

Cyclopropanation of Some Michael Acceptors with Thiophenium Bis(methoxycarbonyl)methylides

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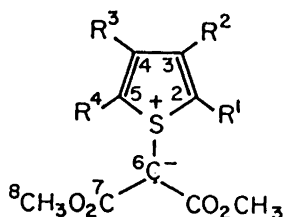
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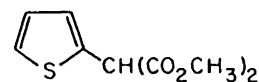
The reaction between a series of thiophenium bis(methoxycarbonyl)methylides and some Michael acceptors was investigated. The reaction products were multifunctional cyclopropane derivatives. Depending on the substituents attached to the thiophene ring, sharp differences were found in the ylide reactivity.

In 1978, Porter *et al.* showed¹ that thiophenium bis(methoxycarbonyl)methylide (**1a**) is unstable at elevated temperatures and rearranges intramolecularly to dimethyl 2-thienylmalonate (**2**). It has also been shown that when both 2- and 5-positions of the thiophene ring are blocked (e.g., as in **1e**) a more complicated rearrangement occurs on thermolysis.² Alternatively, in the presence of Rh(II) acetate or Cu(II) acetylacetonate

Cyclopropanation by sulfur ylides is known to occur with olefins susceptible to Michael addition.⁴ The three alkenes tetracyanoethylene (TCNE) (**3a**), diethyl dicyanofumarate (**3b**) and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ, **4**) whose reactions with **1a** were investigated by us are potential Michael acceptors, and they afforded the fully substituted, multifunctional cyclopropane derivatives **5a**, **5b** and **6**, respec-



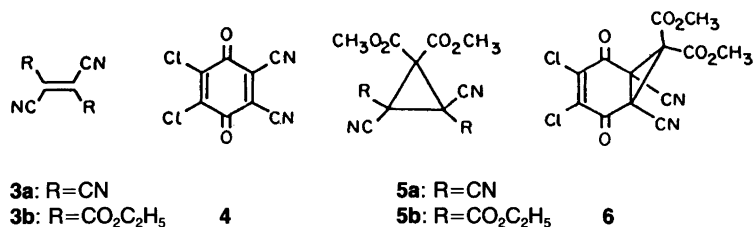
- 1a**: R¹=R²=R³=R⁴=H
1b: R¹=CH₃, R²=R³=R⁴=H
1c: R¹=Cl, R²=R³=R⁴=H
1d: R¹=R⁴=CH₃, R²=R³=H
1e: R¹=R⁴=Cl, R²=R³=H
1f: R¹=R²=R³=R⁴=Cl



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as catalysts, the ylide **1e** effected cyclopropanation of isolated double bonds of olefins at reflux temperature.³ The cyclopropanation was explained by assuming the intermediacy of a bis(methoxycarbonyl)carbene–metal complex as the reactive species, generated by metal-catalysed cleavage of the carbon–sulfur bond of the ylide. In view of these results, we now report our findings concerning the uncatalysed cyclopropanation of some highly electron-poor Michael acceptors by the unsubstituted ylide **1a** under mild conditions.

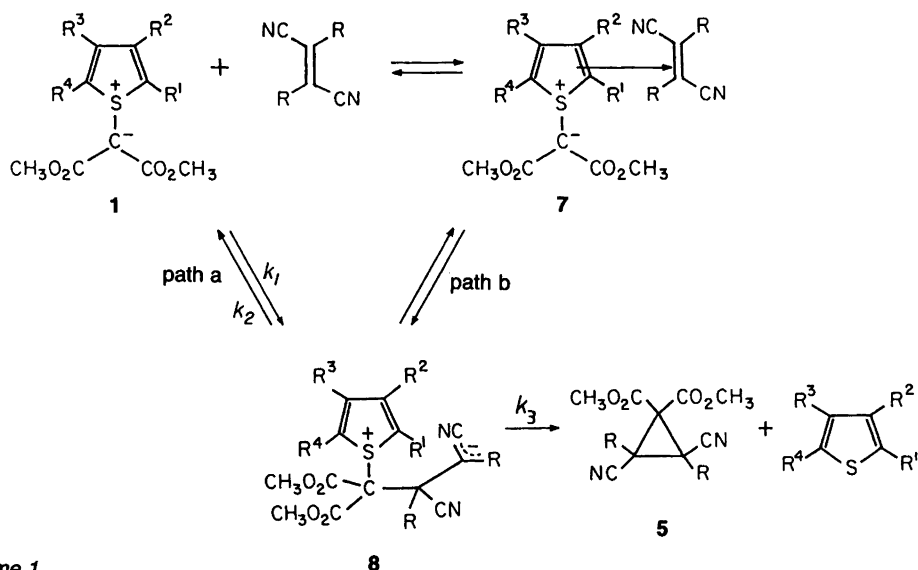
tively, as reaction products. TCNE showed the highest activity towards the ylide, reacting extremely fast even at around 0°C, and the lowest reaction rate was observed for diethyl dicyanofumarate, reacting at 50°C. This difference in reactivity is in accord with the greater activating influence of a cyano group than of the ethoxycarbonyl group on the acceptor, as previously demonstrated in ylide-induced cyclopropanations.⁵ Such findings are in contrast to electrophilic carbene-olefin (or carbenoid-olefin) reactions, whose rates are enhanced by electron-donating but re-



