Cyclopropacycloheptathiophenones and Thiols: Unexpected Rearrangement with Dithiols leading to Benzo- and Cyclo-octa-thiophenes. Spectroscopic and Mechanistic Studies

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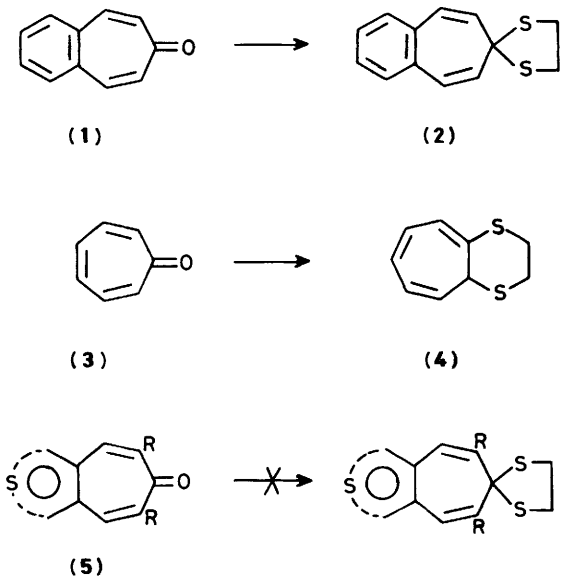
Cyclopropa[3,4]cyclohepta[1,2-*c*]thiophen-5-one reacts in an acidic medium with thiols to give addition or rearrangement compounds: [1,4] addition occurs with ethanethiol, but with 2-mercaptoethanol isomerization of the cyclopropyl ring to a vinyl group occurs, and the thioacetal was not obtained. The most surprising results are observed with ethane-1,2-dithiol and propane-1,3-dithiol, where a benzo[*b*]thiophene is isolated. An *X*-ray analysis of the latter compound and appropriate deuterium labelling experiments led us to propose a possible mechanism for this unexpected reaction pathway.

Thiols and dithiols have been widely used as carbonyl protecting groups for aldehydes and ketones. The reaction generally proceeds in an acidic medium [1] (Lewis acid),[2,3] giving stable intermediates suitable for organic synthesis.

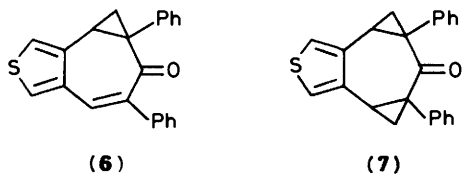
7*H*-Benzocyclohepten-7-one (**1**) and ethane-1,2-dithiol give the expected dithioacetal (**2**), but cyclohepta-2,4,6-trienone (**3**) leads to the bicyclic system (**4**).[4] Under similar experimental conditions, from cyclohepta[*b*]- and -[*c*]thiophenones (**5**), only intractable tars were obtained (see Scheme 1).



Scheme 1.

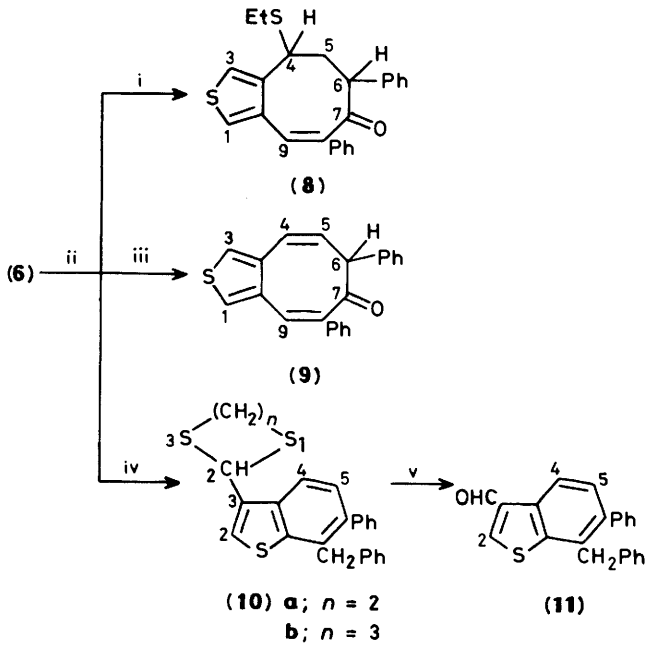
In a previous publication,[5] we reported the synthesis of the mono- and di-cyclopropane compounds (**6**) and (**7**): the increased values of ν_{CO} in both compounds (**6**) and (**7**) (1 655 and 1 683 cm^{-1} respectively) as opposed to the 'anomalous' value, 1 606 cm^{-1}, for (**5**) led us to investigate their behaviour with respect to thiols.

In this paper we describe the reactions of a cyclopropacyclohepta[*c*]thiophenone with certain thiols and give the spectroscopic data of the products. We suggest a plausible mechanism for the observed rearrangement.



