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Reactions of Arylazosulfones with the Conjugate Bases of Active-Methylene Compounds

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Abstract: The reaction between arylazo *p*-tolyl sulfones **1a-f** (Ar-N=N-SO_2-*p*-Tol) and the potassium salts of some active-methylene compounds (CH_2XY: X, Y = CN, COOEt) represents an example of unprecedented behaviour of azosulfones and effectively leads, depending on the nucleophile, to either unsymmetrical (**6-8**) or symmetrical (**9**) tetrasubstituted ethylenes. Of particular interest is the possibility to synthesize, in high yields and mild conditions, polarysed ethylenes [ArNHCX=CXY: X = Y = CN (**6**) or X = COOEt, Y = CN (**7**)] some of which are otherwise not easily accessible. A mechanism involving successive condensation processes is supported by experimental evidence.

Arylazosulfones (Ar-N=N-SO_2Ar', **1**) are well-known, easily accessible[1a,b] covalent adducts of arenediazonium ions whose synthetic and speculative interest stems from their involvement in either ionic or radical processes, depending on the reaction conditions. Thus, for example, the Ar^+ cations, proposed as intermediates[2] in acid-catalysed processes on **1**, are promptly replaced by $Ar^\bullet$ radicals both under basic/reducing conditions[3,4] and in Pd(0)-catalysed reactions,[5] while also Ar^- anions have been hypothesized to form in strongly basic media.[3] The role of temperature and/or solvent polarity in such dichotomous (ionic *vs* radical) behaviour has been evaluated,[6] and the photostimulated homolysis of **1** has been in turn subjected to kinetic investigation.[7]

In the past few years we have devoted particular attention to the employment of azosulfides **2** in the arylation of nucleophiles of different nature in dipolar aprotic solvents (eq 1);[8-12] the process, which has allowed us to achieve conveniently both Ar-S[8,9] and Ar-C[10-12] bond formation, hinges upon intermediate aryl radicals which participate in the efficient propagation cycle of an overall $S_{RN}1$ chain mechanism.

$$\underset{\mathbf{2}}{\text{Ar–N=N–SR}} \xrightarrow[-\text{RS}^-,\ -\text{N}_2]{\text{Nu}^-} \text{ArNu} \qquad (1)$$

R = alkyl, aryl

In the framework of a screening of the behaviour of different covalent adducts of arenediazonium ions towards nucleophiles, we herein report on the peculiar reactivity of arylazo *p*-tolyl sulfones **1a-f** with the potassium salts of some active-methylene compounds.

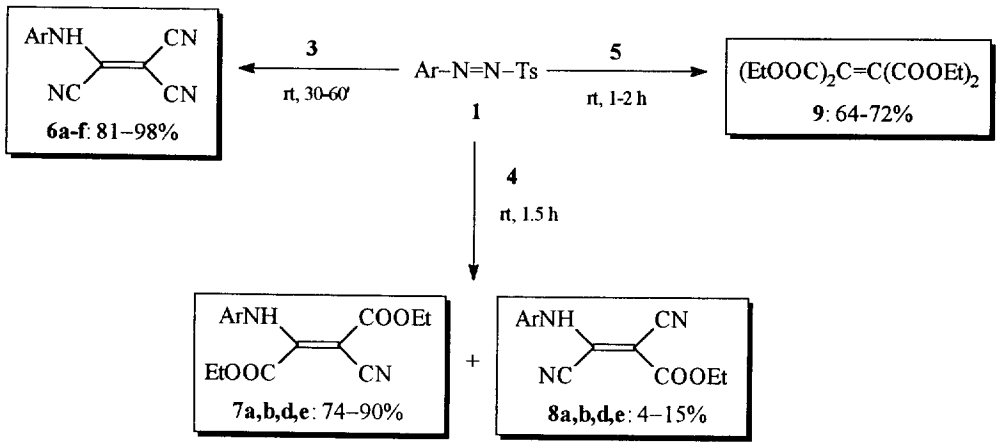
Ar–N=N–Ts

1a: Ar = C_6H_5 **1d**: Ar = 4-ClC_6H_4
1b: Ar = 4-MeC_6H_4 **1e**: Ar = 4-$O_2NC_6H_4$
1c: Ar = 2-MeC_6H_4 **1f**: Ar = 3-$O_2NC_6H_4$

