The Activating Effects of Arylazo Groups on a Double Bond. Preparation and Properties of some Bis(dialkylamino)arylazoethenes and Related Compounds

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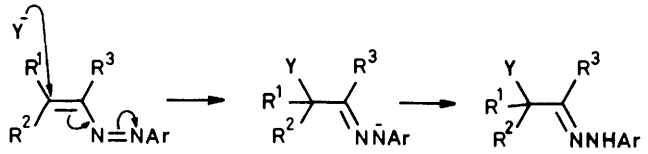
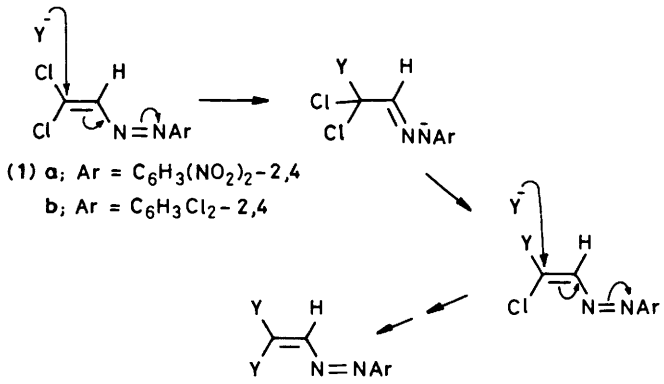
The 1,1-dichloro-2-arylazoethenes (**1**) readily undergo conjugate addition–elimination reactions with amines to give the new azo-olefins (**3**). The n.m.r. and electronic spectra of these compounds, which are highly coloured crystalline solids, indicate that they are strongly polarised enamines. The azo-olefin (**3h**) is formed from compound (**1a**) and thiophenol in sodium hydroxide, but in the presence of sodium carbonate the hydrazone (**8a**) is formed instead. 4-Chlorophenol gives the analogous hydrazone (**8b**). Compound (**3h**) is reduced by thiophenol to the hydrazone (**9**).

Arylazo substituents are known to activate carbon–carbon double bonds towards nucleophilic addition, and 1,4-addition reactions of this type (Scheme 1) have been observed with



Scheme 1.

nucleophiles of many types.[1] We have made use of this activating effect to prepare new azoalkenes by conjugative addition–elimination reactions, and report here the results of reactions of the general type shown in Scheme 2, in which 1,1-dichloro-2-arylazoethenes are used as starting materials. Two azoalkenes of this type, (**1a**)[2] and (**1b**),[3] have previously been isolated as crystalline solids, and were used in this investigation. The aim of the work was to prepare highly polarised azoethenes (**2**) which could have useful chromophores. Nucleophilic addition–elimination reactions of this type are known with β-chloroenones and ββ-dichloroenones.[4] Chattaway and Bennett found that the azo-olefin (**1b**) was converted into ethyl glyoxylate 2,4-dichlorophenylhydrazone by boiling in ethanol,[3] and this conversion can be rationalised as an example of the reaction shown in Scheme 2.

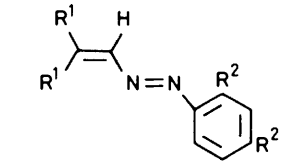


(1) a; Ar = $C_6H_3(NO_2)_2$-2,4
b; Ar = $C_6H_3Cl_2$-2,4

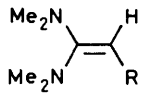
(2)

Scheme 2.

