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Cycloadditions to Pyrrolo[1,2-*c*]thiazoles and Pyrazolo[1,5-*c*]thiazoles

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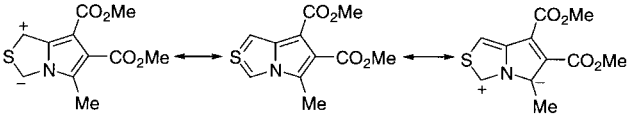
Abstract—The pyrrolo[1,2-*c*]thiazole generated by dehydration of dimethyl 5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate 2-oxide acts as a thiocarbonyl ylide in its cycloaddition to electron deficient alkenes but as an azomethine ylide with electron deficient alkynes. The analogous pyrazolo[1,5-c]thiazole, generated similarly, acts as a thiocarbonyl ylide with both types of dipolarophile. This behaviour is partially explained by Frontier MO theory.

Introduction

Several 'non-classical' 10π-electron heterocyclic-fused-[*c*]thiophenes have been prepared and have been shown to behave as simple thiocarbonyl ylides in [4π+2π] cycloadditions to dipolarophiles.[1] The presence of bridgehead nitrogen atoms, as for example in pyrrolo[1,2-*c*]thiazole **1**, increases the number of resonance forms and raises the possibility of reaction with dipolarophiles across either the thiocarbonyl ylide or azomethine ylide portion of the system.[2]

Several examples of these 'non-classical' systems are known and their participation in [4π+2π] cycloadditions is of interest in the construction of a variety of fused heterocycles.[3] Kane has reported the in situ generation of compound **1** and its reaction with a limited number of alkenic and acetylenic dipolarophiles.[2] Here we report our investigations of the range of dipolarophiles which participate in cycloadditions with **1** and evidence to support the transient existence of the previously unreported pyrazolo-[1,5-*c*]thiazole **2**. Our studies of the pyrrolo- and pyrazolothiazoles **1** and **2** were also prompted by the fact that they can be considered as 'masked' aza- and diazafulvenium methides which we have recently reported.[4a]



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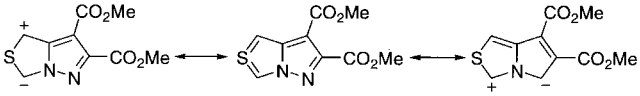

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Results and Discussion

We chose to follow Kane's method[2] for the generation of **1** and to extend this to produce **2** via Pummerer dehydration of the corresponding sulfoxides which can be prepared easily from the parent thiazolidines.

Thiazolidine **4** was prepared from thiazolidine-4-carboxylic acid **3** by heating with acetic anhydride in the presence of dimethyl acetylenedicarboxylate[2] (Scheme 1). Oxidation of **4** with either *m*CPBA (1.2 equiv.) or sodium periodate (1.2 equiv.) gave the corresponding sulfoxide **5** in 84 and 95% yields, respectively. TLC analysis [ethyl acetate–hexane (1:1)] of the reaction mixtures indicated the presence of small amounts of the sulfone[4] which could be removed by careful recrystallisation. However, this purification was time consuming and led to a reduction in overall yield and so a cleaner and more selective method of oxidation was sought.

N-Chlorobenzotriazole[5] is inexpensive, readily prepared and easily handled and has been employed in the quick and efficient oxidation of sulfides to sulfoxides, without concomitant formation of sulfones.[6] Treatment of sulfide **4**

Keywords: dipolar cycloaddition; thiocarbonyl ylide; azomethine ylide; pyrrolo[1,2-*c*]thiazole; pyrazolo[1,5-*c*]thiazole; frontier MO theory.
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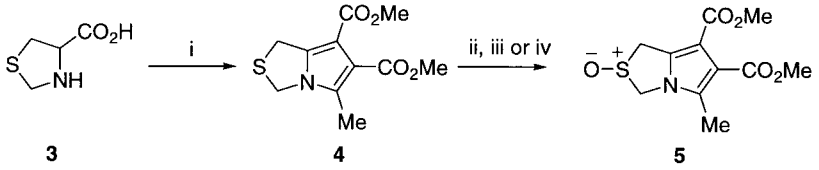


Scheme 1. *Reagents and conditions*: (i) Ac_2O/DMAD/heat; (ii) *m*CPBA (84%); (iii) $NaIO_4$ (95%); (iv) *N*-chlorobenzotriazole (98%).

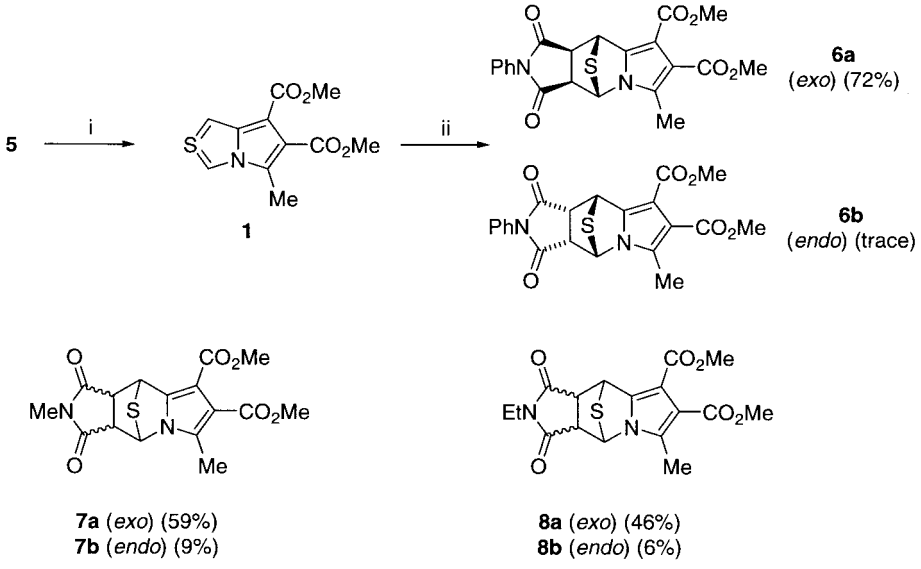
with *N*-chlorobenzotriazole (1 equiv.) in methanol for 1 h gave the desired sulfoxide **5** in 98% yield; this was identical to the sulfoxide **5** reported by Kane.[2]

Kane showed that Pummerer-type dehydration of **5** in boiling acetic anhydride over 3 h led to the transient 'non-classical' pyrrolo[1,2-*c*]thiazole **1** which could be intercepted with *N*-phenylmaleimide to give a mixture of 1:1 cycloadducts in 66% yield.[2] Chromatographic purification and subsequent characterisation showed that these adducts were *exo*- and *endo*-adducts **6a** and **6b** obtained in an *exo*/*endo* ratio of 8.4:1. The *exo*/*endo* assignments of major adduct **6a** and minor adduct **6b** were based on the ^{1}H NMR spectra of these products according to the established procedure of Cava and Potts[7] which involved attributing a larger deshielding effect of the sulfur bridge on the imide α-protons of the *endo*-adduct **6b**. *endo*/*exo* Assignment can also be inferred from the splitting patterns observed in the ^{1}H NMR spectra. On the basis of models, the dihedral angle between the α-imide and sulfur bridge hydrogens is less than 90° in the *endo*-adduct, and these hydrogens are coupled giving a double doublet for the α-imide hydrogens and a doublet for the hydrogens on the sulfur bridge. In the *exo*-adduct the dihedral angle between these protons is close to 90° and as a result only the α-imide hydrogens are coupled together, giving a doublet for the α-imide hydrogens and a singlet for the sulfur bridged hydrogens.

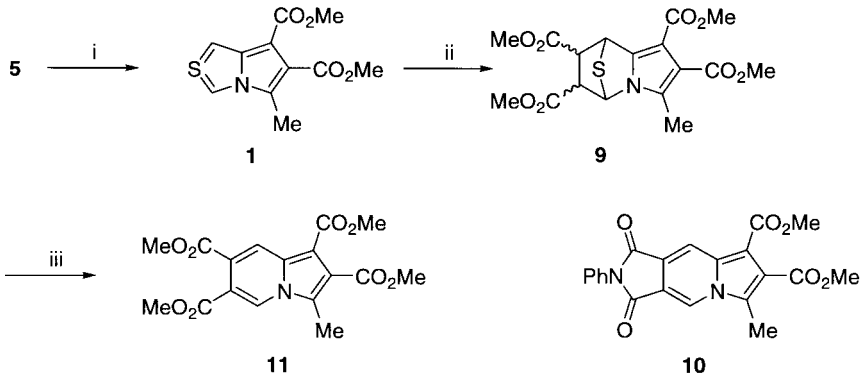
Our own results with pyrrolo[1,2-*c*]thiazole fully support and extend those of Kane.[2] Thus in our hands pyrrolo-[1,2-*c*]thiazole 1, generated from **5** over 4 h in hot acetic anhydride in the presence of *N*-phenylmaleimide, underwent a smooth cycloaddition to give a mixture of 1:1 adducts which after purification were determined to be the major *exo*-adduct **6a** (72% yield) and the minor *endo*-adduct **6b** (only a trace amount by TLC) (Scheme 2). The ^{1}H NMR spectrum of the major cycloadduct showed doublet signals at δ 3.48 and δ 3.52 corresponding to the imide α-H and singlets at δ 5.50 and δ 6.04 corresponding to the sulfur bridge-H. This is consistent with the data previously obtained for the *exo*-cycloadduct by Kane.[2] These adducts are formed by addition of the dipolarophile across the thiocarbonyl ylide portion of the 'non-classical' thiazole **1**. Similar [4π+2π] addition across the thiocarbonyl portion of the betaine **1** by two other substituted maleimides gave the corresponding cycloadducts **7a**–**b** and **8a**–**b**.