tarded by electron-withdrawing substituents attached to the olefinic double bond.

The reported cyclopropanation of TCNE by diazomethane and diphenyldiazomethane is apparently not a carbene reaction. In these cases, 1,3-dipolar cycloaddition of the diazoalkanes to the double bond of TCNE occurs to yield first a pyrazoline, which then readily loses nitrogen to give the cyclopropane derivative.^{6,7} Ethyl diazoacetate, with the electron-attracting carboxy group, has been reported to undergo cycloaddition to the nitrile group of TCNE without the formation of the cyclopropane derivative.⁷ Our attempt to prepare **5a** by reacting TCNE with dimethyl diazomalonate in the presence of rhodium acetate was unsuccessful. Electron-attracting groups (especially cyano groups), on the other hand, will favor a Michael-type reaction by stabilizing the developing negative charge in the dipole intermediate **8** during the nucleophilic ad-

dition of the ylide to the acceptor (Scheme 1). On mixing the reagents in different aprotic solvents, a yellow color (λ_{\max} 346 nm in the case of **1a** + TCNE) appeared instantly and faded rapidly. This indicates that the reaction may involve the initial formation of the charge transfer (CT) complex **7** (π -complex), which evolves to the dipolar intermediate **8** (path b) which then collapses to the product. CT complex formation is reversible: donor, acceptor and complex exist in equilibrium,⁸ and we are not aware of any method which allows an unambiguous decision as to whether the CT complex is an intermediate during the reaction or not. Therefore, a direct nucleophilic attack of the ylide on TCNE (path a) seems to be an equally satisfactory mechanistic explanation. In many other examples described in the literature (see Ref. 4), no mention has been found of initial CT complex formation between reacting ylides and Michael acceptors. Although the



Scheme 1.

Table 1. ^{13}C NMR chemical shifts (ppm) for thiophenium ylides^a.

Ylide	C-2,C-5	C-3,C-4	C-6	C-7	C-8	R ¹ =R ⁴ =CH ₃
1a	130.88	133.54	49.85	165.54	51.37	–
1b	133.39	128.91	50.86	164.35 166.03	51.71	–
1f	131.50	127.55	50.61	163.96 165.47	51.84 52.08	–
1d	140.82	128.44	51.98	165.88	51.04	12.55

^a δ values in CDCl₃ relative to TMS.

stereochemistry of the acceptor in these cyclopropanations which proceed through a zwitterion such as **8** does not necessarily determine the stereochemistry of the product, both **3b** and **5b** have identical configuration (the thermodynamically more stable one) as confirmed by X-ray crystallography. Cyclopropanation of DDQ (**4**) was regioselective, taking place at the more reactive cyano group-substituted double bond, as shown by X-ray structural analysis.

We also investigated the influence of the thiophene ring substituents in the ylides **1b**, **1c**, **1d**, **1e** and **1f** on the course of the reaction with TCNE. The relative reaction rates were estimated only qualitatively by measuring intensities of developing and disappearing carbonyl absorption bands in the infrared spectra of samples taken from the reaction mixtures at regular intervals. Both 2-methylthiophenium ylide (**1b**) and 2-chlorothiophenium ylide (**1c**) reacted rapidly with TCNE at room temperature, and the reaction rates were qualitatively indiscernible from that for **1a**. An equally fast corresponding reaction was observed for the 2,5-dimethyl compound **1d**, and no starting materials could be detected after ca. 15–20

min reaction time at room temperature. On the other hand, the 2,5-dichlorothiophenium ylide (**1e**) did not react with TCNE at room temperature.