Results and Discussion

We successively examined the behaviour of four thiols: ethanethiol, 2-mercaptoethanol, ethane-1,2-dithiol, and propane-1,3-dithiol. Scheme 2 summarizes the results of our



Scheme 2. *Reagents:* i, EtSH; ii, TsOH, toluene; iii, $HOCH_2CH_2SH$; iv, $HS(CH_2)_nSH$; v, SO_2Cl_2–CH_2Cl_2, SiO_2–H_2O

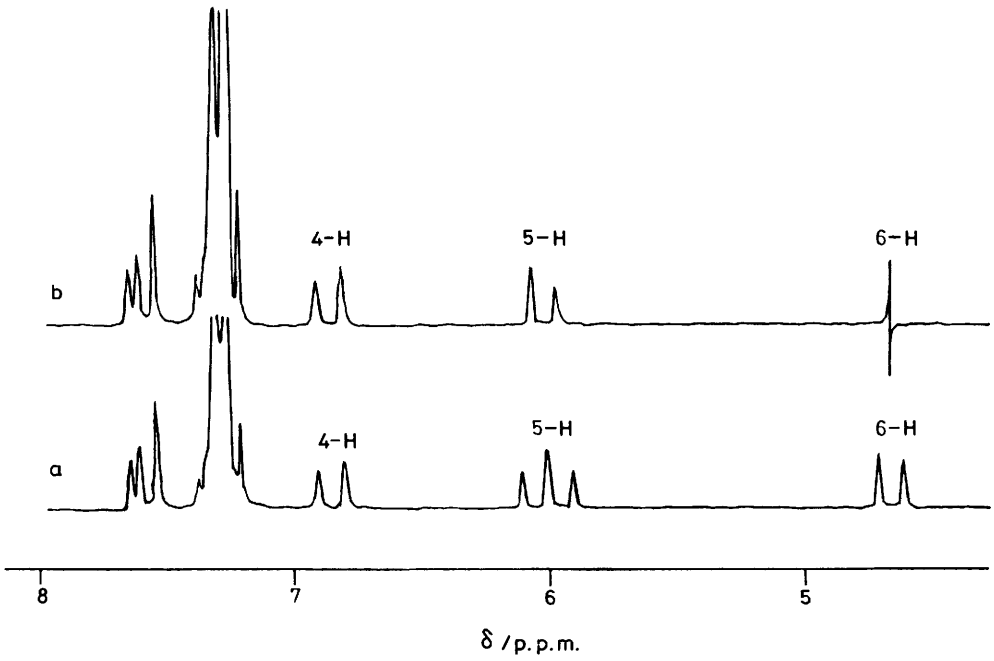
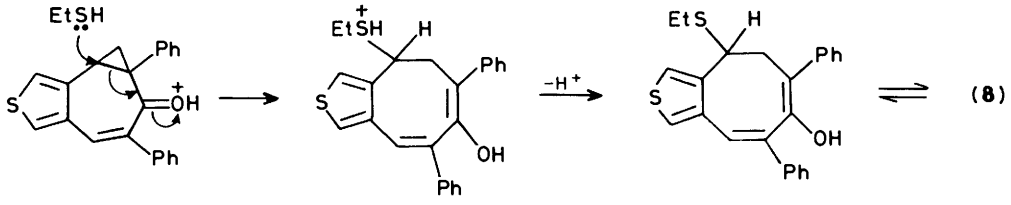
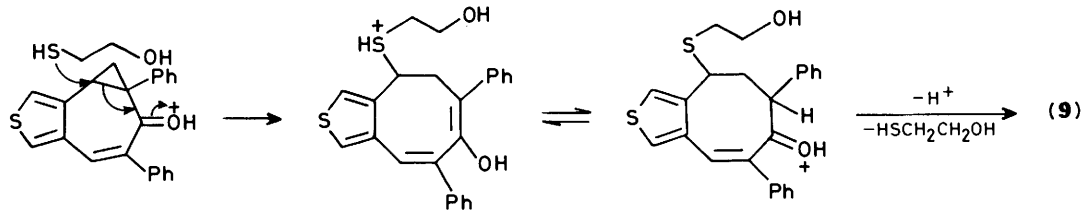


Figure 1. ^{1}H N.m.r. spectra (δ scale) of compound (**9**): *a*, normal spectrum; *b*, after irradiation of 6-H



Scheme 3.



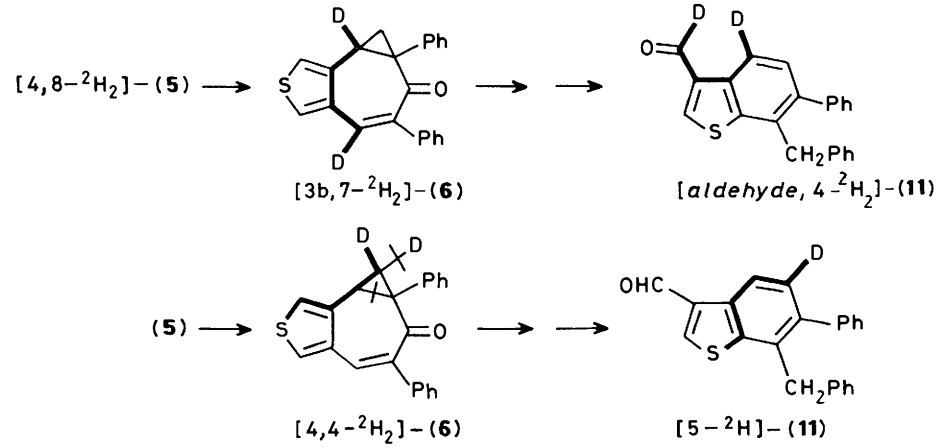
Scheme 4.

