

## Thermal and Photochemical Reactions of Charge-transfer Complexes of Tetracyanoethylene–Toluene Systems

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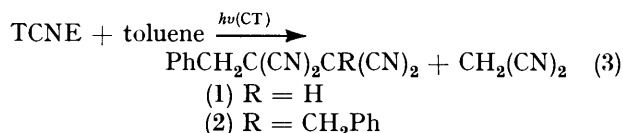
Irradiation of the charge-transfer (CT) absorption bands of tetracyanoethylene (TCNE)–toluene systems gave 3-phenylpropane-1,1,2,2-tetracarbonitrile. TCNE–xylene systems gave a similar addition product on both irradiation of the CT bands and heating under reflux. These reactions proceed through electron-transfer followed by proton-transfer. TCNE reacts with methanol thermally in the presence of *NN*-dimethyl-*p*-toluidine to yield dicyanoketen dimethylacetal which alkylates the toluidine to give eventually *NNN*-trimethyl-*p*-toluidinium 2,2-dicyano-1-methoxyethenolate. *m*-Toluidine reacted similarly and the corresponding toluidinium salt was obtained in addition to a tricyanovinylated product. Irradiation of *NN*-dimethyl-*p*-toluidine with TCNE in methanol gave a diphenyl derivative together with *N*-cyanomethyl-*N*-methyl-*p*-toluidine through radical reactions of the thermal reaction products, *NNN*-trimethyl-*p*-toluidinium salts.

TETRACYANOETHYLENE (TCNE) is a typical electron acceptor and readily forms stable charge-transfer complexes with electron donors.<sup>1</sup> The thermal reactions of TCNE with aromatic compounds activated by electron-donating substituents have been studied extensively.<sup>2</sup> For instance, the tricyanovinylolation of aromatic amines with TCNE occurred with *para*-substitution *via* charge-transfer complexes.<sup>3</sup> The tricyanovinylolation of toluene with TCNE in the presence of  $\text{AlCl}_3$  takes place at the *para*-position of the benzene ring.<sup>4</sup>

In previous papers we described novel substitutions of several charge-transfer complexes of 1,2,4,5-tetracyanobenzene (TCNB)–toluene<sup>5</sup> and 7,7,8,8-tetracyanoquinodimethane (TCNQ)–toluene systems<sup>6</sup> on irradiation of their charge-transfer absorption bands. In continuing our studies on reactions induced by charge-transfer excitation of electron donor–acceptor systems, we have examined the photochemical reactions of TCNE–toluene systems and found that 1,2-photoaddition of toluene to TCNE takes place on irradiation<sup>7</sup> in a similar manner as for TCNQ–toluene complexes.

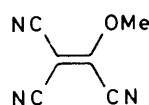
### RESULTS AND DISCUSSION

**TCNE–Toluene Systems.**—The charge-transfer (CT) absorption band of the TCNE–toluene complex is at 410 nm.<sup>8</sup> On irradiating at this wavelength a solution of TCNE (0.032M) in toluene with a medium-pressure mercury arc through a Pyrex filter for 30 h at room temperature, a large portion of the starting TCNE was recovered, but trace amounts of 3-phenylpropane-1,1,2,2-tetracarbonitrile (1), 1,4-diphenylbutane-2,2,3,3-tetracarbonitrile (2) and malononitrile (3), whose structures were deduced from the g.c.–mass-spectra and n.m.r. spectra, were detected in the reaction mixture.

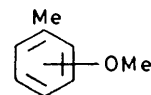


The reaction rate, however, greatly increased in the presence of methanol; *e.g.* on irradiation of a solution of TCNE (0.11M) and toluene (4.4M) in methanol with a

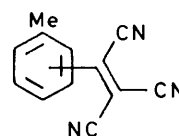
medium-pressure mercury arc for 3 h, (1) and tricyanovinyl methyl ether (4) were obtained in 12 and 30% yields, respectively. Trace amounts of the substitution products (5) and tricyanovinylated products (6), whose structures were deduced from g.c.–mass-spectra, were also detected in the reaction mixture. The accelerating effect of methanol on photochemical reactions of electron-donor–acceptor systems has been well documented<sup>5,6,9</sup> and the present reaction may proceed in a similar manner to that of TCNQ–toluene–methanol<sup>6</sup> or arene–triethylamine–methanol systems.<sup>5,6,9</sup>