Even at 50°C the reaction proceeded quite sluggishly, and after 30 h the reaction mixture consisted of ca. 70% of product **5a** and 30% of starting ylide. The tetrachlorothiophenium ylide **1f** was found to be completely unreactive. After stirring with TCNE at 50–55°C for two days, no product was detected and the starting ylide could be recovered. Since the steric bulk of the chlorine atom and that of the methyl group are quite similar, the striking difference in the behaviour of **1d** and **1e** – and the complete unreactivity of **1f** – suggest that the reactivity of these ylides is affected mainly by electronic rather than by steric effects of the substituents attached to the thiophene moiety.

Although a large number of sulfur ylides are described in the literature, the reported variation in the substituents on the sulfur site of these compounds (as in our case) is very limited, and does not allow a comparison of our results with those previously reported.

Table 2. Reaction of thiophenium bis(methoxycarbonyl)methylides with TCNE.

Ylide	Solvent	Temp./°C	Reaction time	Yield of 5a /%
1a	Acetone	0-R.t.	15–20 min	90 ^a
1b	Acetone	R.t.	20 min	91 ^a
1c	Acetone	R.t.	25–30 min	88 ^a
1d	Acetonitrile	R.t.	15–20 min	89 ^a
1e	Acetonitrile	50–55	30 h	70 ^b
1f	Acetonitrile	50–55	48 h	0 ^c

^aIsolated yield of crude product. ^bEstimated from the IR spectrum. ^cNo product detected.

Fig. 1. ORTEP perspective drawing of **5b** with atom numbering. Ellipsoids are of 50 % probability.

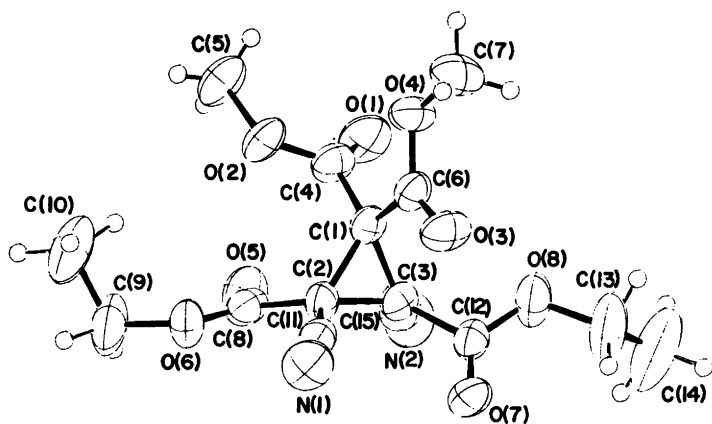


Fig. 2. ORTEP perspective drawing of **6** with atom numbering. Ellipsoids are of 50 % probability.

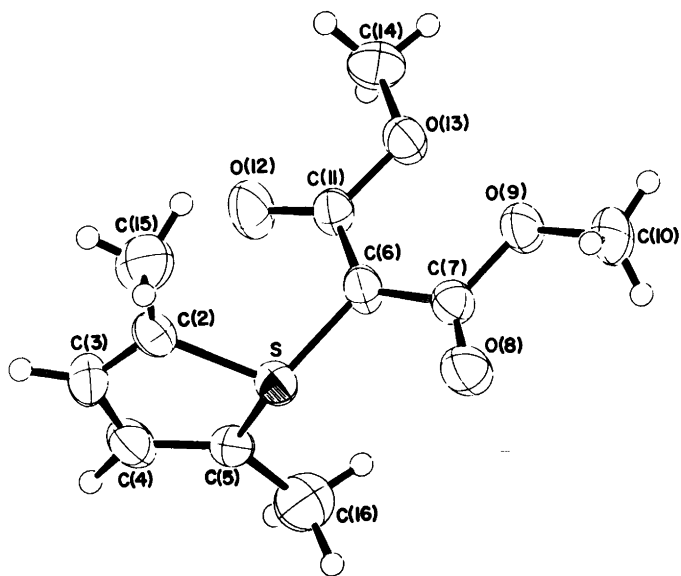
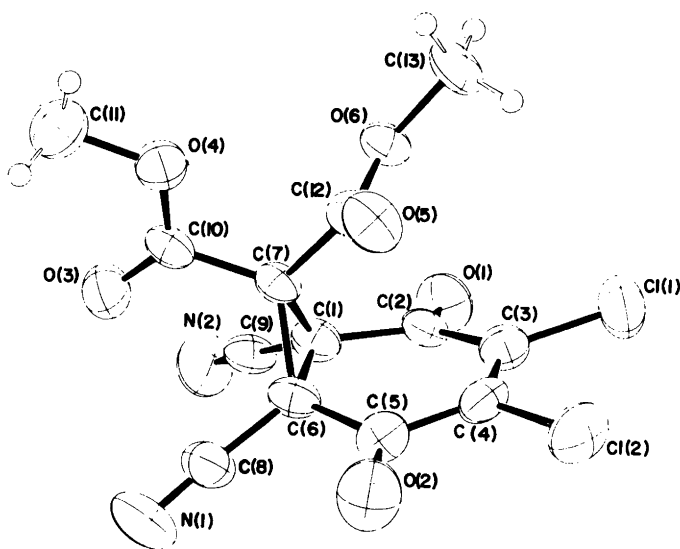


