Mechanism of the Reaction of 1,3-Diaryltriazenes with Tetracyanoethylene in the Presence of Acetic Acid

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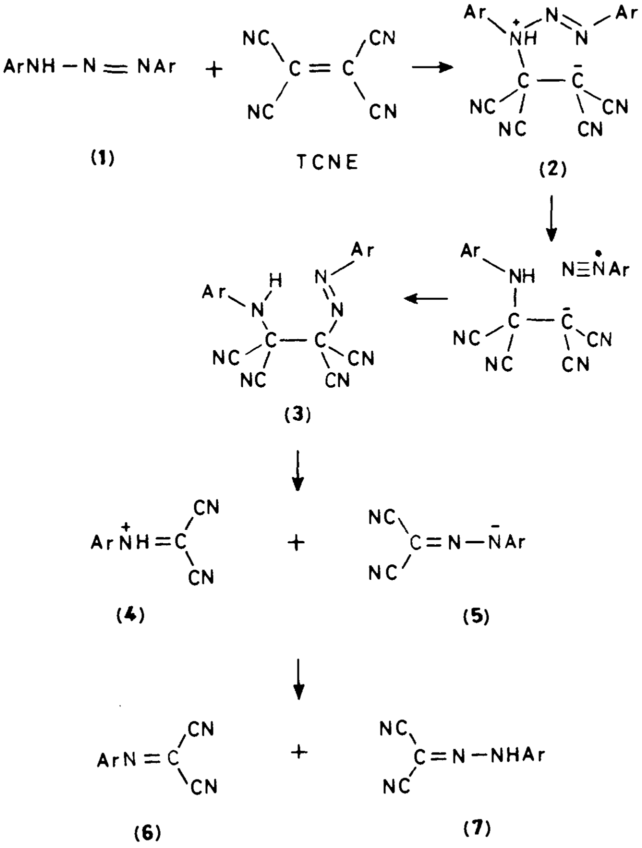
The mechanism for the reaction of 1,3-diaryltriazenes with tetracyanoethylene (TCNE) in the presence of acetic acid, giving Schiff's bases and arylhydrazonomalononitriles, has been investigated. The intermediacy of arylazomalononitriles was confirmed by crossover experiments using an arylamine different from the component of the triazene. The route to the azo compounds *via* TCNE–triazene adducts had already been established by a tracer experiment using an ^{15}N-labelled triazene. However, the crossover experiments, as well as the result of the reaction of a triazene with the TCNE–2,6-dimethylaniline adduct, revealed an alternative route *via* TCNE–ArNH$_2$ adducts in the presence of acetic acid.

Recently we have demonstrated that the reaction of 1,3-diaryltriazenes (**1**) with tetracyanoethylene (TCNE) in methanol to give Schiff's bases (**6**) and arylhydrazonomalononitriles (**7**) proceeds *via* a mechanism involving TCNE–triazene adducts (**2**) and arylazodicyanomethyl(arylamino)malononitriles (**3**) as transient intermediates (Scheme 1);[1] we were able to rule out a cycloaddition–fragmentation mechanism as proposed by Camaggi and his co-workers (Scheme 2).[2] Evidence supporting the mechanism was provided by a tracer experiment with an ^{15}N-labelled triazene. However, we had already realized the importance of the azo compound (**3**) as the key intermediate in the reaction; the tracer experiment was performed to make doubly sure.

We were not aware originally of the results of the Camaggi group, and were examining this reaction for our own purpose, with the expectation that a cycloadduct might be isolated. We were interested in the ability of triazenes to form transient cycloadduct-type intermediates with the active oxygen atom of peroxybenzoic acid acting as an electrophilic reagent like TCNE (Scheme 3).[3] Although the formation of both the Schiff's bases (**6**) and the hydrazones (**7**) was observed under our conditions as well, the possibility of intermediacy of a cycloadduct was entirely ruled out by crossover experiments.



