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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<sub>2</sub>-p-Tol) and the potassium salts of some active-methylene compounds (CH<sub>2</sub>XY: 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<sub>2</sub>Ar', 1) are well-known, easily accessible<sup>1a,b</sup> 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<sup>+</sup> cations, proposed as intermediates<sup>2</sup> in acid-catalysed processes on 1, are promptly replaced by Ar<sup>+</sup> radicals both under basic/reducing conditions<sup>3,4</sup> and in Pd(0)-catalysed reactions,<sup>5</sup> while also Ar<sup>-</sup> anions have been hypothesized to form in strongly basic media.<sup>3</sup> The role of temperature and/or solvent polarity in such dichotomous (ionic *vs* radical) behaviour has been evaluated,<sup>6</sup> and the photostimulated homolysis of 1 has been in turn subjected to kinetic investigation.<sup>7</sup>

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);<sup>8-12</sup> the process, which has allowed us to achieve conveniently both Ar-S<sup>8,9</sup> and Ar-C<sup>10-12</sup> bond formation, hinges upon intermediate aryl radicals which participate in the efficient propagation cycle of an overall  $S_{\rm RN}$  chain mechanism.

$$\begin{array}{c} Ar-N=N-SR & \xrightarrow{Nu^{-}} & ArNu \\ 2 & & \\ R = alkyl, aryl \end{array}$$
(1)

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.

$1a: Ar = C_6H_5$	$1d: Ar = 4 - ClC_6H_4$
1b: $Ar = 4 - MeC_6H_4$	$le: Ar = 4 - O_2 NC_6 H_4$
1c: $Ar = 2 - MeC_6H_4$	If: $Ar = 3 - O_2 NC_6 H_4$

#### **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, <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy, and, in some cases, by comparison with authentic samples;<sup>13-15</sup> the stereochemistry of the previously unreported 7a,e and 8a,e has been assigned by analogy (IR, <sup>1</sup>H- and <sup>13</sup>C-NMR) with the known 7b,d and 8b,d.<sup>14</sup>



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<sub>2</sub> throughout, as well as the recovery of ArNH<sub>2</sub> 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):<sup>16</sup> 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,<sup>17</sup> testifying to behaviour similar to the  $S_{RN}1$  azosulfide/arenethiolate system previously investigated.<sup>8</sup>

Expt	Ar	Yield of <b>6</b> (%) <sup>b,c</sup>
1	C <sub>6</sub> H <sub>5</sub> (1a)	87
2	4-MeC <sub>6</sub> H <sub>4</sub> (1b)	98
3	$2-MeC_{6}H_{4}(1c)$	81 <sup>d</sup>
4	4-ClC <sub>6</sub> H <sub>4</sub> (1d)	98
5a	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> (1e)	97
5b	*	98d
6	$3-O_2NC_6H_4$ (1f)	98

Table 1. Results of the reactions between azosulfones 1 and 3 in DMSO.<sup>a</sup>

<sup>*a*</sup>Nu/1 molar ratio = 10, if not otherwise specified. <sup>*b*</sup>Yields (vs 1) refer to chromatographically pure products. <sup>*c*</sup>TsNH<sub>2</sub> always isolated in consistent yields. <sup>*d*</sup>Nu/1 molar ratio = 2.5.

Table 2. Results of the reactions between azosulfones 1 and 4 in DMSO.<sup>a</sup>

Expt	Ar	Yield (%) <sup>b,c</sup>	
		7	8
1	C <sub>6</sub> H <sub>5</sub> (1a)	82	9
2	4-MeC <sub>6</sub> H <sub>4</sub> (1b)	74	15
3	4-ClC <sub>6</sub> H <sub>4</sub> (1d)	90	4
4	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> (1e)	77	8

<sup>a</sup>Nu/1 molar ratio = 2. <sup>b</sup>Yields (vs 1) refer to chromatographically pure products. <sup>c</sup>TsNH<sub>2</sub> always isolated in consistent yields.

Table 3. Results of the reactions between azosulfones 1 and 5 in DMSO.<sup>a</sup>

Expt	Ar	Yield of <b>9</b> (%) <sup>b</sup>
1	C <sub>6</sub> H <sub>5</sub> (1a)	66
2	$4-MeC_{6}H_{4}$ (1b)	64
3a	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> (1e)	47 <sup>c</sup>
3b	*	72 <sup>d</sup>

<sup>*a*</sup>Nu/1 molar ratio = 2.2, if not otherwise specified. <sup>*b*</sup>Yields (vs 1) refer to chromatographically pure 9; ArNH<sub>2</sub> and TsNH<sub>2</sub> always isolated in consistent yields. <sup>*c*</sup>Diethyl bis[(4-nitrophenyl)amino]malonate [(4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NH)<sub>2</sub>C(COOEt)<sub>2</sub>, 10] also isolated (18%). <sup>*d*</sup>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<sup>16</sup>) 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*-nitroderivative 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).