Fig. 3. ORTEP perspective drawing of **1d** with atom numbering. Ellipsoids are of 50 % probability.

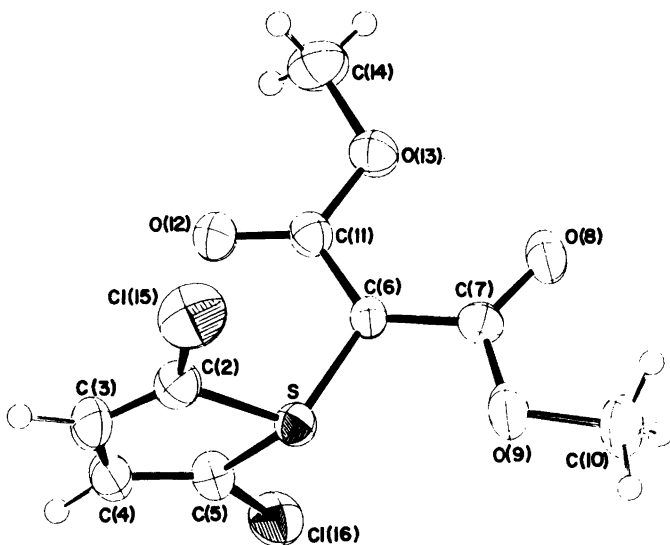


Fig. 4. ORTEP perspective drawing of **1e** with atom numbering. Ellipsoids are of 50 % probability.

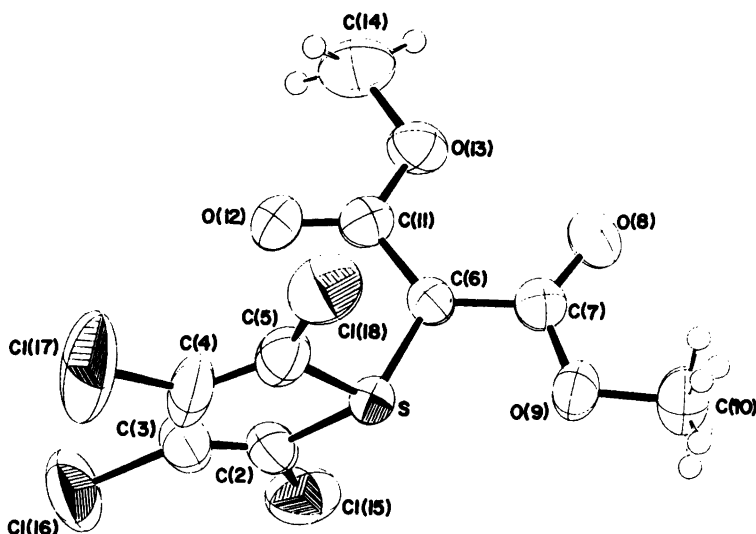


Fig. 5. ORTEP perspective drawing of **1f** with atom numbering. Ellipsoids are of 50 % probability.