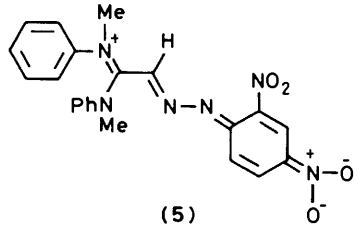
When primary or secondary aimines were added to solutions of the azoethenes (**1**) in dichloromethane at room temperature, the colour of the solutions rapidly changed from red to violet,



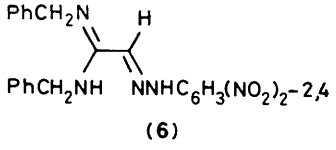
(3) a; $R^1 = Me_2N$, $R^2 = NO_2$
b; R^1 = PhNMe, $R^2 = NO_2$
c; R^1R^1 = $MeNCH_2CH_2NMe$, $R^2 = NO_2$
d; R^1 = 1-Piperidin-1-yl, $R^2 = NO_2$
e; R^1 = Cyclohexylamino, $R^2 = NO_2$
f; $R^1 = Me_2N$, R^2 = Cl
g; R^1 = Piperidin-1-yl, R^2 = Cl
h; R^1 = PhS, $R^2 = NO_2$



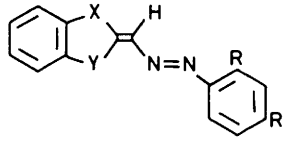
(4) a; R = NO_2
b; R = CO_2Me



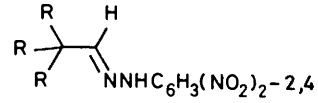
(5)



(6)



(7) a; X = NMe, Y = S, R = NO_2
b; X = NMe, Y = S, R = Cl
c; X = Y = S, R = NO_2



(8) a; R = PhS
b; R = 4-ClC_6H_4O

and then intensified. The new azoethenes (**3a**—**g**) were isolated by evaporation of the solutions after a short time. The amines were used in excess in these reactions; it did not prove possible to displace selectively one of the chloro substituents by using a deficiency of the amine. The azo-olefins, which were isolated in good yield, are deep red or violet crystalline solids.

We found that the same products (**3a**—**e**) could also be obtained in good yield from chloral 2,4-dinitrophenylhydrazone and the appropriate amines. We assume that the azo-olefin (**1a**) is an intermediate in these reactions.

The ^{1}H n.m.r. spectra of the products, recorded at 220 MHz, show two general features which indicate the high degree of polarisation of the double bond. The first of these is that substituents *cis* and *trans* to the arylazo groups are not distinguishable in the n.m.r. spectra. For example, the four methyl groups in compound (**3a**) appear as a 12 H singlet at δ 3.18 and the two methylene groups of (**3c**) appear as a 4 H singlet at δ 3.75. This equivalence is characteristic of highly polarised olefins with a low barrier to rotation about the double bond.[5] It is useful to compare the spectrum of compound (**3a**) with those of analogous enamines (**4**) bearing other types of electron-withdrawing substituent. The β-dimethylamino groups are reported to be equivalent in the n.m.r. spectrum of (**4a**),[6] but not in that of (**4b**).[7]

The second characteristic feature of the spectra of these compounds is the large chemical shift of the vinylic protons. In compound (**3a**), for example, the signal is at δ 7.35, compared with δ 6.30 in (**4a**)[6] and δ 3.96 in (**4b**).[7] It has been suggested that the position of this absorption can be correlated with the 'enamenic' character of the compound, those with the smaller chemical shifts being the more nucleophilic.[6] Compounds (**3**) are thus best formulated as highly polarised enamines with a low barrier to rotation about the double bond. The vinylic signal moves further downfield on addition of a drop of trifluoroacetic acid to the solution; for example, the vinylic signal in the piperidine derivative (**3**) moves from δ 7.45 to 8.15.

Electronic absorption spectra of compounds (**1**) and (**3**) are summarised in the Table. All the 2,4-dinitrophenylazo-olefins (**3**) show intense absorption bands at wavelengths above 500 nm. In the corresponding 2,4-dichlorophenylazo-olefins the absorption is at *ca.* 80 nm lower wavelength. These compounds can be regarded as donor–acceptor chromogens in which the lone pair orbital on the donor group is aligned with the π-electron system.[8] The absorption maxima and their intensities are expected to be influenced by the capacity of the substituents (particularly those *trans* to the azo group) to donate an electron pair, and by steric interactions which can affect the planarity of the system. The 2,4-dinitrophenylazo group is a better acceptor than the 2,4-dichlorophenylazo group, as indicated by the bathochromic shift in absorption of compound (**3d**) compared with (**3g**). The absorption maximum of (**3b**) is at appreciably longer wavelength than that of (**3a**), probably because the phenylmethylamino group increases the conjugation pathway in the charge-separated mesomeric form (**5**). The anomalous absorption maximum of the benzylamine derivative (**6**) indicates that it may exist, at least partly, as its hydrazone tautomer in dilute solution.

