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Synthesis and Nitrosation Reactions of π-Extended 1,3-Dithiol-2-ylidene Systems

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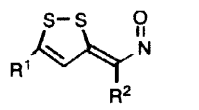
Abstract: New 1,3-dithiol-2-ylidene derivatives, notably π-extended systems, have been synthesised by Wittig reactions of phosphorane and phosphonate ester derivatives of 1,3-dithiole with activated ketones and α,β-unsaturated ketones. Nitrosation reactions of a range of these π-extended systems, results in the formation of nitroalkenes, via unstable nitrosoalkene intermediates, which, in general, could not be isolated. The X-ray crystal structure of 1-(4,5-dicarbomethoxy-1,3-dithiol-2-ylidene)-1-cyano-1-phenyl-methane reveals a small degree of intramolecular electron transfer from the dithiole ring to the conjugated cyano group.

INTRODUCTION

Nitrosoalkenes are extremely reactive species which cannot generally be isolated, evidence for their formation usually being provided by trapping reactions, primarily in a Diels-Alder reaction.[1] Stabilisation of nitrosoalkenes has, however, been achieved by strong conjugative interaction between the C=C and N=O bonds[2] or by participation of the nitroso group in intramolecular O···S interactions, in which considerable π-electron delocalisation and additional heteroatomic stability can result *e.g.* system **1**.[3] Based on the initial work of Lakshmikantham and Cava,[4] in which nitroso derivative **3** was obtained as a stable solid by reaction of 1,3-dithiol-2-ylidene system **2** with *iso*-amylnitrite, we investigated the use of a variety of 1,3-dithiol-2-ylidenes, *e.g.* **4**[5] and 1,3-diselenol-2-ylidenes **6**[6] in analogous reactions. These reactions led to the formation of the stable nitrosoalkenes **5** and **7**, respectively. X-Ray crystallography established that in the solid state these compounds have *cisoid* resonance-stabilised structures **5** and **7**, which accounts for their high stability, rather than *transoid* structures **5'** and **7'**. Early work[4] on **3** did not identify the *cisoid* structures.



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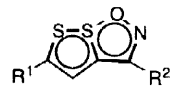

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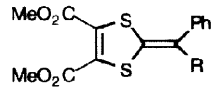
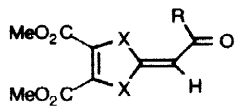
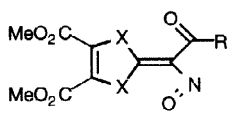


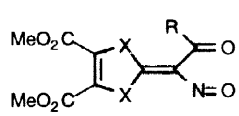
2 R = H
3 R = NO



4 X = S; R = Me
6 X = Se; R = H



5 X = S; R = Me
7 X = Se; R = H



5', 7'

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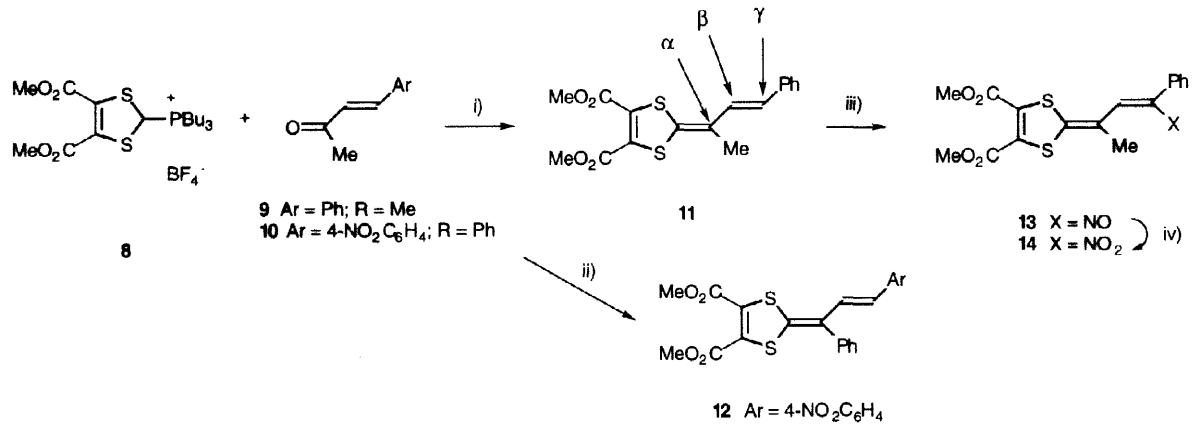
PII: S0040-4020(98)00118-5

Recently, Gowenlock *et al.* reported some new analogues of **5** and based on NMR studies they assigned a *cisoid* structure in solution,[7] and Cava *et al.* have reported the synthesis and nitrosation reactions of an extended tetrathiafulvalene derivative in which the primary reason for the stability of the nitroso product was an intramolecular S···O interaction.[8] Herein, we report the synthesis of new 1,3-dithiol-2-ylidene derivatives and the nitrosation reactions of these systems at a vinylic site.

RESULTS AND DISCUSSION

We wished to explore the possibility that the electron donating effects of the 1,3-dithiole ring[9] could lead to reaction at a more distant site in a π-conjugated chain attached to C(2). The γ-carbon (see structure **11**) could, in principal, be nucleophilic and to determine if a reaction could occur there, we needed to block the α site. To achieve this, we reacted the well-known 1,3-dithiole Wittig reagent **8**[10] with *trans*-4-phenyl-3-butene-2-one **9**. Although this Wittig reagent has been shown to react with ketones and α,β-unsaturated aldehydes,[6] to our knowledge it had not been shown to react with α,β-unsaturated ketones. Attempts to form **11** following the procedure previously described for α,β-unsaturated aldehydes failed. This was attributed to two factors: i) the steric effect of the substituent attached to the carbonyl carbon, and ii) the reduced electrophilicity of the carbonyl group. In an attempt to induce irreversible deprotonation of **8**, and hence promote reaction of the ylide, a stronger base was employed.[11] Thus, addition of **9** to a mixture of **8** and *n*-butyllithium in THF at -78°C, led to the formation of the desired product **11**, albeit in low yield (15%) (Scheme 1). This compound was now a candidate for nitrosation of the more remote γ-vinyl site, since the α-site was blocked by the methyl group.