Considering the above-suggested multistep mechanism (Scheme 1) each step may be rate-determining. Since we found UV-spectral evidence for initial CT complex formation both with the reactive and with the unreactive ylides, this step cannot be rate-determining. X-ray analysis revealed a shortening of the C–S ylide bond (more C=S bond character) in the chloro compounds, which may indeed influence the nucleo-

philic step. In order to gain additional information, relative charge densities on the ylide carbon ($S^+ - C^-$), a possible indication of its nucleophilicity, were estimated from ^{13}C chemical shifts (Table 1). These data, however, failed to correlate with the observed differences in reactivity. One can also suggest that differences in aromaticity of the thiophene ring in the reacting ylides would control the energy gain in the rearomatiza-

tion occurring during the thiophene moiety expulsion step. In this respect, however, no correlation was found between representative bond lengths (see below) and reaction rates for the ylides **1d**, **1e** and **1f**. All these considerations, therefore, do not provide a decisive explanation of the great difference in reactivity observed for **1a** and **1f**. One may speculate that the overall reaction rate is controlled by the ratio of the rate constants k_1 and k_2 (Scheme 1), a greater k_2 being associated with ylides of greater stability. The observed thermal stability of the ylides is **1a** < **1e** \ll **1f**.

Further studies on the dependence of the reaction rates of different ylides on steric and electronic properties of various substituents on sulfur may yield a more satisfactory explanation of our results.

Discussion of the crystallographic results

ORTEP⁹ perspective drawings of molecules **5b**, **6**, **1d**, **1e** and **1f**, including atom labels are shown in Figs. 1, 2, 3, 4 and 5 respectively. Molecule **5b** has its cyano groups disposed *trans* with respect to the cyclopropane ring plane, as displayed in Fig. 1. Its geometry is rather regular. Molecule **6**, however, exhibits some interesting features regarding the shape of the substituted DDQ moiety. Fig. 2 shows clearly that the attachment of the bis(methoxycarbonyl)methylide group occurs to the more active double bond of the DDQ bearing the two cyano groups. Bond lengths of the DDQ moiety (Table 4), excluding the single bond at C(1)–C(6), are in close agreement with the corresponding values in the structure of DDQ itself¹⁰ and in the charge-transfer complex DDQ-phenanthrene.¹¹ Among the various bond angles, C(2)–C(1)–C(6) and C(5)–C(6)–C(1) are af-

fected most, the angle closure being ca. 3° compared to the corresponding values in the DDQ molecule. Indeed, this conservation of angles at C(1) and C(6) is expected in those cases where the double bond is replaced by a three-membered ring. Owing to the cyclopropanation, the almost planar six-membered ring of DDQ converts into a remarkably non-planar cyclohexene ring. This ring adopts a slightly deformed boat conformation with the flaps at C(2) and C(5) bending out the ring mean plane, away from the cyclopropane ring. Deviations of atoms from the mean plane of the six-membered ring are given in Table 5 for comparison with the corresponding values in DDQ. Molecules **1d**, **1e** and **1f** are three thiophenium bis(methoxycarbonyl)methylides with the thiophene ring substituted by methyl and chlorine atoms at various positions. Selected bond lengths and θ values are presented in Table 6, together with the analogous values for the unsubstituted molecule **1a**. The data in Table 6 reveal remarkable shortening of the ylide S–C(6) bond starting from the dimethyl derivative **1d** through the unsubstituted molecule **1a** to the dichloro and tetrachloro derivatives. The thiophene S–C(2) and S–C(5) bonds are significantly longer for **1d**, **1e** and **1f** than for **1a**, indicating reduction of aromaticity with substitution in these compounds. However, the lengths of the C(2)–C(3) and C(4)–C(5) double bonds are determined too inaccurately to warrant a detailed discussion of this effect. The sulfur atom in the dichloro and tetrachloro derivatives is more pyramidal than in the unsubstituted and dimethyl compounds, as indicated by the θ values shown in Table 6. Moreover, it seems that there is a certain correlation between these values and the ylide bond lengths, in the sense that larger angles correspond to shorter bonds.

Table 3. Experimental details of data collection.

	5b	6	1d	1e	1f
Radiation	MoK α	MoK α	MoK α	MoK α	MoK α
Scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
ω -Scan speed/ ^o min ⁻¹	3	3	3	3	2
ω -Scan width/ ^o	1.1	1.1	1.1	1.1	1.2
2 θ -Scan range/ ^o	5–48	5–46	5–46	5–46	5–50
Background on each side of the peak/sec	10	10	10	10	10

Table 4. Selected bond lengths (Å) and angles (°) in the substituted DDQ moiety of **6**. E.s.d.'s are given in parentheses.

