Keten Dithioacetals. Part 22.[1] Reaction of Polarised Ketoketen Dithioacetals with Dimethyl Acetylenedicarboxylate

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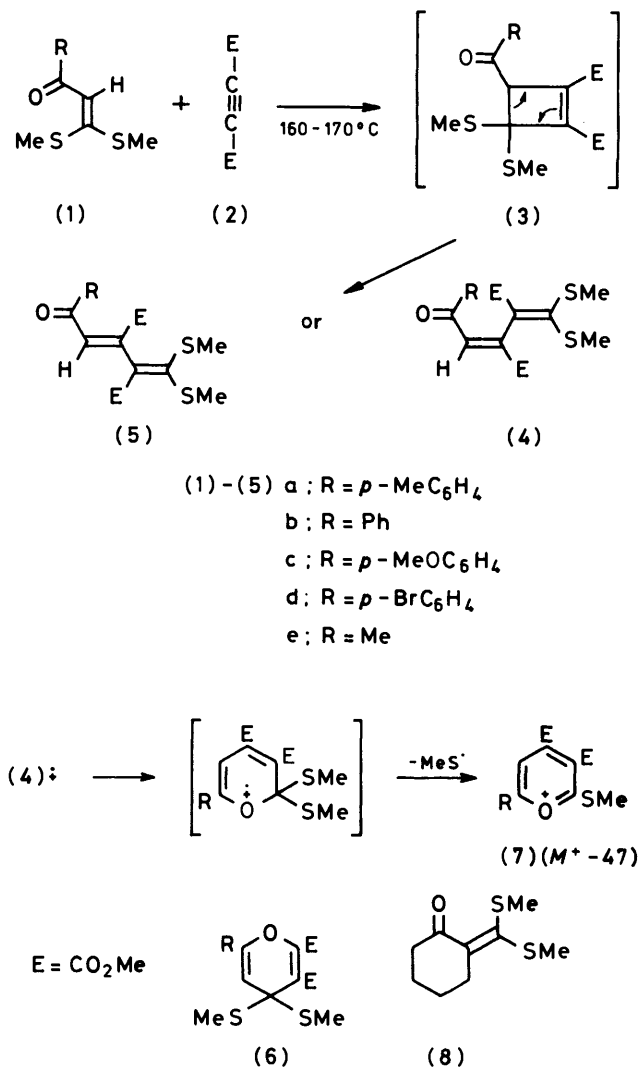
Ketoketen dithioacetals (1a—e) react with dimethyl acetylenedicarboxylate (2) to give open-chain dienes (4a—e) respectively. The formation of these dienes is explained through ring opening of the cyclobutene formed by [2 + 2]cycloadditions of (1) and (2). The cyclic ketoketen dithioacetal (9) reacted with (2) to give an unusual compound, which was characterized as thiapyran-2-one (10). A plausible mechanism for the formation of (10) has been suggested.

While the reactions of simple keten O,O-, S,S-, O,N-, S,N-, and N,N-acetals,[2-4] and enamines [5] with activated acetylenes have been reported in the literature to proceed through [2 + 2]cycloadditions, the conjugated vinylketen O,O- and dithioacetals with activated acetylenes are known to give either [4 + 2]cycloaddition products or open-chain Michael adducts.[6,7] Similarly thioacylketen dithioacetals react with dimethyl acetylenedicarboxylate (DMAD) to give the corresponding Diels–Alder adducts.[8-10] However, the behaviour of polarized ketoketen dithioacetals with DMAD has received very little attention and the easy accessibility of these compounds from a wide variety of active methylene compounds warrants a systematic investigation. The present study was therefore undertaken as a part of our interest in the chemistry of ketoketen dithioacetals.[1]

When the ketoketen dithioacetal (1a), derived from acetophenone, was treated with DMAD (2) in benzene at room temperature, it was recovered unchanged. However (1a) was found to react with (2) in refluxing xylene and, after 20 h, a 1 : 1 adduct was isolated in 20% yield. The yield of the adduct was further improved to 60% when (1a) and (2) were heated neat at 170—180 °C. The 1 : 1 adduct was characterized as the diene (4a), apparently the result of cleavage of the cyclobutene ring (3) arising from the [2 + 2]cycloaddition of the reactants (Scheme 1). The corresponding [4 + 2]cycloadduct (6) was not detected from the reaction mixture. Of the two possible geometrical isomers (4a) and (5a), the isomeric structure (4a) was assigned on the basis of the chemical-shift value of the vinylic proton. Thus the ^{1}H n.m.r. signal for the vinylic proton which appeared at δ 6.60 in (1a) was shifted to lower field (δ 7.40) in (4a) indicating strong deshielding due to the *cis*-methoxycarbonyl group on the adjacent carbon atom. The strong band at 1 630 cm^{-1} in the i.r. spectrum due to the aromatic carbonyl group confirms the open-chain structure (4a), ruling out the formation of the [4 + 2]cycloadduct (6). The ketoketen dithioacetals (1b—e) similarly reacted with DMAD (2) under identical conditions to yield the novel push-pull dienes (4b—e), respectively, in 52—58% overall yields. The spectral and analytical data of (4b—e) are described in Tables 1 and 2 respectively. The mass spectral fragmentations of the dienes (4) showed extremely weak molecular ion peaks (Table 1), while the major fragment ions arose from M^+ (4) (Scheme 1) *via* electrocyclic ring closure followed by loss of a methylmercapto group to give even-electron ions (7), which gave the base peaks ($M^+ - 47$) (Scheme 1).