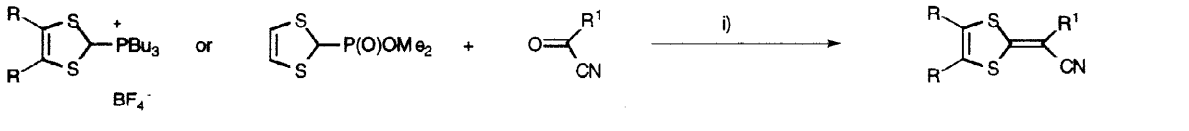
Nitrosation of **11** with *iso*-amylnitrite in dichloromethane at 0°C[4,5] for 1 h, afforded a new product which showed a single vinyl peak from CβH in the proton NMR spectrum, and not a doublet of doublets as seen in **11**, which clearly suggested that substitution had occurred at the γ-vinyl site. The mass spectrum showed fragments which corresponded to both the nitroso compound **13** [*m/z* (CI) 378 (MH^+)] and the nitro species **14** [*m/z* (CI) 394 (MH^+)]. A parent-daughter scan showed both species **13** and **14** exhibited different breakdown patterns, establishing that the two compounds existed independently, with **14** presumably being formed by the *in situ* oxidation of the initially formed nitroso product **13**.



Scheme 1; Reagents and Conditions. i) ^{n}BuLi, THF, -78°C, **9**; ii) ^{n}BuLi, THF, -78°C, **10**; iii) $^i C_5H_{11}ONO$, CH_2Cl_2, 0°C; iv) air.

Although compound **11** possessed a blocking group at the α site, it lacked an electron withdrawing group at the site of nitrosation, which had previously been found to stabilise the nitrosoalkene system.[5,6] Attempts were, therefore, made to prepare analogue **12** from 4-nitro-chalcone **10**. Utilising the procedure optimised for the formation of **11**, and despite repeated attempts, compound **12** could be obtained in only 3% yield. This low reactivity of **8** and **10** was attributed primarily to steric hindrance of the carbonyl group, which was not overcome by the potentially activating effect of the *para*-nitro group on the phenyl ring. Indeed, **8** had previously been shown to be unreactive towards benzophenone, presumably for steric rather than electronic reasons.[10] The nitrosation of **12** was not attempted due to the small amount of product obtained and the expected low yield of the nitrosation step itself.

We, therefore, turned to strongly electron withdrawing substituents, *viz.* nitrile and trifluoromethyl groups, as 'α-site blockers'. It was envisaged that these groups should have the dual advantages of promoting the Wittig reaction, and assisting in the stabilisation of the subsequent nitrosoalkenes.[6,12] To determine the conditions under which acyl cyanides would react with 1,3-dithiole Wittig reagents, the simple derivatives **17** were reacted with reagents **8** and **15**[13] and Wadsworth-Emmons reagent **16**[14] to afford the alkenes **18** (Scheme 2). The diester derivatives **18a-d** were isolated in 52-74% yields, whereas products **18e** and **18f** were obtained in lower yields (27-28%).



8, R = CO_2Me
15, R = MeS

16

17

18	R	R^1
a	CO_2Me	Me
b	CO_2Me	Ph
c	CO_2Me	4-Cl-C_6H_4
d	CO_2Me	4-MeO-C_6H_4
e	MeS	Ph
f	H	Ph

Scheme 2; Reagents and Conditions. i) **8**, **15** or **16**, Base (Et_3N or nBuLi), THF, **17**.

The single-crystal X-ray structure of **18b** was determined (Fig. 1). The dithiole ring is planar and the planes of the ester substituents at C(4) and C(5) form dihedral angles of 25° and 33° with it. There is a slight twist (4.6°) around the C(2)=C(3) bond, while the phenyl ring plane is inclined by 24° to the bonding plane of C(2). Thus push-pull electron transfer from the dithiole ring through the C(2)=C(3) bond to the cyano acceptor group occurs within an essentially planar moiety. In (1,3-dithiol-2-ylidene)-aryl-methanes with H or Me-substituents in place of CN the exocyclic C=C bond *a* (average 1.338 Å)[15] is close to the standard double bond (1.331 Å)[16] and the two adjacent C-S bonds of the dithiole ring (*b*) are significantly longer (average 1.762 Å) than the other two (*c*, avg. 1.734 Å). The intramolecular charge transfer in **18b** manifests itself in lengthening of the bond *a* to 1.370(3) Å, shortening of *b* (average 1.749 Å) and slight lengthening of *c* (average 1.744 Å). Similar effects have been observed earlier in the analogue of **18** with R = Me, R^1 = CO_2Me[17] and in the dicyano-derivative (R = COMe, H, R^1 = CN).[18] Also, the C(1)-C(2) bond in **18b** (1.430(4) Å) is marginally shorter than usual C(sp^2)-CN bonds, *eg.* in benzonitriles (1.438-1.458 Å in the most accurate structures).[19]