RESULTS AND DISCUSSION

Tables 1-3 collect the results of the reactions between arylazo *p*-tolyl sulfones **1** and the potassium salts of malononitrile (**3**), ethyl cyanoacetate (**4**) and diethyl malonate (**5**), respectively, in DMSO (Scheme 1). The structure of isolated compounds **6-9** has in every case been ascertained through IR, ^{1}H- and ^{13}C-NMR spectroscopy, and, in some cases, by comparison with authentic samples;[13-15] the stereochemistry of the previously unreported **7a,e** and **8a,e** has been assigned by analogy (IR, ^{1}H- and ^{13}C-NMR) with the known **7b,d** and **8b,d**.[14]

Scheme 1



The system herein thus represents an effective access to either tetrakis(ethoxycarbonyl)ethylene (**9**) or *N*-vinylanilines, whereby *e.g.* *N*-(tricyanovinyl)anilines **6** and *N*-[1,2-bis(ethoxycarbonyl)-2-cyanovinyl]anilines **7** are easily formed in high to practically quantitative yields irrespective of electronic and/or steric effects of substituents in Ar. Of course, the formation of compounds **6-9**, accompanied by $TsNH_2$ throughout, as well as the recovery of $ArNH_2$ in the reactions with potassium diethyl malonate, imply that azosulfones **1** undergo a nitrogen-nitrogen bond cleavage along the reaction coordinate. Such unprecedented behaviour of azosulfones is in open contrast with that experienced with azosulfides **2** which, in like conditions, prove arylating agents towards the same nucleophiles, leading to ArCHXY (X, Y = CN, COOEt):[16] the arylation yields depend on the nature of Ar, but compounds like **6-9** have never been detected. The peculiarity of the results of Tables 1-3 is even more evident when recalling that the use of **1** in the aryl transfer to group-VI nucleophiles such as

selenolates or tellurolates has been reported,[17] testifying to behaviour similar to the $S_{RN}1$ azosulfide/arenethiolate system previously investigated.[8]

Table 1. Results of the reactions between azosulfones **1** and **3** in DMSO.[a]

Expt	Ar	Yield of **6** (%)[b,c]
1	C_6H_5 (**1a**)	87
2	4-MeC_6H_4 (**1b**)	98
3	2-MeC_6H_4 (**1c**)	81[d]
4	4-ClC_6H_4 (**1d**)	98
5a	4-$O_2NC_6H_4$ (**1e**)	97
5b	"	98[d]
6	3-$O_2NC_6H_4$ (**1f**)	98

[a]Nu/**1** molar ratio = 10, if not otherwise specified. [b]Yields (*vs* **1**) refer to chromatographically pure products. [c]$TsNH_2$ always isolated in consistent yields. [d]Nu/**1** molar ratio = 2.5.

Table 2. Results of the reactions between azosulfones **1** and **4** in DMSO.[a]

Expt	Ar	Yield (%)[b,c]	
		7	**8**
1	C_6H_5 (**1a**)	82	9
2	4-MeC_6H_4 (**1b**)	74	15
3	4-ClC_6H_4 (**1d**)	90	4
4	4-$O_2NC_6H_4$ (**1e**)	77	8

[a]Nu/**1** molar ratio = 2. [b]Yields (*vs* **1**) refer to chromatographically pure products. [c]$TsNH_2$ always isolated in consistent yields.

Table 3. Results of the reactions between azosulfones **1** and **5** in DMSO.[a]

Expt	Ar	Yield of **9** (%)[b]
1	C_6H_5 (**1a**)	66
2	4-MeC_6H_4 (**1b**)	64
3a	4-$O_2NC_6H_4$ (**1e**)	47[c]
3b	"	72[d]

[a]Nu/**1** molar ratio = 2.2, if not otherwise specified. [b]Yields (*vs* **1**) refer to chromatographically pure **9**; $ArNH_2$ and $TsNH_2$ always isolated in consistent yields. [c]Diethyl bis[(4-nitrophenyl)amino]malonate [$(4\text{-}O_2NC_6H_4NH)_2C(COOEt)_2$, **10**] also isolated (18%). [d]Nu/**1** molar ratio = 10.