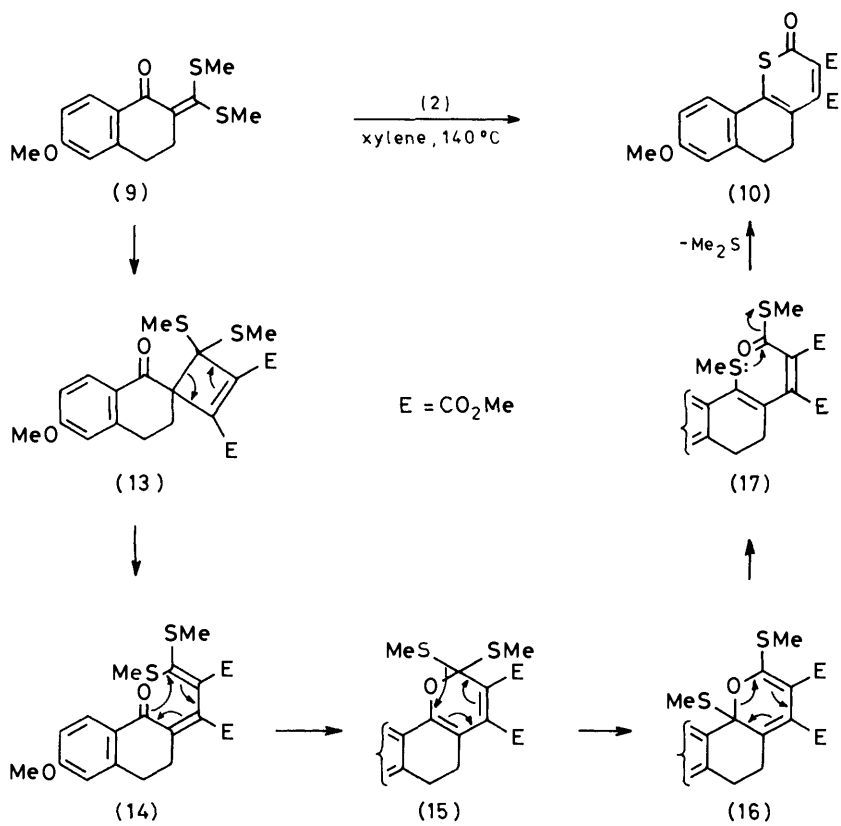
The cyclic ketoketen dithioacetal (8) having *cis*-configuration of carbonyl and bismethylthiomethylene groups did not yield any identifiable product under varying conditions. Either the unchanged compound (8) was recovered under mild conditions or an intractable tar was obtained at higher temperature. Similarly (9) and DMAD (2) under mild conditions did not react, but they gave a bright yellow crystalline solid in low yield (16%) when the reactants were heated in a steel bomb in xylene. The product was characterized as the thiapyran-2-one (10) (Scheme 2) on the basis of analytical and spectral data. It showed in its mass spectrum, the molecular ion peak at *m/z* 360 (72%) ($C_{10}H_{16}O_6S$). The i.r. spectrum showed two strong absorption bands at 1 740 and 1 720 cm^{-1} which were



Scheme 1.

Table 1. Spectral data for dimethyl 4,4-bismethylthio-1-aroyl (or acyl)butadiene-2,3-dicarboxylates (4b—e)