(4)



(5) *o*- and *p*- derivatives

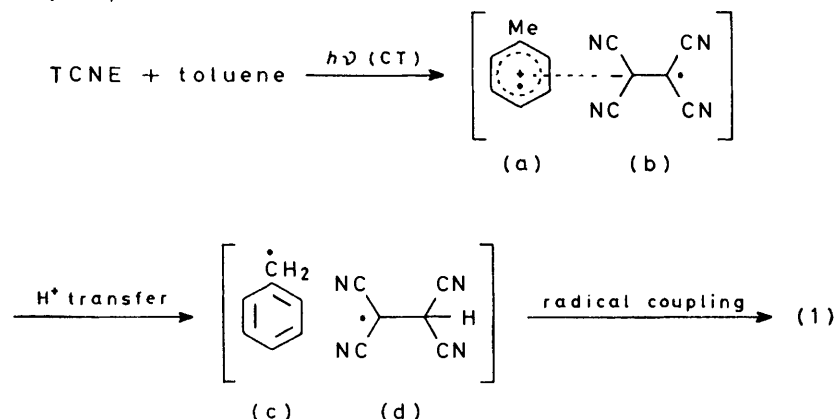


(6) *o*-, *m*-, and *p*- derivatives

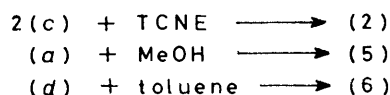
The formation of (4) was also observed in a thermal reaction. When a mixture of TCNE (0.11M), methanol (15 ml) and toluene (15 ml) was set aside for 3 h at room temperature, (4) was obtained in 30% yield. Therefore, the formation of (4) in the photochemical reaction is independent of the excited-state reaction. Dickenson *et al.* reported that in the presence of a catalyst such as urea the reaction of TCNE with ethanol gave tricyanovinyl ethyl ether, but in the absence of a catalyst only tar-like products were obtained.<sup>10</sup> The replacement of one cyano-group of TCNE by the methoxy-group in the presence of toluene must be a similar reaction.

Recently Kimura and Achiba reported that on irradiation of a solution of TCNE in 2-methyltetrahydrofuran glass containing toluene, the TCNE radical anion and the toluene radical cation were formed, and detected spectroscopically.<sup>11</sup> Considering their result, we conclude that the present reaction must be initiated by

## Major process



## Minor processes



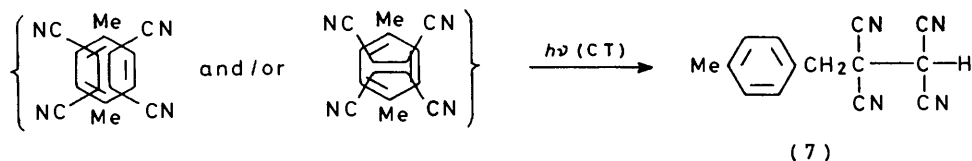
SCHEME 1

photo-induced electron-transfer from toluene to TCNE; the resulting radical cation-anion pair then undergoes proton-transfer to give the radical pair which then couples yielding (1) as shown in Scheme 1, which also explains the formation of small amounts of by-products.

