1,2,3-Thiadiazol-3-ium-3-methanide (ylide) 1,3-dipoles: cycloaddition–rearrangement sequences leading to substituted 1-(2-vinylthioethenyl)pyrazole systems: azolium 1,3-dipoles

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Alkylation of 4,5-diaryl-1,2,3-thiadiazoles and 1,2,3-benzothiadiazoles with trimethylsilylmethyl trifluoromethanesulfonate occurred at N-3. Treatment of the salts with CsF generated new 1,2,3-thiadiazol-3-ium-3-methanide 1,3-dipoles. These gave *in situ* cycloaddition–rearrangement reactions with some alkyne and alkene dipolarophiles leading to new substituted 1-(2-vinylthioethenyl)pyrazole systems, where a second molecule of dipolarophile was added at the thiol SH which was generated by opening of the thiadiazole ring. ^{1}H, ^{13}C and ^{15}N NMR spectra are reported, as well as X-ray crystal structures on dimethyl 1-{(*Z*)-2-[(*Z*)-1,2-bis(methoxycarbonyl)-vinylthio]-1,2-diphenylethenyl}-1*H*-pyrazole-3,4-dicarboxylate **6a** and 1-[(*Z*)-2-cyanoethylthio-1,2-diphenylethenyl]-4,5-dihydro-1*H*-pyrazole-3-carbonitrile **10**. The X-ray data on **6a** suggested a weak chalcogen effect from the pyrazole 2-N to the nearby S-atom.

There are two possible quaternisation sites on the 1,2,3-thiadiazole ring.[1] Quaternisation of azoles with trimethylsilylmethyl trifluoromethanesulfonate followed by desilylation with CsF, a procedure originally developed with Schiff bases,[2,3] has been used to generate unstable exocyclic azolium methanide (ylide) 1,3-dipoles.[4–7] These are synthetically useful intermediates because the azole-embedded 1,3-dipoles may undergo unexpected cycloaddition–rearrangement sequences driven by the loss of azole aromaticity in the first cycloaddition step. For an ambident system like the 1,2,3-thiadiazole ring the synthetic opportunities would depend on the initial quaternisation site. Herein we investigate these reactions for the substituted 1,2,3-thiadiazole system **1**.

Quaternisation occurred exclusively at N-3 giving compounds **2** which opened a route to the new 1,3-dipoles **3**. The reactions of these are the first examples of cycloadditions of exocyclic azolium methanide 1,3-dipoles where the azole-embedded 2π-part of the 1,3-dipole is a nitrogen–nitrogen double bond. In the previously known cases the azole-embedded 2π-part of the 1,3-dipole was a carbon–nitrogen double bond. The cycloaddition–rearrangement sequences with some alkyne and alkene dipolarophiles are examined.

Results and discussions

Sequential reaction pathways

When the 1,2,3-thiadiazoles **1** were heated at 80 °C in trimethylsilylmethyl trifluoromethanesulfonate the salts **2** were obtained quantitatively as sticky red gums. Quaternisation of higher azole N-atoms normally causes a large upfield shift (≥100 ppm) in the ^{15}N NMR signal of the quaternised N-atom and a smaller shift (*ca.* 25 ppm) on the other N-atoms.[8,9] With the 1,2,3-thiadiazoles trimethylsilylmethyl quaternisation at N-3 was indicated by a particularly large shielding shift of *ca.* −160 ppm for this N-atom (Scheme 1). A similar effect has previously been noted for methylation by L'abbé *et al.*[1] A deshielding shift of *ca.* 6 ppm in the carbon-13 NMR signal of C-4 also supported quaternisation at N-3 (Scheme 1) as did all of the subsequent chemistry. We did not encounter quaternisation at N-2 and expected signals from an N-2 alkyl isomer were not found in the NMR spectra of the immediate (unworked) alkylation products. Due to the nature of these sticky salts **2** they were not purified but used immediately to generate the unstable 1,3-dipoles **3**.

Thus the 1,3-dipoles **3** were generated at ambient temperatures in dichloromethane by treating the salts **2** with CsF in the presence of an excess of dipolarophile. In each case a three-step sequence of reactions was encountered: (i) cycloaddition, (ii) 1,4 or 1,2 elimination in the cycloadduct with N–S bond cleavage thereby generating a 1-alkenylpyrazole species containing a β-SH in the alkenyl moiety, and (iii) capture of a second molecule of dipolarophile by addition of this SH group. Thus the new products **6**, **7**, **10**, **11**, **12** (Table 1) were obtained from the appropriate dipoles and dipolarophiles (Scheme 1). The products **6** and **11** were formed from 4,5-diarylthiadiazoles and dialkyl acetylenedicarboxylates. The reaction was regioselective with methyl propiolate as dipolarophile and gave the regioisomers **12** as the sole products. With acrylonitrile as dipolarophile the 1,3-dipole **3a** also displayed a regioselective reaction and gave the product **10**. The reaction of 1,2,3-benzothiadiazol-3-ium-3-methanide (**3**, R^1–R^2 = C_4H_4) with dimethyl acetylenedicarboxylate was less clean than the others but it followed the same pathway and the 2-pyrazol-1-ylthiophenol derivative **7** was isolated in 17% yield along with decomposition gums.