The stoichiometry of the process leading to vinylanilines **6-8** (eq 2) is clearly indicated by the fact that no appreciable decrease in the yield of **6e** is observed (cf. entries 5a and 5b of Table 1) when decreasing the nucleophile to substrate molar ratio from the value of 10 (commonly employed in the reactions with azosulfides[16]) to a value of 2.5, while even a 2.0 Nu/**1** ratio leads to overall (**7** + **8**) almost quantitative yields in the reactions with potassium ethyl cyanoacetate (Table 2). A similar stoichiometry can be advanced for the reaction with potassium diethyl malonate (eq 2'); in such system anyway, at least in the case of the *p*-nitro-derivative **1e**, better yields of **9** are obtained with a higher Nu/**1** molar ratio since the reaction carried out with the stoichiometric ratio also leads to the formation of diethyl bis[(4-nitrophenyl)amino]malonate (**10**) as a by-product (cf. entries 3a and 3b of Table 3).

$$\underset{\mathbf{1}}{\text{Ar–N=N–Ts}} + \underset{\mathbf{3,4}}{2^-\text{CHXY}} \longrightarrow \underset{\mathbf{6\text{-}8}}{\text{ArNHCX=CXY}} + \text{TsNH}^- + \text{Y}^- \qquad (2)$$

$$\underset{\mathbf{1}}{\text{Ar–N=N–Ts}} + \underset{\mathbf{5}}{2^-\text{CH(COOEt)}_2} \longrightarrow \underset{\mathbf{9}}{(\text{EtOOC})_2\text{C=C(COOEt)}_2} + \text{TsNH}^- + \text{ArNH}^- \qquad (2')$$

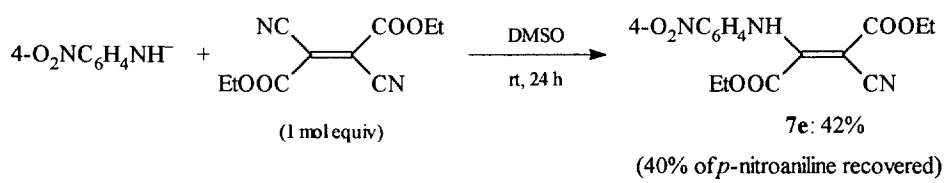
From a mechanistic point of view, the nature of compounds **6-8** as well as the formation of **9**, together with $ArNH_2$, in the reaction with potassium diethyl malonate suggests an initial redox process leading to a tetrasubstituted ethylene, followed, when a suitable leaving group is present,[14,18] by a nucleophilic vinylic substitution (Scheme 2). Such a possibility, though, can be easily dismissed (at least as the main route) on the

Scheme 2

$$\underset{\mathbf{1}}{\text{Ar–N=N–Ts}} + \underset{\mathbf{3\text{-}5}}{2^-\text{CHXY}} \xrightarrow[-\text{TsNH}^-]{} \text{ArNH}^- + \text{CXY=CXY} \xrightarrow{-\text{Y}^-} \mathbf{6\text{-}8}$$

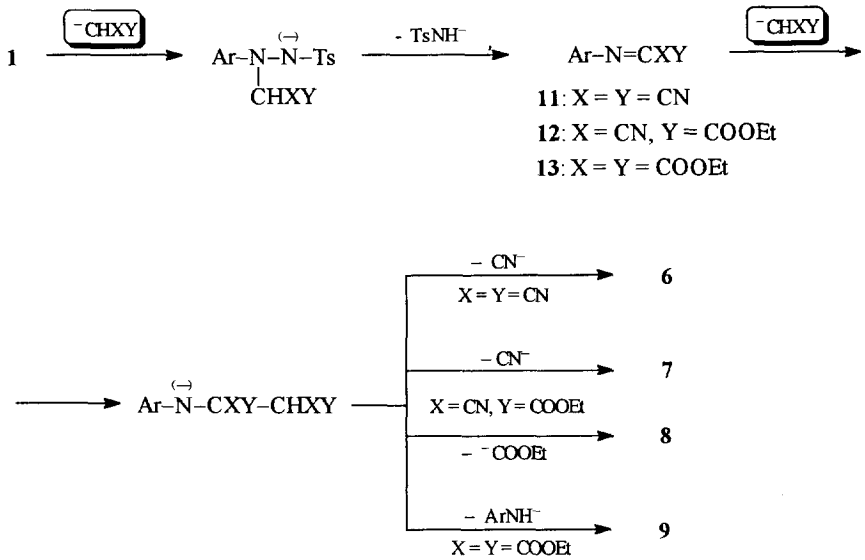
grounds of the extraordinary efficiency (high yields coupled with short reaction times) of the overall process leading herein to **6-8**, irrespective of unfavourable electronic (expts 5 or 6 of Table 1 and expt 4 of Table 2) or steric (expt 3 of Table 1) substituent effects in Ar.[19] Further definitive evidence opposing Scheme 2 comes from the result obtained from the model reaction of Scheme 3, where, in similar conditions, the formation of the expected product **7e** proved to be much slower than that observed in the reaction between **1e** and potassium ethyl cyanoacetate (expt 4 of Table 2).