**TCNE-*p*-Xylene Systems.**—The charge-transfer absorption spectra of TCNE-*p*-xylene systems have been well examined and it was suggested that the two CT absorption peaks (405 and 450 nm) correspond to two configurations of the complex.<sup>8</sup> On irradiation of these

On the other hand, in the absence of methanol a solution of TCNE (0.085M) in *p*-xylene gave (7) in 30% yield when refluxed for 5 h. The formation of (7) both thermally and photochemically is somewhat analogous to the case of the TCNQ-mesitylene system<sup>6</sup> and can be explained in terms of the chemical pseudoexcitation concept proposed by Fukui *et al.*<sup>12</sup>

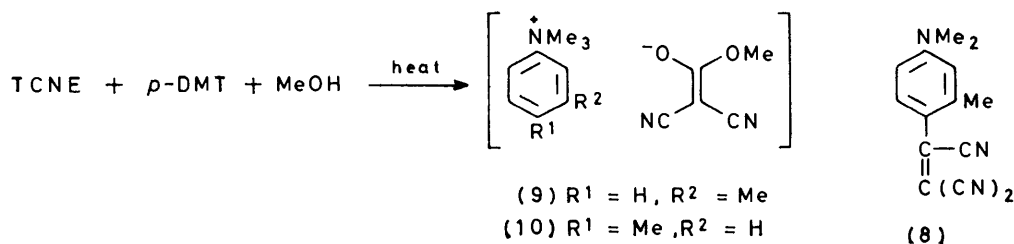
**TCNE-*NN*-Dimethyltoluidine Systems.**—(a) *Thermal reactions.* It has been well established that TCNE in acetonitrile readily reacts with various arylamines,



bands, a mixture of TCNE (0.057M), *p*-xylene (35 ml) and methanol (35 ml) with a Pyrex-filtered medium-pressure mercury arc (100 W) for 5 h gave a similar 1 : 1 adduct (7) to that of the TCNE-toluene system in 25% yield. In the absence of methanol, irradiation under similar conditions did not yield (7) but the starting TCNE was largely recovered (80%).

When a mixture of TCNE, *p*-xylene, and methanol was refluxed for 5 h only tar-like products were obtained.

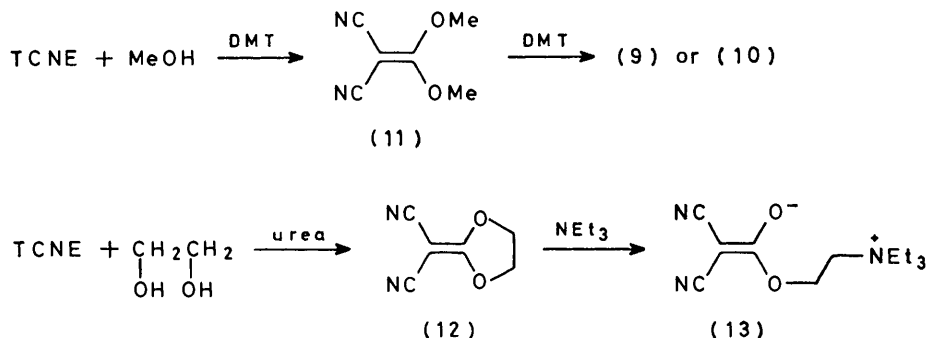
attacking the ring to give 4-tricyanovinylarylamines, but with *NN*-dimethyl-*p*-toluidine (*p*-DMT) no tricyanovinylolation was detected.<sup>3</sup> We found, however, that in methanol the reaction proceeded differently. When a mixture of TCNE, *m*-DMT and methanol was set aside for 7 h at room temperature, the tricyanovinylated product (8)<sup>13</sup> was obtained in only 8% yield. The major product was the quaternary toluidinium salt (9) in 70% yield. Similarly, the reaction of TCNE with



*p*-DMT in methanol gave only the corresponding salt (10) in 88% yield.