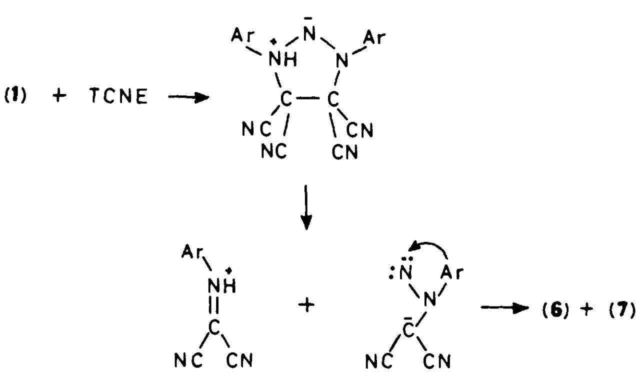
Scheme 1.

Results and Discussion

Mechanism of the Reaction of 1,3-Diaryltriazenes with TCNE.—The reaction of 1,3-diaryltriazenes (**1**) with TCNE was examined in benzene because of the relatively high solubility of TCNE, and was found to proceed with remarkable ease in the presence of acetic acid (10%) to give the Schiff's bases (**6**) and the hydrazones (**7**) in excellent yields. It seemed to us that the process (**2**) ⟶ (**3**) might be regarded as an extension of the well known rearrangement of 1,3-diphenyltriazene to *p*-aminoazobenzene under acidic conditions. The effect of the added acid was therefore investigated, in the expectation that the final products (**6**) and (**7**) might result from heterolysis of the azo compounds (**3**). In the acetic acid–benzene mixture, the triazenes (**1**) behave as mild diazonium coupling reagents because of the equilibrium (i).

$$\mathrm{ArNH{-}N{=}NAr + AcOH \rightleftharpoons ArNH_2 + ArN_2^+\ {}^-OAc} \quad \text{(i)}$$

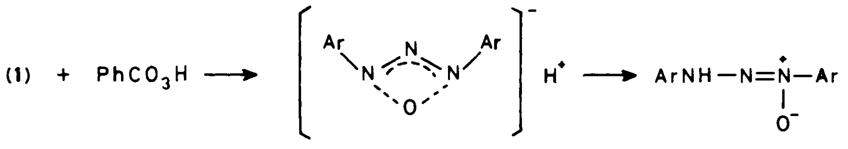
Addition of acetylacetone to the system gave the corresponding coupling product, $\mathrm{Ac_2C{=}NNHAr}$, in good yield. Furthermore, the reactivity of the amine $\mathrm{ArNH_2}$ towards TCNE is much greater than that of the triazene ArNH-N=NAr: the second-order rate constant for the triazene (**1b**) (Ar = *p*-$\mathrm{MeC_6H_4}$), as determined by monitoring the disappearance of



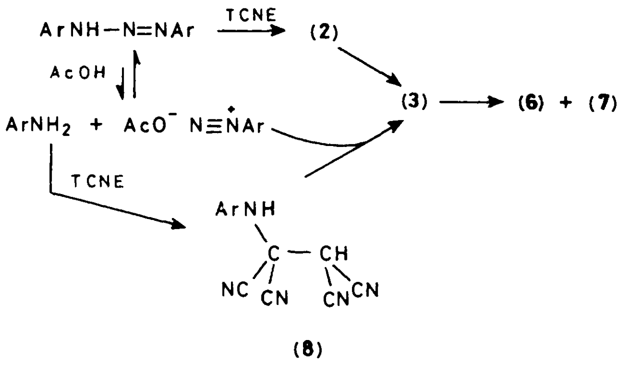
Scheme 2.

Table. Reactions of triazenes with TCNE in 1:9 (v/v) acetic acid–benzene, and crossover experiments

			Products (mol/mol of triazene)					
			Schiff's base		Hydrazone		Tricyanoethylene	
Triazene (equiv.)	*p*-Toluidine (equiv.)	TCNE (equiv.)	**(6a)**	**(6b)**	**(7a)**	**(7b)**	**(10a)**	**(10b)**
(1a) 1.0 (0.05M)	0	1.0	0.85		0.88		0	
(1a) 1.0 (0.025M)	1.0	2.1	0.39	0.37	0.86	0	0.38	0.40
(1a) 1.0 (0.025M)	3.1	4.3	0.21	0.56	0.82	0	0.58	2.13
(1b) 1.0 (0.05M)	0	1.0		0.89		0.89		0
(1c) 1.0 (0.025M)	0	1.0	0.33	0.58	0.58	0.36	0	0



Scheme 3.