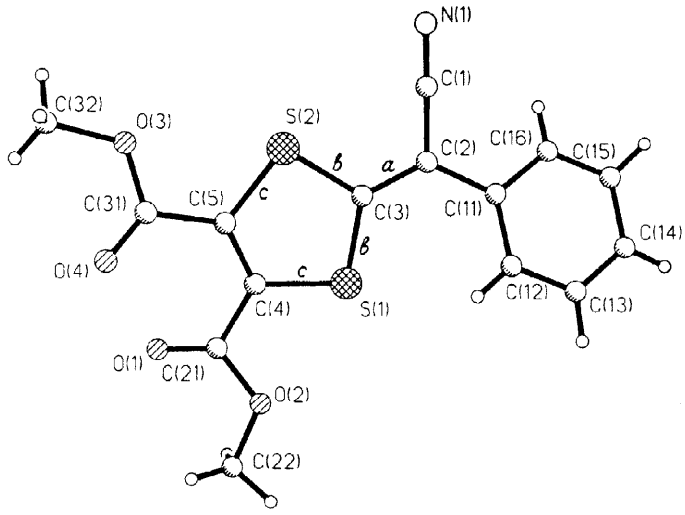
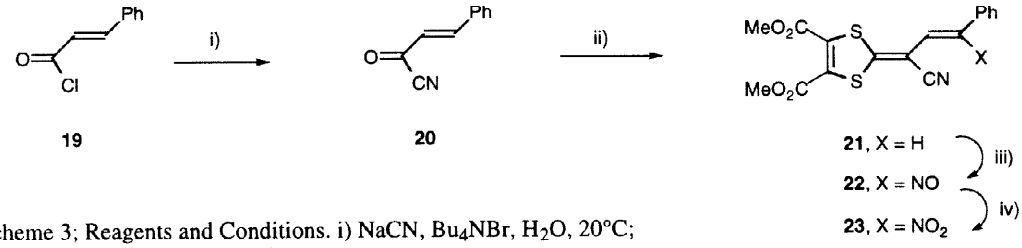


Fig. 1. **Molecular structure of 18b.** Bond distances (Å): S(1)-C(3) 1.743(2), S(2)-C(3) 1.755(2), S(1)-C(4) 1.748(2), S(2)-C(5) 1.740(2), C(4)-C(5) 1.351(3), C(2)-C(3) 1.370(3), C(1)-C(2) 1.430(4), C(2)-C(11) 1.477(3), N(1)-C(1) 1.145(3).

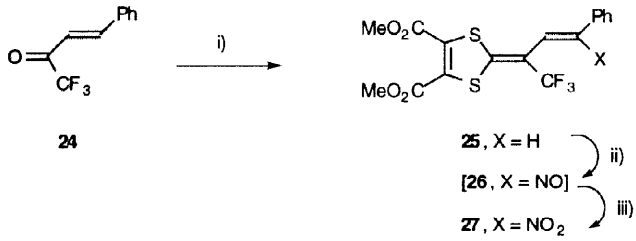
Having determined that simple acyl cyanides successfully underwent Wittig and Wadsworth-Emmons reactions with **8**, **15** and **16**, we extended the reactions to vinyl acyl cyanide **20** (obtained in 98% yield following the procedure described by Koenig and Weber,[20] from cinnamoyl chloride **19**). Reaction of **8** and **20** (n-BuLi as base) gave the desired dithiol-2-ylidene **21** in 22% yield as a yellow crystalline solid (Scheme 3). This reaction demonstrated the enhanced reactivity of the systems substituted with electron-withdrawing groups over the simple ketones described previously.

Nitrosation of **21** was attempted *via* the usual procedure and, after two hours, t.l.c. evidence indicated that a reaction had occured and that no starting material remained. The proton NMR spectrum of the reaction product showed the loss of the characteristic vinyl pattern, and mass spectrometric analysis of the isolated product again indicated the presence of both the nitroso [*m/z* (CI) 389 (MH^+)] and the nitro derivatives, **22** and **23**, respectively. A parent-daughter scan again clearly demonstrated that the two molecules **22** and **23** existed independently. Presumably therefore, **23** was formed by air-oxidation of the initially formed nitroso derivative **22** under the reaction conditions or during work up. Separation of compounds **22** and **23** was attempted by flash column chromatography on silica gel. We have previously observed that under these conditions oxidation of the nitroso species to the corresponding nitro derivative is possible.[12] Indeed, in this case, chromatography led to the isolation only of the pure nitro compound **23** in 62% yield.



Scheme 3; Reagents and Conditions. i) NaCN, Bu_4NBr, H_2O, 20°C; ii) **8**, ^nBuLi, THF, -78°C; iii) $^iC_5H_{11}ONO$, CH_2Cl_2, 0°C; iv) air or SiO_2

Similarly, the commercially-available ketone **24**, gave the π-extended compound **25** in 80% yield. Since the trifluoromethyl group is highly electron withdrawing, we were able to employ triethylamine as the base in the Wittig reaction (Scheme 4). The three fluorine atoms in **25** led to the usual *AB* vinyl pattern in the proton NMR spectrum being further split into a doublet of doublets of quartets, the coupling constants of which were dependent on the number of bonds between the proton and the fluorine group. By comparison of the $J_{H\text{-}F}$ values, the vinyl protons can be assigned, since $^{3}J_{H\text{-}F}$ will be greater than $^{4}J_{H\text{-}F}$. In this case, the $J_{H\text{-}F}$ values are 1.6 and 0.9 Hz; thus the proton with the former $J_{H\text{-}F}$ value is the one lying closest to the trifluoromethyl group, *i.e.* the peak at δ 6.77 ppm. The proton-decoupled fluorine spectrum of **25** showed, as expected, a singlet due to the three equivalent fluorine nuclei.