The intense absorption bands of the azo-olefins (**3**) are removed by the addition of acid. A marked colour change from deep red or purple to orange is observed when a drop of acid is added to the solutions, the absorption maxima of which are below 450 nm. For example, the maximum for (**3b**) moves to 400 nm (ε 30 000) and for (**3g**), to 376 nm (ε 18 000), on addition of a drop of hydrochloric acid to the solutions. The change is reversible, at least over a short period of time: addition of alkali restores the original absorption maxima. The compounds are thus good visual indicators.

As an exception to the above general reaction, benzylamine was found to react with the azo-olefin (**1a**) to give a product which, on the basis of its i.r. and n.m.r. spectra, is best formulated as the hydrazone (**6**). Its visible absorption maximum is also different from those of the azo-olefins (**3**) (Table). The n.m.r. spectrum shows the four benzylic hydrogens as a singlet at δ 4.72. When the sample was cooled to −80 °C the signal was observed to split into a doublet (T_c −47 °C, separation 33.4 Hz) and the free energy of activation for the change was calculated as 44.6 kJ mol^{-1}.

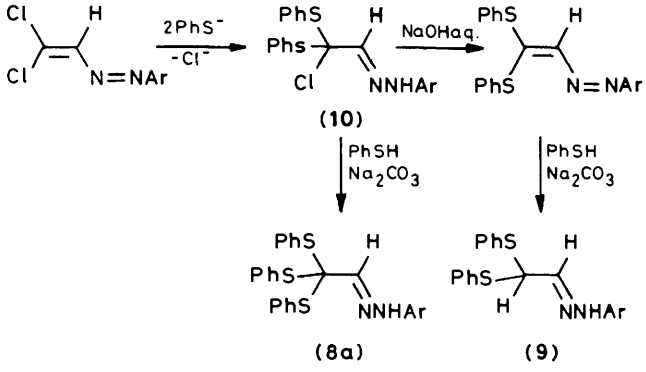
Table. Electronic absorption spectra of azo-olefins in dichloromethane

Compd.	$\lambda_{max.}$/nm (ε/l cm^{-1} mol^{-1})	
(**1a**)	337 (24 000)	454 (600)
(**1b**)	341 (20 000)	446 (700)
(**3a**)	346 (7 000)	524 (41 000)
(**3b**)	365 (10 000)	541 (38 000)
(**3c**)	339 (5 800)	512 (53 000)
(**3d**)	350 (8 300)	532 (50 000)
(**3e**)	356 (11 000)	511 (30 000)
(**3f**)	298 (1 600)	444 (31 000)
(**3g**)	322 (6 600)	448 (29 000)
(**3h**)		449 (22 000)
(**6**)*	355 (11 000)	497 (1 800)
(**7a**)		556 (42 000)
(**7b**)		479 (41 000)

* Formulated as a hydrazone rather than as an azo-olefin (see text).

Reactions of the azoalkenes (**1**) with some oxygen and sulphur nucleophiles were also investigated. 2-Methylaminothiophenol gave the addition–elimination products (**7**) in high yield. These compounds both absorb at long wavelength (Table), presumably because the substituent donor groups are held in the plane of the acceptor group. The n.m.r. spectrum of (**7b**) indicates that it is a mixture of geometrical isomers. Benzene-1,2-dithiol reacted with (**1a**) to give a product for which the n.m.r. and electronic spectra are consistent with structure (**7c**), but it could not be obtained analytically pure despite repeated attempts. Reaction with thiophenol, carried out in a two-phase system with aqueous sodium hydroxide, gave the azo-olefin (**3h**) in high yield. The phenylthio group is a much poorer electron donor than the dialkylamino groups, as indicated by the lower absorption maximum of (**3h**) (Table).