Scheme 4.

the methyl peak of the triazene relative to a peak of an internal standard (tetramethylsuccinonitrile) in the n.m.r. spectrum, is *ca.* 2.0 × 10^{-2} l mol^{-1} s^{-1} in 1:9 (v/v) CD_3CO_2D–benzene at 31 °C. However, under the same conditions *p*-toluidine completely disappears immediately after mixing the toluidine and TCNE (1.5 equiv.) solutions, while the reaction in benzene is much slower (*ca.* 1.0 × 10^{-2} l mol^{-1} s^{-1}), indicating that the formation of the blue-coloured charge-transfer complex between *p*-toluidine and TCNE is almost diffusion-controlled in the presence of acetic acid. These findings suggest that both TCNE–triazene and TCNE–$ArNH_2$ adducts, (**2**) and (**8**), might be responsible for the formation of the azo compounds (**3**) under the present conditions (Scheme 4). It is reasonable to assume that the negative charge of ionic intermediates (*e.g.* charge-transfer complexes, zwitterionic species, and ion pairs) is highly stabilized through hydrogen bonding or protonation in the presence of acetic acid.

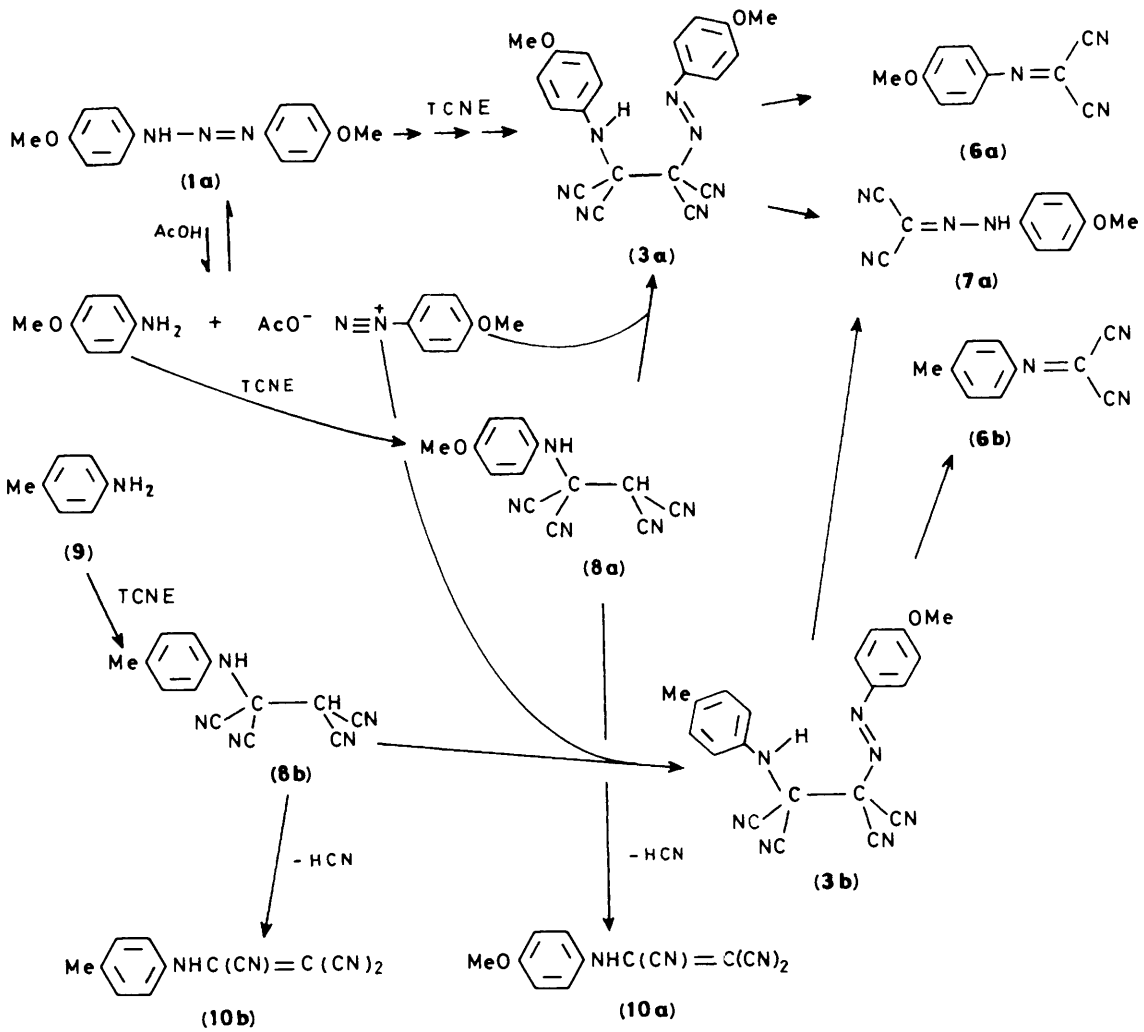
The intermediacy of the TCNE–$ArNH_2$ adducts (**8**) was confirmed by crossover experiments using an amine different from the component of the triazene (Scheme 5 and Table). An equimolar mixture of 1,3-bis-*p*-methoxyphenyltriazene (**1a**) and TCNE in 1:9 (v/v) acetic acid–benzene gave the corresponding