$$Ar-N=N-Ts + 2^{-}CHXY \longrightarrow ArNHCX=CXY + TsNH^{-} + Y^{-}$$
(2)  
1 3.4 6-8

$$Ar-N=N-Ts + 2^{-}CH(COOEt)_{2} \longrightarrow (EtOOC)_{2}C=C(COOEt)_{2} + TsNH^{-} + ArNH^{-}$$
(2')  

$$1 \qquad 5 \qquad 9$$

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, <sup>14,18</sup> 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

 $Ar-N=N-Ts + 2^{-}CHXY \longrightarrow ArNH^{-} + CXY=CXY \longrightarrow 6-8$   $1 \quad 3-5 \quad -TsNH^{-}$ 

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.<sup>19</sup> 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 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<sup>-</sup> prevailing, as expected, over both ArNH<sup>-</sup> and <sup>-</sup>COOEt and the latter having a chance only in the presence of cyano groups in the  $\alpha$  and  $\beta$  positions.







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<sup>20</sup> or anilines<sup>21</sup> 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

$$\frac{\text{Ph-N=C(COOEt)}_2 + 5}{13a} \xrightarrow{\text{DMSO}}_{\text{rt, 50'}} (EtOOC)_2 C=C(COOEt)_2} \frac{13a}{12000} (1.2 \text{ mol equiv}) + 5 \xrightarrow{\text{rt, 50'}}_{\text{rt, 50'}} (EtOOC)_2 C=C(COOEt)_2 + 5 \xrightarrow{\text{rt, 50'}}_{\text{rt, 50'}} (EtOOC)_2 + 5 \xrightarrow{\text{rt, 50'}}_{\text{rt, 50'}$$

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.

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

#### 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<sup>13,14</sup>) represents a not trivial target from a synthetic standpoint, given the interest of polarized ethylenes, *e.g.* as precursors of heterocyclic systems.<sup>22</sup>

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<sup>23</sup>) is often exploited<sup>24,25</sup> for preparative purposes, notwithstanding well-acknowledged<sup>25</sup> 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. <sup>1</sup>H- or <sup>13</sup>C-NMR spectra were taken in CDCl<sub>3</sub> (unless otherwise stated) on a Varian Gemini 200 spectrometer; TMS was used as internal standard and chemical shifts are reported as  $\delta$  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

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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<sup>26</sup> 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<sub>2</sub>Cl<sub>2</sub>, Et<sub>2</sub>O 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  $CH_2Cl_2$ :<sup>1a</sup> 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); <sup>1</sup>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<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S 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.:<sup>7</sup> mp 118.5-119.0 °C).

(4-Nitrophenyl)azo p-tolyl sulfone (1e): mp 135.0-136.0 °C (EtOH) (lit.:<sup>4c</sup> 135-136 °C). (3-Nitrophenyl)azo p-tolyl sulfone (1f): mp 114.5-115.0 °C (EtOH) (lit.:<sup>4c</sup> 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, <sup>12b</sup> the nucleophile being generated *in situ* from equimolar amounts of Bu<sup>t</sup>OK and CH<sub>2</sub>XY. 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 tic analysis of aliquots quenched with 3% HCl. Usual work-up involved pouring of the reaction mixture into ice/3% HCl and extraction with Et<sub>2</sub>O. After drying (Na<sub>2</sub>SO<sub>4</sub>) 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<sub>2</sub>) and anilines were identified by comparison with commercial samples.

*N-(Tricyanovinyl)aniline* (6a): mp 170 °C (dec.) (toluene) (lit.:<sup>13</sup> 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,<sup>20</sup> is not in agreement with the <sup>13</sup>C-NMR spectrum of

the product herein (in CD<sub>3</sub>COCD<sub>3</sub>): 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.:<sup>13</sup> 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); <sup>1</sup>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); <sup>13</sup>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<sup>-1</sup> (CO st.). Found: C, 62.63; H, 5.44; N, 9.91%. (C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub> 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 petro-leum) (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.:<sup>14</sup> 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); <sup>1</sup>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); <sup>13</sup>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<sup>-1</sup> (CO st.). Found: C, 54.17; H, 4.42; N, 12.46%. (C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O<sub>6</sub> 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); <sup>1</sup>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); <sup>13</sup>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<sup>-1</sup> (CO st.). Found: C, 64.73; H, 4.52; N, 17.45%. (C<sub>13</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub> 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.:<sup>14</sup> 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.:<sup>14</sup> 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); <sup>1</sup>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); <sup>13</sup>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<sup>-1</sup> (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); <sup>1</sup>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); <sup>13</sup>C-NMR: 13.93, 64.56, 73.93, 113.85, 125.90, 140.58, 148.27, 167.10; IR: 3342 (NH st.), 1748 cm<sup>-1</sup> (CO st.). Found: C, 52.60; H, 4.76; N, 12.85%. (C<sub>19</sub>H<sub>20</sub>N<sub>4</sub>O<sub>8</sub> 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<sup>1</sup>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<sup>1</sup>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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