Product structures

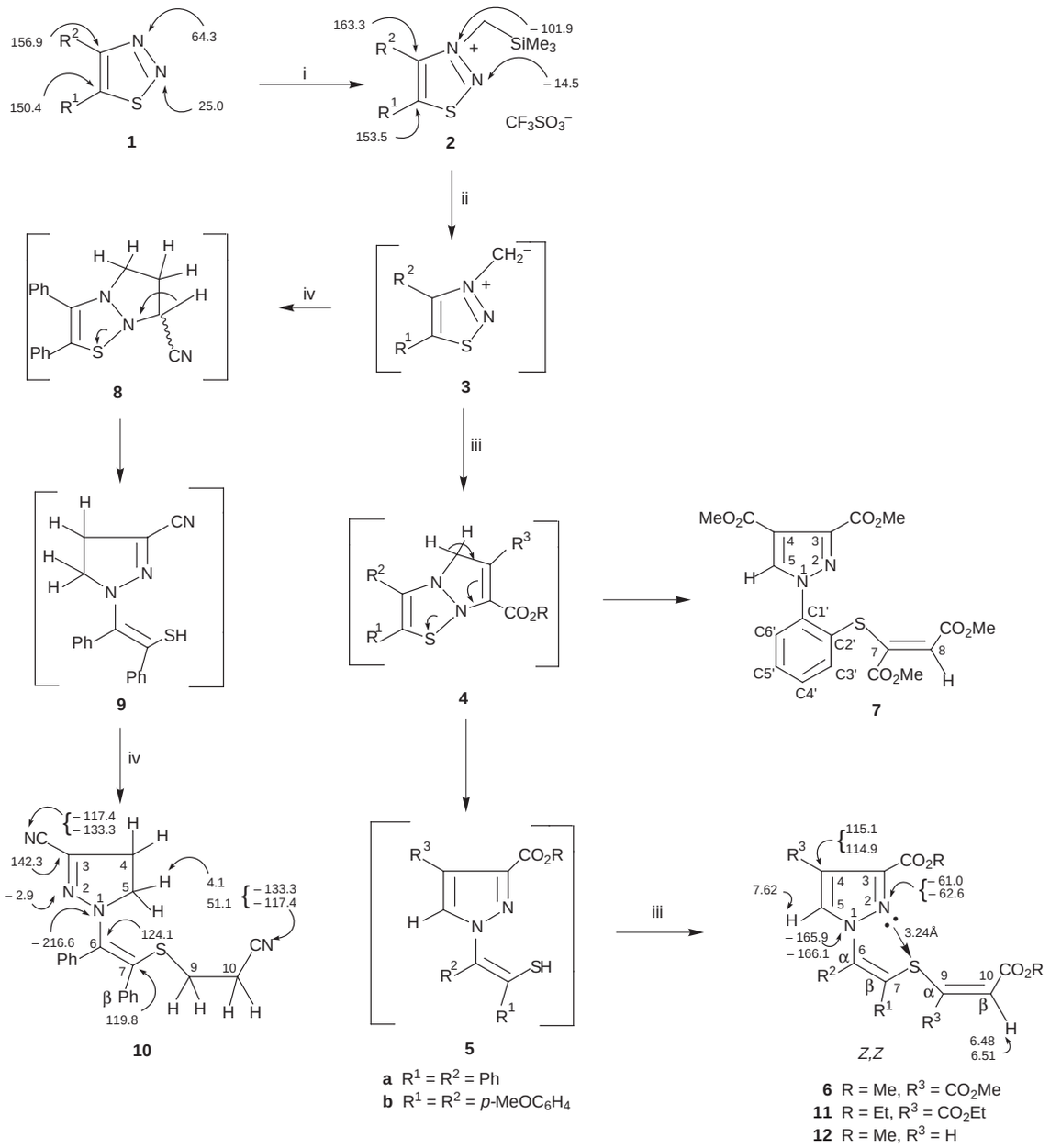
The structures of the new products were established from microanalyses, IR and ^{1}H, ^{13}C and ^{15}N NMR spectra which showed all of the expected signals. X-Ray crystal structures of compounds **6a** (Fig. 1) and **10** (Fig. 2) supported the spectral assignments and the proposed sequential reaction pathways. The combination of the X-ray and NMR data showed some interesting structural features around the pyrazole N-1 site of these new substituted 1-alkenylpyrazole derivatives. For the compounds **6a** and **11a** in the *solid state* the molecules exhibited a single *Z*,*Z* isomeric form only, with *Z* structures for the alkene moieties (Scheme 1, Fig. 1). In this there appears to be a weak chalcogen effect from the pyrazole 2-N lone pair to the nearby S (3.24 Å) atom.† Chalcogen 'fractional' bonding from O and N atoms to S, Se and Te has aroused renewed interest recently.[10,11]

† This distance is 0.11 Å less than the sum of the atomic van der Waals radii (*cf.* G. L'abbé, L. Bastin, W. Dehaen and L. Van Meervelt, *J. Chem. Soc., Perkin. Trans. 1*, 1994, 2895).