Schiff's base (**6a**) (85%) and the hydrazone (**7a**) (88%). The addition of 1 equiv. of *p*-toluidine (**9**) and a further 1 equiv. of TCNE resulted in the formation of the *p*-methyl derivative (**6b**) of the Schiff's base (37%) at the expense of (**6a**) (39%), while the yield of (**7a**) was not affected and no detectable amount of the *p*-methyl derivative (**7b**) of the hydrazone was obtained. Further addition of *p*-toluidine and TCNE led to an increase in the yield of (**6b**) relative to (**6a**). On the other hand, 1-*p*-methoxyphenyl-3-*p*-tolyltriazene (**1c**) afforded both (**6b**) and (**7b**) together with (**6a**) and (**7a**). The results clearly indicate that the Schiff's base (**6b**) obtained in the crossover experiments is formed through the process (**8b**) ⟶ (**3b**), but not *via* an unsymmetrical triazene (**1c**). It follows that the reaction of the triazene (**1a**) with TCNE proceeds exclusively *via* the azo intermediate (**3a**) to give the Schiff's base (**6a**) and the hydrazone (**7a**).

Camaggi and his co-workers reported that the azo compound (**3c**), thought to intervene in the reaction (ii) of the (**10c**)–NaCN

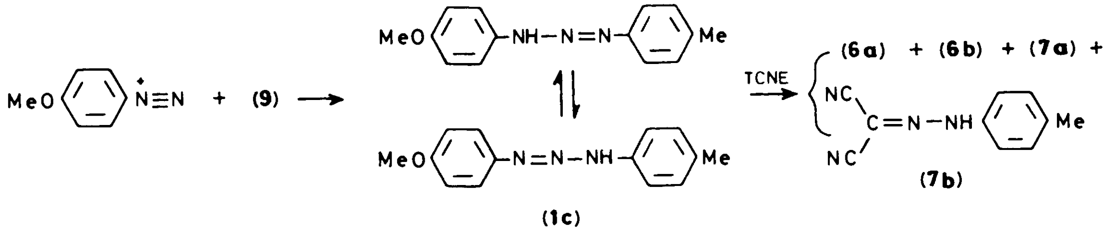
$$\underset{\textbf{(10c)}}{p\text{-ClC}_6\text{H}_4\text{–NH–C(CN)=C(CN)}_2} \xrightarrow{\text{NaCN}} \underset{\text{(solid)}}{p\text{-ClC}_6\text{H}_4\text{–NH–C(CN)}_2\text{–C(CN)}_2\text{Na}}$$