When the reaction of compound (**1a**) with thiophenol was carried out in dichloromethane in the presence of solid sodium carbonate, a different product, the hydrazone (**8a**), was isolated in good yield. We considered that this might have resulted from the addition of thiophenol to the azo-olefin (**3h**), but this proved not to be the case. Compound (**3h**) was reduced by thiophenol in the presence of sodium carbonate, the product being the hydrazone (**9**) (Scheme 3). Compound (**8a**) was converted only



Scheme 3.

very slowly into the azo-olefin (**3h**) by aqueous sodium hydroxide, so it appears that the products (**3h**) and (**8a**) are formed from compound (**1a**) by independent routes. A possible explanation, illustrated in Scheme 3, is that an intermediate (**10**) is long-lived in the presence of the weaker base and is able to

react further with thiophenol, but it is rapidly converted into compound (**3h**) by aqueous sodium hydroxide.

4-Chlorophenol reacted with the azo-olefin (**1a**) in the presence of sodium acetate to give the hydrazone (**8b**) in moderate yield. When (**1a**) was heated in methanol, methyl glyoxylate 2,4-dinitrophenylhydrazone was formed. The azo-olefin (**1a**) also reacted readily with pyrocatechol but the product could not be characterised.

We have thus shown that the azo-olefins (**1**) readily undergo addition–elimination reactions and that the new azo-olefins (**3**) derived from their reaction with amines are highly polarised enamines.

Experimental

I.r. spectra were recorded using a Perkin-Elmer 125 spectrometer as KBr discs, except where indicated otherwise. U.v. and visible spectra were recorded on a Pye Unicam SP8-100 spectrophotometer using 1 cm quartz cells and dry redistilled dichloromethane as solvent. ^{1}H N.m.r. spectra were recorded on a Perkin-Elmer R34 instrument at 220 MHz in $CDCl_3$ except where indicated otherwise. Mass spectra were recorded on A.E.I. MS12 or MS902 instruments at 70 eV using a direct insertion probe. Melting points are uncorrected.

Chloral 2,4-dinitrophenylhydrazone, m.p. 150 °C (lit.,[9] 152—143 °C), 1,1-dichloro-2-(2,4-dinitrophenylazo)ethene (**1a**), m.p. 108—109 °C (lit.,[2] 108—110 °C), and 1,1-dichloro-2-(2,4-dichlorophenylazo)ethene (**1b**), m.p. 82—83 °C (lit.,[3] 84 °C) were prepared by literature procedures.

General procedure for reaction with amines.—Method A. The azoalkene (**1a**) (2 mmol) was dissolved in dichloromethane (50 cm^3) and the amine (20 mmol) was added. After 2 h the solvent and the excess amine were removed on the rotary evaporator and the residue was crystallised.

Method B. Trichloroacetaldehyde 2,4-dinitrophenylhydrazone was used in place of the azoalkene (**1a**) in the procedure described for Method A.

Method C. The azoalkene (**1b**) was used in the procedure of Method A. The following were prepared by these methods:

(a) Aqueous dimethylamine gave, by method B, the *azo-olefin* (**3a**) (96%), m.p. 154—155 °C (decomp.) (from dichloromethane–cyclohexane) (Found: C, 47.1; H, 5.4; N, 27.3. $C_{12}H_{16}N_6O_4$ requires C, 46.8; H, 5.2; N, 27.3%); $\nu_{max.}$ 1 570, 1 515, 1 320, and 825 cm^{-1}; δ 3.18 (12 H), 7.35 (1 H), 7.73 (1 H, d), 8.15 (1 H, dd), and 8.55 (1 H, d); *m/z* 281 (28%), 183 (54), and 72 (100) (no M^+).