Scheme 3



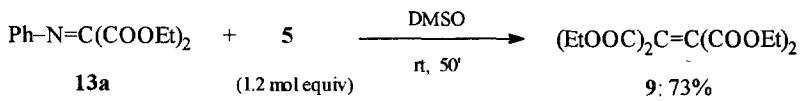
Scheme 4 outlines a fully ionic pathway whereby the formation of an N-C bond precedes that of the C-C bond and the final outcome is the result of two successive condensations initiated by the nucleophilic attack of the carbanion respectively onto the original N=N and onto an intermediate iminic C=N double bond; the nature of the actual product would thus be essentially governed by a competition between leaving groups in the final elimination step, with CN^- prevailing, as expected, over both $ArNH^-$ and ^-COOEt and the latter having a chance only in the presence of cyano groups in the α and β positions.

Scheme 4



To our knowledge, condensation following nucleophilic attack onto the N=N double bond of azosulfones has never been reported; nevertheless, processes very similar to those hypothesized in Scheme 4 on the intermediate imino derivatives **11-13** have been already observed with carbanions[20] or anilines[21] as nucleophiles. Further support to the participation of imino compounds in the system herein comes from the outcome of the reaction between the independently synthesized **13a** and potassium diethyl malonate (Scheme 5): together with aniline, the main isolated product is tetrakis(ethoxycarbonyl)ethylene **9**, with a yield comparable to that of expt 1 of Table 3. On the other hand, the failure to isolate **13a** even in a reaction carried out between equimolar amounts of **1a** and **5** (*i.e.* with a Nu/**1** molar ratio lower than the stoichiometric one

Scheme 5



required by eq 2') suggests that the consumption of **13a** is faster than its formation; definitive confirmation of the involvement of iminic intermediates in the reaction between the *p*-nitrophenylazo sulfone **1e** and potassium diethyl malonate comes from the formation of the bis[(4-nitrophenyl)amino]derivative **10** (Table 3, expt 3a), most likely deriving from trapping of **13e** by the 4-nitrophenylamide anion (Scheme 6): an excess of carbanion (expt 3b) restores the full competitivity of the route leading to **9**, as only traces of **10** have been detected by tlc. Thus, Scheme 4 must be regarded as a very likely reaction mechanism, supported by consistent experimental evidence.

Scheme 6

$$\underset{\textbf{13e}}{4\text{-}O_2NC_6H_4N{=}C(COOEt)_2} + 4\text{-}O_2NC_6H_4NH^- \xrightarrow{H^+} \underset{\textbf{10}}{(4\text{-}O_2NC_6H_4NH)_2C(COOEt)_2}$$

CONCLUSIONS

The system herein can be regarded as an efficient overall redox process (eqs 2 or 2'), where arylazosulfones effectively accomplish the oxidative coupling of anions of active-methylene compounds to eventually furnish symmetrical (**9**) or unsymmetrical (**6-8**) tetrasubstituted ethylenes. Indeed, the possibility of a straightforward access to vinylanilines such as **6** or **7** (and in particular to the ones characterized by electron-withdrawing-substituted Ar moieties, whose attainment via the classical nucleophilic vinylic substitution is practically precluded[13,14]) represents a not trivial target from a synthetic standpoint, given the interest of polarized ethylenes, *e.g.* as precursors of heterocyclic systems.[22]

Moreover, on the grounds of the proposed mechanism, azosulfones **1** can be regarded as convenient synthetic equivalents of nitrosoarenes: in particular, the involvement of the latter in condensations with active-hydrogen compounds (the Ehrlich-Sachs reaction[23]) is often exploited[24,25] for preparative purposes, notwithstanding well-acknowledged[25] severe limitations due to the poor availability of nitrosoarenes themselves and to competitive nitrone formation. Accordingly, further investigations into the reactivity of **1** are in progress.

