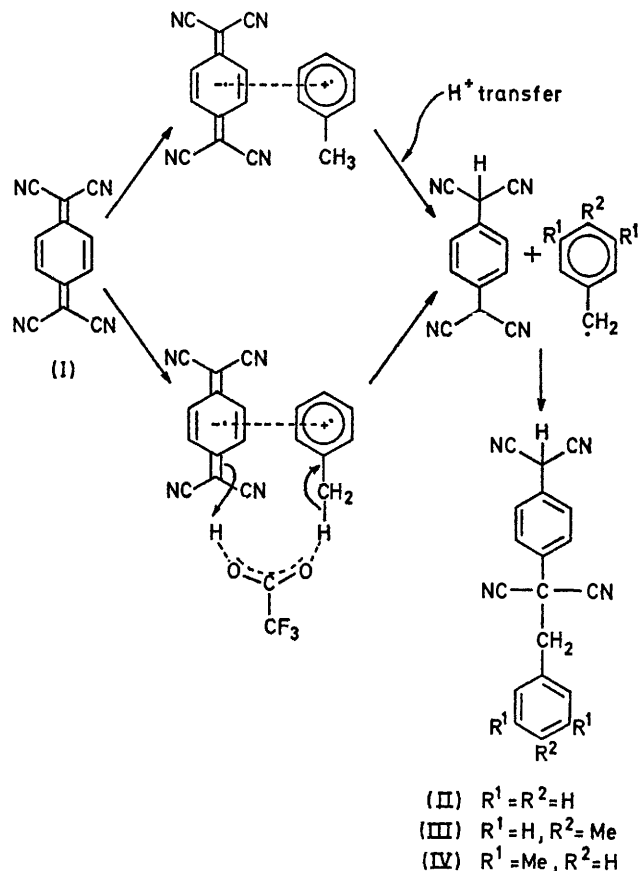
THE 1,4-photoaddition of tertiary amines to benzene has been investigated by Bryce-Smith and his co-workers and a proton-transfer step in the excited state of the charge-transfer complex has been proposed.¹ We have already reported that photo-induced addition occurs in the TCNB-toluene charge-transfer complex,² and we now report that toluene also undergoes photoaddition to TCNQ.

Irradiation of a solution of TCNQ (I) in toluene with a medium-pressure mercury arc for 10 h at room temperature gave (II), m.p. 163°, (28%) along with a small amount of 1,2-diphenylethane. When the reaction was carried out under reflux, the yield of (II) increased to 60%. The TCNQ-*p*-xylene complex behaved similarly, to give (III), m.p. 172°. In order to demonstrate that the reaction was caused by irradiation within the charge-transfer band, irradiation of the TCNQ-*p*-xylene system by a glass-filtered high-pressure arc (500 W; $\lambda > 420$ nm) under continuous heating gave (III) as sole product (74%). The TCNQ-mesitylene system underwent a similar reaction simply when heated, to give (IV), m.p. 154°.

The rate of formation of the 1,6-adduct (III) increased approximately ninefold in the presence of $\text{CF}_3\cdot\text{CO}_2\text{H}$ (0.5M) and fivefold with MeOH (1M). These results are similar to those reported by Bryce-Smith.¹ We propose that the reaction involves a proton transfer step in the excited charge-transfer complex, as in the Scheme.

The photoinduced 1,6-addition of tetrahydrofuran to TCNQ has been reported,³ but the mechanism of this reaction is quite different from that of the additions reported here.

In the presence of trifluoroacetic acid, the photochemical reaction of the TCNQ-toluene complex is accelerated, whereas that of the TCNB-toluene complex is quenched.² In the latter case, Stern-Volmer plots of ϕ^{-1} vs. $[\text{CF}_3\cdot\text{CO}_2\text{H}]$ showed the lifetime (τ) of the charge-transfer complex to be



SCHEME

3.5×10^{-8} s, in fair agreement with the τ_f value obtained from fluorescence measurements.⁴

(Received, 20th October 1972; Com. 1786.)

¹ D. Bryce-Smith, M. T. Clarke, A. Gilbert, G. Klunklin, and C. Manning, *Chem. Comm.*, 1971, 916.

² A. Yoshino, M. Ohashi, and T. Yonezawa, *Chem. Comm.*, 1971, 97.

³ J. Diekman and C. J. Pederson, *J. Org. Chem.*, 1963, 28, 2879.

⁴ T. Kobayashi, K. Yoshihara, and S. Nagakura, *Bull. Chem. Soc. Japan*, 1971, 44, 2603.