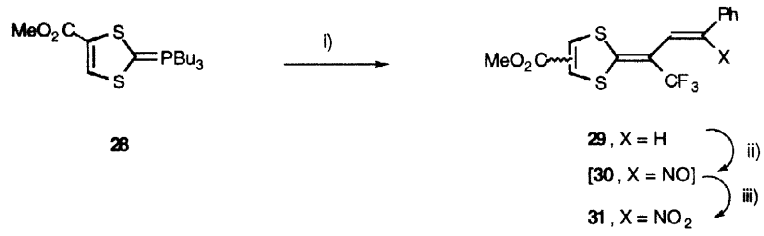


Scheme 4 Reagents and conditions. i) **8**, Et_3N: ii) $^{i}C_5H_{11}ONO$, CH_2Cl_2, 0°C; iii) air

Nitrosation of compound **25** using the standard protocol led to the formation of a yellow product in 52% yield, which was shown to be solely the nitro derivative **27** [*m/z* (CI) 448 (MH^+)], both before and after chromatographic purification. In this case, oxidation of the (presumably) initially formed nitroso derivative **26** to the more stable nitro compound **27** could not be prevented.

Having synthesised compounds **21** and **25** which provided the factors necessary for the nitrosation reaction to proceed at the γ site (*i.e.* **20** and **24** reactive enough for the Wittig reaction, and the products were blocked at the α-nitrosation site) we turned our attention to analogues possessing only one ester group to determine whether nitrosation reactions were still feasible.

The mono-ester Wittig reagent **28** cannot be isolated as its fluoroboric acid salt,[12] and, instead, was generated and trapped in 'one pot'. Initial attempts showed that the acyl cyanide, **20** was insufficiently reactive for the 'one pot' reaction, and no Wittig reaction occurred. This effect was attributed to the previously observed reduced reactivity of the α,β-unsaturated derivatives, which had hindered approaches to **10** and **14**. However, the *in situ* trapping of **28** with **24** afforded the desired system **29** in 47% yield (Scheme 5).



Scheme 5; Reagents and Conditions. i) **24**; ii) $^{i}C_5H_{11}ONO$, CH_2Cl_2, 0°C; iii) air

The proton NMR spectrum confirmed that **29** was an equimolar mixture of isomers: the ester group appeared as two distinct singlets arising from the s-*cis* and the s-*trans* isomers. Nitrosation of **29** under the

standard conditions gave an oil which, after purification was shown to be the nitro derivative **31** in 76% yield. Presumably, as above, the nitroso derivative **30** is an unstable precursor to nitroalkene **31** and **30** was not observed, even in the mass spectrum of the crude material.

CONCLUSIONS

Reactions with α,β-unsaturated ketones seem to be at the limit of the reactivity of the versatile Wittig reagent **8**. This was well illustrated by the fact that unless strongly electron withdrawing groups are present at the carbonyl carbon, the yields of the Wittig reactions were very low. Reagents **8**, **15** and **16** have, however, been shown to react with simple acyl cyanides to afford products incorporating a nitrile group in close proximity to the dithiole ring. Further reactions of the nitrile functionality may lead to the development of new compounds based on the rich chemistry of this reactive functionality.

We have established that the more remote vinyl sites of π-extended 1,3-dithiol-2-ylidene systems are sufficiently activated to undergo a nitrosation reaction. The nitrosoalkenes which are formed in these reactions are, however, not stable and very readily oxidise to the more stable nitro systems either during the reaction or on purification. It is clear from this work, and that reported by Cava *et. al.*,[8] that the dipolar nature of these nitrosoalkenes is not the major factor in determining their stability. The instability of **13**, **22**, **26** and **30** clearly demonstrates the importance of the intramolecular O···S and O···Se interactions we have previously reported,[5,6] in stablising the highly reactive nitrosoalkene moiety in systems **5** and **7**.

EXPERIMENTAL

General. Details of equipment used and general procedures are the same as those reported recently.[21]

2-(4,5-Dicarbomethoxy-1,3-dithiol-2-ylidene)-4-phenyl-but-3-ene (11).
To a stirring solution of Wittig reagent **8** (510 mg, 1 mmol) in dry tetrahydrofuran (50 mL) at -78°C was added, dropwise, *n*-butyllithium (0.63 mL, 1 mmol, 1.6 M in hexanes) which turned the solution deep red. After 0.5 h, 4-phenyl-but-3-en-2-one **9** (152 mg, 1 mmol) was added dropwise. The reaction temperature was maintained at -78°C for 1.5 h and then allowed to warm to ambient temperature over 2.5 h. The reaction was poured into water (20 mL) and extracted with dichloromethane (3 x 10 mL). The combined organic phases were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* to yield a deep red oil, which was purified by recrystallisation from dichloromethane/methanol (1:10 $^{v}/_{v}$) to yield 53 mg (15%) of **11** as an orange solid; m.p. 130-132°C. (Found C, 58.32; H, 4.53; $C_{17}H_{16}O_4S_2$ requires C, 58.64; H, 4.62%) *m/z* (CI) 349(MH^+, 100%); ν_{max} (KBr)/cm^{-1} 3054, 2986, 1736 and 1235; δ_H ($CDCl_3$) 7.3 (m, 5H), 6.71 (d, *J*= 15 Hz, 1H), 6.42 (d, *J*= 15 Hz, 1H), 3.85 (s, 6H), and 1.90 (s, 3H).