EXPERIMENTAL

Melting points were determined on a Büchi 535 apparatus and are uncorrected. ^1H- or ^{13}C-NMR spectra were taken in $CDCl_3$ (unless otherwise stated) on a Varian Gemini 200 spectrometer; TMS was used as internal standard and chemical shifts are reported as δ values (ppm). IR Spectra (nujol mull) were recorded on a Perkin-Elmer 881 Infrared Spectrophotometer.

Materials

Petroleum ether and light petroleum refer to the fractions with bp 40-60 °C and 80-100 °C, respectively. Dimethylsulfoxide (DMSO) was used as received after storage over molecular sieves (4 Å). Methylene chloride

for the synthesis of azosulfones was distilled over P_2O_5 before use. Sodium *p*-toluenesulfinate and potassium *tert*-butoxide were commercial products used as received.

Malononitrile, ethyl cyanoacetate and diethyl malonate were commercial samples, distilled before use. (*E*)-1,2-Dicyano-1,2-bis(ethoxycarbonyl)ethylene[26] and diethyl phenyliminomalonate **(13a)**[24b] were synthesized according to literature methods.

Column chromatographies were performed on silica gel using petroleum ether and gradients (or appropriate mixtures) with CH_2Cl_2, Et_2O or AcOEt as eluants, the solvents being distilled before use.

Arylazosulfones **1a-f**

The title compounds were prepared in high yields by arenediazonium tetrafluoroborate/sodium *p*-toluenesulfinate coupling in anhydrous CH_2Cl_2:[1a] the method has been reported to afford (*E*)-isomers.

Phenylazo p-tolyl sulfone (**1a**): mp 88.6-90.1 °C (EtOH) (lit.:[27] mp 90-91 °C).

(4-Methylphenyl)azo p-tolyl sulfone (**1b**): mp 92.4-93.6 °C (toluene/petroleum ether) (lit.:[27] 96-97 °C).

(2-Methylphenyl)azo p-tolyl sulfone (**1c**): mp 73.0-75.0 °C (dec.) (toluene/petroleum ether); ^{1}H NMR: 2.28 (3H, s), 2.48 (3H, s), 7.40 (6H, m) and 7.83 (2H, AA' of AA'BB', *J* 8.3 Hz). Found: C, 61.43; H, 5.11; N, 10.06; S, 11.48%. ($C_{14}H_{14}N_2O_2S$ requires: C, 61.29; H, 5.14; N, 10.21; S, 11.69%).

(4-Chlorophenyl)azo p-tolyl sulfone (**1d**): mp 112.2-113.4 °C (toluene/petroleum ether) (lit.:[7] mp 118.5-119.0 °C).

(4-Nitrophenyl)azo p-tolyl sulfone (**1e**): mp 135.0-136.0 °C (EtOH) (lit.:[4c] 135-136 °C).

(3-Nitrophenyl)azo p-tolyl sulfone (**1f**): mp 114.5-115.0 °C (EtOH) (lit.:[4c] 113-114 °C).

Reactions of arylazosulfones with the potassium salts of active-methylene compounds

The reactions were carried out under argon, according to a reported general procedure,[12b] the nucleophile being generated *in situ* from equimolar amounts of Bu^tOK and CH_2XY. The azosulfone concentration was 0.06 M in the reactions with **3**, 0.12 M in those with **4** and **5**: typically, a solution of the azosulfone (1.9 mmol) in DMSO (15 ml or 10 ml, respectively) was dropped under stirring into a solution of the nucleophile in the same solvent (15 ml or 5 ml, respectively), the reaction progress being monitored by tlc analysis of aliquots quenched with 3% HCl. Usual work-up involved pouring of the reaction mixture into ice/3% HCl and extraction with Et_2O. After drying (Na_2SO_4) the solvent was rotoevaporated and the residue chromatographed on silica-gel. In the reactions with potassium diethyl malonate the relevant anilines (with the only exception of the weakly basic *p*-nitroaniline) remained in the acidic aqueous phase and could be recovered; furthermore, excess diethyl malonate was most conveniently distilled off prior to the chromatographic separation. *p*-Toluenesulfonamide ($TsNH_2$) and anilines were identified by comparison with commercial samples.