observations. Ethanethiol reacts with cyclopropacyclohepta[*c*]thiophenone (**6**) in the presence of toluene-*p*-sulphonic acid (TsOH) in refluxing toluene to give the cyclooctane (**8**). The elemental analysis and mass spectral data [*m/z* 390 (M^+), 329, $(M - SEt)^+$] confirm the molecular formula $C_{24}H_{22}OS_2$. The i.r. spectrum contains a strong carbonyl absorption (ν_{CO} 1 677 cm^{-1}), and the ^{1}H n.m.r. spectrum contains an SEt group signal, and a vinyl proton resonance but no cyclopropyl signal. The formation of compound (**8**) can be explained by means of a [1,4] addition of thiol to the protonated cyclopropacycloheptathiophenone. After proton abstraction, the Michael adduct tautomerizes into the ketone (**8**) (see Scheme 3).

Under the same experimental conditions, 2-mercaptoethanol gives different results: in the mass spectrum of compound (**9**), the molecular peak appears at the same *m/z* value (328, M^+) as in the starting cyclopropacycloheptathiophenone. The ^{1}H n.m.r. spectrum shows a vinyl group which displays a coupling constant with a CHPh moiety (see Figure 1). The carbonyl absorption (ν_{CO} 1 669 cm^{-1}) is consistent with formula (**9**). In an acidic medium (TsOH) the cyclopropyl ring isomerizes to its vinyl analogue through Michael and reverse-Michael reactions, as shown in Scheme 4.

The reactivity of dithiols is completely different:[6] ethane-1,2-dithiol and propane-1,3-dithiol add to compound (**6**) with the loss of the carbonyl absorption. The cyclopropyl signals disappear from the n.m.r. spectrum and 13 aromatic protons may be observed in the low-field region. Near 3 p.p.m., a four-proton multiplet for (**10a**) [6 H multiplet for (**10b**)] is characteristic of a dithiolane (dithiane) moiety. The mass spectral data gave the molecular formulae $C_{24}H_{20}S_3$ and $C_{25}H_{22}S_3$ for (**10a**) and (**10b**), respectively.

These spectral data give an equivocal structure for compound (**10**). The removal of the protecting group, in accordance with Hojo's procedure,[7] leads to an aldehyde



Scheme 5.

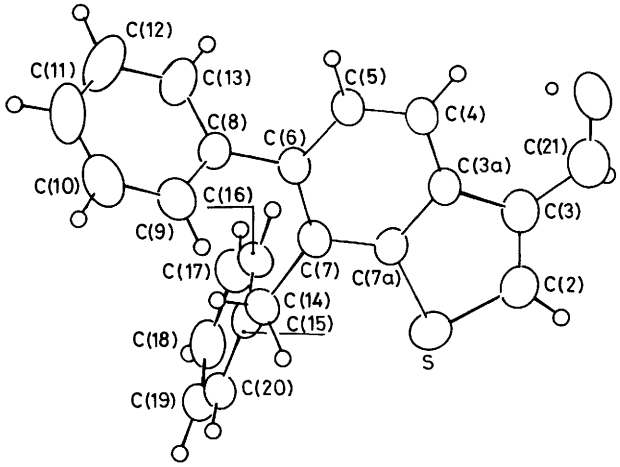


Figure 2. ORTEP View of compound (11) showing the crystallographic numbering scheme used

(11) whose structure has been solved by *X*-ray analysis. The structure consists of discrete molecules as shown in Figure 2, with the aldehyde function on the carbon atom C(3) of the thiophene ring. Each molecule consists of two *ortho*-condensed and coplanar rings (a thiophene ring and a six-membered ring). The oxygen atom is well separated from this plane (0.12 Å) which contains the C(8), C(14), and C(21) atoms. The angle between the two phenyl groups is 94° and the angles between the thiophene and each of these planes are respectively 126 and 98°. The presence of the aldehyde function does not modify the bond lengths of the thiophene ring. The C(2)–C(3) (1.354 Å) and C(3)–C(3a) (1.448 Å) distances are respectively a little longer and a little shorter than similar bonds (1.277 and 1.509 Å) in 'arenobishomotropones.'[8] The bond lengths of the three six-membered rings are very close to the mean values of 1.386, 1.388, and 1.398 Å. There are no intermolecular contacts that are less than the sum of the Van der Waals radii.