Bond lengths			
C(1)–C(2)	1.511(9)	C(4)–C(5)	1.46(1)
C(1)–C(6)	1.52(1)	C(4)–Cl(2)	1.715(8)
C(1)–C(9)	1.465(9)	C(5)–C(6)	1.51(1)
C(2)–C(3)	1.49(1)	C(5)–O(2)	1.19(1)
C(2)–O(1)	1.192(8)	C(6)–C(8)	1.452(9)
C(3)–C(4)	1.35(1)	C(8)–N(1)	1.13(1)
C(3)–Cl(1)	1.698(7)	C(9)–N(2)	1.13(1)
Angles			
C(2)–C(1)–C(6)	118.2(6)	C(3)–C(4)–Cl(2)	120.8(5)
C(2)–C(1)–C(9)	111.3(5)	C(5)–C(4)–Cl(2)	115.7(5)
C(6)–C(1)–C(9)	119.6(5)	C(3)–C(4)–C(5)	123.4(7)
C(1)–C(2)–C(3)	117.3(5)	C(4)–C(5)–C(6)	118.1(6)
C(1)–C(2)–O(1)	120.1(6)	C(4)–C(5)–O(2)	121.8(7)
C(3)–C(2)–O(1)	122.6(6)	C(6)–C(5)–O(2)	120.1(7)
C(2)–C(3)–Cl(1)	114.7(5)	C(1)–C(6)–C(5)	118.0(5)
C(4)–C(3)–Cl(1)	123.5(6)	C(1)–C(6)–C(8)	119.1(6)
C(2)–C(3)–C(4)	121.6(6)	C(5)–C(6)–C(8)	112.4(6)

Experimental

Melting points were measured in open capillaries and are uncorrected. IR spectra were recorded with a Perkin-Elmer 298 spectrophotometer. A Bruker AM-400 WB spectrometer was used at 400.13 and 100.61 MHz to record ¹H and ¹³C NMR spectra, respectively. TMS and CDCl₃ were used as internal standards, unless otherwise

Table 5. Deviations ($\times 10^{-3}$ Å) of atoms of **6** from the mean-plane of the six-membered ring. The corresponding values for the DDQ molecule are given for comparison. The eqn. of the plane in an orthogonal system is given by: $0.7537X + 0.5675Y + 0.3314Z - 32.9565 = 0$, where $X_{||}^a$, $Y_{||}^c$ and $Z_{||}^c$. An asterisk denotes an atom not included in the mean-plane calculation.

DDQ			6		
C(1)	4	-57	C(9)*	-1	602
C(2)	-10	122	N(1)*	113	1162
C(3)	-2	-75	N(2)*	-12	1138
C(4)	19	-42	O(1)*	-8	404
C(5)	-24	106	O(2)*	-97	317
C(6)	13	-53	Cl(1)*	-10	-216
C(8)*	61	604	Cl(2)*	71	-105

stated (δ scale). Molecular weight determinations were made by high resolution MS on a Varian Matt-711 double-focusing instrument operating at 70 eV, by direct inlet. The thiophenium ylides were prepared by literature methods.^{12,13}

Dimethyl 2,2,3,3-tetracyanocyclopropane-1,1-dicarboxylate (5a). The reaction conditions used for the reaction of TCNE with ylides **1a–1f** are summarized in Table 2. A typical procedure is the following: to a magnetically stirred mixture of **1a** (0.21 g, 1 mmol) in ice-cold acetone* (6 ml) was added TCNE (**3a**) (0.14 g, 1.1 mmol) in small portions. After each addition a dark-yellow colour developed which then faded very fast. After the addition was completed (2–3 min), stirring was continued at room temperature for 10–15 min and the resulting pale yellow solution was concentrated (water pump). Trituration of the solid residue with cold benzene, gave the crude crystalline product **5a** (0.23 g, 90%). Recrystallization from 2-propanol gave an analytical sample, m.p. 164 °C; ν_{\max} (CHCl₃) 1770 cm⁻¹; δ_{H} 4.55 (s); HRMS: M^+ 258.0350 (C₁₁H₆N₄O₄ requires $M = 258.0389$).

* Note the differences in solvent, reaction temperature and time for **1e** and **1f** given in Table 2.

Table 6. Selected bond lengths (Å) and θ -values ($^\circ$) for various thiophenium ylides. θ is the angle between the thiophenium ring mean-plane and the vector defined by the bond from sulfur to the ylid carbon.