N-(Tricyanovinyl)aniline (**6a**): mp 170 °C (dec.) (toluene) (lit.:[13] mp 176 °C). The tautomeric 1,1,2-tricyano-2-phenyliminoethane structure, reportedly isolated on one occasion from the condensation between nitrosobenzene and the potassium salt of malononitrile,[20] is not in agreement with the ^{13}C-NMR spectrum of

the product herein (in CD_3COCD_3): 64.44, 111.40, 112.14, 113.98, 125.52, 129.51, 130.44, 137.83, 141.41.

4-Methyl-N-(tricyanovinyl)aniline (**6b**): mp 169 °C (dec.) (toluene) (lit.:[13] mp 174 °C).

2-Methyl-N-(tricyanovinyl)aniline (**6c**): mp 129 °C (dec.) (toluene) (lit.:[13] mp 129-130 °C).

4-Chloro-N-(tricyanovinyl)aniline (**6d**): mp 154 °C (dec.) (EtOH) (lit.:[13] mp 160 °C).

4-Nitro-N-(tricyanovinyl)aniline (**6e**): mp 167 °C (dec.) (toluene) (lit.:[13] mp 170 °C).

3-Nitro-N-(tricyanovinyl)aniline (**6f**): mp 179 °C (dec.) (toluene) (lit.:[13] mp 171 °C).

(Z)-N-[2-Cyano-1,2-bis(ethoxycarbonyl)vinyl]aniline (**7a**): mp 78.4-79.5 °C (petroleum ether/toluene); ^{1}H-NMR: 1.17 (3H, t, *J* 7.1 Hz), 1.37 (3H, t, *J* 7.1 Hz), 4.26 and 4.32 (2H in all, two partially overlapped q, *J* 7.1 Hz), 7.13 (2H, m), 7.36 (3H, m), 11.1 (1H, br s); ^{13}C-NMR: 13.50, 14.26, 61.66, 63.54, 74.68, 115.83, 123.16, 127.53, 129.62, 137.19, 159.04, 160.92, 167.78; IR: 3221 (NH st.), 2211 (CN st.), 1746 (CO st.), 1670 cm^{-1} (CO st.). Found: C, 62.63; H, 5.44; N, 9.91%. ($C_{15}H_{16}N_2O_4$ requires: C, 62.49; H, 5.59; N, 9.72%).

(Z)-N-[2-Cyano-1,2-bis(ethoxycarbonyl)vinyl]-4-methylaniline (**7b**): mp 101.8-103.0 °C (light petroleum) (lit.:[14] mp 103-104 °C).

(Z)-4-Chloro-N-[2-cyano-1,2-bis(ethoxycarbonyl)vinyl]aniline (**7d**): mp 97.5-98.0 °C (MeOH) (lit.:[14] mp 99.5-100.5 °C).

(Z)-N-[2-Cyano-1,2-bis(ethoxycarbonyl)vinyl]-4-nitroaniline (**7e**): mp 136.2-136.9 °C (light petroleum); ^{1}H-NMR: 1.31 and 1.39 (6H in all, two partly overlapped t, *J* 7.1 Hz), 4.35 and 4.38 (4H in all, two partly overlapped q, *J* 7.1 Hz), 7.21 and 8.25 (2H each, AA'BB', *J* 8.8 Hz), 11.32 (1H, br s); ^{13}C-NMR: 13.63, 14.18, 62.40, 64.27, 78.76, 114.76, 122.04, 125.43, 142.76, 145.69, 156.95, 160.61, 167.25; IR: 3216 (NH st.), 2216 (CN st.), 1731 (CO st.), 1678 cm^{-1} (CO st.). Found: C, 54.17; H, 4.42; N, 12.46%. ($C_{15}H_{15}N_3O_6$ requires: C, 54.05; H, 4.54; N, 12.61%).