Mechanism.—It should be pointed out that ethanethiol and 2-mercaptoethanol give different results even under the same conditions. The reactivity of dithiols seems to be specific: only in such cases is the rearrangement observed. The same dithiols do not react in the presence of such Lewis acids as aluminium chloride and boron trifluoride–ether. The rearrangement proceeds in a protic medium. In other respects, substituents on the thiophene ring, in the α and α′ positions, inhibit the reaction pathway.

Using deuteriated analogues of compound (6), we examined the consequences of this substitution on the n.m.r. spectrum of the product: starting from [3b,7-$^2H_2$] (6) the aldehydic proton and the 4-H doublet (*J* 8.4 Hz) [*aldehyde*-4]- have disappeared in (11) leaving the 5-H signal as a single line (see Scheme 5 and Figure 3). Given the high deuterium level in [*aldehyde*-4-$^2H_2$]-(11) the impossibility of a carbon–deuterium scission must necessarily imply a carbon–carbon double bond cleavage. This hypothesis was verified starting from the *gem*-dideuteriated analogue [4,4-$^2H_2$]-(6) and isolating compound [5-^2H]-(11), the n.m.r. spectrum of the latter showing an aldehydic proton and a singlet for 4-H, with only a single deuterium atom remaining in the place of 5-H. Here too the deuterium level is very high (at least 90% with respect to the remaining proton), and we observed no deuterium incorporation in any other position. The loss of one of the two cyclopropyl deuterium atoms indicates the concomitant three-membered ring opening, occurring at the final step of cyclization.

These results have led us to propose a possible mechanism for the rearrangement of compound (6) (see Scheme 6). After protonation the cyclopropacyclohepta[*c*]thiophenone (6) undergoes a [1,4] addition with ethanedithiol, followed by prototropy. The Michael adduct (i) tautomerizes to a protonated ketone (ii) which undergoes a non-classical rearrangement, with nucleophilic sulphur attack at C-8 followed by C(7)–C(8) bond cleavage resulting from the electrophilic character of the oxonium. This step proceeds through a transfer of electrons between a soft nucleophile and a hard acid. Two subsequent tautomeric displacements generate the substituted carbocation (iii). This electrophilic species attacks the α carbon atom of the thiophene ring. Loss of the cyclopropyl hydrogen with simultaneous ring opening allows the formation of the bicyclic system (iv). A dehydration finally leads to the benzo[*b*]thiophene dithioacetal (10).

One of the referees has suggested that the conversion of compound (6) into (10) might proceed *via* the cyclo-octathiophenone (9) (formed by a Michael–reverse–Michael process analogous to that observed with 2-mercaptoethanol). However, treatment of compound (9) with ethane-1,2-dithiol gave only an 8% yield of the benzo[*b*]thiophene (10), compared with the 40% yield obtained starting from compound (6), so it would appear that this alternative route is not a significant one.

Although the [1,4] addition of thiols on α,β-unsaturated ketones is well known,[9] the electronic transfer (ii)→(iii) is not as well documented. To our knowledge, only one reaction