	1a	1d	1e	1f
S–C(2)	1.745(7)	1.772(5)	1.778(6)	1.792(7)
C(2)–C(3)	1.326(6)	1.330(7)	1.307(8)	1.313(12)
C(3)–C(4)	1.439(10)	1.443(8)	1.450(9)	1.458(15)
C(4)–C(5)	1.320(8)	1.324(7)	1.316(8)	1.333(12)
S–C(5)	1.743(4)	1.769(5)	1.782(6)	1.768(7)
S–C(6)	1.711(4)	1.717(5)	1.693(5)	1.694(7)
θ	49.7	48.2	53.4	54.8

Dimethyl trans-2,3-diethoxycarbonyl-2,3-dicyanocyclopropane-1,1-dicarboxylate (5b). A mixture of **1a** (0.21 g, 1 mmol) and diethyl dicyanofumarate (**3b**) (0.22 g, 1 mmol) in acetonitrile (6 ml) was stirred magnetically at 50 °C for 3 h. After evaporation of the solvent at reduced pressure, the residue was triturated with ether to give a white crystalline product (0.15 g), m.p. 100–102 °C. A second crop (0.06 g) was obtained when the concentrated mother liquor was kept in the refrigerator; this increased the total yield to 60%. The analytical sample had m.p. 102–103 °C (benzene/petroleum ether) ν_{\max} (CHCl₃) 1767 cm⁻¹; δ_{H} 1.39 (3H, t), 3.88 (3H, s), 4.40 (2H, q); HRMS: M^+ 352.0958 (C₁₅H₁₆N₂O₈ requires $M = 352.0907$).

Dimethyl 1,6-dicyano-3,4-dichlorobicyclo[4.1.0]hept-3-ene-2,5-dione-7,7-dicarboxylate (6). (a) To an ice-cold, magnetically stirred suspension of the ylide (0.107 g, 0.05 mmol) in dry acetone (4 ml) was added DDQ (0.12 g, 0.55 mmol) in small portions. During the addition a dark red colour developed. The mixture was kept in a refrigerator overnight and the yellow-brown solution was then evaporated to dryness under reduced pressure. The orange coloured crude solid (0.18 g) was purified by chromatography on silica gel (Woelm; 7 g) using ethyl acetate/methanol (98/2) as eluent. The title compound was obtained as a bright yellow solid (0.142 g, 80%). Crystallization from benzene gave an analytical sample, m.p. 213–215 °C; ν_{\max} (KBr) 1780, 1756, 1728 cm⁻¹; δ_{H} (CD₃COCD₃) 3.85 (s), 4.02 (s); HRMS: M^+ 355.9603 (C₁₃H₆Cl₂N₂O₆ requires $M = 355.9600$).

(b) In an alternative procedure, using the same amounts as described above, the ylide was added

in small portions to a solution of DDQ in acetone at room temperature. Stirring was continued until the red colour of the solution turned to yellow-brown (ca. 1 h). Evaporation of the solvent and recrystallization of the residue from benzene gave **6** in 73% yield.

X-Ray crystallographic data and structure determination

Crystals of **5b** were prepared from benzene/hexane as transparent prisms, crystal size 0.165 × 0.30 × 0.33 mm, formula C₁₅H₁₆N₂O₈, F.W. = 352.1, lattice triclinic, $a = 11.403(5)$, $b = 9.738(4)$, $c = 8.694(4)$ Å, $\alpha = 102.27(5)$, $\beta = 98.94(5)$, $\gamma = 65.71(5)^\circ$, $V = 857.3$ Å³, space group $P\bar{1}$, $Z = 2$, $F(000) = 368$, $D_{\text{calc}} = 1.365$ g cm⁻³, μ (MoK α) = 0.72 cm⁻¹, No. of unique F_{obs} 2565, No. of F_{obs} at the final refinement stage 1640, criterion for omitting reflections $F_o \leq 3 \sigma(F_o)$, $R = 0.066$, $R_w = 0.056$, weighting scheme = $2.035/\sigma^2(F_o)$.