Table 1 Substrates and products

Entry	Substrate	Mp/°C	Yield (%)	Dipolarphile	Product	Mp/°C	Yield (%)[f]
1	**1a**	92–93	50	DMAD[a]	**6a**	177–178	88
2	**1b**	86–87	45	DMAD[a]	**6b**	162–164	90
3	**1** (R^1–R^2 = C_4H_4)	36	55	DMAD[a]	**7**	—[e]	17
4	**1a**	92–93	50	AN[b]	**10**	134–135	86
5	**1a**	92–93	50	DEAD[c]	**11a**	142–143	81
6	**1b**	86–87	45	DEAD[c]	**11b**	—[e]	70
7	**1a**	92–93	50	MPP[d]	**12a**	202–204	59
8	**1b**	86–87	45	MPP[d]	**12b**	—[e]	58

[a] Dimethyl acetylenedicarboxylate. [b] Acrylonitrile. [c] Diethyl acetylenedicarboxylate. [d] Methyl propiolate. [e] Gum. [f] Yields over two steps from **1**.



Scheme 1 *Reagents*: (i) $Me_3SiCH_2OSO_2CF_3$; (ii) CsF; (iii) R^3–C≡C–CO_2R; (iv) CH_2=CHCN. Shown are some ^1H, ^{13}C and ^{15}N NMR shifts for series **a** including **6a**, and the numbering system applied to the vinylthioethenyl substituent.

The effect may be strengthened in the molecules herein due to conjugation of the pyrazole ring with the 1-N alkenyl group. In this structure **6** the pyrazole 5-H is lying over the plane of the α-alkenyl phenyl ring (R^2) with a distance to the phenyl ring centroid of 3.74 Å, which is close enough to cause significant shielding of the 5-H atom.[12] Interestingly on dissolution of the compounds **6a** and **11a** in NMR solvents an isomerisation of the 1-N alkenyl α–β bond (C-6, C-7) (Scheme 1) occurred giving approximately 1 : 1 mixtures of the *Z*,*Z* and *E*,*Z* forms of the molecules in solution, thus displaying double sets of signals. No isomerisation occurred on the S-vinyl unit, which is more remote from the pyrazole ring. In the form with the *E*-alkenyl structure bonded to the pyrazole 1-N the pyrazole H-5 no longer experienced the shielding of the alkenyl α-phenyl group, which is now *trans* to it, and H-5 appeared out of the aromatic envelope at δ 8.98, the normal position[13,14] for a pyrazole H-5

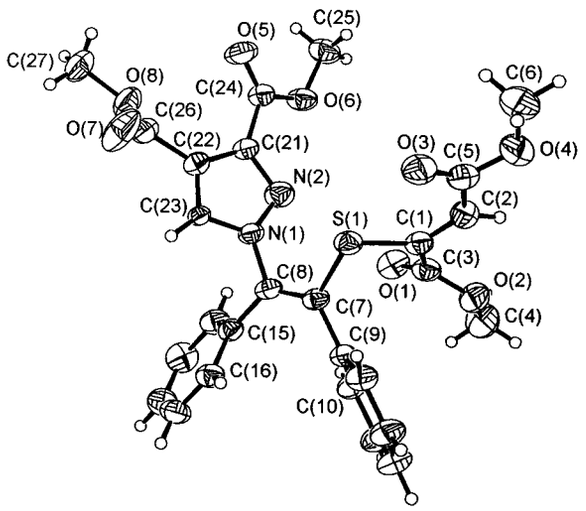


Fig. 1 X-Ray crystal structure of **6a**.

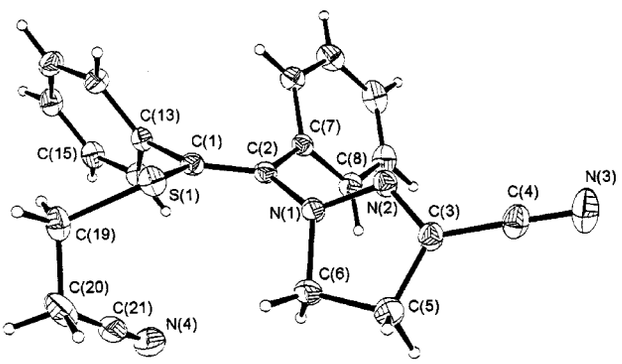


Fig. 2 X-Ray crystal structure of **10**.

