Photosubstitution in Some Charge-transfer Complexes of Toluene

By AKIRA YOSHINO, MAMORU OHASHI,* and TEIJIRO YONEZAWA

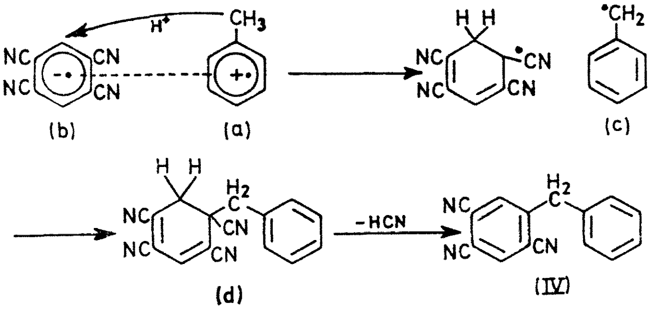
(*Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan*)

Summary A novel photo-induced substitution in some charge-transfer complexes of toluene probably proceeds *via* a proton-transfer step in the excited state of the complexes.

PHOTO-INDUCED addition of the benzene–maleic anhydride charge-transfer complex has been investigated in detail[1] and a zwitterionic intermediate, formed by rapid combination of a radical anion/radical cation pair, has been postulated.[2]

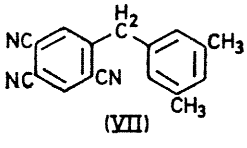
We have investigated the photoreaction of the well known charge-transfer complexes of toluene with 1,2,4,5-tetracyanobenzene (I),[3,4] pyromellitic dianhydride (II),[5] and tetramethyl pyromellitate (III)[6] and have found that a novel substitution reaction takes place, which is accounted for in terms of proton transfer from a radical cation to a radical anion in the excited state of the complexes (Scheme 1).

Irradiation of (I) in toluene with a high-pressure mercury arc for 10 h at room temperature gave (IV), m.p. 137°, M^+ *m/e* 243, in 68% yield along with a small amount of 1,2-diphenylethane (V). When the reaction was carried out in the presence of trifluoroacetic acid (0·5 M-solution), the starting material was recovered quantitatively, which supports the participation of a proton-transfer step. The charge-transfer band (315 nm) of the toluene–(I) system is so close to the absorption band of (I) (314 nm)[4] that specific irradiation on the charge-transfer band was almost impossible. In order to demonstrate that the reactions can be caused by irradiation within the charge-transfer band, we carried out a similar experiment using the mesitylene–(I) system, where the charge-transfer band alone (355 nm)[4] could be irradiated by means of an acetone-filtered high-pressure mercury arc. In this case, (VII) m.p. 179°, was isolated as sole reaction product in 93% yield. This result demonstrates clearly that the substitution reaction proceeds *via* the charge-transfer complex.



SCHEME 1

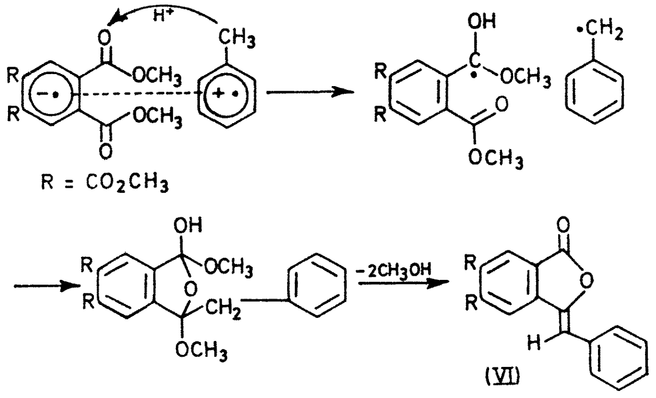
Irradiation of (II) under similar conditions gave (V) as a major product.



(VII)

Irradiation of (III) in toluene under similar conditions gave (VI),[7] m.p. 215°; M^+ *m/e* 338, in 25% yield, along with a comparable amount of (V).

Although the (III)–toluene system does not display any charge-transfer bands in the ground state, it is quite possible to form an exciplex upon irradiation.[6] Scheme 2 represents a reaction mechanism similar to that of Scheme 1. In this case the proton transfer from toluene to a carbonyl group of (III) is somewhat similar to the first step of the acyloin condensation, while in the case of Scheme 1, the first step of the Birch reduction will be recalled.



SCHEME 2

In the case of the toluene–(II) complex it is not clear to which position the proton transfer occurs; however, the formation of (V) in high yield suggests that the benzyl radical is more free than in the case of (I) and (III).

(*Received, October 29th, 1970; Com.* 1876.)

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[7] The same reaction has been reported independently by K. Fukui, S. Shigemitsu, and Y. Odaira, Abstracts of the Annual Photochemistry Symposium, Kyoto, Nov. 19, 1970, p. 88.