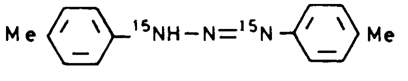
$$\xrightarrow{p\text{-ClC}_6\text{H}_4\overset{+}{\text{N}}\equiv\text{NBF}_4^-} \underset{\textbf{(3c)}}{p\text{-ClC}_6\text{H}_4\text{–NH–C(CN)}_2\text{–C(CN)}_2\text{–N=N–C}_6\text{H}_4\text{Cl-}p} \longrightarrow \textbf{(10c)} \quad \text{(ii)}$$

adduct with *p*-chlorophenyldiazonium tetrafluoroborate, has no ability to produce the corresponding Schiff's base and hydrazone. However, no definitive evidence for the presence of the (**10c**)–NaCN adduct and the azo compound (**3c**) was presented. The *N*-tricyanovinylamine (**10c**) is an acid, and is readily extracted with aqueous Na_2CO_3; thus it is conceivable that a solid obtained from (**10c**) and NaCN may not be the adduct but the sodium salt of (**10c**), *p*-ClC_6H_4–NNa–C(CN)=C(CN)$_2$. After recognizing that their mechanism was inconsistent with ours, we examined the reaction under their conditions [1,3-bis-*p*-tolyltriazene (**1b**) in methanol without added acids] as reported in our preliminary communication.[1] The difference in frequency between the N–H stretching vibrations of ^{15}N-labelled and unlabelled compounds are easily discernible in high-resolution i.r. spectra.[4] The spectrum of the hydrazone obtained from the reaction of the doubly labelled [1,3-$^{15}N_2$]triazene (**1d**) with TCNE in methanol shows that the



Scheme 5.