Dehydration of **5** in the presence of dimethyl fumarate (1.2 equiv.) gave a mixture of products **9** (55%) (Scheme 3). These cycloadducts could not be separated and the complexity of the ^{1}H NMR spectrum made stereochemical assignment of this mixture impossible. However, we have observed that the cycloadducts **6a**/**6b** lose hydrogen sulfide on treatment with two equivalents of sodium methoxide[3a,7b,8] to give the corresponding indolizine **10**, the structure of which was confirmed by signals at δ 2.66 (s, 3H, 6-CH_3), 3.97 (s, 3H, ester CH_3), 3.98 (s, 3H, ester CH_3), 7.51 (s, 5H, N–*Ph*), 8.51 (s, 1H, Ar-H) and 8.72 ppm (s, 1H, Ar-H) in the ^{1}H NMR spectrum.

Similarly, this mixture of cycloadducts **9** underwent elimination of hydrogen sulfide on reaction with sodium methoxide (2 equiv.) to afford indolizine **11**, the structure of which was established by signals at δ 2.59 (s, 3H, 5-CH_3),



Scheme 2. *Reagents and conditions*: (i) Ac_2O/heat; (ii) *N*-phenylmaleimide.



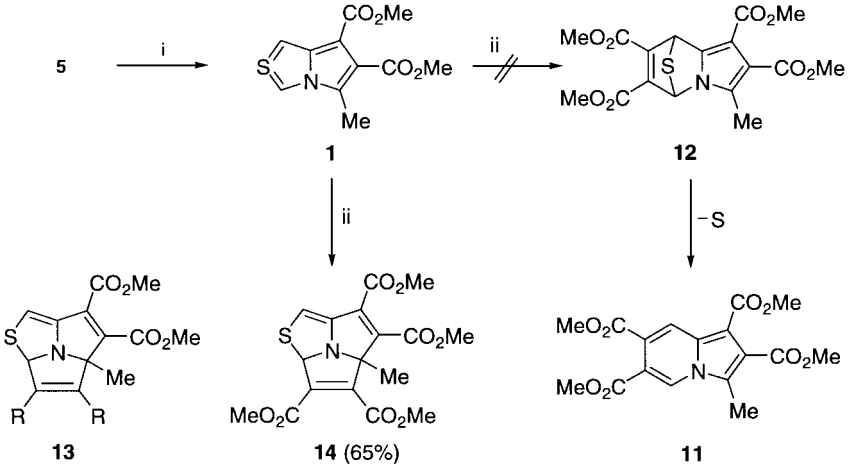
Scheme 3. *Reagents and conditions*: (i) Ac_2O/heat; (ii) dimethyl fumarate (55%) or dimethyl maleate (61%); (iii) $NaOMe/CH_2Cl_2$ (85 and 79%, respectively).

3.92 (s, 3H, ester CH_3), 3.93 (s, 3H, ester CH_3), 3.95 (s, 3H, ester CH_3), 3.96 (s, 3H, ester CH_3), 8.30 (s, 1H, Ar-H) and 8.47 ppm (s, 1H, Ar-H) in the ^{1}H NMR spectrum. A similar inseparable mixture of cycloadducts (61%) (which was cleanly desulfurised to give indolizine **11**) was obtained from reaction of **1** and dimethyl maleate. Surprisingly other olefinic dipolarophiles such as maleic anhydride, tetracyanoethylene, norbornadiene and tropone all failed to give adducts with 'non-classical' system **1**.

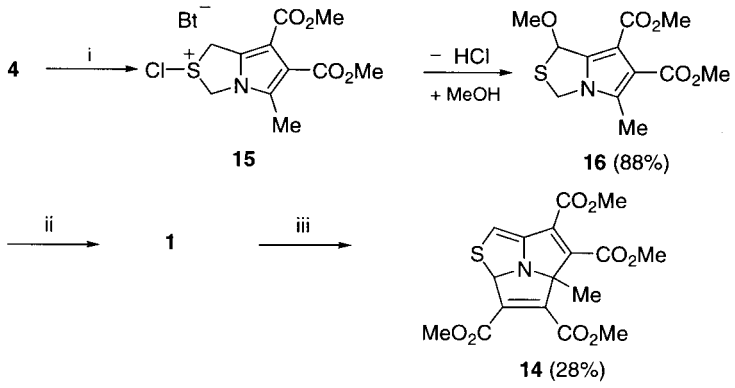
Dehydration of **5** in the presence of activated acetylenes might have been expected to give indolizines **11** via addition across the thiocarbonyl ylide portion of the 'non-classical' thiazole **1** and subsequent desulfurisation of the initial adducts **12**. However, Kane[2] reported that the reaction of **5** and DMAD in boiling acetic anhydride over 3 h led to a complex mixture, from which he isolated a colourless solid in low yield (15%). MS and elemental analysis showed that the product was a 1:1 adduct of the 'non-classical' thiazole and the acetylene. The structure of the adduct was established as **14** by the observation of the *C*-methyl group at 1.67 ppm, diagnostic of the Δ^3-pyrroline structure. The corresponding *C*-methyl in the indolizine structure is to be expected at ca. 2.6 ppm. Thiazolo[2,3,4-*cd*]pyrrolizine **14** results from cycloaddition across the azomethine ylide portion of the 'non-classical' system **1** (Scheme 4).

In our hands, sulfoxide **5** was dehydrated in boiling acetic anhydride in the presence of DMAD (1.2 equiv.) over 4 h to give a complex mixture. Crystallisation from methanol gave thiazolo[2,3,4-*cd*]pyrrolizine **14** as a yellowish powder in an improved yield of 65%. Structural assignment of **14** was based on signals at δ 1.69 (s, 3H, Δ^3-pyrroline-CH_3), 3.78 (s, 12H, ester CH_3), 4.99 (s, 1H, 6a-H) and 5.75 ppm (s, 1H, 2-H) which correspond with the data obtained by Kane and are different from the spectrum obtained for indolizine **11** prepared from aromatisation of the cycloadduct of dimethyl fumarate and **1**. We hoped to extend this reaction to prepare a number of these interesting heterocyclic compounds. However, although an analogous reaction occurred with diethyl acetylenedicarboxylate (1.2 equiv.) to give (**13**, R=CO_2Et) (41%), dibenzoyl acetylene and diphenylacetylene failed to react.

Although oxidation of **4** with *N*-chlorobenzotriazole in methanol for 1 h gave the sulfoxide **5** in high yield, an interesting reaction was observed when the reaction mixture was left for a prolonged period (ca. 24 h) before work-up with aqueous base (Scheme 5). The isolated crystalline material was not the sulfoxide **5**, but the unexpected 1-methoxysulfide **16**. ^{1}H NMR spectral analysis confirmed the structure of **16** with signals at δ 2.38 (s, 3H, 5-CH_3), 3.37 (s, 3H, 1-OCH_3), 3.82 (s, 6H, ester CH_3), 4.83 (d, 1H, J=10 Hz, 3-H), 5.06 (d, J=10 Hz, 3-H) and 6.23 (s, 1H,



Scheme 4. *Reagents and conditions*: (i) Ac_2O/heat; (ii) DMAD.



Scheme 5. *Reagents and conditions*: (i) *N*-chlorobenzotriazole; (ii) benzene/heat; (iii) DMAD.

1-H). Presumably, **16** is formed from the *S*-chlorosulfide **15** by elimination of HCl and attack by methanol. We anticipated that we could generate our desired 'non-classical' thiazole by thermal elimination of methanol from methoxide **16**. Indeed when sulfide **16** was heated in benzene in the presence of DMAD for 2 h, removal of the solvent in vacuo and purification of the residue afforded the expected thiazolo[2,3,4-*cd*]pyrrolizine **14** in 28% yield. Therefore sulfide **16** offers a novel and milder route to the 'non-classical' thiazole system **1** and may allow more thermally sensitive dipolarophiles to be trapped in situ.

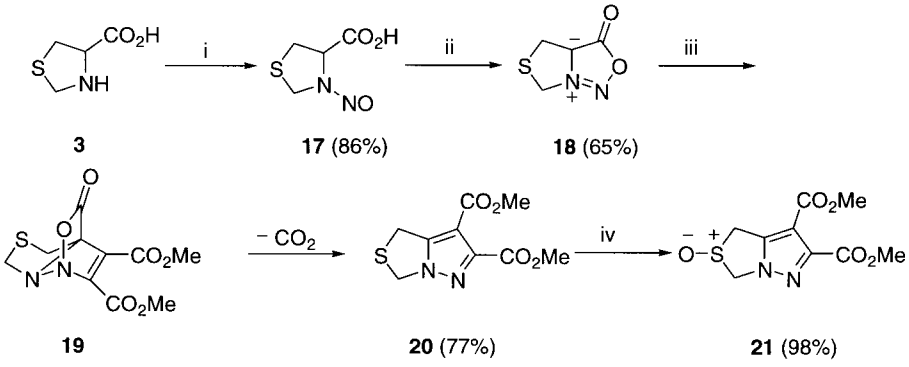
We next turned our attention to the previously unreported 'non-classical' pyrazolo[1,5-*a*]thiazole **2**.

Commercially available thiazolidine-4-carboxylic acid **3** was nitrosated under standard conditions to give *N*-nitrosothiazolidine-4-carboxylic acid **17** (Scheme 6). Treatment of **17** with TFAA in anhydrous ether[9] furnished the previously unreported sydnone **18** in moderate yield. Sydnone **18** is stable and has a long shelf-life. In agreement with its expected mesoionic reactivity, **18** underwent a [4π+2π] cycloaddition to DMAD followed by spontaneous extrusion of carbon dioxide from the initial adduct **19** to give the fused thiazole **20** in high yield. Finally oxidation of **20** with sodium periodate under standard conditions afforded the desired sulfoxide **21** in almost quantitative yield.