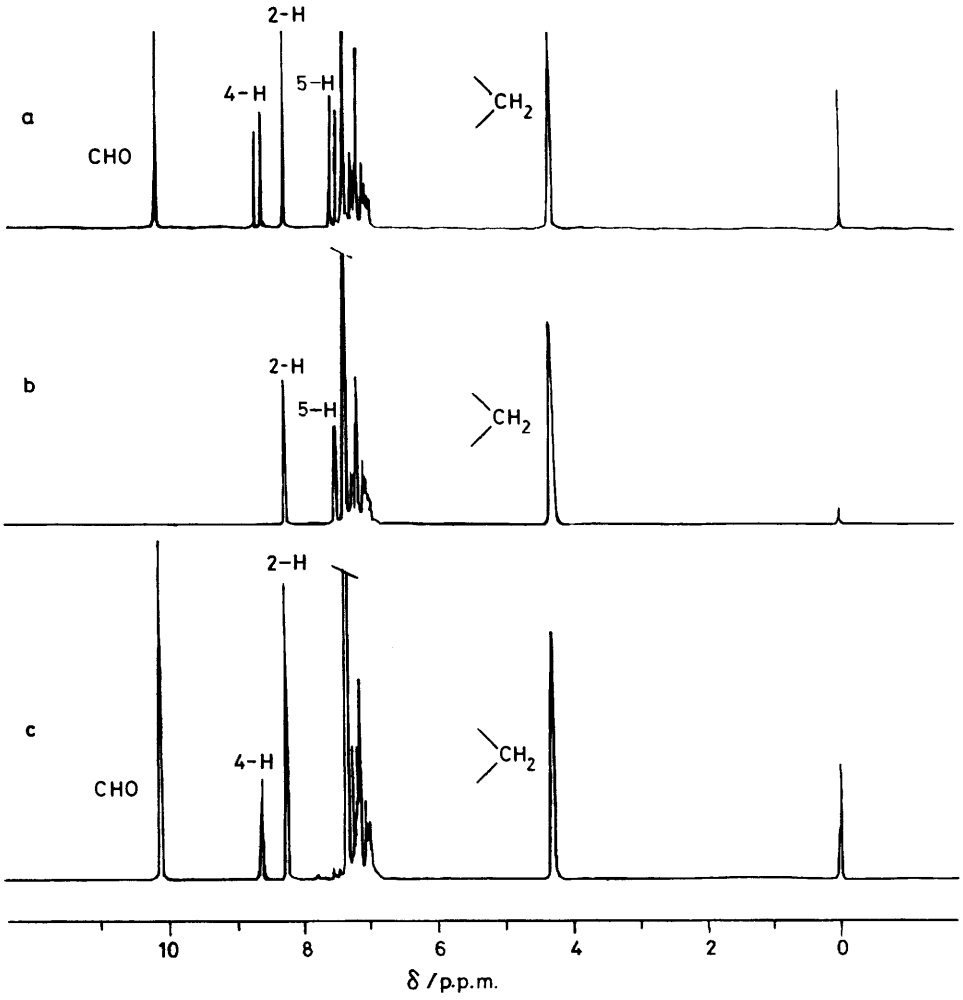
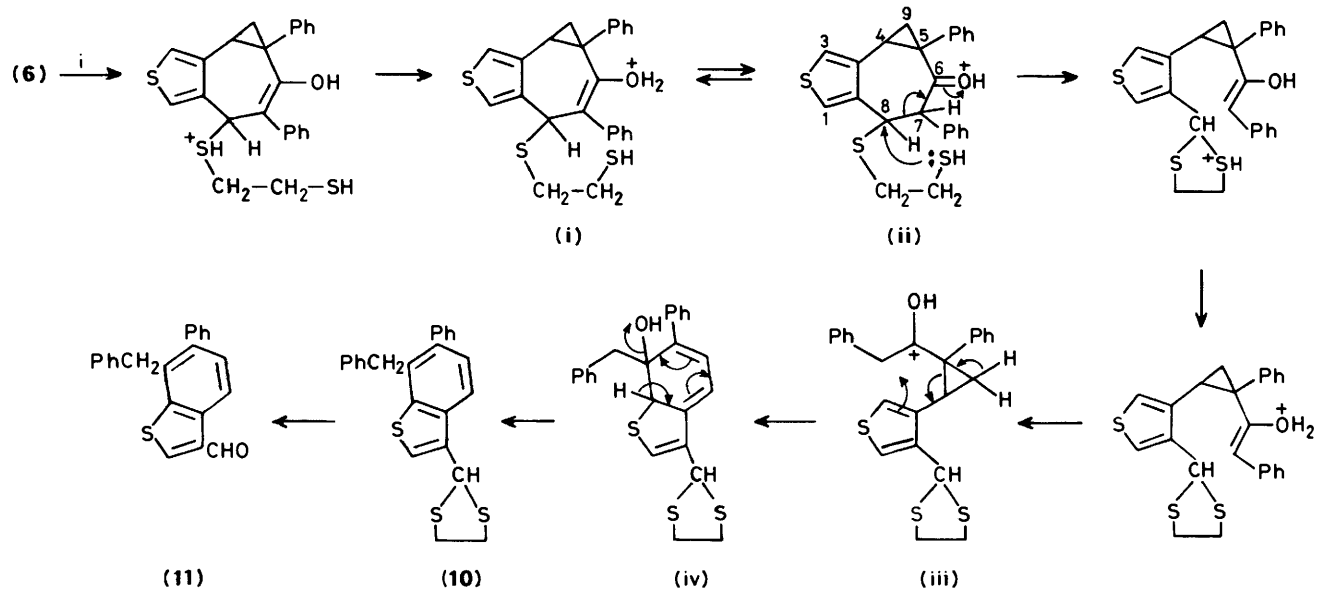


Figure 3. ^{1}H N.m.r. spectra (δ scale) of the three aldehydes: a, (**11**), b, [*aldehyde*-4-$^2H_2$]-(**11**), and c, [5-^{2}H]-(**11**)



Scheme 6. *Reagents:* i, $HSCH_2CH_2SH$, H^+

Table 1. Atomic co-ordinates ($\times 10^4$) with e.s.d.s in parentheses

	x	*y*	*z*
S	9 948(1)	1 179(1)	3 876(1)
C(2)	490(5)	−569(4)	3 540(3)
C(3)	9 264(4)	−1 518(3)	2 728(2)
C(3a)	7 784(4)	−820(3)	2 326(2)
C(7a)	7 983(4)	668(3)	2 886(2)
C(4)	6 291(4)	−1 400(3)	1 496(2)
C(5)	5 071(4)	−482(3)	1 265(2)
C(6)	5 279(4)	1 021(3)	1 827(2)
C(7)	6 758(4)	1 627(3)	2 663(2)
C(8)	3 870(4)	1 893(3)	1 481(2)
C(9)	1 880(4)	1 276(4)	1 360(2)
C(10)	535(5)	2 052(5)	1 016(3)
C(11)	1 169(6)	3 433(5)	788(3)
C(12)	3 138(6)	4 041(4)	891(2)
C(13)	4 494(5)	3 274(3)	1 230(2)
C(14)	7 079(4)	3 194(3)	3 345(2)
C(15)	6 589(4)	3 246(3)	4 428(2)
C(16)	5 306(4)	2 066(3)	4 661(2)
C(17)	4 787(5)	2 191(4)	5 646(2)
C(18)	5 543(5)	3 474(4)	6 407(2)
C(19)	6 837(5)	4 663(4)	6 184(2)
C(20)	7 337(4)	4 534(3)	5 203(2)
C(21)	9 482(6)	−3 069(4)	2 330(3)
O	8 364(4)	−4 001(3)	1 664(2)