Crystals of **6** were grown from benzene as yellow prisms, crystal size 0.22 × 0.28 × 0.35 mm, formula C₁₃H₆Cl₂N₂O₆, F.W. = 356.0, lattice orthorhombic, $a = 40.936(9)$, $b = 19.122(4)$, $c = 7.708(2)$ Å, $V = 6033.6$ Å³, space group $Fdd2$, $Z = 16$, $F(000) = 2880$, $D_{\text{calc}} = 1.573$ g cm⁻³, μ (MoK α) = 4.03 cm⁻¹, No. of unique F_{obs} 1130, No. of F_{obs} at the final refinement stage 999, criterion for omitting reflections $F_o \leq 3 \sigma(F_o)$, $R = 0.035$, $R_w = 0.035$, weighting scheme = $1.053/\sigma^2(F_o)$.

Crystals of **1d** grew from acetonitrile as transparent prisms, crystal size 0.13 × 0.30 × 0.40 mm, formula C₁₁H₁₄O₄S, F.W. = 242.3, lattice monoclinic, $a = 12.984(7)$, $b = 8.459(4)$, $c = 11.463(6)$ Å, $\beta = 112.07(5)^\circ$, $V = 1166.8$ Å³,

space group $P2_1/c$, $Z = 4$, $F(000) = 512$, $D_{\text{calc}} = 1.380 \text{ g cm}^{-3}$, $\mu(\text{MoK}\alpha) = 2.25 \text{ cm}^{-1}$, No. of unique F_{obs} 1542, No. of F_{obs} at the final refinement stage 1102, criterion for omitting reflections $F_o \leq 3 \sigma(F_o)$, $R = 0.06$, $R_w = 0.054$, weighting scheme = $1.606/\sigma^2(F_o)$.

Crystals of **1e** were grown from acetonitrile as pale yellow prisms, crystal size $0.20 \times 0.25 \times 0.35 \text{ mm}$, formula $\text{C}_9\text{H}_8\text{Cl}_2\text{O}_4\text{S}$, F.W. = 283.1, lattice orthorhombic, $a = 16.587(8)$, $b = 9.325(5)$, $c = 7.389(4) \text{ \AA}$, $V = 1142.9 \text{ \AA}^3$, space group $P2_12_12_1$, $Z = 4$, $F(000) = 576$, $D_{\text{calc}} = 1.646 \text{ g cm}^{-3}$, $\mu(\text{MoK}\alpha) = 6.71 \text{ cm}^{-1}$, No. of unique F_{obs} 942, No. of F_{obs} at the final refinement stage 804, criterion for omitting reflections $F_o \leq 3 \sigma(F_o)$, $R = 0.036$, $R_w = 0.033$, weighting scheme = $1.070/\sigma^2(F_o)$.

Crystals of **1f** were grown from acetonitrile as flat yellow plates, crystal size $0.11 \times 0.33 \times 0.59 \text{ mm}$, formula $\text{C}_9\text{H}_6\text{Cl}_4\text{O}_4\text{S}$, F.W. = 352.0, lattice monoclinic, $a = 10.639(4)$, $b = 9.277(4)$, $c = 7.273(3) \text{ \AA}$, $\beta = 102.35(5)^\circ$, $V = 701.2 \text{ \AA}^3$, space group $P2_1$, $Z = 2$, $F(000) = 352$, $D_{\text{calc}} = 1.668 \text{ g cm}^{-3}$, $\mu(\text{MoK}\alpha) = 9.09 \text{ cm}^{-1}$, No. of unique F_{obs} 1304, No. of F_{obs} at the final refinement stage 1161, criterion for omitting reflections $F_o \leq 3 \sigma(F_o)$, $R = 0.051$, $R_w = 0.057$, weighting scheme $1/[\sigma^2(F_o) + 0.004 F_o^2]$.

Crystals of diffraction quality were mounted on a Philips PW 1100/20 four-circle diffractometer, and accurate cell parameters were derived from 25 carefully centered reflections. Intensities were collected with graphite monochromated radiation under the measuring conditions described in Table 3. Absorption corrections were applied only for **1f**, and intensities for all five crystals were corrected for L_p and reduced to lists of structure factors.

The structures were solved by direct methods and Patterson synthesis using MULTAN¹⁴ and SHELX 77.¹⁵ Non-hydrogen atoms were refined anisotropically, and hydrogens isotropically. Unit weights were introduced at the initial stages and statistical weights at the final stages of the refinement.

Tables of final fractional coordinates, anisotropic temperature factors, bond lengths and angles, as well as lists of observed and calculated structure factors are available on request from

the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, U.K.

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