containing a deshielding CO_2R group at C-4. The separate *Z*,*Z*- and *E*,*Z*-isomers did not appear to be in dynamic equilibrium in solution as the spectra were not changed by heating or cooling between −60 and 80 °C. When the solvent was removed the solids recovered were the normal *Z*,*Z* forms **6a** and **11a** (Fig. 1, Scheme 1). As expected this phenomenon did not occur with compound **7** where isomerisation of the pyrazole 1-N alkenyl moiety cannot occur. The phenomenon also did not occur with compounds **10** and **12**, where the substituents at C-9 are H-atoms, suggesting that the isomeric mixture may be delicately balanced due to interactions between substituents at C-7 and C-9 at either side of the S-atom. The packing in the solid state may favour the *Z*,*Z* form. The X-ray crystal structure of compound **10** shows that the partially reduced pyrazole ring, with the aromatic conjugation removed, is now rotated away and not aligned for possible chalcogen bonding between N-2 and the S-atom (Scheme 1, Fig. 2). In the case of compounds **6b** and **11b** the two isomeric forms, *Z*,*Z* and *E*,*Z*, were both found to be present in a 1:1 ratio in the solid products isolated directly from the reaction. Extensive chromatographic work failed to separate the individual *Z*,*Z* and *E*,*Z* forms. The influence of the *p*-methoxy substituent in the phenyl rings of these compounds relative to **6a** and **11a** again suggests that isomerism of the pyrazole 1-N alkenyl double bond is delicately balanced and the preferred form may vary with the physical state of the compound, either solid state or solution. Another interesting feature of the 1-N β-thioalkenylpyrazole system is that the expected deshielding at the N-vinyl α-carbon (C-6) and shielding at the N-vinyl β-carbon (C-7) due to enamine vinyl resonance[15] are not observed since the presence of the β S-atom partially cancels out the enamine effect by introducing a reverse thio-vinyl resonance contribution ($-C^{-}H-CH=S^{+}-$). Hence the signals for the α- and β-alkenyl carbons (C-6 and C-7) in the compounds **6**, **10**, **11** and **12** appeared in the normal alkene shift range (Scheme 1).

Experimental

Mps were measured on an Electrothermal apparatus. NMR spectra were measured on a JEOL GXFT 400 NMR machine and IR spectra on a Perkin-Elmer 983G spectrophotometer. ^1H and ^{13}C shifts are from Me_4Si, ^{15}N shifts are from CH_3NO_2 and *J* values are in Hz. Assignments were supported by COSY, DEPT and off-resonance decoupled spectra (ds). The 1,2,3-thiadiazoles **1** were prepared from the reaction of $SOCl_2$ with the *p*-tolylsulfonylhydrazone or semicarbazone of the appropriate ketone, the so-called Hurd–Mori reaction, on which we have previously reported[16] a detailed kinetic and mechanistic study. 1,2,3-Benzothiadiazole was prepared by a literature procedure.[17] The following examples show typical procedures.

4,5-Diphenyl-3-trimethylsilylmethyl-1,2,3-thiadiazol-3-ium triflate 2a

4,5-Diphenyl-1,2,3-thiadiazole (0.25 g, 1.05 mmol) and trimethylsilylmethyl trifluoromethanesulfonate (0.42 cm^3, 2.1 mmol) were heated at 80 °C for 12 h, under a reflux condenser. The resultant mixture was cooled to ambient temperature giving **2a** in quantitative yield as a red gum; $\delta_H(CDCl_3)$ 0.27 (s, 9H, $SiMe_3$), 4.4 (s, 2H, CH_2-N), 7.15–7.48 (m, 6H, $H_{m,p}$, Ph), 7.54–7.63 (m, 4H, H_o, Ph); δ_C −1.3 ($SiMe_3$), 47.1 (N-CH_2), 163.3 (C-4), 153.5 (C-5), 123.8, 124.2 (C-1′ of 4-C-Ph and 5-C-Ph), 129.2, 129.7 (C-3′ of 4-C-Ph and 5-C-Ph), 130.0, 130.3 (C-2′ of 4-C-Ph and 5-C-Ph), 132.2, 132.3 (C-4′ of 4-C-Ph and 5-C-Ph); $\delta_N(CDCl_3, CH_3NO_2)$ −14.5 (N-2), −101.9 (N-3). Compound **2a** was used directly as the residue and not purified further.

Dimethyl 1-{(*Z*)-2-[(*Z*)-1,2-bis(methoxycarbonyl)vinylthio]-1,2-diphenylethenyl}-1*H*-pyrazole-3,4-dicarboxylate 6a (Table 1, entry 1)

A solution of compound **2a**, obtained as described, in dry dichloromethane (4 cm^3) was treated with dimethyl acetylenedicarboxylate (0.69 cm^3, 5.5 mmol) followed by CsF (450 mg, 3.0 mmol), stirred at ambient temperature for 24 h, filtered to remove insoluble salts and evaporated under reduced pressure. The residue in dichloromethane (2 cm^3) was placed on a silica gel-60 column (70–230 mesh ASTM). Elution with a gradient mixture of dichloromethane–diethyl ether (1:0–30:1 v/v) gave the product **6a**, mp 177–178 °C (from CH_2Cl_2–hexane) (0.49 g, 88% over two steps from **1a**) (Found: C, 60.5; H, 4.6; N, 5.2. $C_{27}H_{24}N_2O_8S$ requires C, 60.4; H, 4.5; N, 5.2%); ν_{max}(mull)/cm^{-1} 1749.3, 1726.2, 1717.5 (ester C=O); $\delta_H(CDCl_3)$ (1:1 mixture of *Z*,*Z* and *E*,*Z* isomers) 3.52, 3.53, 3.72, 3.75, 3.76, 3.83, 3.87, 3.89 (s, 3H each, OMe), 6.48, 6.51 (s, 1H each, β-vinylic 10-CH), 6.84–6.86 (m, 2H, Ph), 7.06–7.14 (m, 1H, Ph), 7.21 (s, 10H, Ph), 7.24–7.27 (m, 1H, Ph), 7.35–7.37 (m, 3H, Ph), 7.59–7.63 (m, 3H, Ph), 7.62 (s, 1H, 5-CH, *Z*,*Z*-form), 8.98 (s, 1H, 5-CH, *E*,*Z*-form); δ_C 51.7, 51.8, 52.0, 52.1, 52.4, 53.1 (each OMe), 164.9, 164.8, 164.1, 162.0, 161.9, 161.8, 161.5 (each C=O), 114.9, 115.1 (C-4), 144.8, 144.4, 143.8, 143.7 (C-3 and C-9) 135.2, 134.9, 134.2, 133.9 (C-6 and C-7) 124.8, 124.0 (C-10) 136.9, 137.6 (C-5) 133.9, 131.1, 129.5, 129.4, 129.3, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 127.9 (Aromatic CH), overlap of some signals from both isomers; $\delta_N(CDCl_3, CH_3NO_2)$ −61.0, −62.6 (N-2), −165.9, −166.1 (N-1).