Compound	M.p. (°C)	Yield (%)	$\nu_{max.}$(KBr) (cm^{-1}) Ester CO	Arom/ alph CO	δ_H($CDCl_3$)	*m/z*
(4b)	122—124	52	1 722, 1 703	1 628	2.20 (s, 3 H, SCH_3), 2.35 (s, 3 H, SCH_3), 3.6 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 7.17 (s, 1 H, olefinic), 7.25—7.65 (m, 5 H, aromatic)	366 (8%) 319 (100%)
(4c)	130—132	58	1 725—1 704	1 625	2.30(s, 3 H, SCH_3), 2.45 (s, 3 H, SCH_3), 3.65 (s, 3 H, OCH_3), 3.8 (s, 3 H, OCH_3), 3.9 (s, OCH_3), 7.55 (s, 1 H), 6.80—7.75 (m, A_2B_2, 4 H aromatic)	396 (2%) 349 (100%)
(4d)	112—113	56	1 710, 1 730	1 640	2.22 (s, 3 H, SCH_3), 2.43 (s, 3 H, SCH_3), 3.65 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 7.48 (s, 1 H, olefinic), 7.30—7.40 (m, A_2B_2, aromatic)	444, 446 (1%) 397, 399 (100%)
(4e)	135—136	52	1 712, 1 685	1 645	2.22 (s, 3 H, SCH_3), 2.30 (s, 3 H, SCH_3), 2.48 (s, 3 H, CH_3), 3.67 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 7.67 (s, 1 H, olefinic)	304 (2%) 257 (100%)



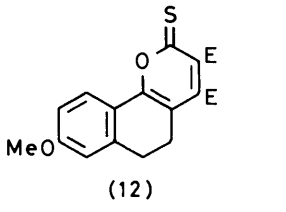
Scheme 2.

due to the ester carbonyl groups. The other strong band at 1 625 cm^{-1} was assigned to the thiapyran-2-one carbonyl group, which is in agreement with the reported values (1 620—1 634 cm^{-1}).[11,12] The ^{1}H n.m.r. spectrum ($CDCl_3$) exhibited an A_2B_2 quartet at δ 3.08 (4 H) due to four methylene protons. The three closely spaced singlets which appeared at δ 3.80, 3.85, and 3.86 were assigned to the methoxy and two methoxycarbonyl protons. The aromatic protons exhibited signals at δ 6.79 (d, *J* 2.5 Hz, 4-H), 6.86 (dd, *J* 7 and 2.5 Hz, 2-H), and 8.02 (d, *J* 7 Hz, 1-H). The u.v. spectrum (MeOH) of (10) showed absorption bands at $\lambda_{max.}$ 233 (log ε 4.08), 310 (4.15), 336 (4.20), and 348sh nm (3.99), thus ruling out the alternative pyran-2-thione[13,14] structure (12), which shows characteristic absorption in the visible region (above 400 nm).[11] Final confirmation of the thiapyran-2-one structure (10) was derived from its ^{13}C n.m.r. spectrum (Figure). The characteristic signal at δ 184 was assigned to the thiopyran carbonyl carbon, while the thiocarbonyl carbon of pyran-2-thione is reported to appear at δ 196.[15]

The mechanistic pathway for the conversion of (9) into (10) thus appears to be an interesting series of rearrangements (Scheme 3). The formation of cyclobutene *via* [2 + 2]cycloaddition followed by ring opening and electrocyclic ring closure in succession to give compound (15) is logical. The intermediate (15) appears to undergo either an interesting 1,5-suprafacial shift of the methylthio group or a stepwise

Table 2. Analytical data for compounds (4b—e)

Compound	Mol. formula	Analysis Calc. % (Found %) C	H
(4b)	$C_{17}H_{18}O_5S_2$	55.73 (55.4)	4.91 (4.45)
(4c)	$C_{18}H_{20}O_6S_2$	54.82 (54.5)	5.07 (5.3)
(4d)	$C_{17}H_{17}BrO_5S_2$	45.84 (45.45)	3.82 (3.55)
(4e)	$C_{12}H_{16}O_5S_2$	47.36 (46.9)	5.26 (5.35)



(12)

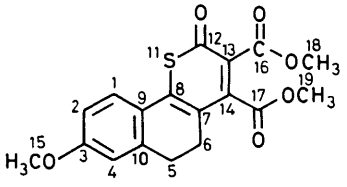
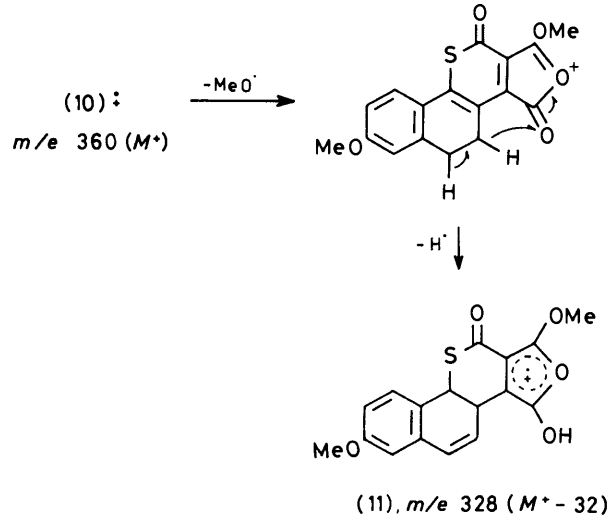


Figure. ^{13}C N.m.r. chemical shifts of compound (10) in $CDCl_3$ (measured at 40 MHz) recorded as δ (p.p.m.)