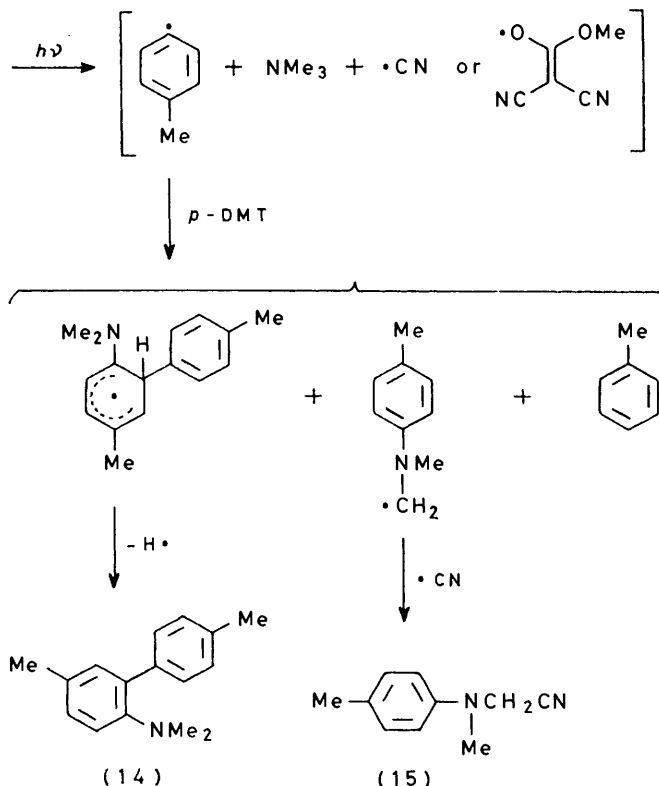
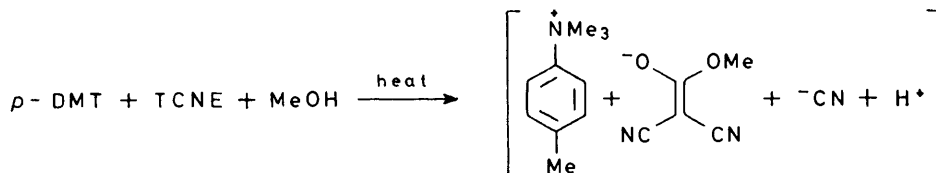
Middleton and Engelhart reported some years ago that TCNE is easily converted into dicyanoketen di-

acetal (11) in the presence of urea in methanol, and that such acetals act as alkylating agents.<sup>13</sup> For instance, the acyclic acetal (12), prepared from TCNE and ethylene glycol, alkylates triethylamine to give the zwitterion (13) quantitatively. In view of their observa-



methyacetal (11) in the presence of urea in methanol, and that such acetals act as alkylating agents.<sup>13</sup> For instance, the acyclic acetal (12), prepared from TCNE and ethylene glycol, alkylates triethylamine to give the zwitterion (13) quantitatively. In view of their observa-

tions we concluded that in our case *p*- or *m*-DMT can act as a catalyst as urea does and (11) must be formed in the reaction mixture, which then methylates *p*- or *m*-DMT to give the salts (9) or (10). In fact the acetal



SCHEME 2

(b) *Photochemical reactions.* Since *p*-DMT is a more powerful electron donor than toluene, the same type of photo-induced electron-transfer reaction as mentioned above was expected. However, the photochemical reaction of this system proceeded in an entirely different manner. Irradiation of a mixture of TCNE and *p*-DMT in methanol with a Pyrex-filtered medium-pressure mercury arc for 6.5 h gave *NN*-dimethyl-*o*-(*p*-tolyl)-*p*-toluidine (14) and *N*-cyanomethyl-*N*-methyl-*p*-toluidine (15). Since the thermal reaction of *p*-DMT with TCNE in methanol gives the salt (9) as mentioned before, the photochemical reaction between TCNE and *p*-DMT must be preceded by thermal salt formation. In fact irradiation of the salt (9) in the presence of *p*-DMT gave (14) in 41% yield but no (15) was detected.

The photochemical reactions of quaternary anilinium salts have been well examined by Walsh and Long, and a radical mechanism was proposed through photo-induced electron-transfer to the quaternary cation from the counter anion.<sup>15</sup> Referring to their mechanism we propose the mechanism of the present reaction to be as follows. The photo-induced electron-transfer to the quaternary toluidinium cation is possible from both the cyanide and the 2,2-dicyano-1-methoxyethenolate anions. This electron-transfer may result in the formation of the *p*-tolyl radical which then adds to *p*-DMT to give (14), or abstracts a hydrogen from the *N*-methyl group of *p*-DMT to give a radical which then couples with the cyano-radical yielding (15) as shown in Scheme 2.

#### EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. T.l.c. was performed with silica gel GF-254 (Merck). I.r. spectra were taken with a JASCO model IRA-1 instrument, u.-v. spectra were obtained with a Hitachi 124 spectrophotometer, and n.m.r. spectra were recorded with Hitachi R-24 and R-20B instruments with tetramethylsilane as internal standard. Mass spectra were recorded with a Hitachi RMU-6MG instrument equipped with a direct/in-beam ion source; ionizing energy 20 eV, source temperature ca. 200 °C.

TCNE, purchased from Eastman Co., was recrystallized twice from chlorobenzene and then purified by sublimation *in vacuo* before use. *p*- and *m*-DMT were distilled from sodium before use. Dicyanoketen dimethylacetal (11) was prepared by Middleton's procedure.<sup>13</sup> An authentic specimen of *NN*-dimethyl-4-tricyanovinyl-*m*-toluidine (8) was prepared by McKusick's method.<sup>2</sup>

*Photochemical Reactions of TCNE-Toluene Systems.*—(a) A solution of TCNE (289 mg) in toluene (70 ml) was irradiated by means of a 100-W medium-pressure mercury arc through a Pyrex filter under nitrogen for 30 h. The solvent was removed *in vacuo* and the residue was treated with chloroform. From the undissolved solid TCNE was recovered in 80% yield. The chloroform solution was concentrated and chromatographed on silica gel with chloroform elution. This yielded a trace amount of solid (ca. 1 mg), which spectral data suggested was 1,4-diphenylbutane-2,2,3,3-tetracarbonitrile (2);  $\delta(\text{CDCl}_3)$  7.47 (10 H, s) and 3.65 (4 H, s);  $m/e$  310 ( $M^+$ , 11), 219 (4), 155 (11), and 91 (100); and a red oil (8 mg) which was shown to be a mixture of 3-phenylpropane-1,1,2,2-tetracarbonitrile (1) and

malononitrile by direct comparison of the spectral data with those of the authentic specimens.

(b) Irradiation of a mixture of TCNE (203 mg), toluene (30 ml), and acetonitrile (40 ml) under similar conditions for 3 h resulted in recovery of the starting TCNE (89%).

*Photochemical Reaction of a TCNE-Toluene-Methanol System.*—A mixture of TCNE (1.078 g), toluene (35 ml) and methanol (40 ml) was irradiated under similar conditions for 3 h. Chromatography on silica gel with chloroform elution gave four fractions in addition to recovered TCNE (52%). From fraction 1 a mixture of *o*- and *p*-methoxytoluene (14 mg) was obtained, which were identified by direct comparison of the g.c.-mass-spectral and n.m.r. spectral data with those of authentic specimens. From fraction 2 a solid was obtained, which was a mixture of *o*-, *m*-, and *p*-tricyanovinyltoluene (3 mg); the n.m.r. spectrum of the mixture exhibited peaks at  $\delta(\text{CCl}_4)$  7.4 (4 H, m) and 2.5 (3 H, m); g.c.-mass spectra showed three compounds: compound A,  $m/e$  193 ( $M^+$ , 50), 166 (100), 139 (35), and 117 (7); compound B,  $m/e$  193 ( $M^+$ , 100), 166 (72), 139 (27), 117 (10), and 91 (12); and compound C,  $m/e$  193 ( $M^+$ , 100), 166 (73), 139 (31), 117 (9), and 91 (8). From fraction 3 tricyanovinyl methyl ether (4) was obtained as a yellow oil (163 mg, 31%) (Found:  $M^+$ , 133.026 5.  $\text{C}_6\text{H}_5\text{N}_3\text{O}$  requires  $M$ , 133.027 6);  $\nu_{\text{max}}$  (neat) 2 230, 1 590, 1 460, 1 330, 1 240, and 1 040  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$  4.34 (s);  $m/e$  133 ( $M^+$ , 95), 107 (100), 105 (24), 92 (22), 79 (14), 78 (8), and 67 (24). From fraction 4, 3-phenylpropane-1,1,2,2-tetracarbonitrile (1) was isolated as red needles (104 mg, 12%), m.p. 110–113 °C (from benzene-cyclohexane) (Found: C, 70.7; H, 3.35; N, 25.20.  $\text{C}_{13}\text{H}_9\text{N}_4$  requires C, 70.9; H, 3.66; N, 25.44%);  $\nu_{\text{max}}$  (KBr) 2 120, 1 440, 770, and 690  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$  7.5 (5 H, m), 4.18 (1 H, s), and 3.69 (2 H, s);  $m/e$  220 ( $M^+$ , 2), 193 (100), 166 (37), 139 (19), and 91 (25).