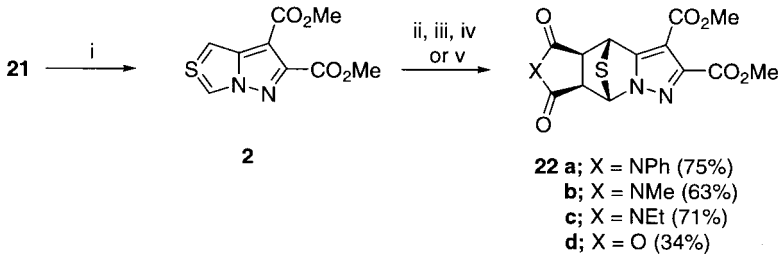
Pummerer-type dehydration of sulfoxide **21** in boiling acetic anhydride in the presence of *N*-phenylmaleimide gave exclusively adduct **22a** after 3 h (Scheme 7). Chromatographic purification and subsequent characterisation showed that this adduct was the *exo*-adduct. This *exo* assignment was based on comparison with the *endo*/*exo* adducts obtained from cycloaddition of **1** to *N*-methylmaleimide. The imide α-protons of adduct **22a** were observed to be simple doublets at δ 3.53 and 3.69 ppm, consistent with the proposed *exo*-structure.

This adduct arises by addition of the dipolarophile across the thiocarbonyl portion of **2** in a similar fashion to pyrrolo[1,2-*c*]thiazole **1**. Similar [4π+2π] cycloadditions were also observed with *N*-methyl- and *N*-ethylmaleimide and with maleic anhydride to give the corresponding *exo*-adducts **22b–d** (Scheme 7). Dehydration of **21** in the presence of either dimethyl fumarate or dimethyl maleate gave a mixture of stereoisomeric products **23** which once again proved impossible to separate. However, elimination of hydrogen sulfide from these adducts with sodium methoxide afforded the expected pyrazolo[1,5-*a*]pyridine **24** (Scheme 8).

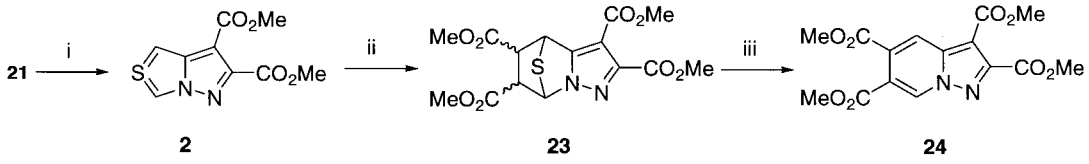
Dehydration of **21** in the presence of activated acetylenes, such as DMAD, was expected to give the tricyclic system **25** (R=CO_2Me) via [4π+2π] addition across the azomethine imine portion of **2** in a similar fashion to that observed by Kane for **1**.[2] In the event, the reaction of **21** and DMAD in boiling acetic anhydride over 4 h led to a complex mixture, from which a colourless solid was isolated in moderate yield (Scheme 9). Spectroscopic and elemental analysis of this adduct established the structure as the pyrazolo[1,5-*a*]pyridine **24** obtained from cycloaddition across the thiocarbonyl



Scheme 6. *Reagents and conditions*: (i) $NaNO_2$/HCl; (ii) TFAA/Et_2O; (iii) xylene/DMAD/heat; (iv) $NaIO_4$.



Scheme 7. *Reagents and conditions*: (i) Ac_2O/heat; (ii) *N*-phenylmaleimide; (iii) *N*-methylmaleimide; (iv) *N*-ethylmaleimide; (v) maleic anhydride.



Scheme 8. *Reagents and conditions*: (i) Ac_2O/heat; (ii) dimethyl fumarate (60%) or dimethyl maleate (adduct not isolated); (iii) $NaOMe/CH_2Cl_2$ (76% from dimethyl fumarate adduct; in the case of dimethyl maleate overall yield of **24** from **22** is 43%).

ylide portion of **2** and subsequent loss of sulfur from the initial adduct **26** (R=CO_2Me). Similar pyrazolo[1,5-*a*]pyridines, **27a** and **27b**, respectively, were also observed in the cycloadditions of diethyl acetylenedicarboxylate and dibenzoylacetylene; however, no cycloadduct was observed in the case of the less reactive diphenylacetylene.

Using the semi-empirical molecular modeling package (MOPAC/PM3)[10] we calculated the energies of the HOMO and LUMO in molecules **1** and **2** (Fig. 1). The relative energies of these orbitals indicate that additions to activated acetylenes and alkenes should be dipole-HOMO controlled in both cases.

$$\Delta E_{covalent} = 2\,\frac{(C_d^{HO}C_a^{LU}\Delta\beta_{ad} + C_{d'}^{HO}C_{a'}^{LU}\Delta\beta_{a'd'})^2}{E_D^{HO} - E_A^{LU}} \qquad (1)$$

Examination of the amplitudes of the coefficients in the HOMO appears to suggest that a mixture of products via addition across both the thiocarbonyl ylide and the azomethine ylide or imine portion of **1** and **2**, respectively would result. However, this does not take into account the contribution of $\Delta\beta$ (β=the resonance integral) to the covalent term of the general perturbation equation (Eq. (1)). The value of $\Delta\beta$ depends on the nature of the bonds being formed and is greater for C–C than C–N bonds (i.e. C–N bonds are weaker than C–C bonds). In the case of **1**, addition via both modes leads to two new carbon–carbon bonds and the preferred mode is therefore finely balanced. In the case of **2**, addition across the thiocarbonyl ylide leads

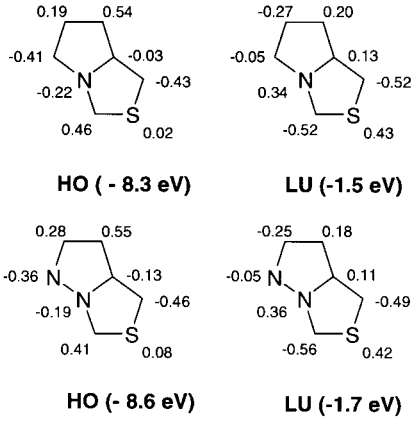
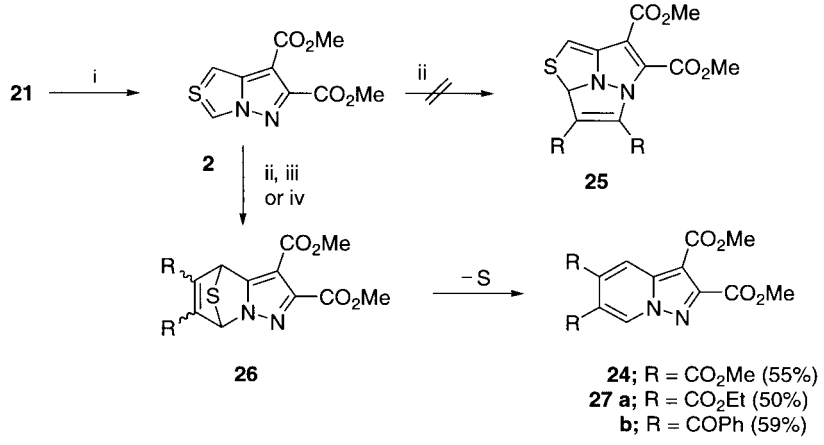


Figure 1. MO coefficients of 'non-classical' thiazoles **1** and **2**.



Scheme 9. *Reagents and conditions*: (i) Ac_2O/heat; (ii) DMAD; (iii) diethyl acetylenedicarboxylate; (iv) dibenzoyl acetylene.

to two new carbon–carbon bonds, whilst addition across the azomethine imine portion leads to the formation of a carbon–carbon and a carbon–nitrogen bond. Hence, the exclusive formation of the pyrazolo[1,5-*a*]pyridine adducts with **2** and the formation of both types of adduct in the case of **1** is not unexpected. However, why electron deficient acetylenes and electron deficient alkenes add by different modes to **1** remains unexplained.

Experimental

^{1}H NMR spectra were recorded on either a Bruker ACE 200 (200 MHz) instrument or a Varian Gemini 300 (300 MHz) instrument. ^{13}C and ^{13}C DEPT spectra were recorded on the Varian Gemini 300 (300 MHz) instrument. All spectra were recorded using tetramethylsilane (TMS) as the internal reference. Infra-red spectra were recorded in the range of 4000–600 cm^{-1} using a Perkin–Elmer 298 instrument. Mass spectra were recorded on a VG Analytical 7070E or a Trio 1000 Quadrapole GC mass spectrometer. Microanalyses were performed in the University of Liverpool Department of Chemistry microanalytical laboratory using a Carlo Erba elemental analyzer and melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. All reagents were of commercial quality and solvents were dried, where necessary, using standard procedures.

Dimethyl 5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate (4). Sulfide **4** was prepared according to the method published by Kane.[2] Thiazolidine-4-carboxylic acid (5.3 g, 40 mmol) and DMAD (7.4 mL, 1.5 equiv., 60 mmol) gave *dimethyl 5-methyl-1*H,*3*H-*pyrrolo[1,2-*c*]-*thiazole-6,7-dicarboxylate* as cream coloured needles, mp 133°C, lit.[2] 131–132°C. (Found: C, 51.8; H, 5.1; N, 5.5. $C_{11}H_{13}NSO_4$ requires C, 51.8; H, 5.1 and N, 5.5%); ν_{max} (Nujol®) 2926, 2855, 1718, 1703, 1536, 1449, 1419, 1389, 1376, 1301, 1258, 1208, 1165, 1093, 1050, 972, 886, 800, 781, 768, 741, 724 and 665 cm^{-1}; δ_H ($CDCl_3$) 2.37 (s, 3H, 5-CH_3), 3.80 (s, 3H, ester CH_3), 3.84 (s, 3H, ester CH_3), 4.27 (s, 2H, 1,1-H) and 4.92 (s, 2H, 3,3-H); δ_C ($CDCl_3$) 11.5 (CH_3), 30.2 (CH_2), 47.4 (CH_2), 51.3 (CH_3), 51.5 (CH_3), 107.1, 116.6, 130.5, 139.7, 164.0 (C=O) and 165.3 (C=O). *m/z* M^+ 255 (24%), 223 (100) 178 (41), 165 (37) and 137 (42). Accurate mass: 255.0565, $C_{11}H_{13}NO_4S$ requires 255.0565.