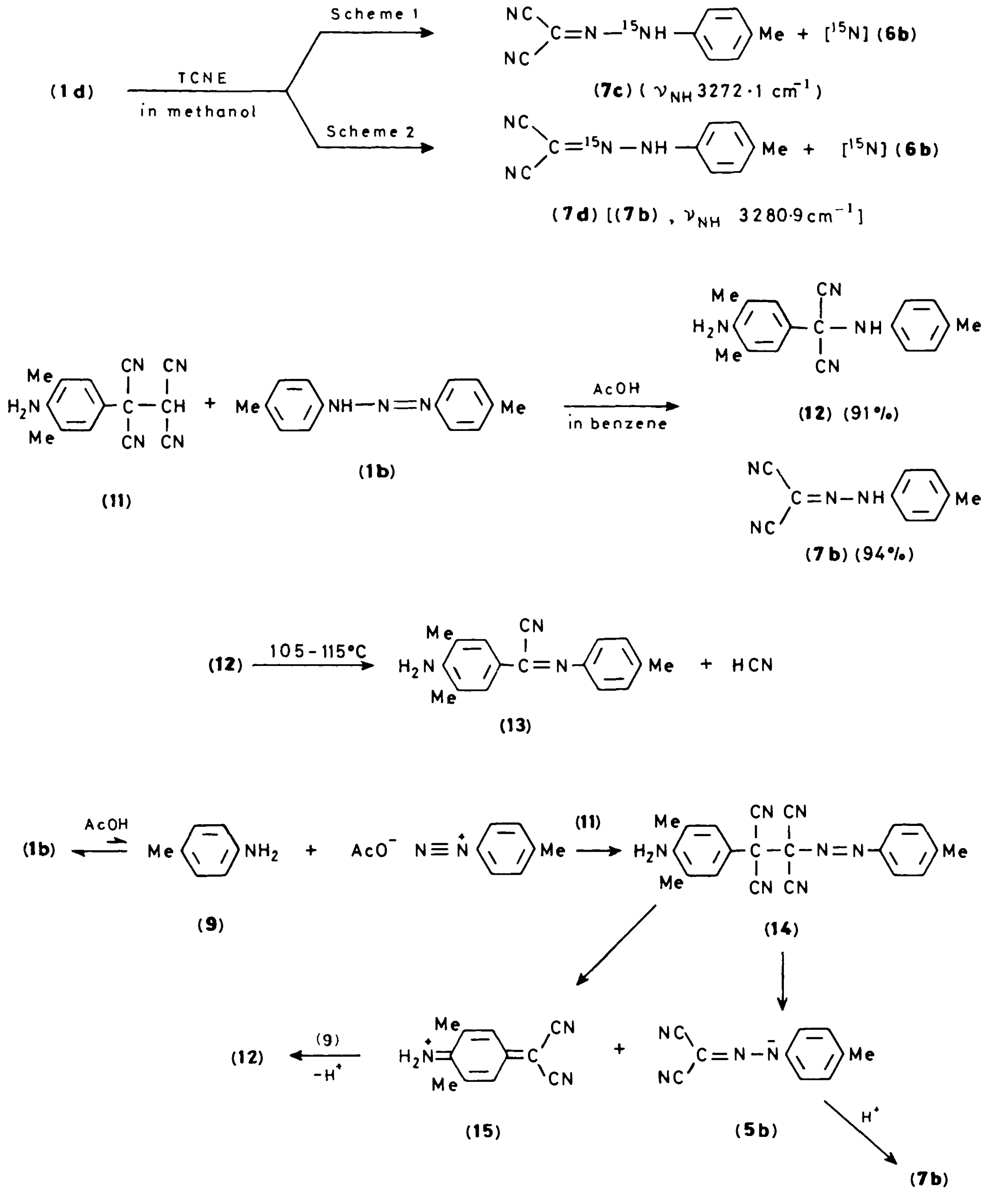


(1b) unlabelled
(1d) labelled

product is the [^{15}N] hydrazone (**7c**), as expected from Scheme 1, but not the [^{15}N]hydrazone (**7d**), which should be formed as a result of aryl migration as shown in Scheme 2.

Consequently, it is concluded that the final products (**6**) and (**7**) are formed from the cation (**4**) and the hydrazone anion (**5**), which are generated by the heterolysis of a carbon–carbon bond in the azo compound (**3**) under any conditions. However, the possibility of a concerted retro-ene mechanism for the fragmentation of the azo compound (**3**) remains unexcluded. It is noteworthy that the 'π-acid' TCNE is able to cause the diazonium migration of (**1**) [*i.e.* (**2**) ⟶ (**3**)] like a normal Brønsted acid.

Reaction of TCNE–2,6-Dimethylaniline Adduct with 1,3-*Bis*-p-*tolyltriazene in the Presence of Acetic Acid*.—TCNE–ArNH$_2$ adducts (**8**) are unstable under the reaction conditions and quickly lose HCN to yield the tricyanovinylamine (**10**), unless they are trapped.[5] However, the isolation of the adduct (**11**) has been reported as an exceptional case.[6] To test the applicability of the process illustrated in Schemes 4 and 5, we studied diazonium coupling to the adduct (**11**) by means of the reagent (**1b**) in 1 : 10 (v/v) acetic acid–benzene. The reaction readily occurred at room temperature to give the hydrazone (**7b**) and the malononitrile (**12**) in high yields. When heated above 105 °C or maintained in hot methanol, the malononitrile (**12**) was



Scheme 6.

quantitatively converted into the Schiff's base (**13**) with loss of HCN. The results strongly support the heterolysis of a carbon–carbon bond in the initially formed azo intermediate (**14**), since a retro-ene-type reaction is sterically impossible in this case. The formation of the malononitrile (**12**) is therefore explicable in terms of nucleophilic attack by *p*-toluidine (**9**) on the resulting cation (**15**) (Scheme 6).