*Thermal Reactions of TCNE-Toluene Systems.*—(a) Heating under reflux for 1 h a solution of TCNE (60 mg) in toluene (35 ml) resulted only in almost quantitative recovery of the starting TCNE.

(b) A mixture of TCNE (407 mg), toluene (15 ml) and methanol (15 ml) was refluxed for 1.5 h. The solvent was removed and the residue was chromatographed on silica gel. Elution with chloroform gave (4) and malononitrile (3) in 17 and 7% yields, respectively.

*Photochemical Reactions of TCNE-*p*-Xylene Systems.*—(a) Irradiation of a solution of TCNE (520 mg) in *p*-xylene (70 ml) with a Pyrex-filtered medium-pressure mercury arc (100 W) for 5 h under nitrogen resulted only in recovery of unreacted TCNE (413 mg).

(b) A mixture of TCNE (510 mg), *p*-xylene (35 ml) and methanol (35 ml) was irradiated under similar conditions for 5 h. The solvent was removed and the residue was chromatographed on silica gel to yield the addition product, 3-*p*-tolylpropane-1,1,2,2-tetracarbonitrile (7), as colourless needles (195 mg), m.p. 112–113 °C (from benzene-cyclohexane) (Found: C, 71.7; H, 4.19; N, 24.08.  $\text{C}_{14}\text{H}_{10}\text{N}_4$  requires C, 71.8; H, 4.30; N, 23.92%);  $\nu_{\text{max}}$  (KBr) 1 930, 1 820, 1 630, 1 530, 1 450, 1 290, 840, and 750  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$  7.32 (4 H, s), 4.17 (1 H, s), 3.50 (2 H, s), and 2.40 (3 H, s);  $m/e$  234 ( $M^+$ , 3), 207 (100), 206 (45), 180 (13), 179 (16), 165 (13), 153 (10), 105 (41), and 91 (18), together with unreacted TCNE (76 mg).

*Thermal Reactions of TCNE-*p*-Xylene Systems.*—(a) A solution of TCNE (218 mg) in *p*-xylene (20 ml) was refluxed for 5 h. The solvent was removed and the residue was

chromatographed on silica gel to give recovered TCNE (131 mg) and (7) as colourless needles (32 mg).

(b) A mixture of TCNE (207 mg), *p*-xylene (10 ml) and methanol (10 ml) was refluxed for 5 h. The solvent was removed and the residue was chromatographed on silica gel but neither TCNE nor (7) was detected.

**Thermal Reaction of TCNE with *p*-DMT in Methanol.**—A methanol solution (20 ml) of TCNE (289 mg) and *p*-DMT (2 ml) was set aside for 18 h. The solvent was evaporated off *in vacuo* and the residue was chromatographed on silica gel. Elution with chloroform gave *NNN*-trimethyl-*p*-toluidinium 2,2-dicyano-1-methoxyethenolate (10) (547 mg, 88% yield), m.p. 93–95 °C [from chloroform–acetone (1 : 1)] (Found: C, 65.7; H, 6.95; N, 15.45.  $C_{15}H_{19}N_3O_2$  requires C, 65.9; H, 7.01; N, 15.37%);  $\nu_{\max}$  (KBr) 2 190 and 2 170  $cm^{-1}$ ;  $\lambda_{\max}$  (MeCN) 231 ( $\epsilon$   $7.5 \times 10^3$ ) nm;  $\delta$ (CDCl<sub>3</sub>) 7.79 (2 H, d, *J* 9 Hz), 7.41 (2 H, d, *J* 9 Hz), 3.75 (9 H, s), 3.60 (3 H, s), and 2.45 (3 H, s); *m/e* (in-beam electron-impact, 20 eV) 150 (6), 135 (100), 134 (94), 119 (8), 107 (6), 93 (6), 91 (6), and 59 (10).