Table 2. Molecular dimensions

(a) Bond lengths (Å)

S–C(2)	1.715(3)	S–C(7a)	1.744(3)
C(2)–C(3)	1.354(4)	C(3)–C(3a)	1.448(4)
C(3a)–C(7a)	1.399(4)	C(3a)–C(4)	1.395(4)
C(4)–C(5)	1.379(4)	C(5)–C(6)	1.411(4)
C(6)–C(7)	1.396(4)	C(7)–C(7a)	1.409(4)
C(7)–C(14)	1.508(4)	C(6)–C(8)	1.495(4)
C(14)–C(15)	1.517(4)	C(3)–C(21)	1.468(4)
C(21)–O	1.203(4)		
		C(8)–C(9)	1.393(4)
C(15)–C(16)	1.390(4)	C(9)–C(10)	1.396(4)
C(16)–C(17)	1.391(4)	C(10)–C(11)	1.378(5)
C(17)–C(18)	1.373(4)	C(11)–C(12)	1.379(5)
C(18)–C(19)	1.393(5)	C(12)–C(13)	1.393(4)
C(19)–C(20)	1.382(4)	C(13)–C(8)	1.392(4)
C(20)–C(15)	1.385(4)		

(b) Bond angles (°)

C(7a)–S–C(2)	91.3(1)	S–C(2)–C(3)	113.6(2)
C(2)–C(3)–C(3a)	112.4(3)	C(3)–C(3a)–C(7a)	113.3(2)
C(3a)–C(7a)–S	111.4(2)	C(3)–C(3a)–C(4)	130.0(3)
C(3a)–C(4)–C(5)	118.5(3)	C(4)–C(5)–C(6)	122.8(3)
C(5)–C(6)–C(7)	119.8(2)	C(6)–C(7)–C(7a)	116.4(2)
C(7)–C(7a)–C(3a)	123.9(2)	C(5)–C(6)–C(8)	117.1(2)
C(7)–C(6)–C(8)	123.1(2)	C(6)–C(7)–C(14)	124.7(2)
C(7a)–C(7)–C(14)	118.9(2)	C(7)–C(14)–C(15)	114.9(2)
C(2)–C(3)–C(21)	121.7(3)	C(3a)–C(3)–C(21)	125.9(3)
C(3)–C(21)–O	125.0(3)		

involving a carbon–carbon double bond cleavage has been reported,[10] and in a different system. These authors also describe the formation of the Michael adduct alone under the same conditions (similar substituents and strength of the Lewis acid): we observed similar behaviour with ethanethiol in place of ethanedithiol.

Conclusion

The behaviour of the cyclopropacyclohepta[*c*]thiophenone towards thiols would thus appear to be unique: the anticipated product with a protected carbonyl group was never obtained. The nature of the product depends on the nature of the thiol. In the case of dithiols the observed rearrangement is a novel process: the mechanism has been established using deuteriated analogues of the cyclopropacyclohepta[*c*]thiophenone.

Table 3. Least-squares planes (distances of atoms from the plane are given in Å)

Plane 1						
S	0.001	C(2)	0.011	C(3)	−0.002	C(3a)	−0.009
C(4)	0.000	C(5)	0.005	C(6)	0.006	C(7)	0.004
C(7a)	−0.009	C(8)*	0.032	C(14)*	−0.052	C(21)*	−0.018
O*	−0.117						
Plane 2						
S	−0.002	C(2)	0.003	C(3)	−0.002	C(3a)	−0.001
C(4)*	0.020	C(5)*	0.030	C(6)*	0.035	C(7)*	0.014
C(7a)	0.000	C(8)*	0.068	C(14)*	−0.036	C(21)*	−0.021
O*	−0.113						
Plane 3						
C(8)	0.010	C(9)	−0.005	C(10)	−0.003		
C(11)	0.006	C(12)	−0.001	C(13)	−0.007		
Plane 4						
C(15)	−0.002	C(16)	0.003	C(17)	−0.003		
C(18)	0.000	C(19)	0.002	C(20)	−0.001		

Angles between planes
1 and 3: 126° 1 and 4: 98° 3 and 4: 92°

* Atom not included in the least-squares calculation.