(E)-N-[1,2-Dicyano-2-(ethoxycarbonyl)vinyl]aniline (**8a**): mp 83.2-84.2 °C (petroleum ether); ^{1}H-NMR: 1.39 (3H, t, *J* 7.1 Hz), 4.35 (2H, q, *J* 7.1 Hz), 7.42 (5H, m), 11.16 (1H, br s); ^{13}C-NMR: 14.12, 62.60, 83.78, 110.42, 114.63, 123.10, 128.42, 129.95, 136.21, 137.81, 166.52; IR: 3200 (NH st.), 2248 (CN st.), 2213 (CN st.), 1686 cm^{-1} (CO st.). Found: C, 64.73; H, 4.52; N, 17.45%. ($C_{13}H_{11}N_3O_2$ requires: C, 64.72; H, 4.60; N, 17.42%).

(E)-N-[1,2-Dicyano-2-(ethoxycarbonyl)vinyl]-4-methylaniline (**8b**): mp 113.5-115.0 °C (light petroleum) (lit.:[14] 116.5-116.7 °C).

(E)-4-Chloro-N-[1,2-dicyano-2-(ethoxycarbonyl)vinyl]aniline (**8d**): mp 163.1-164.0 °C (MeOH) (lit.:[14] 165.0-165.5 °C).

(E)-N-[1,2-Dicyano-2-(ethoxycarbonyl)vinyl]-4-nitroaniline (**8e**): mp 151.5-152.9 °C (light petroleum/toluene); ^{1}H-NMR: 1.41 (3H, t, *J* 7.1 Hz), 4.39 (2H, q, *J* 7.1 Hz), 7.52 and 8.35 (2H each, AA'BB', *J* 9.1 Hz), 11.40 (1H, br s); ^{13}C-NMR: 14.05, 63.34, 87.60, 110.23, 113.67, 122.29, 125.67, 135.85, 141.30, 146.27, 166.00; IR: 3200 (NH st.), 2248 (CN st.), 2212 (CN st.), 1681 cm^{-1} (CO st.). Found: C, 54.43; H, 3.44; N, 19.61%. ($C_{13}H_{10}N_4O_4$ requires: C, 54.55; H, 3.52; N, 19.57%).

Tetrakis(ethoxycarbonyl)ethylene (**9**): mp 54.2-55.1 °C (lit.:[15] mp 58 °C).

Diethyl bis[(4-nitrophenyl)amino]malonate (**10**): mp 171.7-173.0 °C (EtOH); ^{1}H-NMR: 1.12 (6H, t, *J*

7.1 Hz), 4.27 (4H, q, *J* 7.1 Hz), 6.31 (2H, s), 6.87 and 8.07 (4H each, AA'BB', *J* 7.1 Hz); ^{13}C-NMR: 13.93, 64.56, 73.93, 113.85, 125.90, 140.58, 148.27, 167.10; IR: 3342 (NH st.), 1748 cm^{-1} (CO st.). Found: C, 52.60; H, 4.76; N, 12.85%. ($C_{19}H_{20}N_4O_8$ requires: C, 52.78; H, 4.66; N, 12.96%).

Reaction between potassium 4-nitrophenylamide and (E)-1,2-dicyano-1,2-bis(ethoxycarbonyl)ethylene

The experimental conditions employed were similar to those relevant to the reaction between **1e** and potassium ethyl cyanoacetate (expt 4 of Table 2): potassium *p*-nitrophenylamide (0.9 mmol) was generated from equimolar amounts of the parent aniline and Bu^{t}OK in DMSO (5 ml), prior to addition of the ethylene derivative (0.9 mmol) in DMSO (2.5 ml). The reaction progress was monitored as described above; after 24 h at room temperature usual work-up yielded a crude residue which was chromatographed on silica-gel to afford **7e** (42%) together with unreacted *p*-nitroaniline (40%).

Reaction between diethyl phenyliminomalonate (13a) and potassium diethyl malonate

A solution of **13a** (1.6 mmol) in DMSO (6 ml) was dropped into a solution of 1.2 molar equivalents of the nucleophile in the same solvent (7 ml), generated from equimolar amounts of diethyl malonate and Bu^{t}OK. After 50 min at room temperature usual work-up yielded a residue which was distilled bulb-to-bulb to afford pure **9** in 73% yield.

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