Dimethyl 5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate 2-oxide (5). *Method A (Oxidation with 3-chloroperoxybenzoic acid).* Sulfoxide **5** was prepared according to the method published by Kane.[2] 3-Chloroperoxybenzoic acid (90%) (4.8 g, 24 mmol) and dimethyl 5-methyl-3-thienyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate **4** (5.5 g, 22 mmol) gave *dimethyl 5-methyl-1*H,*3*H-*pyrrolo[1,2-*c*]*thiazole-6,7-dicarboxylate 2-oxide* (4.9 g, 84%) as colourless flakes, mp 134–136°C, lit.[2] 135–137°C. (Found: C, 48.8; H, 4.8; N, 5.1. $C_{11}H_{13}NSO_5$ requires C, 48.7; H, 4.8 and N, 5.2%); ν_{max} (Nujol®) 2926, 2856, 1712, 1536, 1455, 1376, 1295, 1208, 1164, 1092, 1056 and 779 cm^{-1}; δ_H ($CDCl_3$) 2.35 (s, 3H, 5-CH_3), 3.79 (s, 3H, ester CH_3), 3.83 (s, 3H, ester CH_3), 4.24 (d, 1H, J=18 Hz, 1-CH_2), 4.39 (d, 1H, J=18 Hz, 1-CH_2), 4.78 (d, 1H, J=12 Hz, 3-CH_2) and 4.99 (d, 1H, J=12 Hz, 3-CH_2); δ_C ($CDCl_3$) 11.5 (CH_3), 51.5 (CH_3 ester), 51.6 (CH_3 ester), 53.4 (CH_2), 67.8 (CH_2), 110.6, 117.2, 131.8, 134.9, 163.5 (C=O ester) and 164.8 (C=O ester); *m/z* M^+ 271 (33%), and 223 (100). Accurate mass: 271.0514, $C_{11}H_{13}NO_5S$ requires 271.0515.

Method B (Oxidation with sodium periodate). Sulfoxide **5** was prepared by adapting the method published by Nakayama.[11] Sodium periodate (12.32 g, 1.2 equiv., 58 mmol) and dimethyl 5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]-thiazole-6,7-dicarboxylate **4** (12.28 g, 48 mmol) gave *dimethyl 5-methyl-1*H,*3*H-*pyrrolo[1,2-*c*]*thiazole-6,7-dicarboxylate 2-oxide* (12.40 g, 95%) as colourless flakes which had identical physical and spectroscopic properties to those of the sulfoxide prepared by method A.

Method C (Oxidation with N*–chlorobenzotriazole). N*-Chlorobenzotriazole (7.37 g, 48 mmol) dissolved in methanol (100 mL) (DO NOT WARM TO EFFECT SOLUTION) was slowly added to a solution of dimethyl 5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate **4** (12.28 g, 48 mmol) in methanol (1500 mL) at −78°C. After stirring for 1 h the almost clear reaction mixture was allowed to warm to room temperature and 4% (w/v) sodium hydroxide solution (1000 mL) added. After stirring for ten minutes the reaction mixture was extracted with dichloromethane (3×1000 mL), washed with water (500 mL), brine (500 mL) and the combined organic fractions dried over anhydrous magnesium sulfate. Concentration in vacuo gave a yellowish oil which crystallised on standing. Recrystallisation of the crude residue from methanol gave *dimethyl 5-methyl-1*H,*3*H-*pyrrolo[1,2-*c*]*thiazole-6,7-dicarboxylate 2-oxide* (12.79 g, 98%) as colourless flakes which had identical physical and spectroscopic properties to those of the sulfoxide prepared by method A.

Dimethyl 1-methoxy-5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]-thiazole-6,7-dicarboxylate (16). *N*-Chlorobenzotriazole (1.84 g, 12 mmol) dissolved in methanol (25 mL) (DO NOT WARM TO EFFECT SOLUTION) was slowly added to a solution of dimethyl 5-methyl-1*H*,3*H*-pyrrolo-[1,2-*c*]thiazole-6,7-dicarboxylate (3.07 g, 12 mmol) in methanol (400 mL) at −78°C. After stirring for 24 h the almost clear reaction mixture was allowed to warm to room temperature and 4% (w/v) sodium hydroxide solution (250 mL) added. After stirring for 10 min the reaction mixture was extracted with dichloromethane (3×250 mL), washed with water (150 mL), brine (150 mL) and the combined organic fractions dried over anhydrous magnesium sulfate. Concentration in vacuo gave a yellowish oil which crystallised on standing. Recrystallisation of the crude residue from methanol gave *dimethyl 1-methoxy-5-methyl-1*H,*3*H-*pyrrolo[1,2-*c*]*thiazole-6,7-dicarboxylate* (3.01 g, 88%) as light brown flakes, mp 126–128°C. (Found: C, 50.3; H, 5.3; N, 4.8. $C_{12}H_{15}NSO_5$ requires C, 50.5; H, 5.3 and N, 4.9%); ν_{max} (Nujol®) 2924, 1712, 1539, 1454, 1385, 1298, 1255, 1216, 1168, 1100, 1078, 942, 890, 799, 772 and 728 cm^{-1}; δ_H ($CDCl_3$) 2.38 (s, 3H, 5-CH_3), 3.37 (s, 3H, 1-OCH_3), 3.82 (s, 6H, 2×ester CH_3), 4.83 (d, 1H, J=10 Hz, 3-H), 5.06 (d, 1H, J=10 Hz, 3-H) and 6.27 (s, 1H, 1-H); δ_C ($CDCl_3$) 11.2 (CH_3), 46.5 (CH_2), 51.5 (CH_3 ester), 51.5 (CH_3 ester), 55.6 (CH_3 ether),

84.8 (CH), 108.9, 117.0, 131.2, 138.0, 163.6 (C═O ester) and 165.1 (C═O ester); *m/z* M^+ 285 (16%), 254 (100) and 222 (28).

General procedure for generation and trapping of 'non-classical' thiazole (1)

Dimethyl 5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate 2-oxide **5** (0.27 g, 1.0 mmol) and the appropriate dipolarophile (1.2 mmol) in acetic anhydride (5 mL) were heated to reflux for 4 h. The reaction mixture was cooled to room temperature and the solvent removed in vacuo. The resulting residue was triturated with methanol to give the cycloadduct which was further purified by flash chromatography and/or recrystallisation from the appropriate solvent.

Dimethyl 1,3-dioxo-4,9-epithio-2,3,3a,4,9,9a-hexahydro-6-methyl-2-phenyl-1*H*-pyrrolo[3,4-*f*]indolizine-7,8-dicarboxylate (6a). Dimethyl 5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]-thiazole-6,7-dicarboxylate 2-oxide **5** (0.27 g, 1.0 mmol) and *N*-phenylmaleimide gave after recrystallisation from methanol (*exo*-adduct) *dimethyl 1,3-dioxo-4,9-epithio-2,3,3a,4,9,9a-hexahydro-6-methyl-2-phenyl-1*H-*pyrrolo-[3,4-*f]*indolizine-7,8-dicarboxylate* as a colourless powder, mp 210–212°C, lit.[2] 210–211°C. (Found: C, 59.1; H, 4.4; N, 6.5. $C_{21}H_{18}N_2SO_6$ requires C, 59.2; H, 4.3 and N, 6.6%); ν_{max} (Nujol®) 2930, 1714, 1699, 1654, 1595, 1462, 1378, 1308, 1193, 1146, 1093, 919, 843, 785 and 737 cm^{-1}; δ_H ($CDCl_3$) 2.46 (s, 3H, 5-CH_3), 3.48 (d, 1H, *J*=8 Hz, imide α-H), 3.51 (d, 1H, *J*=8 Hz, imide α-H), 3.83 (s, 3H, ester CH_3), 3.86 (s, 3H, ester CH_3), 5.50 (s, 1H, sulfur bridge-H), 6.04 (s, 1H, sulfur bridge-H), 7.26–7.28 and 7.44–7.51 (m, 5H, Ar-H); *m/z* M+ 426 (12%), 392 (10), 360 (11), 274 (37), 253 (100), 221 (33), 163 (23), 135 (14).

Dimethyl 1,3-dioxo-4,9-epithio-2,3,3a,4,9,9a-hexahydro-2,6-dimethyl-1*H*-pyrrolo[3,4-*f*]-indolizine-7,8-dicarboxylate (7a, *exo*) and (7b, *endo*). Dimethyl 5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate 2-oxide **5** (0.27 g, 1.0 mmol), *N*-methylmaleimide (0.13 g, 1.2 equiv., 1.2 mmol) gave after chromatography [ethyl acetate–hexane (1:1)] and crystallisation from chloroform–ethanol (*exo*-adduct) *dimethyl 1,3-dioxo-4,9-epithio-2,3,3a,4,9,9a-hexahydro-2,6-dimethyl-1*H-*pyrrolo[3,4-*f]*indolizine-7,8-dicarboxylate* (0.21 g, 59%) as a colourless powder, mp 190–192°C. (Found: C, 52.8; H, 4.4; N, 7.7. $C_{16}H_{16}N_2SO_6$ requires C, 52.7; H, 4.4 and N, 7.7%); ν_{max} (Nujol®) 2926, 1726, 1699, 1462, 1377, 1307, 1206, 1154 and 1093 cm^{-1}; δ_H ($CDCl_3$) 2.44 (s, 3H, 5-CH_3), 3.03 (s, 3H, N–CH_3), 3.33 (d, 1H, *J*=8 Hz, imide α-H), 3.36 (d, 1H, *J*=8 Hz, imide α-H), 3.82 (s, 3H, ester CH_3), 3.86 (s, 3H, ester CH_3), 5.39 (s, 1H, sulfur bridge-H), and 5.93 (s, 1H, sulfur bridge-H); δ_C ($CDCl_3$) 11.3 (CH_3), 25.4 (CH_2), 50.8 (CH), 51.6 (CH_3 ester), 51.8 (CH_3 ester), 51.9 (CH), 53.5 (CH), 67.0 (CH), 107.8, 114.3, 131.4, 140.3, 162.8 (C═O ester), 164.9 (C═O ester), 173.3 (C═O amide) and 174.0 (C═O amide); *m/z* M^+ 364 (26%), 332 (22), 253 (100), 221 (37), 163 (28), 135 (23), and (*endo*-adduct) *dimethyl 1,3-dioxo-4,9-epithio-2,3,3a,4,9,9a-hexahydro-2,6-dimethyl-1*H-*pyrrolo-[3,4-*f]*indolizine-7,8-dicarboxylate* (0.03 g, 9%) as a colourless powder, mp 206–208°C. Found: C, 52.7; H, 4.3; N, 7.7. $C_{16}H_{16}N_2SO_6$ requires C, 52.7; H, 4.4 and N, 7.7%); ν_{max} (Nujol®) 2925, 1726, 1698, 1462, 1377, 1306, 1206, 1154 and 109 cm^{-1}; δ_H ($CDCl_3$) 2.34 (s, 3H, 5-CH_3), 2.54 (s, 3H, N–CH_3), 3.83 (s, 3H, ester CH_3), 3.86 (s, 3H, ester CH_3), 4.00 (dd, 1H, *J*=4, 7 Hz, imide α-H), 4.02 (dd, 1H, *J*=4, 7 Hz, imide α-H), 5.44 (d, 1H, *J*=4 Hz, sulfur bridge-H), and 6.02 (d, 1H, *J*=4 Hz, sulfur bridge-H); δ_C ($CDCl_3$) 10.9 (CH_3), 24.5 (CH_3), 50.8 (CH), 51.9 (CH_3 ester), 52.1 (CH_3 ester), 53.4 (CH), 55.9 (CH), 67.4 (CH), 107.8, 114.3, 132.2, 138.1, 162.8 (C═O ester), 164.9 (C═O ester), 172.0 (C═O amide) and 174.0 (C═O amide); *m/z* M^+ 364 (34%), 332 (18), 253 (100), 221 (37), 163 (31), 135 (20).