(b) *N*-Methylaniline gave, by method B, the *azo-olefin* (**3b**) (63%), m.p. 154—156 °C (from ethyl acetate–hexane) (Found: C, 61.1; H, 4.8; N, 19.7. $C_{22}H_{20}N_6O_4$ requires C, 61.1; H, 4.6; N, 19.4%); $\nu_{max.}$ 1 590, 1 500, 1 320, and 740 cm^{-1}; δ 3.45 (6 H), 6.98—7.40 (12 H, m), 8.10 (1 H, dd), and 8.50 (1 H, d); *m/z* 404 (M^+ − 28), 402, and 105 (base).

(c) *N,N'*-Dimethylethylenediamine gave, by method B, the *azo-olefin* (**3c**) (87%), m.p. 184—187 °C (from dichloromethane–cyclohexane) (Found: C, 47.2; H, 4.7; N, 27.5. $C_{12}H_{14}N_6O_4$ requires C, 47.1; H, 4.6; N, 27.5%); $\nu_{max.}$ 1 570, 1 430, 1 315, and 830 cm^{-1}; δ[$(CD_3)_2SO$] 3.26 (6 H), 3.75 (4 H), 7.47 (1 H, d), 7.68 (1 H, vinylic H), 7.98 (1 H, dd), and 8.36 (1 H, d); *m/z* 278 (M^+ − 28), 187 and 56 (base).

(d) Piperidine gave, by method B, the *azo-olefin* (**3d**) (98%), m.p. 165—167 °C (from dichloromethane–cyclohexane) (Found: C, 55.5; H, 6.4; N, 21.7. $C_{18}H_{24}N_6O_4$ requires C, 55.7; H, 6.2; N, 21.7%); $\nu_{max.}$ 1 590, 1 490, 1 330, and 830 cm^{-1}; δ 1.80 (12 H), 3.52 (8 H), 7.45 (1 H), 7.73 (1 H, d), 8.17 (1 H, dd), and 8.63 (1 H, d); *m/z* 361, 360 (M^+ − 28), and 94 (base).

(e) Cyclohexylamine gave, by method A, the *azo-olefin* (**3e**) (81%), m.p. 150—151 °C (from dichloromethane–cyclohexane) (Found: C, 57.7; H, 6.9; N, 19.9. $C_{20}H_{28}N_6O_4$ requires C, 57.7; H, 6.8; N, 20.2%); $\nu_{max.}$ 3 270 (NH), 1 610, 1 540, and 1 330 cm^{-1}; δ 0.70—1.75 (20 H, m), 3.38 (2 H, m), 7.40 (1 H, d), 7.50 (1 H, vinylic H), 7.98 (1 H, dd), and 8.48 (1 H, d).

(f) Benzylamine gave, by method A, the 2,4-*dinitrophenylhydrazone* (**6**) (45%), m.p. 125—127 °C (from dichloromethane–hexane) (Found: N, 19.0; *m/z* 432.1529. $C_{22}H_{20}N_6O_4$ requires N, 19.4; *m/z* 432.1546); $\nu_{max.}$ 3 420 (NH), 3 280 (NH), 1 630, 1 610, 1 510, and 1 325 cm^{-1}; δ 4.72 (4 H), 7.25—7.35 (10 H, m), 8.02 (1 H, imine H), 8.28 (1 H, dd), and 9.05 (1 H, d).

(g) Aqueous dimethylamine gave, by method C, the *azo-olefin* (**3f**) (91%), m.p. 132—134 °C (from cyclohexane) (Found: C, 50.5; H, 5.7; N, 19.5. $C_{12}H_{16}Cl_2N_4$ requires C, 50.2; H, 5.8; N, 19.5%), $\nu_{max.}$ 1 570, 1 540, 1 520, and 1 300 cm^{-1}; δ 3.30 (12 H), 7.00 (1 H), 7.13 (1 H, dd), 7.38 (1 H, d), and 7.52 (1 H, d); *m/z* 290/288/286 (M^+) and 42 (base).