C-1	133.5d	C-7	129.3	C-14	146.2
C-2	112.5d	C-8	144.5	C-15	55.3q
C-3	161.0	C-9	136.0	C-16	163.4
C-4	114.9d	C-10	143.1	C-17	164.8
C-5	34.5t	C-12	184.0	C-18	52.6q
C-6	26.9t	C-13	138.9	C-19	52.6q



(11), *m/e* 328 (M^+ − 32)

Scheme 3.

elimination–addition process leading to the dihydropyran intermediate (16). In the subsequent steps, the intermediate (16), which is susceptible to electrocyclic ring opening, undergoes cleavage to give an activated *S*-methyl ester intermediate (17), which on intramolecular ring closure and elimination of dimethyl sulphide yields the thiopyranone (10).

The mass spectrum of (10) exhibited an interesting fragmentation pattern. The molecular ion peak at *m/z* 360 (72%) was followed by the most intense peak at *m/z* 328 (M^+ − 32, 100%, $C_{17}H_{12}OS$), which is possibly due to the ion (11) (Scheme 3). Although the loss of methanol in preference to the carbon monoxide in (10) appears to be unusual,[16] the presence of the adjacent methoxycarbonyl favours elimination of methanol to give the ion (11), as shown in Scheme 3.[17]

Experimental

I.r. spectra were determined on a Perkin-Elmer 297 spectrophotometer, while the u.v. spectrum was run on a Beckmann UV-26 spectrophotometer. ^1H N.m.r. spectra were determined on a Varian EM-390 90 MHz n.m.r. spectrometer using $SiMe_4$ as internal reference.

Reactions of Aryl (or Alkyl) 3,3-Bis(methylthio)vinyl Ketones (1a)—(1e) *with Dimethyl Acetylenedicarboxylate* (2).—(*a*) Reaction of 2,2-bismethylthiovinyl *p*-methyl phenyl ketone (1a) with DMAD (2) in xylene. A solution of the ketone (1a) (2.38 g, 0.01 mol) and DMAD (2) (3.7 g, 0.22 mol) in dry xylene was refluxed for 20 h. Xylene was evaporated off under reduced pressure and the residue was chromatographed on a silica-gel column. Elution with benzene–hexane (1 : 1) yielded *dimethyl* 1,1-*bismethylthio*-4-(p-*toluoyl*)-*buta*-1,3-*diene*-2,3-*dicarboxylate* (4a) (0.76 g, 20%) as pale yellow solid which was crystallised from ether–hexane, m.p. 110—112 °C, $\nu_{max.}$ (KBr) 1 728, 1 708, and 1 630 cm^{-1}; δ($CDCl_3$) 2.2 (s, 3 H, SCH_3), 2.35 (s, 3 H, SCH_3), 2.4 (s, 3 H, CH_3), 3.65 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 7.4 (s, 1 H, vinylic), and 7.05—7.60 (m A_2B_2, 4 H, arom) (Found: C, 56.4; H, 5.55. $C_{18}H_{20}O_5S_2$ requires C, 56.84; H, 5.26%).

(*b*) *General procedure.* A mixture of the keten dithioacetal (1) (0.01 mol) and DMAD (2) (0.02 mol) was heated at 170—180 °C for 6—7 h until the starting material had disappeared completely (t.l.c.). The reaction mixture was passed through a silica-gel column. Elution with benzene–hexane (1 : 1) yielded pure compounds (4a—e), which were further purified by crystallization from ether–hexane (Table 1).

Reaction of (9) *with DMAD* (2).—A solution of compound (9) (2.1 g, 0.008 mol) and DMAD (2) (1.42 g, 0.1 mol) in dry xylene (20 ml) was heated in a sealed tube at 160—170 °C for 33 h. Xylene was removed under reduced pressure and the residue was chromatographed on a silica-gel column. Elution with 6% ethyl acetate in hexane gave *compound* (10) as a bright yellow crystalline solid (0.43 g, 16%), m.p. 141—143 °C (spectral data in text) (Found: C, 60.25; H, 4.75; S, 8.55. $C_{18}H_{16}O_6S$ requires C, 60.0; H, 4.75; S, 8.88%); *m/z* 360 (M^+, 72), 329 (53), 328 (100), 313 (19.7), 300 (14), 272 (14), 269 (27.7), 243 (19), and 242 (44).

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