Dimethyl 1,3-dioxo-4,9-epithio-2,3,3a,4,9,9a-hexahydro-2-ethyl-6-methyl-1*H*-pyrrolo[3,4-*f*]indolizine-7,8-dicarboxylate (8a, *exo*) and (8b, *endo*). Dimethyl 5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate 2-oxide **5** (0.27 g, 1.0 mmol) and *N*-ethylmaleimide (0.15 g, 1.2 equiv., 1.2 mmol) gave after chromatography [ethyl acetate–hexane (1:1)] and crystallisation from chloroform–ethanol (*exo*-adduct) *dimethyl 1,3-dioxo-4,9-epithio-2,3,3a,4,9,9a-hexahydro-2-ethyl-6-methyl-1*H-*pyrrolo[3,4-*f]*indolizine-7,8-dicarboxylate* (0.17 g, 46%) as a colourless powder, mp 212–213°C. (Found: C, 54.0; H, 4.8; N, 7.4. $C_{17}H_{18}N_2SO_6$ requires C, 54.0; H, 4.8 and N, 7.4%); ν_{max} (Nujol®) 2926, 1777, 1699, 1533, 1456, 1378, 1348, 1302, 1205, 1153, 1093, 911 and 783 cm^{-1}; δ_H ($CDCl_3$) 1.18 (t, 3H, *J*=7 Hz, CH_3CH_2-N), 2.44 (s, 3H, 5-CH_3), 3.29 (d, 1H, *J*=7 Hz, imide α-H), 3.32 (d, 1H, *J*=7 Hz, imide α-H), 3.59 (q, 2H, *J*=7 Hz, CH_3CH_2-N), 3.82 (s, 3H, ester CH_3), 3.85 (s, 3H, ester CH_3), 5.39 (s, 1H, sulfur bridge-H), and 5.93 (s, 1H, sulfur bridge-H); δ_C ($CDCl_3$) 11.3 (CH_3), 12.5 (CH_3), 34.5 (CH_2), 50.6 (CH), 51.6 (CH_3 ester), 51.8 (CH_3 ester), 52.0 (CH), 53.3 (CH), 67.1 (CH), 107.8, 114.3, 131.4, 140.4, 163.1 (C═O ester), 164.9 (C═O ester), 173.1 (C═O amide) and 173.8 (C═O amide); *m/z* M^+ 378 (23%), 346 (15), 253 (100), 221 (35), 163 (21), 135 (19), and (*endo*-adduct) *dimethyl 1,3-dioxo-4,9-epithio-2,3,3a,4,9,9a-hexahydro-2-ethyl-6-methyl-1*H-*pyrrolo[3,4-*f]*indolizine-7,8-dicarboxylate* (0.02 g, 6%) as a colourless powder, mp dec. 234–235°C. (Found: C, 53.9; H, 4.7; N, 7.4. $C_{17}H_{18}N_2SO_6$ requires C, 54.0; H, 4.8 and N, 7.4%); ν_{max} (Nujol®) 2926, 1778, 1699, 1532, 1456, 1378, 1347, 1302, 1205, 1153, 1093, 910 and 783 cm^{-1}; δ_H ($CDCl_3$) 0.77 (t, 3H, *J*=7 Hz, CH_3CH_2-N), 2.35 (s, 3H, 5-CH_3), 3.16 (q, 2H, *J*=7 Hz, CH_3CH_2-N), 3.82 (s, 3H, ester CH_3), 3.85 (s, 3H, ester CH_3), 4.01 (dd, 1H, *J*=4, 7 Hz, imide α-H), 4.06 (d, 1H, *J*=4, 7 Hz, imide α-H), 5.44 (d, 1H, *J*=4 Hz, sulfur bridge-H), and 6.02 (d, 1H, *J*=4 Hz, sulfur bridge-H); δ_C ($CDCl_3$) 10.8 (CH_3), 12.0 (CH_3), 34.0 (CH_2), 50.5 (CH), 51.6 (CH_3 ester), 51.7 (CH_3 ester), 52.0 (CH), 53.3 (CH), 56.1 (CH), 108.7, 114.4, 132.1, 138.1, 162.9 (C═O ester), 164.7 (C═O ester), 172.0 (C═O amide) and 173.8 (C═O amide); *m/z* M^+ 378 (33%), 346 (9), 253 (100), 221 (27), 163 (17), 135 (11).

Dimethyl 1,3-dioxo-2,3-dihydro-6-methyl-2-phenyl-1*H*-pyrrolo[3,4-*f*]indolizine-7,8-dicarboxylate (10). A solution of sodium methoxide (0.38 mL, 30% wt. soln., 2.0 equiv., 2.0 mmol) added slowly to a solution of dimethyl 1,3-dioxo-4,9-epithio-2,3,3a,4,9,9a-hexahydro-6-methyl-2-phenyl-1*H*-pyrrolo[3,4-*f*]indolizine-7,8-dicarboxylate **6a** (0.43 g, 1.0 mmol) dissolved in anhydrous dichloromethane

(10 mL). After stirring for 2 h, the reaction was quenched with saturated ammonium chloride solution (10 mL). The dichloromethane layer was separated and dried over anhydrous sodium sulfate. The organics were filtered and concentrated in vacuo to give a dark residue. Purification by flash column chromatography [ethyl acetate–hexane (1:1)] gave *dimethyl 1,3-dioxo-2,3-dihydro-6-methyl-2-phenyl-1*H*-pyrrolo[3,4-*f*]indolizine-7,8-dicarboxylate* (0.25 g, 63%) as a yellowish powder, mp dec. 210–211°C, lit.[2] 209–211. (Found: C, 64.2; H, 4.0; N, 7.1. $C_{21}H_{16}N_2O_6$ requires C, 64.3; H, 4.1 and N, 7.1%); ν_{max} (Nujol®) 2926, 2856, 1721, 1699, 1696, 1683, 1654, 1460, 1377, 1240, 1219, 1117, 1072 and 738 cm^{-1}; δ_H ($CDCl_3$) 2.66 (s, 3H, 6-CH_3), 3.97 (s, 3H, ester CH_3), 3.98 (s, 3H, ester CH_3), 7.51 (s, 5H, N–Ph), 8.51 (s, 1H, Ar-H) and 8.82 (s, 1H, Ar-H). *m/z* M^+ 392 (6%), 360 (32), 274 (100), 180 (13), 77 (13).

Tetramethyl 3-methylpyrrolo[1,2-*a*]pyridine-1,2,6,7-tetracarboxylate (11). *Method A (via Dimethyl fumarate).* Dimethyl 5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate 2-oxide (0.54 g, 2.0 mmol), dimethyl fumarate (0.46 g, 3.2 mmol) and acetic anhydride (10 mL) were heated to reflux for 4 h. The reaction mixture was cooled to room temperature and the solvent removed in vacuo. The resulting dark residue was triturated with methanol and the crude brown mixture of isomers collected by filtration (0.43 g, 55%). The mixture was used without further purification. A solution of sodium methoxide (0.38 mL, 30% wt. soln., 2.0 equiv., 2.0 mmol) was added slowly to a solution of the crude mixture of isomers (0.40 g, 1.0 mmol) dissolved in anhydrous dichloromethane (10 mL). After stirring for 2 h, the reaction was quenched with saturated ammonium chloride solution (10 mL). The dichloromethane layer was separated and dried over anhydrous sodium sulfate. The organics were filtered and concentrated in vacuo to give a dark residue. Recrystallisation from benzene-petroleum ether gave *tetramethyl 3-methylpyrrolo[1,2-*a*]pyridine-1,2,6,7-tetracarboxylate* as a yellowish powder (0.31 g, 85%), mp 133–135°C. (Found: C, 56.3; H, 4.7; N, 3.8. $C_{17}H_{17}NO_8$ requires C, 56.2; H, 4.7 and N, 3.9%); ν_{max} (Nujol®) 2930, 1256, 1733, 1709, 1654, 1536, 1462, 1378, 1305, 1279, 1256, 1237, 1193, 1171, 1134, 1082, 1043, 968, 902, 846, 821, 806, 783, 772 and 741 cm^{-1}; δ_H ($CDCl_3$) 2.59 (s, 3H, 5-CH_3), 3.92 (s, 3H, ester CH_3), 3.94 (s, 3H, ester CH_3), 3.95 (s, 3H, ester CH_3) and 3.96 (s, 3H, ester CH_3), 8.29 (s, 1H, Ar-H), 8.47 (s, 1H, Ar-H); δ_C ($CDCl_3$) 10.1 (5-CH_3), 51.7 (CH_3 ester), 52.5 (CH_3 ester), 52.8 (CH_3 ester), 52.9 (CH_3 ester), 106.5, 117.6, 122.1 (CH), 122.7, 124.9, 125.4, 125.9 (CH), 132.5, 163.5 (C═O), 165.7 (2×C═O), 166.6 (C═O); *m/z* M^+ 363 (37%), 332 (48), 245 (100).