Experimental

^{1}H N.m.r. spectra were obtained on a Jeol FX-100 spectrometer in $CDCl_3$ solutions. Chemical shifts are reported in p.p.m. downfield from internal $SiMe_4$. Multiplicities are given as follows: singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). Mass spectra were recorded in the electron-impact mode with a Finnigan 3300 spectrometer: ionizing energy, 30—70 eV; ionizing current, 0.4 mA; operating temperature, 250—400 °C. I.r. spectra were measured as KBr discs on a Perkin-Elmer 580 B spectrometer. Analyses were performed by the 'Service Central d'Analyse du C.N.R.S.'.

Determination of Crystal and Molecular Structure.—Crystal Data. $C_{22}H_{16}OS$ (**11**), Space group $P\bar{1}$, a = 7.067(2), b = 9.266(2), c = 13.396(2) Å, α = 102.95(2), β = 99.56(2), γ = 101.06(2)°, U = 833.51 Å^3, Z = 2, D_c = 1.30 g cm^{-3}, μ(Cu-K_α) = 1.70 cm^{-1}, λ(Cu-K_α) 1.541 78 Å. 3 247 Reflections were measured of which 2 382 had $I > \sigma(I)$. $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ 0.045.

X-Ray data collection. The crystal of approximate dimensions (0.01 × 0.02 × 0.01 cm^3) was mounted on a Nonius CAD 4 diffractometer and data were collected for the scan range 1.00 + 0.14 tanθ. Scan θ/scan ω = 4/3. Independent reflections were measured within the θ limit 4—70°. Absorption and extinction corrections were not applied. The structure was solved using MULTAN 78.[11] The sulphur, carbon, and oxygen atoms were then refined anisotropically. The hydrogen atoms were placed by difference Fourier and refined isotropically. The structure was refined by full-matrix least-squares using SHELX 76[12] on an IRIS 80 computer at the University of Nancy Computer Centre. The final unweighted R value was 0.045. Atomic co-ordinates are listed in Table 1, details of interatomic distances and angles in Table 2, and least-squares planes in Table 3. The anisotropic thermal parameters and hydrogen

positions are given in a Supplementary Publication (SUP. No. 56168, 3 pp.).* Observed and calculated structure factors are available on request from the editorial offices.

4a,6-*Diphenyl*-4,4a-*dihydrocyclopropa*[3,4] *cyclohepta*-[1,2-c]*thiophen*-5(3bH)-*one* (**6**).—Compound (**6**) was prepared as previously reported.[5]

4a,6-*Diphenyl*-4,4a-*dihydrocyclopropa*[3,4]*cyclohepta*[1,2-c]-*thiophen*-5(3bH)-*one*[3b,7-$^2H_2$]-(**6**).—(*a*) *Preparation of* [4,8-$^2H_2$]-5,7-*diphenylcyclohepta*[c]*thiophen*-6-*one* [4,8-$^2H_2$]-(**5**). Similar experimental conditions were employed as in the preparation of compound (**5**).[13] To a methanolic solution (300 ml) of [*aldehyde*-$^2H_2$] thiophene-3,4-dicarbaldehyde[14] (4.12 g; 30×10^{-3}M) and dibenzyl ketone (6.48 g; 31×10^{-3}M) was added dropwise an aqueous solution of sodium hydroxide (3.60 g in 30 ml H_2O). The reaction mixture was allowed to stand overnight and then quenched in ice–water. After extraction (CH_2Cl_2) the organic layers were washed and evaporated giving a yellow solid. Crystallization from ethanol (300 ml) afforded [4,8-$^2H_2$]-(**5**) as bright yellow *crystals* (6.40 g, 68%), m.p. 167 °C (Found: C, 79.5; O, 5.1; S, 9.6. $C_{21}H_{12}D_2OS$ requires C, 79.71; O, 5.05; 10.13%).

(*b*) *Cyclopropanation of compound* [4,8-$^2H_2$]-(**5**). Compound [3b,7-$^2H_2$] (**6**) was prepared by the general method described in a previous paper,[5] from trimethylsulphoxonium iodide (2.20 g; 10×10^{-3}M), sodium hydride (0.50 g of 50% dispersion in mineral oil, 10×10^{-3}M), and [4,8-$^2H_2$]-(**5**) (3.16 g; 10×10^{-3}M) in DMF (50 ml). After crystallization (ether–hexane) [3b,7-$^2H_2$]-(**6**) was obtained as colourless *needles* (1.90 g, 58%), m.p. 158 °C (Found: C, 79.9; O, 4.9; S, 9.1. $C_{22}H_{14}D_2OS$ requires C, 79.96; O, 4.84; S, 9.70%).

[4,4-$^2H_2$]-4a,6-*Diphenyl*-4,4a-*dihydrocyclopropa*[3,4]*cyclohepta*[1,2-c]*thiophen*-5(3bH)-*one*[4,4-$^2H_2$]-(**6**).—Compound [4,4-$^2H_2$]-(**6**) was prepared as above. The ylide was generated from [$^2H_9$]trimethylsulphoxonium iodide[15] (1.25 g; 5.46×10^{-3}M), sodium hydride (0.30 g; 6.25×10^{-3}M) in [^2H]DMF (15 ml).† A solution of compound (**5**) (1.43 g; 4.55×10^{-3}M) in [^2H]DMF (10 ml) was then added at 0 °C. The *product* [4,4-$^2H_2$]-(**6**) was isolated as above (1.13 g, 63%), m.p. 158 °C (Found: C, 79.5; O, 5.2; S, 9.7. $C_{22}H_{14}D_2OS$ requires C, 79.96; O, 4.84; S, 9.70%).