Similarly obtained was **6b**: mp 162–164 °C (CH_2Cl_2–hexane) (90% over two steps from **1b**) (Found: C, 58.6; H, 5.0; N, 4.3. $C_{29}H_{28}N_2O_{10}S$ requires C, 58.4; H, 4.7; N, 4.7%); ν_{max}(mull)/cm^{-1} 1733, 1719 (ester C=O); $\delta_H(CDCl_3)$ (1:1 mixture of *Z*,*Z* and *E*,*Z* isomers) 3.55, 3.56, 3.64, 3.70, 3.75, 3.76, 3.85, 3.86, 3.84, 3.89, 3.90 (s, 24H, 4′-OMe, CO_2Me, overlap), 6.47, 6.48 (s, 1H each, β-vinylic 10-CH), 6.62, 6.72, 6.86 (8H overlapping ds, AA′BB′, 3′-CH of 4′-$MeOC_6H_4$ for both isomers), 6.76, 7.14,

7.20, 7.51 (8H overlapping ds, AA′BB′, 2′-CH of 4′-$MeOC_6H_4$ for both isomers), 7.64 (s, 1H, 5-CH, *Z*,*Z*-form), 8.95 (s, 1H, 5-CH, *E*,*Z*-form); δ_C($CDCl_3$) 51.6, 51.7, 51.8, 51.9, 52.3, 52.4, 53.0 (overlapping 4′-OMe), 55.0, 55.1 (overlapping CO_2Me), 164.9, 164.7, 164.1, 163.9, 161.8, 161.5, 160.1, 159.6, 159.5 (overlapping C=O and C-4′ of 4′-$MeOC_6H_4$), 114.2 (C-4), 145.7, 144.7, 144.2, 143.9 (C-3 and C-9), 137.7, 137.0 (C-5), 123.5, 124.1 (C-10), 136.5, 134.9, 132.3, 131.6 (C-6, C-7), 132.6, 132.1, 131.1, 130.9 (C-2′ of 4′-$MeOC_6H_4$), 113.5, 113.7, 113.8, 113.9 (C-3′ of 4′-$MeOC_6H_4$), 128.5, 128.4, 127.8 (C-1′ of 4′-$MeOC_6H_4$).

Diethyl 1-{(*Z*)-2-[(*Z*)-1,2-bis(ethoxycarbonyl)vinylthio]-1,2-bis(4′-methoxyphenyl)ethenyl}-1*H*-pyrazole-3,4-dicarboxylate 11b (Table 1, entry 6)

A solution of compound **2b**, a red gum obtained from **1b** (1.05 mmol) as described, in dry dichloromethane (4 cm^3) was treated with diethyl acetylenedicarboxylate (3.39 cm^3, 21.2 mmol) followed by CsF (450 mg, 3.0 mmol), stirred at ambient temperature for 24 h, filtered to remove insoluble salts and evaporated under reduced pressure. The residue in dichloromethane (2 cm^3) was placed on a silica gel-60 column (70–230 mesh ASTM). Elution with a gradient mixture of dichloromethane–diethyl ether (1 : 0–30 : 1 v/v) gave the product **11b** a gum (0.48 g, 70% over two steps from **1b**); ν_{max}(mull)/cm^{-1} 1733.8, 1719.5 (ester C=O); δ_H($CDCl_3$) (1 : 1 mixture of *Z*,*Z* and *E*,*Z* isomers) 1.12–1.17 and 1.24–1.38 (overlapping triplets, 24H, OCH_2CH_3), 3.71, 3.76, 3.77, 3.82 (s, 3H each, 4′-OMe), 3.94–3.99 (m, 4H, OCH_2CH_3), 4.20–4.40 (m, 12H, OCH_2CH_3), 6.46, 6.49 (s, 1H each, β-vinylic 10-CH), 6.62, 6.72, 6.86, (8H overlapping ds, AA′BB′, 3′-CH of 4′-$MeOC_6H_4$ for both isomers), 6.76, 7.14, 7.20, 7.55 (8H overlapping ds, AA′BB′, 2′-CH of 4′-$MeOC_6H_4$ for both isomers), 7.62 (s, 1H, 5-CH, *Z*,*Z*-form), 8.96 (s, 1H, 5-CH, *E*,*Z*-form); δ_C 13.7, 13.8, 13.9, 14.0 (overlapping OCH_2CH_3), 55.1, 55.2 (overlapping 4-OMe), 60.5, 60.9, 61.0, 61.5, 62.1, 62.4 (overlapping OCH_2CH_3), 164.7, 164.6, 163.7, 162.0, 161.8, 161.3, 161.1, 159.6 (overlapping C=O and C-4′ of 4′-$MeOC_6H_4$), 114.9 (C-4), 145.9, 144.9, 144.4 (C-3 and C-9), 131.6, 134.9 (C-6, C-7), 124.4, 123.7 (C-10), 137.6, 136.7 (C-5), 132.7, 132.2, 131.0, 130.9 (C-2′ of 4′$MeOC_6H_4$), 113.6, 113.7, 113.8, 113.9 (C-3′ of 4′$MeOC_6H_4$), 127.8, 127.9, 128.7 (C-1′ of 4′$MeOC_6H_4$); δ_N($CDCl_3$, CH_3NO_2) −63.3, −64.8 (N-2), −158.8, −169.6 (N-1). On evaporation of the NMR solution containing the mixture of *Z*,*Z* and *E*,*Z* isomers of **11b** both forms were present in the *solid state* but pure samples could not be obtained despite extensive chromatographic work.