Method B (via Dimethyl maleate). Tetramethyl 3-methylpyrrolo[1,2-*a*]pyridine-1,2,6,7-tetracarboxylate **12** was prepared from dimethyl maleate using the procedure detailed in method A. Dimethyl 5-methyl-1*H*,3*H*-pyrrolo-[1,2-*c*]thiazole-6,7-dicarboxylate 2-oxide **5** (0.54 g, 2.0 mmol) and dimethyl maleate (0.4 mL, 3.2 mmol) gave after desulfurisation *tetramethyl 3-methylpyrrolo[1,2-*a*]-pyridine-1,2,6,7-tetracarboxylate* (0.35 g, 48% overall yield from sulfoxide) as a yellowish powder which had identical physical and spectroscopic properties as the product prepared by method A.

Tetramethyl 4a,6a-dihydro-4a-methylthiazolo[2,3,4-*cd*]-pyrrolizine-3,4,5,6-tetracarboxylate (14). *Method A (via Sulfoxide **5**).* Dimethyl 5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate 2-oxide **5** (0.27 g, 1.0 mmol) and dimethyl acetylenedicarboxylate (0.12 mL, 1.2 mmol) using the general procedure for generation and trapping of thiazole **1** gave *tetramethyl 4a,6a-dihydro-4a-methylthiazolo[2,3,4-*cd*]pyrrolizine-3,4,5,6-tetracarboxylate* (0.26 g, 65%) as a colourless powder, mp 238–240°C, lit.[2] 239–241°C. (Found: C, 51.6; H, 4.3; N, 3.6. $C_{17}H_{17}NSO_8$ requires C, 51.7; H 4.3, and N, 3.5%); ν_{max} (Nujol®) 3440, 2926, 2856, 2358, 1726, 1671, 1641, 1456, 1437, 1377, 1334, 1289, 1222, 1169, 1140, 1127, 1087, 1056, 1018, 960, 940, 859, 827, 803, 784 and 670 cm^{-1}; δ_H ($CDCl_3$) 1.69 (s, 3H, 4a-CH_3), 3.78 (s, 12H, ester CH_3), 4.99 (s, 1H, 6a-H) and 5.75 (s, 1H, 2-H); δ_C ($CDCl_3$) 29.3 (5-CH_3), 52.2 (2×CH_3 ester), 52.6 (2×CH_3 ester), 60.6 (CH), 78.7 (CH), 86.4, 94.8, 134.1, 137.6, 141.5, 142.5, 161.9 (C═O ester), 162.4 (C═O ester), 163.9 (C═O ester) and 164.2 (C═O ester); *m/z* M^+ 395 (69%), 304 (100), 253 (33), 221 (19), 163 (21), 135 (17).

*Method B (via 1-Methoxysulfide **17**).* Dimethyl 1-methoxy-5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate (0.27 g, 1.0 mmol) was suspended in benzene (2 mL) with dimethyl acetylenedicarboxylate (1.2 mL, 1.2 mmol) and heated to reflux for 2 h. The reaction mixture was cooled to room temperature and the solvent removed in vacuo. The resulting dark residue was triturated with methanol and the crude brown product collected by filtration. Recrystallisation from methanol afforded *tetramethyl 4a,6a-dihydro-4a-methylthiazolo[2,3,4-*cd*]pyrrolizine-3,4,5,6-tetracarboxylate* (0.11 g, 28%) as a colourless powder which had identical physical and spectral properties to the material isolated from the cycloaddition of dimethyl 5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate 2-oxide and DMAD.

5,6-Diethyl-3,4-dimethyl 4a,6a-dihydro-4a-methylthiazolo[2,3,4-*cd*]pyrrolizine-3,4,5,6-tetracarboxylate (13) (R=CO_2Et). Dimethyl 5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate-2-oxide **5** (0.27 g, 1.0 mmol) and diethyl acetylenedicarboxylate (0.19 mL, 1.2 mmol) using the general procedure for generation and trapping of thiazole **1** gave *5,6-diethyl-3,4-dimethyl 4a,6a-dihydro-4a-methyl-thiazolo[2,3,4-*cd*]pyrrolizine-3,4,5,6-tetracarboxylate* (0.17 g, 41%) as a yellowish powder, mp 216–218°C. (Found: C, 53.7; H, 4.9; N, 3.2. $C_{19}H_{21}NSO_8$ requires C, 53.9; H, 5.0 and N, 3.3%); ν_{max} (Nujol®) 2926, 1721, 1683, 1660, 1644, 1462, 1377, 1322, 1262, 1224, 1135, 1108, 1084, 1053, 1018, 858, 840, 800 and 722 cm^{-1}; δ_H ($CDCl_3$) 1.26–1.32 (m, 6H, 2×$CH_3CH_2CO_2$–), 1.70 (s, 3H, 4a-CH_3), 3.74 (s, 3H, ester CH_3), 3.78 (s, 3H, ester CH_3), 4.12–4.36 (m, 4H, 2×$CH_3CH_2CO_2$–), 4.99 (s, 1H, 6a-H) and 5.76 (s, 1H, 2-H); δ_C ($CDCl_3$) 13.9 ($CH_3CH_2CO_2$–), 14.0 ($CH_3CH_2CO_2$–), 29.3 (5-CH_3), 52.2 (2×CH_3CO_2–), 60.5 (CH), 61.8 (CH_2), 61.9 (CH_2), 78.8 (CH), 86.5, 94.9, 134.2, 137.7, 141.6, 142.4, 161.31 (C═O ester), 162.8 (C═O ester), 163.9 (2×C═O ester); *m/z* M^+ 423 (100%), 364 (38), 332 (75), 253 (84), 221 (51), 163 (43), 135 (37).

***N*-Nitrosothiazolidine-4-carboxylic acid (17).** Concentrated hydrochloric acid was slowly added dropwise

(CARE!) to a suspension of thiazolidine-4-carboxylic acid (13.32 g, 0.1 mol) in water (50 mL) until the suspension dissolved. To the vigorously stirring solution was then added slowly via a dropping funnel sodium nitrite (10.35 g, 0.15 mol) dissolved in water (50 mL). Shortly after the addition was complete a vigorous evolution of gas (CAUTION!) occurred and the initial red colour faded to give a pale yellow solution. After stirring for 12 h the reaction mixture was extracted with ethyl acetate (3×100 mL) and the combined organic fractions were then washed with water (100 mL), brine (100 mL) and dried over anhydrous magnesium sulfate. Concentration in vacuo gave a yellowish oil which crystallised on trituration with petroleum ether to give N-*nitrosothiazolidine-4-carboxylic acid* (13.95 g, 86%) as pale yellow crystals, mp 98–99°C, lit.[12] 101–102°C. (Found: C, 29.8; H, 3.7; N, 17.0. $C_4H_6N_2SO_3$ requires C, 29.6; H, 3.7 and N, 17.3%); ν_{max} (Nujol®) 2928, 2855, 2576, 1739, 1462, 1432, 1387, 1345, 1259, 1222, 1201, 1129, 1010, 955, 928, 871, 852, 819, 762, 750, 720 and 693 cm^{-1}; *m/z* M^+ 162 (1%), 132 (100), 104 (15), and 88 (94).

4*H*,6*H*-Thiazolo[3,4-*c*][1,2,3]oxadiazolium-3-oxide (18). Trifluoroacetic anhydride (5.37 mL, 38 mmol) was slowly added to a suspension of *N*-nitrosothiazolidine-4-carboxylic acid (6.08 g, 38 mmol) in anhydrous diethyl ether (400 mL) at 0°C. The reaction mixture was stirred at 0°C for 6 h and then allowed to warm to room temperature. After stirring at room temperature for 24 h the solution was filtered and the crude product was thoroughly washed with *cold* diethyl ether (20 mL) to give *4*H,*6*H-*thiazolo[3,4-*c*][1,2,3]oxadiazolium-3-oxide* (3.51 g, 65%) as colourless crystals, mp 88–90°C. (Found: C, 33.4; H, 2.7; N, 19.5. $C_4H_4N_2SO_2$ requires C, 33.3 H, 2.8 and N, 19.4%); ν_{max} (Nujol®) 3439, 2926, 2857, 2352, 1725, 1520, 1456, 1377, 1316, 1235, 1187, 1106, 1025, 899, 789, 737, 711 and 62 cm^{-1}; δ_H ($CDCl_3$) 4.03 (t, 2H, *J*=2.0 Hz, CH_2) and 5.40 (t, 2H, *J*=2.0 Hz, CH_2); *m/z* M^+ 144 (26%), 114 (100) and 86 (26).

Dimethyl 1*H*,3*H*-pyrazolo[1,5-*c*]thiazole-6,7-dicarboxylate (20). 4*H*,6*H*-Thiazolo[3,4-*c*][1,2,3]oxadiazolium-3-oxide **17** (14.5 g, 0.10 mol) and dimethyl acetylenedicarboxylate (19.8 mL, 1.6 equiv., 0.16 mol) in xylene (60 mL) were heated at reflux for 3 h under a positive flow of dry nitrogen. The reaction was cooled to room temperature and the solvent removed in vacuo to give a brown crystalline mass which was recrystallised from methanol to give *dimethyl 1*H,*3*H-*pyrazolo[1,5-*c*]thiazole-6,7-dicarboxylate* (18.76 g, 77%) as cream coloured needles, mp 123–128°C. (Found: C, 44.5; H, 4.2; N, 11.5. $C_9H_{10}N_2SO_4$ requires C, 44.6; H, 4.1 and N, 11.6%); ν_{max} (Nujol®) 3443, 2923, 2857, 1734, 1697, 1550, 1504, 1464, 1377, 1330, 1299, 1231, 1203, 1181, 1149, 1079, 990, 889, 860, 820, 793, 770, 720, 646 cm^{-1}; δ_H ($CDCl_3$) 3.85 (s, 3H, ester CH_3), 3.96 (s, 3H, ester CH_3), 4.31 (t, 2H, *J*=2 Hz, 1-CH_2) and 5.25 (t, 2H, *J*=2 Hz, 3-CH_2); δ_C ($CDCl_3$) 28.3 (CH_2), 50.4 (CH_2), 51.9 (CH_3), 52.6 (CH_3), 108.7, 148.3, 149.2, 160.9 (C=O ester) and 161.8 (C=O ester); *m/z* M^+ 242 (2%), and 210 (100).