The intermediate azo compounds (3) and (14) are too unstable to be isolated, suggesting that both the cation [(4) or (**15**)] and the hydrazone anion (5) generated from the azo intermediate are highly stabilized by delocalization through the electron-donating amino group and through the diaza-allylic system bearing two electron-withdrawing cyano groups, respectively.

Experimental

I.r. spectra were recorded with a Hitachi 260-30 spectrometer. ^1H N.m.r. spectra were taken with a Varian EM-390 spectrometer (internal standard Me_4Si). Known compounds were prepared by standard literature procedures.

Reactions of 1,3-*Diaryltriazenes with TCNE.*—To a solution of (**1a**) (0.259 g, 1.0 mmol) in benzene (10 ml) was added a solution of TCNE (0.134 g, 1.04 mmol) in 1:4 acetic acid–benzene (10 ml) with stirring. The mixture was left overnight, then washed with aqueous 5% Na_2CO_3 repeatedly, and finally with water, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was extracted with hot hexane (3 × 20 ml), and the combined extracts were treated with Norit (30 mg). Removal of the solvent left p-*methoxyphenyliminomalononitrile* (**6a**) (0.158 g, 85%), m.p. 97 °C (orange needles from hexane); $\nu_{max.}$ (KBr) 2 220 (m, CN) and 2 200 cm^{-1} (m, CN); δ($CDCl_3$) 3.92 (s, 3 H), 7.00 (d, *J* 9 Hz, 2 H), and 7.74 (d, *J* 9 Hz, 2 H) (Found: C, 64.8; H, 3.7; N, 22.8. $C_{10}H_7N_3O$ requires C, 64.9; H, 3.8; N, 22.7%). The aqueous layer was treated with Norit (30 mg), acidified with acetic acid, and extracted with CH_2Cl_2. Removal of the solvent left *p*-methoxyphenylhydrazonomalononitrile (**7a**) (0.177 g, 88%); m.p. 149 °C (decomp.) (from aqueous ethanol), identical with an authentic sample (lit.,[7] m.p. 150 °C). Under the same conditions, (**1b**) gave (**6b**) (89%) and (**7b**) (89%), whereas in the absence of acetic acid the reaction mixture turned dark brown to afford (**7b**) only in 45% yield. Analogously, the unsymmetrical triazene (**1c**) gave four products: (**6a**) (33%), (**6b**) (58%), (**7a**) (58%), and (**7b**) (36%) (yields being determined by n.m.r. in $CDCl_3$).

Crossover Experiments.—To a stirred solution of (**1a**) (0.129 g, 0.50 mmol) and *p*-toluidine (0.055 g, 0.51 mmol) in benzene (10 ml) was added a solution of TCNE (0.136 g, 1.06 mmol) in 1:4 (v/v) acetic acid–benzene (10 ml) at room temperature (23 °C); the mixture was left overnight. A yellow solid (0.022 g) which precipitated was found to be an 83:17 (**10a**)–(**10b**) mixture from the n.m.r. spectrum in pyridine. The reaction solution was worked up as already described; the organic layer gave a yellow solid (0.076 g), the n.m.r. spectrum ($CDCl_3$) of which showed that this fraction contained mainly (**6a**) and (**6b**) in the ratio 51:49. A small peak (less than 10%) due to an unidentified species was found in each of the methoxy and methyl regions; the yields of (**6**) were therefore determined by using an internal standard (tetramethylsuccinonitrile); (**6a**) (39%); (**6b**) (37%). The product obtained from the aqueous layer amounted to 0.156 g; its composition [(**7a**):(**7b**):(**10a**):(**10b**)] determined by the n.m.r. measurement in pyridine, was 60:0:15:25. The products from (**1a**) (0.50 mmol), *p*-toluidine (1.56 mmol), and TCNE (2.17 mmol) were similarly analysed.