Similarly obtained was **11a**: mp 142–143 °C (CH_2Cl_2–hexane) (81% over two steps from **1a**) (Found: C, 62.7; H, 5.2; N, 4.4. $C_{31}H_{32}N_2O_8S$ requires C, 62.8; H, 5.4; N, 4.7%); ν_{max}(mull)/cm^{-1} 1747.5, 1728.4, 1717.8 (ester C=O); δ_H($CDCl_3$) (1 : 1 mixture of *Z*,*Z* and *E*,*Z* isomers) 1.12–1.16 and 1.23–1.38 (overlapping triplets, 24H, OCH_2CH_3), 3.93–3.98 and 4.18–4.39 (overlapping quartets, 16H, OCH_2CH_3), 6.47, 6.52 (s, 1H each, β-vinylic 10-CH), 6.84–6.86 (m, 2H, Ph), 7.08–7.26 (m, 10H, Ph), 7.35–7.36 (m, 4H, Ph), 7.63–7.65 (m, 4H, Ph), 7.58 (s, 1H, 5-CH, *Z*,*Z*-form), 9.00 (s, 1H, 5-CH, *E*,*Z*-form); δ_C($CDCl_3$) 13.7, 13.9, 14.0, 14.1 (overlapping OCH_2CH_3), 60.6, 60.7, 61.0, 61.1, 61.5, 62.5 (overlapping OCH_2CH_3), 164.6, 164.4, 163.6, 163.5, 161.9, 161.7, 161.6, 161.1 (C=O), 115.1, 115.0 (C-4), 124.4, 125.3 (C-10), 145.1, 144.5, 143.9 (C-3 and C-9, overlap), 137.6, 137.5, 136.6, 135.9, 135.5, 135.3, 134.1, 134.0 (C-6, C-7, C-5, C-1′, overlap), 131.3, 129.8, 129.6, 129.4, 128.7, 128.5, 128.4, 128.3, 128.1 (Aromatic C-H), overlap of some signals from both isomers.

Methyl 1-{(*Z*)-2-[(*Z*)-2-methoxycarbonylvinylthio]-1,2-diphenylethenyl}-1*H*-pyrazole-3-carboxylate 12a (Table 1, entry 7)

A solution of **2a**, prepared as described, in dry CH_2Cl_2 (4 cm^3) was treated with methyl propiolate (4.24 cm^3, 47.6 mmol) followed by CsF and worked up as described. Excess methyl propiolate was first eluted with CH_2Cl_2 and elution with a mixture of dichloromethane–diethyl ether (30 : 1 v/v) gave the product **12a**, mp 202–204 °C (from CH_2Cl_2–hexane) (0.26 g, 59%) (Found: C, 65.4; H, 4.8, N, 6.5. $C_{23}H_{20}N_2O_4S$ requires C, 65.6; H, 4.8; N, 6.6%); ν_{max}(mull)/cm^{-1} 1724, 1691 (ester C=O); δ_H($CDCl_3$) 3.68, 3.93 (s, each 3H, OMe), 5.72 (d, 1H, *J* 10.3, 9-CH), 6.73 (d, 1H, 10-CH, NOE ds, enhancement from 9-CH, 12.2%), 6.97 (d, 1H, 4-CH, *J* 1.5, NOE ds, enhancement from 5-CH, 4.6%), 7.63 (d, 1H, 5-CH), 6.87–6.89 and 7.05–7.12 (m, 6H, $H_{m,p}$, Ph), 7.30–7.36 (m, 4H, H_o, Ph); δ_C 51.4, 52.0 (OMe), 166.6, 162.6 (C=O), 109.7 (C-4), 113.8 (C-10), 144.6 (C-9), 137.5, 136.9, 135.9 (C-3, C-6, C-7, C-1′, Ph, overlap), 133.2 (C-5), 130.9, 129.1, 128.9, 128.4, 128.0 (Ar, CH); δ_N($CDCl_3$, CH_3NO_2) −65.2 (N-2), −158.2 (N-1).