Dimethyl 1*H*,3*H*-pyrazolo[1,5-*c*]thiazole-6,7-dicarboxylate 2-oxide (21). Sodium periodate (10.23 g, 1.2 equiv., 48 mmol) dissolved in water (200 mL) was slowly added to a stirring solution of dimethyl 1*H*,3*H*-pyrazolo[1,5-*c*]-thiazole-6,7-dicarboxylate (10.23 g, 40 mmol) in methanol (700 mL) at 0°C. The cooling bath was then removed and the reaction mixture was allowed to warm to room temperature. After stirring at room temperature for 48 h, the reaction mixture was filtered and the filtrate extracted with chloroform (3×500 mL). The combined organic fractions were then washed with water (250 mL), brine (250 mL) and dried over anhydrous magnesium sulfate. Concentration in vacuo gave a yellowish oil which crystallised on standing. Recrystallisation of the crude residue from methanol gave *dimethyl 1*H,*3*H-*pyrazolo[1,5-*c*]thiazole-6,7-dicarboxylate 2-oxide* (10.69 g, 98%) as colourless flakes, mp 133–135°C. (Found: C, 41.9; H, 3.9; N, 10.9. $C_9H_{10}N_2SO_5$ requires C, 41.9; H, 3.9 and N, 10.7%); ν_{max} (Nujol®) 3446, 3006, 2958, 2849, 2352, 2314, 2090, 1730, 1633, 1555, 1488, 1464, 1439, 1397, 1375, 1310, 1231, 1230, 1176, 1134, 1118, 1076, 988, 947, 895, 865, 818, 788, 770, 736, 701, 678, 666 cm^{-1}; δ_H ($CDCl_3$) 3.86 (s, 3H, ester CH_3), 3.96 (s, 3H, ester CH_3), 4.28 (d, 1H, *J*=17 Hz, 3-H), 4.55 (d, 1H, *J*=17 Hz, 3-H), 5.13 (d, 1H, *J*=12 Hz, 1-H) and 5.35 (d, 1H, *J*=12 Hz, 1-H); δ_C ($CDCl_3$) 52.1 (CH_3 ester), 52.4 (CH_3 ester), 52.8 (CH_2), 71.7 (CH_2), 111.1, 145.7, 148.9, 161.3 (C=O ester) and 161.4 (C=O ester); *m/z* M^+ 258 (2%), 226 (30), 196 (37), 151 (100), 59 (30).

General procedure for generation and trapping of 'non-classical' thiazole (2)

Dimethyl 5-methyl-1*H*,3*H*-pyrazolo[1,5-*a*]thiazole-6,7-dicarboxylate 2-oxide **21** (0.26 g, 1.0 mmol) and the appropriate dipolarophile (1.2 mmol) in acetic anhydride (5 mL) were heated to reflux for 4 h. The reaction mixture was cooled to room temperature and the solvent removed in vacuo. The resulting residue was triturated with methanol to give the cycloadduct which was further purified by flash chromatography and/or recrystallisation from the appropriate solvent.

Dimethyl 1,3-dioxo-4,9-epithio-2,3,3a,4,9,9a-hexahydro-2-phenyl-1*H*-pyrazolo[1,5-*a*]pyrrolo[3,4-*c*]pyridine-7,8-dicarboxylate (22a). Dimethyl 1*H*,3*H*-pyrazolo[1,5-*c*]thiazole-6,7-dicarboxylate 2-oxide **21** (0.26 g, 1.0 mmol), *N*-phenylmaleimide (0.21 g, 1.2 mmol) gave after recrystallisation from methanol (*exo*-adduct) *dimethyl 1,3-dioxo-4,9-epithio-2,3,3a,4,9,9a-hexahydro-2-phenyl-1*H-*pyrazolo[1,5-*a*]-pyrrolo-[3,4-*c*]pyridine-7,8-dicarboxylate* (0.31 g, 75%) as a colourless powder, mp 202–203°C. (Found: C, 55.3; H, 3.6; N, 10.1. $C_{19}H_{15}N_3SO_6$ requires C, 55.2; H, 3.6 and N, 10.2%); ν_{max} (Nujol®) 2923, 2857, 1757, 1718, 1501, 1460, 1393, 1289, 1193, 1136, 1076 and 889 cm^{-1}; δ_H ($CDCl_3$) 3.53 (d, 1H, *J*=6 Hz, imide α-H), 3.69 (d, 1H, *J*=6 Hz, imide α-H), 3.92 (s, 3H, ester CH_3), 3.96 (s, 3H, ester CH_3), 5.52 (s, 1H, sulfur bridge-H) and 6.28 (s, 1H, sulfur bridge-H), 7.23–7.28 and 7.45–7.56 (m, 5H, Ar-H); δ_C ($CDCl_3$) 50.7 (CH), 51.2 (CH), 52.4 (CH_3 ester), 52.8 (CH_3 ester and CH), 71.2 (CH), 108.2, 126.4 (2×CH), 129.5 (3×CH), 146.0, 151.3, 161.1 (C=O ester), 161.4 (C=O ester), 171.4 (C=O amide) and 172.5 (C=O amide); *m/z* M^+ 413 (18%), 379 (85), 348 (100), 240 (91), 203 (26), 77 (31), 59 (36).

Dimethyl 1,3-dioxo-4,9-epithio-2,3,3a,4,9,9a-hexahydro-2-methyl-1*H*-pyrazolo[1,5-*a*]pyrrolo[3,4-*c*]pyridine-7,8-dicarboxylate (22b). Dimethyl 1*H*,3*H*-pyrazolo[1,5-*c*]thiazole-6,7-dicarboxylate 2-oxide **21** (0.26 g, 1.0 mmol) and

N-methylmaleimide (0.14 g, 1.2 mmol) gave after recrystallisation from methanol (*exo*-adduct) *dimethyl 1,3-dioxo-4,9-epithio-2,3,3a,4,9,9a-hexahydro-2-methyl-1*H-*pyrazolo-[1,5-*a*]pyrrolo-[3,4-*c*]pyridine-7,8-dicarboxylate* (0.22 g, 63%) as a colourless powder, mp 232–233°C. (Found: C, 47.9; H, 3.7; N, 11.9. $C_{14}H_{13}N_3SO_6$ requires C, 47.9; H, 3.7 and N, 12.0%); ν_{max} (Nujol®) 2926, 2856, 1779, 1739, 1703, 1699, 1683, 1559, 1462, 1377, 1315, 1211, 1188, 1133, 1072, 973, 888, 830, 805, 795, 776 and 720 cm^{-1}; δ_H ($CDCl_3$) 3.04 (s, 3H, N–CH_3), 3.36 (d, 1H, *J*=7 Hz, imide α-H), 3.52 (d, 1H, *J*=7 Hz, imide α-H), 3.89 (s, 3H, ester CH_3), 3.86 (s, 3H, ester CH_3), 5.40 (s, 1H, sulfur bridge-H) and 6.17 (s, 1H, sulfur bridge-H); δ_C ($CDCl_3$) 25.5 (CH_3), 50.8 (CH), 52.6 (CH), 52.7 (CH_3 ester), 52.8 (CH_3 ester), 53.0 (CH), 70.9 (CH), 108.1, 131.7, 145.9, 151.3, 160.5 (C═O ester), 161.4 (C═O ester), 172.3 (C═O amide) and 173.3 (C═O amide); *m/z* M^+ 351 (16%), 286 (30), 240 (100), 203 (28), 59 (23).

Dimethyl 1,3-dioxo-4,9-epithio-2-ethyl-2,3,3a,4,9,9a-hexahydro-1*H*-pyrazolo[1,5-*a*]pyrrolo[3,4-*c*]pyridine-7,8-dicarboxylate (22c). Dimethyl 1*H*,3*H*-pyrazolo[1,5-*c*]thiazole-6,7-dicarboxylate 2-oxide **21** (0.26 g, 1.0 mmol) and *N*-ethylmaleimide (0.16 g, 1.2 mmol) gave after recrystallisation from methanol (*exo*-adduct) *dimethyl 1,3-dioxo-4,9-epithio-2-ethyl-2,3,3a,4,9,9a-hexahydro-1*H-*pyrazolo[1,5-*a*]-pyrrolo[3,4-*c*]pyridine-7,8-dicarboxylate* (0.26 g, 71%) as a colourless powder, mp 230–231°C. (Found: C, 49.1; H, 4.0; N, 11.2. $C_{15}H_{15}N_3SO_6$ requires C, 49.3; H, 4.1 and N, 11.5%); ν_{max} (Nujol®) 3771, 3625, 3369, 2925, 2858, 1777, 1703, 1650, 1576, 1459, 1376, 1302, 1132, 1072, 888, 805, 720 cm^{-1}; δ_H ($CDCl_3$) 1.19 (t, 3H, *J*=7 Hz, N–CH_2CH_3), 3.34 (d, 1H, *J*=7 Hz, imide α-H), 3.50 (d, 1H, *J*=7 Hz, imide α-H), 3.61 (q, 2H, *J*=7 Hz, N–CH_2CH_3), 3.91 (s, 3H, ester CH_3), 3.95 (s, 3H, ester CH_3), 5.42 (s, 1H, sulfur bridge-H) and 6.18 (s, 1H, sulfur bridge-H); δ_C ($CDCl_3$) 12.5 (CH_3), 34.7 (CH_2), 50.6 (CH), 50.7 (CH), 52.3 (CH_3 ester), 52.7 (CH_3 ester and CH), 70.9 (CH), 108.1, 145.8, 151.4, 161.0 (C═O ester), 161.4 (C═O ester), 172.1 (C═O amide) and 173.1 (C═O amide); *m/z* M^+ 365 (16%), 300 (17), 240 (100), 203 (38), 59 (22).