1-(4,5-Dicarbomethoxy-1,3-dithiol-2-ylidene)-1-phenyl-3-(4-nitrophenyl)-prop-2-ene (12).
To a stirring solution of Wittig reagent **8** (512 mg, 1 mmol) in anhydrous tetrahydrofuran (50 mL) at -78°C was added, dropwise, *n*-butyllithium (1.6 M in hexanes) (0.06 mL, 1 mmol). The mixture was stirred at -78°C for 10 minutes, whereupon a solution of 4-nitrochalcone **10** (255 mg, 1 mmol) in anhydrous tetrahydrofuran (10 mL) was added dropwise, and the resultant mixture allowed to warm to 20°C over 16 h. At that time, the solvent was removed *in vacuo* to yield an orange/red solid, which was purified by column chromatography on silica gel with dichloromethane / hexane (1:1 $^{v}/_{v}$) as eluent, followed by recrystallisation from methanol to yield 12 mg (3%) of **12** as a deep red solid; m.p. >250°C. *m/z* (CI) 456 (MH^+, 100%); ν_{max} (KBr)/cm^{-1} 3050,

2994, 1744, 1655 and 1242; δ_H ($CDCl_3$) 8.12 (d, *J*= 8 Hz, 2H), 7.45 (m, 7H), 7.08 (d, *J*= 16 Hz, 1H), 5.97 (d, *J*= 16 Hz, 1H), 3.87 (s, 3H) and 3.78 (s, 3H).

General Procedure for the Formation of 1-Cyano-1-dithiol-2-ylidenes (18)

To a stirred solution of the appropriate Wittig reagent in anhydrous tetrahydrofuran (40 mL) were added sequentially, triethylamine (excess) and the appropriate acyl cyanide. The resultant mixture was stirred at room temperature for 4 h. After this time, the solvent was removed *in vacuo* and the resulting oil dissolved in dichloromethane and purified either by column chromatography or by recrystallisation after precipitation of the crude material.

1-(4,5-Dicarbomethoxy-1,3-dithiol-2-ylidene)-1-cyano-ethane (18a).

Prepared according to the general procedure with reagent **8** (400 mg, 0.79 mmol), triethylamine (1 mL, excess) and pyruvonitrile (55 mg, 0.79 mmol). The crude material was dissolved in dichloromethane (10 mL) and methanol (60 mL) was added to induce precipitation. Recrystallisation from dichloromethane / methanol (1:10 $^v/_v$) afforded **18a** (160mg, 74%) as yellow needles; m.p. 113-115°C. [Found C, 44.39; H, 3.21; N, 5.04: $C_{10}H_9NO_4S_2$ requires C, 44.32; H, 3.35; N, 5.17%] *m/z* (CI) 272(MH^+, 100%); ν_{max} (KBr)/cm^{-1} 2180, 1720 and 1244; δ_H ($CDCl_3$) 3.89 (s, 3H), 3.87 (s, 3H) and 1.86 (3H, s).

1-(4,5-Dicarbomethoxy-1,3-dithiol-2-ylidene)-1-cyano-1-phenyl-methane (18b).

Prepared according to the general procedure with reagent **8** (400 mg, 0.79 mmol), triethylamine (1 mL, excess) and benzoyl cyanide (100 mg, 0.76 mmol). The crude material was dissolved in dichloromethane (10 mL) and methanol (60 mL) was added to induce precipitation. Recrystallisation from dichloromethane / methanol (1:10 $^v/_v$) afforded **18b** (160 mg, 64%) as yellow needles; m.p. 146-148°C. [Found C, 53.8; H, 3.3; N, 4.1: $C_{15}H_{11}NO_4S_2$ requires C, 54.0; H, 3.3; N, 4.2%] *m/z* (EI) 333 ($M^{+\cdot}$ 100%); ν_{max} (KBr)/cm^{-1} 2187, 1755, 1728, 1582, 1508, 1430 and 1240; δ_H ($CDCl_3$) 7.6-7.3 (m, 5H), 3.91 (s, 3H) and 3.87 (s, 3H); δ_C ($CDCl_3$) 158.86, 158.71, 152.50, 133.10, 132.11, 130.87, 129.13, 126.32, 128.52, 117.28, 96.19, 53.7 and 53.65.

1-(4,5-Dicarbomethoxy-1,3-dithiol-2-ylidene)-1-cyano-1-(4-chlorophenyl)-methane (18c).

Prepared according to the general procedure with reagent **8** (1.73 g, 3.6 mmol), triethylamine (2 mL, excess) and 4-chlorobenzoyl cyanide (600 mg, 3.6 mmol). The crude material was dissolved in dichloromethane (10 mL) and methanol (60 mL) was added to induce precipitation. Recrystallisation from dichloromethane / methanol (1:10 $^v/_v$) afforded **18c** (890 mg, 67%) as yellow needles; m.p. 131-133°C. [Found C, 49.15; H, 2.86; N, 3.69: $C_{15}H_{10}NClO_4S_2$ requires C, 48.98; H, 2.74; N, 3.81%] *m/z* (CI) 386 (MNH_4^+, 30%), 384 (MNH_4^+, 65%) and 368 (100%); ν_{max} (KBr) 2190, 1765, 1710, 1575, 1500, 1430 and 1240 cm^{-1}; δ_H ($CDCl_3$)/cm^{-1} 7.6-7.3 (m, 4H), 3.93 (s, 3H) and 3.88 (s, 3H); δ_C ($CDCl_3$) 158.52, 158.34, 152.13, 133.12, 132.45, 131.42, 129.32, 127.17, 128.28, 118.54, 95.42, 52.99 and 52.70.

1-(4,5-Dicarbomethoxy-1,3-dithiol-2-ylidene)-1-cyano-1-(4-methoxyphenyl)-methane (18d).