Similarly obtained was **12b**: a gum (58% over two steps from **1b**); δ_H($CDCl_3$) 3.68, 3.71, 3.80, 3.93 (s, 12H, 4′-OMe), 5.72 (d, 1H, *J* 10.3, 9-CH), 6.79 (d, 1H, 10-CH, overlap with Ar), 6.59–6.64 (m, 2H, 3′-CH of 4′-$MeOC_6H_4$), 6.79–6.84 (m, 4H, 2′-CH, 3′-CH of 4′-$MeOC_6H_4$, overlap), 6.96 (d, 1H, *J* 2.3, 4-CH), 7.28–7.33 (m, 2H, 2′-CH of 4′-$MeOC_6H_4$), 7.59 (d, 1H, 5-CH); δ_C($CDCl_3$) 51.3, 52.0 (CO_2Me), 55.1 (4′-OMe, overlap), 162.6, 159.8, 159.6, 159.3 (C=O, C-4′ of 4′-$MeOC_6H_4$), 109.6 (C-4), 113.6 (C-10), 145.4 (C-9), 136.2, 135.1 (C-3, C-6, C-7, overlap), 130.7, 130.4 (C-2′ of 4′ $MeOC_6H_4$), 113.3, 113.5 (C-3′ of 4′-$MeOC_6H_4$), 128.6, 128.2 (C-1′ of 4′-$MeOC_6H_4$), 133.1 (C-5).

3-Trimethylsilylmethyl-1,2,3-benzothiadiazol-3-ium triflate 2 (R^1–R^2 = C_4H_4)

1,2,3-Benzothiadiazole (0.15 g, 1.1 mmol) and trimethylsilylmethyl trifluoromethanesulfonate (0.42 cm^3, 2.1 mmol) were heated at 80 °C for 12 h under a reflux condenser. The resultant mixture was cooled to ambient temperature giving compound **2** (R^1–R^2 = C_4H_4) in quantitative yield as a dark red gum; δ_H([$^2H_6$]acetone) 0.36 (s, 9H, $SiMe_3$), 5.70 (s, 2H, CH_2-N), 8.35–8.44 (m, 4H, Ar); δ_C −1.5 ($SiMe_3$), 46.4 (N-CH_2), 147.4, 147.0 (C-3a, C-7a), 123.9, 123.2 (C-5, C-6), 119.7, 118.9 (C-4, C-7). The product was used without further purification.

Dimethyl 1-{2-[(*Z*)-1,2-bis(methoxycarbonyl)vinylthio]phenyl}-1*H*-pyrazole-3,4-dicarboxylate 7 (Table 1, entry 3)

A solution of the dark red gum **2** (R^1–R^2 = C_4H_4) (250 mg) (prepared as described) in dry acetone (1 cm^3) and dry dichloromethane (3 cm^3) was treated with dimethyl acetylenedicarboxylate (3.2 cm^3, 25.5 mmol) followed by CsF (1.5 g, 10.0 mmol) and stirred at ambient temperature for 36 h. The solution was filtered to remove insoluble salts and the solvent removed under reduced pressure. The residue in dichloromethane (4 cm^3) was placed on a silica gel-60 column (70–230 mesh ASTM). Excess dimethyl acetylenedicarboxylate was eluted with CH_2Cl_2 after which elution with a mixture of dichloromethane–diethyl ether (30 : 1 by volume) gave the product **7**, a gum (0.08 g, 17%); ν_{max}(mull)/cm^{-1} 1735.6, 1713.4 (ester C=O); δ_H($CDCl_3$) 3.46, 3.75, 3.84, 3.95 (s, 3H each, OMe), 6.55 (s, 1H, 8-CH), 7.36–7.54 (m, 4H, Ar), 8.46 (s, 1H, 5-CH); δ_C 51.9, 52.1, 52.6, 53.1 (OMe), 165.1, 165.0, 164.0, 161.9 (C=O), 144.4 (C-3), 115.6 (C-4), 136.5 (C-5), 140.7 (C-7), 122.9 (C-8), 146.3 (C-1′), 128.8 (C-2′), 127.4 (C-3′), 129.9 (C-4′), 134.3 (C-5′), 130.4 (C-6′). The only other products eluted from the column were intractable resins.

1-[(*Z*)-2-Cyanoethylthio-1,2-diphenylethenyl]-4,5-dihydro-1*H*-pyrazole-3-carbonitrile 10 (Table 1, entry 4)

A solution of compound **2a** (prepared as described from 140 mg of **1a**) in dry CH_2Cl_2 (1 cm^3) was treated with acrylonitrile (30 cm^3, 0.456 mol) followed by CsF (800 mg, 5.33 mmol), stirred at ambient temperature for 24 h, filtered to remove insoluble salts and evaporated under reduced pressure to

Table 2 Crystal data and structure refinement for **6a**[a]