**Thermal Reaction of Dicyanoketen Dimethylacetal (11) with *p*-DMT.**—A mixture of dicyanoketen dimethylacetal (11) (100 mg) prepared by Middleton's procedure<sup>13</sup> and *p*-DMT (2 ml) was set aside for 1.5 h at room temperature. The resulting oil was chromatographed on silica gel to give the salt (10) in 71% yield.

**Thermal Reaction of the TCNE–*m*-DMT–Methanol System.**—A methanol solution (20 ml) of TCNE (293 mg) and *m*-DMT (2 ml) was set aside for 18.5 h. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel. Elution with chloroform–acetone (1 : 1) gave *NN*-dimethyl-4-tricyanovinyl-*m*-toluidine (8), m.p. 134–135 °C (lit.<sup>2</sup> 129–130 °C); *m/e* 236 ( $M^+$ , 100) (8% yield) and *NNN*-trimethyl-*m*-toluidinium 2,2-dicyano-1-methoxyethenolate (9) (70%), m.p. 101–103 °C (Found: C, 65.8; H, 7.25; N, 15.40.  $C_{15}H_{19}N_3O_2$  requires C, 65.9; H, 7.01; N, 15.37%);  $\nu_{\max}$  3 040, 2 190, and 2 170  $cm^{-1}$ ;  $\delta$ (CDCl<sub>3</sub>) 7.5 (4 H, m), 3.73 (9 H, s), 3.57 (3 H, s), and 2.49 (3 H, s); *m/e* (in-beam electron-impact, 20 eV) 150 (1), 136 (10), 135 (100), 134 (96), 120 (5), 119 (8), 118 (4), 93 (10), 91 (4), and 59 (18).

**Photochemical Reaction of the TCNE–*p*-DMT–Methanol System.**—A solution of TCNE (300 mg) and *p*-DMT (10 ml) in methanol (350 ml) was irradiated for 6.5 h by means of a 100-W medium-pressure mercury arc under nitrogen. Chromatographic purification of the products in the usual way gave *NN*-dimethyl-*o*-(*p*-tolyl)-*p*-toluidine (14) as an oil (118 mg);  $\nu_{\max}$  (neat) 2 800 and 820  $cm^{-1}$ ;  $\delta$ (CCl<sub>4</sub>) 7.44 (2 H, d, *J* 8 Hz), 7.14 (2 H, d, *J* 8 Hz), 6.9 (3 H, m), 2.48 (6 H, s), 2.37 (3 H, s), and 2.28 (3 H, s); *m/e* 225 ( $M^+$ , 100), 224 (23), 210 (18), 195 (8), 145 (8), and 105 (3); and *N*-cyanomethyl-*N*-methyl-*p*-toluidine (15) as an oil (140 mg);  $\nu_{\max}$  (neat) 2 800, 2 220, and 810  $cm^{-1}$ ;  $\delta$ (CCl<sub>4</sub>) 7.06 (2 H, d, *J* 9 Hz), 6.72 (2 H, d, *J* 9 Hz), 3.99 (2 H, s), 2.89 (3 H, s),

and 2.26 (3 H, s); *m/e* 160 ( $M^+$ , 100), 159 (25), 134 (14), 120 (45), and 91 (10).

**Photochemical Reaction of (10) in the Presence of *p*-DMT.**—Irradiation of a solution of (10) (269 mg) and *p*-DMT (4 ml) in methanol (70 ml) with a 100-W medium-pressure mercury arc for 4.5 h under nitrogen and work-up in the usual way gave (14) in 41% yield.

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