Prepared according to the general procedure with reagent **8** (290 mg, 0.62 mmol), triethylamine (1 mL, excess) and 4-methoxybenzoyl cyanide (100 mg, 0.62 mmol). The crude material was dissolved in dichloromethane (5 mL) and methanol (60 mL) was added to induce precipitation. Recrystallisation from dichloromethane / methanol (1:10 $^v/_v$) afforded **18d** (116 mg, 52%) as orange plates; m.p. 110-112°C. [Found C, 52.82; H, 3.63; N, 3.62: $C_{16}H_{13}NO_5S_2$ requires C, 52.88; H, 3.61; N, 3.85%] *m/z* (CI) 381 ($MNH_4^{+\cdot}$ 25%) and 364 (MH^+, 100%); ν_{max} (KBr)/ cm^{-1} 2185, 1755, 1710, 1580, 1514, 1430 and 1220; δ_H ($CDCl_3$) 7.4 (d, J = 7 Hz, 2H), 6.95 (d, J = 7 Hz, 2H), 3.90 (s, 3H), 3.86 (3H, s) and 3.84 (s, 3H); δ_C ($CDCl_3$) 159.62, 158.98, 150.75, 132.17, 130.69, 128.13, 125.67, 117.34, 114.53, 96.10, 55.39, 53.76 and 53.64.

1-(4,5-Dithiomethyl-1,3-dithiol-2-ylidene)-1-cyano-1-phenyl-methane (18e).
Prepared according to the general procedure utilising reagent **15** (450 mg, 1 mmol), triethylamine (1 mL, excess) and benzoyl cyanide (800 mg, 6 mmol). The crude material was dissolved in dichloromethane (5 mL) and methanol (60 mL) was added to induce precipitation. Recrystallisation from dichloromethane / methanol (1:10 $^{v}/_{v}$) afforded **18e** (80 mg, 27%) as yellow plates; m.p. 124-126°C. [Found C, 50.44; H, 3.66; N, 4.32: $C_{13}H_{11}NS_4$ requires C, 50.45; H, 3.58; N, 4.53%] *m/z* (CI) 310 (MH^{+} 100%); ν_{max} (KBr)/cm^{-1} 2173, 1584, 1509, 1432, and 1224; δ_H ($CDCl_3$) 7.5 (m, 5H), 2.54 (s, 3H) and 2.43 (s, 3H).

1-(4,5-Dihydro-1,3-dithiol-2-ylidene)-1-cyano-1-phenyl-methane (18f).
To a solution of reagent **16** (500 mg, 0.23 mmol) in anhydrous THF (50 mL) at -78°C was added *n*-butyllithium (1.6 mL, 0.26 mmol). The resultant solution was stirred for 1 h, whereupon benzoyl cyanide (300 mg, 0.23 mmol) was added and the solution allowed to warm to room temperature over 12 h. The solution was diluted with diethyl ether (100 mL) washed with water (2 x 50 mL), dried ($MgSO_4$) and the solvent removed *in vacuo* to afford a yellow oil. Column chromatography on silica gel utilising dichloromethane / hexane (1:3 $^{v}/_{v}$) as the eluent afforded **18f** (70 mg, 28%) as yellow needles; m.p. 83-84°C. [Found C, 60.93; H, 3.11; N, 6.71: $C_{11}H_7NS_2$ requires C, 60.80; H, 3.24; N, 6.45%] *m/z* (CI) 218 (MH^{+} 100%); ν_{max} (KBr)/cm^{-1} 2184, 1580, 1512, 1424, and 1220; δ_H ($CDCl_3$) 7.30 - 7.50 (m, 5H), 6.72 (d, J = 4 Hz, 1H) and 6.55 (d, J = 4 Hz, 1H); δ_C ($CDCl_3$) 159.69, 134.33, 128.95, 127.67, 126.18, 120.09, 119.30 and 118.99.

2-(4,5-Dicarbomethoxy-1,3-dithiol-2-ylidene)-1-cyano-3-phenyl-prop-2-ene (21).
To a solution of Wittig reagent **8** (1.05 g, 2.0 mmol) in dry tetrahydrofuran (50 mL) at -78°C was added *n*-butyl lithium (1.6 M in hexanes) (2 mL, 3.6 mmol) over 0.25 h. The reaction was maintained at -78°C for 1 h, whereupon compound **20** (300 mg, 2 mmol) in dry tetrahydrofuran (10 mL) was added and the reaction was allowed to warm to 20°C before being stirred for 3 days. The resultant solution was poured into water (80 mL) and the mixture extracted with dichloromethane (3 x 50 mL). The combined organic phases were washed, dried ($MgSO_4$) and the solvent removed *in vacuo* to yield a yellow solid. Purification by column chromatography on silica gel with dichloromethane as the eluent afforded **21** (160 mg, 22%) as yellow crystals; m.p. 161-162°C. [Found C, 56.84; H, 3.37; N, 4.05: $C_{17}H_{13}NO_4S_2$ requires C, 56.82; H, 3.64; N, 3.91%] *m/z* (CI) 360 (MH^{+} 100%); ν_{max}(KBr)/ cm^{-1} 3054, 2986, 2211, 1738 and 1265; δ_H($CDCl_3$) 7.34 (m, 5H), 6.76 (d, J= 16 Hz, 1H), 6.38 (d, J= 16 Hz, 1H) 3.89 (s, 3H) and 3.88 (s, 3H).