(h) Piperidine gave, by method C, the *azo-olefin* (**3g**) (53%), m.p. 165—167 °C (from ethyl acetate) (Found: C, 58.6; H, 6.7; N, 15.4. $C_{18}H_{24}Cl_2N_4$ requires C, 58.9; H, 6.5; N, 15.3%); $\nu_{max.}$ 1 500, 1 450, and 1 320 cm^{-1}; δ 1.65 (12 H), 3.33 (8 H, br), 6.95 (1 H), 7.08 (1 H, dd), 7.32 (1 H, d), and 7.45 (1 H, d); *m/z* 370/368/366 (M^+) and 43 (base).

(i) 2-Methylaminothiophenol gave, by method A, the *azo-olefin* (**7a**) (88%), m.p. 205—206 °C (from dichloromethane–hexane) (Found: C, 50.4; H, 3.0; N, 19.7. $C_{15}H_{11}N_5O_4S$ requires C, 50.4; H, 3.1; N, 19.6%); $\nu_{max.}$ 1 610, 1 590, 1 575, 1 520, and 1 330 cm^{-1}; δ(CF_3CO_2H) (conjugate acid spectrum) 4.50 (3 H), 7.90—8.33 (5 H, m), 8.65 (1 H, dd), 9.07 (1 H, imine H), and 9.28 (1 H, d); *m/z* 357 (M^+), 178, and 136 (base).

(j) 2-Methylaminothiophenol gave, by method C, the *azo-olefin* (**7b**) (96%), m.p. 157—158 °C (from cyclohexane) (Found: C, 53.4; H, 3.6; N, 12.3. $C_{15}H_{11}Cl_2N_3S$ requires C, 53.6; H, 3.3; N, 12.5%); $\nu_{max.}$ 1 570, 1 550, and 1 315 cm^{-1}; δ 3.84 and 4.08 (together 3 H, 2:1 ratio) and 7.35—8.31 (8 H, m); *m/z* 339/337/335 (M^+) and 109 (base).

Other Reactions of Azo-olefin (**1a**).—(a) *With benzene-1,2-thiol.* The azo-olefin (0.30 g, 1.03 mmol) was dissolved in dichloromethane (50 cm^3) and a solution of 1,2-dimercaptobenzene[10] (0.175 g, 1.23 mmol) in 20% aqueous sodium hydroxide (30 cm^3) was added. The mixture was stirred rapidly for 3 days. The organic phase was then separated, washed, and dried to give a product formulated as the azo-olefin (**7c**) (0.3 g, 81%), m.p. 150 °C (decomp.) (from dichloromethane–hexane). No satisfactory analysis was obtained; $\nu_{max.}$ 1 610, 1 590, 1 505, and 1 340 cm^{-1}; $\lambda_{max.}$ 538 nm; δ(CH_3CO_2H) (conjugate acid) 8.02 (2 H, m), 8.21 (1 H, d), 8.46 (2 H, m), 8.55 (1 H, dd), 9.13 (1 H), and 9.18 (1 H, d); *m/z* 360 (M^+), 165, and 140 (base).