Dimethyl 1,3-dioxo-4,9-epithio-2-methyl-3a,4,9,9a-tetrahydro-1*H*-pyrazolo[1,5-*a*]furo[3,4-*c*]pyridine-7,8-dicarboxylate (22d). Dimethyl 1*H*,3*H*-pyrazolo[1,5-*c*]thiazole-6,7-dicarboxylate 2-oxide **21** (0.26 g, 1.0 mmol) and maleic anhydride (0.12 g, 1.2 mmol) gave after recrystallisation from methanol (*exo*-adduct) *dimethyl 1,3-dioxo-4,9-epithio-2-methyl-3a,4,9,9a-tetrahydro-1*H-*pyrazolo[1,5-*a*]-furo[3,4-*c*]pyridine-7,8-dicarboxylate* (0.11 g, 34%) as a colourless powder, mp 239–241°C. (Found: C, 46.2; H, 3.0; N, 8.3. $C_{13}H_{10}N_2SO_7$ requires C, 46.2; H, 3.0 and N, 8.3%); ν_{max} (Nujol®) 3441, 3058, 3019, 2926, 2856, 2330, 1867, 1846, 1791,1757, 1723, 1551, 1461, 1436, 1415, 1368, 1319, 1298, 1236, 1259, 1229, 1193, 1171, 1130, 1081, 952, 928, 889, 864, 838, 818, 807, 770, 757, 732 and 664 cm^{-1}; δ_H ($CDCl_3$) 3.72 (d, 1H, *J*=7 Hz, anhydride α-H), 3.86 (d, 1H, *J*=7 Hz, anhydride α-H), 3.91 (s, 3H, ester CH_3), 3.95 (s, 3H, ester CH_3), 5.53 (s, 1H, sulfur bridge-H) and 6.28 (s, 1H, sulfur bridge-H); δ_C (d^6 DMSO) 50.7 (CH), 51.6 (CH), 52.0 (CH_3 ester), 52.4 (CH_3 ester), 53.5 (CH), 71.8 (CH), 106.1, 144.6, 152.3, 161.3 (C═O ester), 162.0 (C═O ester), 170.1 (C═O anhydride) and 170.6 (C═O anhydride); *m/z* M^+ 338 (23%), 307 (18), 240 (100), 234 (33), 203 (60), 59 (44).

Tetramethyl pyrazolo[1,5-*a*]pyridine-2,3,5,6-tetracarboxylate (24). *Method A (via Dimethyl fumarate).* Dimethyl 1*H*,3*H*-pyrazolo[1,5-*c*]thiazole-6,7-dicarboxylate 2-oxide **21** (0.52 g, 2.0 mmol), dimethyl fumarate (0.34 g, 3.2 mmol) and acetic anhydride (10 mL) were heated to reflux for 4 h. The reaction mixture was cooled to room temperature and the solvent removed in vacuo. The resulting dark residue was triturated with methanol and the crude brown mixture of isomers collected by filtration (0.42 g, 60%). The mixture was used without further purification.

A solution of sodium methoxide (0.38 mL, 30% wt. soln., 2.0 equiv., 2.0 mmol) was added slowly to a solution of the crude mixture of isomers (0.38 g, 1.0 mmol) dissolved in anhydrous dichloromethane (10 mL). After stirring for 2 h, the reaction was quenched with saturated ammonium chloride solution (10 mL). The dichloromethane layer was separated and dried over anhydrous sodium sulfate, then filtered and concentrated in vacuo to give a dark residue. Recrystallisation from benzene-petroleum ether gave *tetramethyl pyrazolo[1,5-*a*]pyridine-2,3,5,6-tetracarboxylate* (0.26 g, 76%) as a colourless powder, mp. 133–135°C. (Found: C, 51.2; H, 3.9; N, 7.8. $C_{15}H_{14}N_2O_8$ requires C, 51.4; H, 4.0 and N, 8.0%); ν_{max} (Nujol®) 2925, 2856, 1775, 1728, 1699, 1563, 1529, 1462, 1434, 1377, 1307, 1282, 1251, 1204, 1180, 1154, 1117, 1092, 976, 946, 909, 886, 840, 807, 783, 744 and 710 cm^{-1}; δ_H ($CDCl_3$); 3.96 (s, 3H, ester CH_3), 3.97 (s, 3H, ester CH_3), 3.98 (s, 3H, ester CH_3), 4.05 (s, 3H, ester CH_3), 8.40 (s, 1H, Ar-H) and 9.01 (s, 1H, Ar-H); δ_C ($CDCl_3$) 52.1 (CH_3 ester), 53.2 (3×CH_3 ester), 96.6, 118.7, 120.3 (CH), 132.0, 132.1 (CH), 140.8, 149.8, 161.8 (C═O ester), 162.5 (C═O ester), 164.0 (C═O ester) and 166.2 (C═O ester); *m/z* M^+ 350 (55%), 319 (100), 201 (21).

Method B (via Dimethyl maleate). Tetramethyl pyrazolo-[1,5-*a*]pyridine-2,3,5,6-tetracarboxylate **27a** was prepared from dimethyl maleate using the procedure detailed in method A. Dimethyl 1*H*,3*H*-pyrazolo[1,5-*c*]thiazole-6,7-dicarboxylate 2-oxide **21** (0.52 g, 2.0 mmol) and dimethyl maleate (0.4 mL, 3.2 mmol) gave after desulfurisation *tetramethyl pyrazolo[1,5-*a*]pyridine-2,3,5,6-tetracarboxylate* (0.30 g, 43% overall yield from sulfoxide) as a colourless powder which had identical physical and spectroscopic properties as the product prepared by method A.

Method C (via Dimethyl acetylenedicarboxylate). Dimethyl 5-methyl-1*H*,3*H*-pyrazolo[1,5-*c*]thiazole-6,7-dicarboxylate 2-oxide (0.26 g, 1.0 mmol) and dimethyl acetylenedicarboxylate (0.12 mL, 1.2 mmol) gave after chromatography [ethyl acetate–hexane (1:1)] and recrystallisation from benzene–petroleum ether *tetramethyl pyrazolo[1,5-*a*]pyridine-2,3,5,6-tetracarboxylate*(0.19 g, 55%) as a colourless powder which had identical physical and spectroscopic properties as the product prepared by method A.

5,6-Diethyl-2,3-dimethyl pyrazolo[1,5-*a*]pyridine-2,3,5,6-tetracarboxylate (27a). Dimethyl 5-methyl-1*H*,3*H*-pyrazolo[1,5-*c*]thiazole-6,7-dicarboxylate-2-oxide (0.26 g, 1.0

mmol) and diethyl acetylenedicarboxylate (0.19 mL, 1.2 mmol) using the general procedure for generation and trapping of thiazole **2** gave after chromatography [ethyl acetate–hexane (1:1)] and recrystallisation from benzene–petroleum ether *5,6-diethyl-2,3-dimethyl pyrazolo[1,5-a]-pyridine-2,3,5,6-tetracarboxylate* (0.19 g, 50%) as a colourless powder, mp. dec. 236–238°C. (Found: C, 54.2; H, 4.9; N, 7.2. $C_{17}H_{18}N_2O_8$ requires C, 54.0; H, 4.8 and N, 7.4%); ν_{max} (Nujol®) 3771, 3695, 3369, 2923, 2859, 1730, 1709, 1659, 1639, 1576, 1458, 1376, 1303, 1259, 1236, 1193, 1171, 1134, 1082, 1052, 1018, 968, 902, 846, 821, 805, 772, 741 and 719 cm^{-1}; δ_H ($CDCl_3$); 1.38–1.43 (m, 6H, 2×$CH_3CH_2CO_2$–), 3.96 (s, 3H, ester CH_3), 4.05 (s, 3H, ester CH_3), 4.39–4.48 (m, 4H, 2×$CH_3CH_2CO_2$–), 8.39 (s, 1H, Ar-H) and 9.02 (s, 1H, Ar-H); *m/z* M^+ 378 (100), 347 (69), 305 (68), 201 (28), 59 (26). Accurate mass: 378.1068, $C_{17}H_{18}N_2O_8$ requires 378.1063.

Dimethyl 5,6-dibenzoylpyrazolo[1,5-*a*]pyridine-2,3-dicarboxylate (27b). Dimethyl 5-methyl-1*H*,3*H*-pyrazolo[1,5-*c*]-thiazole-6,7-dicarboxylate-2-oxide (0.26 g, 1.0 mmol), dibenzoylacetylene (0.28 g, 1.2 mmol) gave after chromatography [ethyl acetate–hexane (1:1)] and recrystallisation from methanol *dimethyl 5,6-dibenzoylpyrazolo[1,5-a]pyridine-2,3-dicarboxylate* (0.26 g, 59%) as a brownish powder, mp. 168–170°C. (Found: C, 67.9; H, 4.0; N, 6.3. $C_{25}H_{18}N_2O_6$ requires C, 67.9; H, 4.0 and N, 6.3%); ν_{max} (Nujol®) 2930, 2856, 1740, 1721, 1699, 1673, 1654, 1596, 1524, 1462, 1406, 1377, 1325, 1304, 1230, 1215, 1174, 1071, 980, 886 and 715 cm^{-1}; δ_H ($CDCl_3$); 3.92 (s, 3H, ester CH_3), 4.06 (s, 3H, ester CH_3), 7.44–7.50 (m, 4H, Ar-H), 7.60–7.62 (m, 2H, Ar-H), 7.78–7.85 (m, 4H, Ar-H), 8.34 (s, 1H, 4-H) and 9.01 (s, 1H, 7-H); *m/z* M^+ 442 (40%), 411 (100), 365 (29), 105 (100), 77 (83).

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