Tracer Experiment.—[^{15}N]-*p*-Toluidine hydrochloride (0.28 g) was obtained from *p*-toluoyl chloride (0.88 g) and $^{15}NH_3$ (99%; 250 ml) by a method similar to that described by Fones and White.[8] According to the usual procedures, the [1,3-$^{15}N_2$]-triazene (**1d**) and the [^{15}N]hydrazone (**7c**) were prepared from diazotized [^{15}N]-*p*-toluidine. Compound (**1d**) (27 mg) reacted with TCNE (15.5 mg) in methanol (2 ml) overnight to give the crude hydrazone (20 mg, 90%), which gave yellow crystals, m.p. 169 °C (from ethanol), in agreement with the m.p. of an authentic sample. I.r. absorption spectra were measured with a Nicolet 7199 Fourier transform i.r. spectrometer (resolution 0.5 cm^{-1}; NaCl cell of 1 cm length). The N–H stretching vibrations in CCl_4 (1—1.5 mM) [ν_{NH}/cm^{-1}, $\Delta\nu_{\frac{1}{2}}$ (half-band width)/cm^{-1}, $10^{-3}A$ (integrated absorption intensity)/l mol^{-1} cm^{-2}] were 3280.9, 10, 6.7 for (**7b**) (unlabelled); 3 272.1, 10, 6.2 for (**7c**) (labelled); and 3 272.1, 10, 5.8 for the hydrazone obtained from (**1d**) [ν_{NH} for (**1d**) 3 319.0 cm^{-1}; ν_{NH} for (**1b**) 3 326.9 cm^{-1}].

*Diazonium Coupling to TCNE–*2,6-*Dimethylaniline Adduct.*—To a mixture of (**11**)[6] (0.50 g, 2.0 mmol) and (**1b**) (0.51 g, 2.2 mmol) in benzene (20 ml) was added acetic acid (2 ml) with stirring. The sparingly soluble (**11**) gradually disappeared and yellow precipitates were deposited. After 2 h, benzene (50 ml) was introduced and the mixture was washed with water and extracted with aqueous 5% Na_2CO_3. The aqueous layer was shaken with benzene (10 ml), and the combined benzene layers were washed with water, dried, concentrated to 15 ml *in vacuo*, diluted with hexane (30 ml), and cooled to 5 °C. The resulting precipitates were collected by filtration to give (4-*amino*-3,5-*dimethylphenyl*)-(p-*toluidino*)*malononitrile* (**12**) (0.53 g, 91%) as light brown needles; $\nu_{max.}$(KBr) 3 440 (m, NH_2), 3 360 (m, NH_2), 3 250 (m, NH), and 2 230 cm^{-1} (w, CN); δ($CDCl_3$) 2.23 (s, 6 H), 2.30 (s, 3 H), 3.88 (br s, 3 H), 6.91 (d, *J* 8 Hz, 2 H), 7.12 (d, *J* 8 Hz, 2 H), and 7.35 (s, 2 H) (Found: C, 74.4; H, 6.1; N, 19.15. $C_{18}H_{18}N_4$ requires C, 74.5; H, 6.25; N, 19.3%). The product (**12**) turned yellow at 105—115 °C and melted at 153 °C. It changed quantitatively into the p-*methylphenylimino-analogue* (**13**) when heated in methanol at 60 °C for 1 h; m.p. 153 °C (yellow needles); $\nu_{max.}$(KBr) 3 500 (m, NH_2), 3 405 (s, NH_2), and 2 210 cm^{-1} (w, CN); *m/z* 263 (M^+, 100%), 262 (31), 248 (20), 237 (49), 91 (16), 57 (18), 44 (31), and 40 (24); δ($CDCl_3$) 2.23 (s, 6 H), 2.36 (s, 3 H), 4.06 (br s, 2 H), 7.01 (d, *J* 8 Hz, 2 H), 7.21 (d, *J* 8 Hz, 2 H), and 7.72 (s, 2 H) [Found: C, 77.4; H, 6.4; N, 15.7. $C_{17}H_{17}N_3$ (*M* 263.35) requires C, 77.5; H, 6.5; N, 16.0%). The aqueous layer was acidified with acetic acid to afford (**7b**) (0.35 g, 94%).

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