1,1,1-Trifluoro-2-(4,5-dicarbomethoxy-1,3-dithiol-2-ylidene)-4-phenyl-but-3-ene (25).
To a stirred solution of Wittig reagent **8** (250 mg, 0.5 mmol) in anhydrous tetrahydrofuran (50 mL) at 20°C was added triethylamine (3 mL, excess). To this mixture was added *trans*-1,1,1-trifluoro-4-phenyl-3-buten-2-one, **24** (110 mg, 0.5 mmol) and the resultant solution stirred for 18 h. Removal of the solvent *in vacuo* afforded a viscous oil which was purified by column chromatography on silica gel with dichloromethane as the eluent to afford **25** (160 mg, 80%) as red crystals; m.p. 124-125°C. [Found C, 51.02; H, 3.35: $C_{17}H_{13}F_3O_4S_2$ requires C, 50.83; H, 3.24%] *m/z* (CI) 403(MH^{+}, 100%); ν_{max}(KBr)/ cm^{-1} 3152, 1740 and 1247; δ_H($CDCl_3$) 7.38 (m, 5H), 6.77 (dq, J_{HH}= 16 Hz, $^{3}J_{HF}$= 1.6 Hz, 1H), 6.51 (dq, J_{HH}= 16.5 Hz, $^{4}J_{HF}$= 0.9 Hz, 1H) and 3.87 (s, 6H); δ_F($CDCl_3$) -58.5 (s, 3F).

1,1,1-Trifluoro-2-(4-carbomethoxy-1,3-dithiol-2-ylidene)-4-phenyl-but-3-ene (29).
To a stirred solution of tributylphosphine (0.12 mL, 0.5 mmol) and carbon disulfide (0.03 mL, 0.5 ml) in methanol (20 mL) at 0°C was added methyl propiolate (0.05 mL, 0.5 mmol) followed by *trans*-1,1,1-trifluoro-4-phenyl-3-buten-2-one **24** (113 mg, 0.5 mmol). The resultant solution was stirred at 0°C for 5 min and allowed to warm to ambient temperature whereupon it was stirred for 18h. Removal of the solvent *in vacuo*

gave an oily material which was recrystallised from methanol to afford **29** (43 mg) as yellow needles. The mother liquor was concentrated *in vacuo* and chromatography on silica gel with dichloromethane as the eluent afforded a second crop of **29** (combined yield: 81mg, 47% yield); m.p. 119°C. *m/z* (CI) 345 (MH^+, 100%) ; HRMS Found: 344.01544; $C_{15}H_{11}F_3O_2S_2$ requires 344.01523; ν_{max}(KBr)/ cm^{-1} 3155, 1720 and 1257; $\delta_H(CDCl_3)$[22] 7.35 (m, 10H+2H), 6.8-6.4 5 (m, 4H), 3.8 4 (s, 3H) and 3.83 (s, 3H) $\delta_F(CDCl_3)$ -58.3 (s, 3F), -58.7 (s, 3F).

Nitrosation Reactions of 1,3-Dithiol-2-ylidene Systems: General Procedure.
To a stirring solution of the1,3-dithiole derivative (*ca* 0.1 mmol) in dry dichloromethane (5 mL) at 0°C was added *iso*amyl nitrite (0.5 mL, excess). The solution was stirred at this temperature for 15 min then allowed to warm to ambient temperature and stirred for a further 15 min. After this time the solvent was removed *in vacuo* and the resulting oil either crystallised from methanol (*method a*) or chromatographed on silica gel with dichloromethane as eluent (*method b*).

2-(4,5-Dicarbomethoxy-1,3-dithiol-2-ylidene)-3-nitroso-4-phenyl-but-3-ene (13) and **2-(4,5-Dicarbomethoxy-1,3-dithiol-2-ylidene)-3-nitro-4-phenyl-but-3-ene (14)**
(Method a). An inseparable mixture of the nitroso **13** and nitro **14** species was obtained. *m/z* (CI) 378 (M^++1) (**13**), 394 (M^++1) (**14**); $\delta_H(CDCl_3)$ 8.94 (s, 1H), 7.35 (m, 5H), 3.89 (s, 3H), 3.88 (s, 3H) and 1.25 (s, 3H).

2-(4,5-Dicarbomethoxy-1,3-dithiol-2-ylidene)-1-cyano-3-nitro-3-phenyl-prop-2-ene (23).
(Method b). The product was obtained as a pale yellow solid in 62% yield. m.p. 32-34°C. *m/z* (CI) 405 (MH^+, 100%); HRMS Found: 404.01723; $C_{17}H_{12}N_2O_6S_2$ requires 404.01710; $\delta_H(CDCl_3)$ 7.46 (m, 5H), 4.79 (s, 1H) and 3.80 (s, 6H).

1,1,1-Trifluoro-2-(4,5-dicarbomethoxy-1,3-dithiol-2-ylidene)-3-nitro-4-phenyl-but-3-ene (27).
(Method b). The product was obtained as a yellow solid in 50% yield. m.p. 88-90°C. *m/z* (CI) 448 (MH^+, 100%1); HRMS Found: 447.00688; $C_{17}H_{12}F_3NO_6S_2$ requires 447.00581; ν_{max}(KBr)/ cm^{-1} 3155, 1735, 1561 and 1383; $\delta_H(CDCl_3)$ 7.41 (m, 5H), 5.01 (m, 1H), 3.92 (s, 3H) and 3.88 (s, 3H).

1,1,1-Trifluoro-2-(4-carbomethoxy-1,3-dithiol-2-ylidene)-3-nitro-4-phenyl-but-3-ene (31).
(Method b). The product was obtained as a red/orange oil in 76% yield. *m/z* (CI) 390 (MH^+, 100%); HRMS Found: 388.97898; $C_{15}H_{10}F_3NO_4S_2$ requires 388.98033; ν_{max}(neat)/ cm^{-1} 3155, 1712, 1573 and 1366; $\delta_H(CDCl_3)$[22] 7.43 (m, 10H), 5.07 (m, 2H), 3.85 (s, 3H) and 3.85 (s, 3H).

