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THERMAL 1,6-ADDITION OF THE CHARGE-TRANSFER COMPLEXES OF 7,7,8,8-TETRACYANOQUINODIMETHAN-METHOXYTOLUENE SYSTEMS

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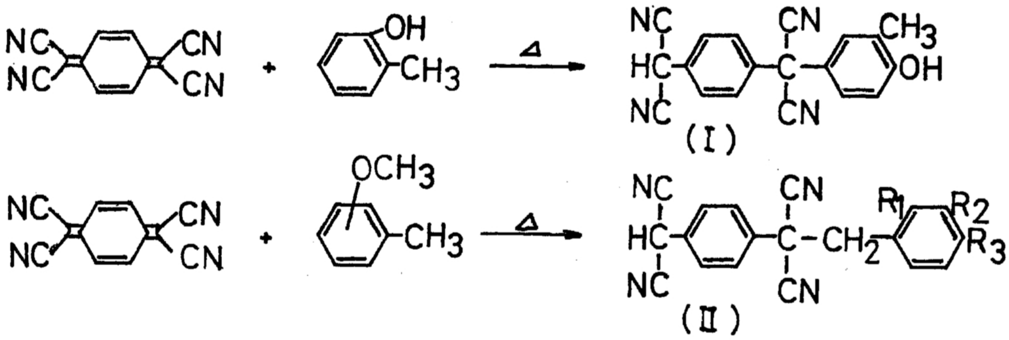
Treatment of TCNQ with *o*-, *m*-, and *p*-methoxytoluene gave the corresponding 1,6-addition products similar to those obtained from the photochemical addition of toluene to TCNQ but different from those obtained from the thermal addition of *o*-cresol to TCNQ. The reaction was accelerated in the presence of a proton donor, suggesting the participation of a proton-transfer step.

It is well known that 7,7,8,8-tetracyanoquinodimethane(TCNQ), a typical electron acceptor, reacts with various electron donors *via* charge-transfer complexes.[1] One recent example was reported by Bespalov et al. where TCNQ reacted with *o*-cresol upon heating to give a *para*-substituted phenol(I) through charge-transfer complex formation.[2] By contrast, in previous results addition took place only at a methyl side chain rather than at an aromatic ring although TCNQ did add both to toluene photochemically and to mesitylene thermally in a 1,6-manner.[3] We have now investigated the thermal addition of TCNQ with methoxytoluenes, more powerful electron donors than toluene. We observed that TCNQ attacked the benzylic methyl groups of methoxytoluenes with overall 1,6-addition, a similar result to that observed in the case of TCNQ-toluene.



(I)

(II)

a $R_1=OCH_3$ $R_2=R_3=H$
b $R_2=OCH_3$ $R_1=R_3=H$
c $R_3=OCH_3$ $R_1=R_2=H$

A typical reaction procedure was as follows: A solution of TCNQ(100 mg) in o-methoxytoluene(20 ml) was refluxed for 3 h. The reaction mixture was red but it gradually turned green. Removal of the excess o-methoxytoluene *in vacuo* gave a brown solid which was washed with hexane and crystallized from CCl_4 to give pale yellow crystals, α,α-dicyano-4-dicyanomethyl-2'-methoxybibenzyl(IIa), mp 89-91°C, MS(20 eV) m/e 326(M^+ 2%) 299(M^+-HCN 19%) 121($CH_3OC_6H_4CH_2{}^+$ 100%), NMR δ in acetone-d_6 3.63(s, 3H) 3.72(s, 2H) 6.20(s, 1H)4) 6.90-7.70(m, 4H) 7.82(s, 4H), in 76% yield. In the same way a mixture of TCNQ(61 mg) and m-methoxytoluene(20 ml) was refluxed for 7 h to give α,α-dicyano-4-dicyanomethyl-3'-methoxybibenzyl(IIb), mp 135-136°C, MS(20 eV) m/e 326(M^+ 10%) 299(3%) 121(100%), NMR δ in $CDCl_3$ 3.42(s, 2H) 3.71(s, 3H) 5.21(s, 1H)4) 6.7-7.4(m, 4H) 7.61(s, 4H), in 85% yield. The TCNQ-p-methoxytoluene system underwent a similar reaction to give α,α-dicyano-4-dicyanomethyl-4'-methoxybibenzyl(IIc), mp 96-98°C, MS(20 eV) m/e 326(M^+ 1%) 299(1%) 121(100%), NMR δ in acetone-d_6 3.73(s, 2H) 3.83(s, 3H) 6.21(s, 1H)4) 6.91 and 7.25(AB quartet, 4H, J=6 Hz) 7.87(s, 4H), in 77% yield. The above data unequivocally demonstrate the reaction site of the methoxytoluenes to be the benzylic methyl groups.

Weak charge-transfer absorption bands similar to those of a TCNQ-mesitylene complex3) were observed at around 520 nm in the UV spectra of TCNQ in methoxytoluenes, but no clear absorption corresponding to TCNQ radical anion5) was detected. The UV spectrum of an anisole-TCNQ system exhibited similar charge-transfer bands but no reaction occurred under similar reaction conditions.

To test for the possible involvement of a proton-transfer step, the above reaction of TCNQ in p-methoxytoluene was repeated in the presence of methanol (5 M). As expected the rate of formation of the adduct IIc increased approximately tenfold. This result indicates the importance of a proton-transfer step in the present reaction.6) The similarity of these reaction features to those observed in the photochemical addition of toluene to TCNQ3) must be accounted for in terms of "pseudo-excitation" proposed by Fukui et al. on reactions of electron donor-acceptor systems.7)

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