(b) *With thiophenol.* (i) The azo-olefin (**1a**) (0.50 g, 1.72 mmol) in dichloromethane (50 cm^3) was stirred with thiophenol (0.22 cm^3, 2.15 mmol) in 20% aqueous sodium hydroxide (30 cm^3) for 24 h. The organic phase yielded the *azo-olefin* (**3h**) (0.69 g, 92%), m.p. 154—156 °C (from ethyl acetate) (Found: C, 54.7; H, 3.3; N, 13.0. $C_{20}H_{19}N_4O_4S_2$ requires C, 54.8; H, 3.2; N, 12.8%); $\nu_{max.}$ 1 590, 1 530, 1 515, and 1 335 cm^{-1}; δ 7.13 (1 H, vinylic H), 7.40—7.80 (11 H, m), 8.36 (1 H, dd), and 8.57 (1 H, d); *m/z* 438 (M^+) and 77 (base). (ii) The azo-olefin (**1a**) (0.30 g, 1.03 mmol) and thiophenol (0.4 cm^3, 3.9 mmol) were stirred in dichloromethane (50 cm^3) with anhydrous sodium carbonate (0.75 g, 7.0 mmol) for 24 h. The organic phase was washed with aqueous sodium hydroxide and water, dried, and evaporated to give the 2,4-*dinitrophenylhydrazone* (**8a**) (0.43 g, 76%), m.p. 153—156 °C (from ethyl acetate–hexane) (Found: C, 56.7; H, 3.6; N, 10.1. $C_{26}H_{20}N_4O_4S_3$ requires C, 56.9; H, 3.7; N, 10.2%); $\nu_{max.}$ 3 270 (NH), 1 615, 1 585, 1 500, and 1 320 cm^{-1}; δ 7.30—7.50 (11 H, m), 7.68 (6 H, m), 8.23 (1 H, dd), and 9.05 (1 H, d).

(c) *With 4-chlorophenol.* The azo-olefin (**1a**) (0.50 g, 1.72 mmol) and 4-chlorophenol (0.50 g, 3.89 mmol) were stirred in acetone (25 cm^3) with sodium acetate (0.75 g, 9.1 mmol) for 24 h.

Column chromatography (silica; ether–hexane 3:7) gave the 2,4-*dinitrophenylhydrazone* (**8b**) (0.40 g, 51%), m.p. 140—142 °C (from ethyl acetate) (Found: C, 51.2; H, 2.7; N, 9.2. $C_{26}H_{17}Cl_3N_4O_7$ requires C, 51.7; H, 2.8; N, 9.3%); $\nu_{max.}$ 3 200 (NH), 1 610, 1 590, 1 500, and 1 320 cm^{-1}; δ 7.18—7.30 (12 H, m), 7.42 (1 H, d), 7.51 (1 H, d), 8.28 (1 H, dd), and 9.04 (1 H, d); *m/z* 475 ($M^+ - C_6H_4ClO$) and 127 (base).

(d) *With methanol.* Attempted recrystallisation of the azo-olefin (**1a**) from methanol gave yellow crystals, identified as methyl glyoxylate 2,4-dinitrophenylhydrazone, m.p. 149—150 °C (lit.,[11] 146 °C); $\nu_{max.}$ 3 180 (NH), and 1 695 cm^{-1} (CO); δ 3.93 (3 H), 7.09 (1 H), 8.14 (1 H, d), 8.42 (1 H, dd), and 9.15 (1 H, d).

Reaction of the Azo-olefin (**3h**) *with Thiophenol.*—Compound (**3h**) (0.20 g, 0.46 mmol) and thiophenol (1.0 ml, 9.77 mmol) were stirred in dichloromethane (25 cm^3) with anhydrous sodium carbonate (0.50 g) for 18 h. The mixture was washed with aqueous sodium hydroxide and water, dried, and evaporated to give 2,2-*bisphenylthioacetaldehyde* 2,4-*dinitrophenylhydrazone* (**9**) (0.18 g, 90%), m.p. 138—139 °C (from dichloromethane–hexane) (Found: C, 54.2; H, 3.7; N, 13.0. $C_{20}H_{16}N_4O_4S_2$ requires C, 54.5; H, 3.6; N, 12.7%); $\nu_{max.}$ 3 270 (NH), 1 610, 1 510, and 1 310 cm^{-1}; δ 5.15 (1 H, d), 7.28—7.60 (12 H, m), 8.27 (1 H, dd), and 9.09 (1 H, d); *m/z* 440 (M^+), 331, 109, and 77 (base).

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