X-Ray Crystallography. Single crystals of **18b** suitable for an X-ray diffraction study were grown by slow evaporation of a dichloromethane solution of the compound. The diffraction experiment was carried out at room temperature on a Rigaku AFC6S 4-circle diffractometer, using graphite-monochromated Mo-K_α radiation, $\bar{\lambda}$=0.71073 Å. *Crystal data:* $C_{15}H_{11}NO_4S_2$, M=333.4, monoclinic, space group $P2_1/n$ (No. 14), a=12.944(4), b=7.391(3), c=16.178(8) Å, β =103.07(3)°, V=1508(1) $Å^3$ (from 20 setting reflections with 5<θ<12°), Z=4, D_c=1.47 $g{\cdot}cm^{-3}$, F(000)=688, μ=3.7 cm^{-1}, orange crystal of 0.5×0.4×0.25 mm. 3535 data with 2θ≤50° were collected in 2θ/ω scan mode, of these 2653 were unique (R_{int}=0.023), 1890 observed with $I \geq 2\sigma(I)$. The structure was solved by direct methods and refined by full-matrix least squares (non-H atoms anisotropic, all H atoms refined isotropically, 243 variables) against F^2 of all data, converging at R(F, obs. data)=0.034, wR(F^2, all data)=0.094, goodness-of-fit 1.03; residual electron density $\Delta\rho_{max}$=0.19, $\Delta\rho_{min}$=-0.25 $eÅ^{-3}$. SHELXTL (Version 5/VMS) software was used. Atomic coordinates and thermal parameters, bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

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REFERENCES AND NOTES

1. Gilchrist, T. L. *Chem. Soc. Rev.* **1983**, *12*, 53.
2. Francotte, E.; Merenyi, R.; Vandenblucke-Coyette V.; Viehe, H. G. *Helv. Chim. Acta* **1981**, *64*, 1208.
3. a) Johnson, P. L.; Paul, I. C. *J. Am. Chem. Soc.* **1969**, *91*, 781. b) Beer, R. J. S.; Gait, R. J. *Chem. Commun.* **1970**, 328. c) Reed, K. I. G. and Paul, I. C. *Chem. Commun.* **1970**, 329. d) Johnson, P. L.; Reed, K. I. G.; Paul, I. C. *J. Chem. Soc. (B)* **1971**, 946. e) Beer, R. J. S.; Cartwright, D.; Gait, R. J.; Harris, D. *J. Chem. Soc (C)* **1971**, 963. f) Dingwall, J. G.; Dunn, A. R.; Reid, D. H.; Wade, K. O. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1360. g) Abazid, M.; Bertrand, H. O.; Christen, M. O.; Burgot, J. L. *J. Chem. Soc., Chem. Commun.* **1994**, 131.
4. Lakshmikantham, M. V.; Cava, M. P. *J. Org. Chem.* **1981**, *46*, 3246.
5. Bryce, M. R.; Chalton, M. A.; Batsanov, A. S.; Lehmann, C. W.; Howard, J. A. K. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2367.
6. Chesney, A.; Bryce, M. R.; Chalton, M. A.; Batsanov, A. S.; Howard, J. A. K.; Fabre, J. M.; Binet, L. *J. Org. Chem.* **1996**, *61*, 2877.
7. Gowenlock, G. B.; Orrell, K. G.; Sik, V.; Vasapallo, G.; Lakshmikantham, M. V.; Cava, M. P. *Polyhedron* **1994**, *13*, 675.
8. Jackson, Y. A.; Parakka, J. P.; Lakshmikantham, M. V.; Cava, M. P. *J. Org. Chem.* **1997**, *62*, 2616.
9. Hansen, T. K.; Becher, J. *Adv. Mater*. **1993**, *5*, 288.
10. Sato, M.; Gonnella, N. C.; Cava, M. P. *J. Org. Chem.* **1979**, *44*, 930.
11. Sallé, M.; Belysamine, A.; Gorgues, A.; Jubault M.; Soyer, N. *Tetrahedron Lett.* **1991**, *32*, 2897.
12. Chalton, M. A. Ph.D. Thesis, University of Durham, **1996**.
13. Moore, A. J.; Bryce, M. R. *Tetrahedron Lett*. **1992**, *33*, 1373.
14. Moore, A. J.; Bryce, M. R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 3157.
15. a) Fourmigué, M.; Johannsen, I.; Boubekeur, K.; Nelson, C.; Batail, P. *J. Amer. Chem. Soc.* **1993**, *115*, 3752. b) van Veggel, F. C. J. M.; Harkema, S. *Acta Crystallogr. Sect. C* **1992**, *48*, 393.
16. Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans.* 2 **1987**, 51.
17. Nakatsu, K.; Yoshie, N.; Yoshioka, H.; Nogami, T.; Shirota, Y.; Shimizu, Y.; Uemiya, T.; Yasuda, N. *Mol. Cryst. Liq. Cryst.* **1990**, *182A*, 59.
18. Komarova, E. N.; Yufit, D. S.; Struchkov, Yu. T.; Drozd, V. N. *Zh. Org. Khim.* **1990**, *26*, 1437.
19. Desiraju, G. R.; Harlow, R. L. *J. Amer. Chem. Soc.* **1989**, *111*, 6757 and references therein.
20. Koenig, K. E.; Weber, W. P. *Tetrahedron Lett.* **1974**, 2275.
21. Bryce, M. R.; Chesney, A.; Lay, A. K.; Batsanov, A. S.; Howard, J. A. K. *J. Chem. Soc., Perkin Trans. 1* **1996**, 2451.
22. The appearance of 2 ester peaks of equal intensities is due to the presence of equimolar amounts of s-*cis* and s-*trans* isomers; no attempt was made to separate the compounds or assign the peaks.