Empirical formula	$C_{27}H_{24}N_2O_8S$
Formula weight	536.54
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 10.605(2)$ Å, $\alpha = 97.974(15)°$ $b = 11.781(2)$ Å, $\beta = 105.989(16)°$ $c = 12.306(3)$ Å, $\gamma = 111.055(12)°$
Volume	1330.0(5) Å^3
Z	2
Density (calculated)	1.340 Mg m^{-3}
Absorption coefficient	0.174 mm^{-1}
$F(000)$	560
Crystal size	0.46 × 0.31 × 0.17 mm
Theta range for data collection	2.20 to 31.94°
Index ranges	$-5 \leqslant 12$; $-17 \leqslant k \leqslant 16$; $-18 \leqslant l \leqslant 17$
Reflections collected	5939
Independent reflections	5305 [R(int) = 0.0617]
Reflections observed (>2σ)	4119
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5305/0/347
Goodness-of-fit on F^2	1.089
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0725$ $wR_2 = 0.2244$
R indices (all data)	$R_1 = 0.0832$ $wR_2 = 0.2348$
Largest diff. peak and hole	0.701 and −0.625 e Å^{-3}

[a] R indices; $R_1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$ (based on F), $wR_2 = [[\Sigma_w(|F_o^2 - F_c^2|)^2]/[\Sigma_w(F_o^2)^2]]^{\frac{1}{2}}$ (based on F^2). $w = 1/[(\sigma F_o)^2 + (0.1626P)^2 + 0.3P]$. Goodness-of-fit = $[\Sigma_w(F_o^2 - F_c^2)^2/(N_{obs} - N_{parameters})]^{\frac{1}{2}}$.

Table 3 Crystal data and structure refinement for **10**[a]

Empirical formula	$C_{21}H_{18}N_4S$
Formula weight	358.45
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 9.2079(10)$ Å, $\alpha = 105.590(15)°$ $b = 10.2328(10)$ Å, $\beta = 99.435(13)°$ $c = 10.764(2)$ Å, $\gamma = 91.538(11)°$
Volume	961.0(2) Å^3
Z	2
Density (calculated)	1.239 Mg m^{-3}
Absorption coefficient	0.180 mm^{-1}
$F(000)$	376
Crystal size	0.41 × 0.37 × 0.17 mm
Theta range for data collection	2.07 to 27.98°
Index ranges	$0 \leqslant h \leqslant 12$; $-13 \leqslant k \leqslant 13$; $-14 \leqslant l \leqslant 14$
Reflections collected	5063
Independent reflections	4612 [R(int) = 0.0192]
Reflections observed (>2σ)	2725
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4612/0/235
Goodness-of-fit on F^2	1.031
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0392$ $wR_2 = 0.1055$
R indices (all data)	$R_1 = 0.0810$ $wR_2 = 0.1172$
Largest diff. peak and hole	0.194 and −0.156 e Å^{-3}

[a] R indices; $R_1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$ (based on F), $wR_2 = [[\Sigma_w(|F_o^2 - F_c^2|)^2]/[\Sigma_w(F_o^2)^2]]^{\frac{1}{2}}$ (based on F^2). $w = 1/[(\sigma F_o)^2 + (0.0604P)^2]$. Goodness-of-fit = $[\Sigma_w(F_o^2 - F_c^2)^2/(N_{obs} - N_{parameters})]^{\frac{1}{2}}$.

remove excess acrylonitrile. The residue in dichloromethane (2 cm^3) was placed on a silica gel-60 column (70–230 mesh ASTM). Elution with dichloromethane gave the product **10**, mp 134–135 °C (from CH_2Cl_2–hexane) (0.12 g, 86%) (Found: C, 70.6; H, 4.9; N, 15.8; $C_{21}H_{18}N_4S$ requires C, 70.4; H, 5.0; N, 15.6%); ν_{max}(mull)/cm^{-1} 2249, 2209 (C≡N), 1638 (C=C); δ_H($CDCl_3$) 2.4 (dd, AA′BB′, 2H, CH_2CN), 2.6 (dd, 2H, SCH_2), 3.08 (m, 2H, 4-CH_2), 4.10 (m, 2H, 5-CH_2), 7.00–7.03 (m, 2H, Ph), 7.10–7.25 (m, 6H, Ph), 7.32–7.39 (m, 2H, Ph); δ_C 18.3 (C-10), 27.5 (C-9), 32.9 (C-4), 51.1 (5-C), 142.3 (C-3), 124.1 (C-6), 119.8 (C-7), 118.1, 114.9 (C≡N), 136.6, 136.0 (C-1′ of Ph), 130.7, 129.9, 128.2, 128.0 (C-2′ and C-3′ of Ph), 127.9, 127.5 (C-4′ of Ph); δ_N($CDCl_3$, CH_3NO_2) −2.9 (N-2), −216.6 (N-1), −117.4, −133.3 (C≡N). The remainder was untractable resin.

X-Ray crystallography

The crystal structures of **6a** and **10** were solved by direct methods, SHELXS-97,[18] and refined by full-matrix least-squares using SHELXL-97.[19] SHELX operations were rendered paperless using ORTEX which was also used to obtain the drawings.[20] Data were corrected for Lorentz and polarization effects but not for absorption. Hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. The non-hydrogen atoms were refined anisotropically. All calculations were performed on a Pentium PC. Crystal data for **6a** are in Table 2 and for **10** in Table 3. CCDC reference number 207/320. See http://www.rsc.org/suppdata/P1/1999/1415 for crystallographic files in .cif format.

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