4-*Ethylthio*-6,8-*diphenyl* -4,5-*dihydrocyclo-octa*[1,2-c]*thiophen*-7(6H)-*one* (**8**).—A mixture of compound (**6**) (0.98 g; 3×10^{-3}M), TsOH (0.57 g; 3×10^{-3}M), and ethanethiol (1.1 ml; 15×10^{-3}M) was refluxed for 5 h in anhydrous toluene (30 ml). After cooling the reaction mixture was slowly added to 2N-NaOH (100 ml) with stirring. The aqueous solution was extracted with diethyl ether and the organic layer washed to pH 7 and dried ($MgSO_4$). After removal of the solvents an oily residue was obtained and chromatographed on SiO_2 (CH_2Cl_2–C_6H_{14}, 1:1). Crystallization from the same mixture gave compound (**8**) (0.25 g, 22%), m.p. 134 °C (Found: C, 74.0; H, 5.9; O, 4.9; S, 15.3. $C_{24}H_{22}OS_2$ requires C, 73.80; H, 5.68; O, 4.10; S, 16.42%); $\nu_{max.}$ 1 677 (C=O), 1 597 (C=C), and 694 cm^{-1} (–Ph); δ 1.18 (3 H, t, *J* 7.20 Hz, CH_3), 2.04 (1 H, ddd, *J* 4.49, 11.87, and 13.36 Hz, 5-H), 2.54 (2 H, q, *J* 7.20 Hz, SCH_2), 2.96 (1 H, ddd, *J* 3.97, 11.87, and 12.94 Hz, 5-H), 4.10 (1 H, dd, *J* 3.97 and 13.36 Hz, CHPh), 4.39 (1 H, dd, *J* 4.49 and 12.94 Hz, CHS), and 7.00—7.70 (13 H, m, arom.); *m/z* 390 (M^+), 329 (M^+ – EtS), and 300 (base).

6,8-*Diphenylcyclo-octa*[1,2-c]*thiophen*-7(6H)-*one* (**9**).—Compound (**6**) (2.62 g; 8×10^{-3}M), TsOH (1.52 g; 8×10^{-3}M), and 2-mercaptoethanol (2.81 ml; 40×10^{-3}M) were refluxed overnight in anhydrous toluene (100 ml). After being cooled and filtered the neutral organic solution was chromatographed on SiO_2 (CH_2Cl_2–C_6H_{14}, 1:1). From the first eluted fractions (R_F *ca.* 0.75) 1,4-dithiane was isolated (0.40 g) (m.p. 111 °C). A second product (R_F *ca.* 0.25) was identified as compound (**9**) (0.78 g, 30%), m.p. 174 °C (Found: C, 78.8; H, 4.9; O, 4.8; S, 9.75. $C_{22}H_{16}OS$ requires C, 80.45; H, 4.91; O, 4.79; S, 9.76%); $\nu_{max.}$ 1 669 (C=O), 1 590 (C=C), 1 095, and 703 cm^{-1}; δ 4.68 (1 H, d, *J* 10.1 Hz, CHPh), 6.02 (1 H, dd, *J* 10.1 and 10.1 Hz, 5-H), 6.89 (1 H, d, *J* 10.1 Hz, 4-H), and 7.00—7.70 (13 H, m, arom.); *m/z* 328 (M^+, base).

7-*Benzyl*-6-*phenyl*-3-(1,3-*dithiolan*-2-*yl*)*benzo*[b]*thiophene* (**10**).—A mixture of compound (**6**) (3.93 g; 12×10^{-3}M), TsOH (2.28 g; 12×10^{-3}M), and ethane-1,2-dithiol (5.00 ml; 60×10^{-3}M) was heated under reflux in anhydrous toluene (100 ml) during 12 h. The resulting brown solution was cooled and treated with 2*N*-NaOH (50 ml). Extraction with diethyl ether and purification on an SiO_2 column (CH_2Cl_2–C_6H_{14}, 1:1) gave a residue which was crystallized from the same solvents to give *compound* (**10a**) (40%), m.p. 155 °C (Found: C, 71.4; H, 5.0; S, 24.0. $C_{24}H_{20}S_3$ requires C, 71.24; H, 4.98; S, 23.77%); $\nu_{max.}$ 1 592 (C=C), 1 490, 1 458, 1 442, 1 432, and 690 cm^{-1}; δ 3.40 (4 H, m, SCH_2CH_2S), 4.24 (2 H, s, CH_2), 5.98 (1 H, d, *J* 1.00 Hz, 2-H), 7.00—7.30 (5 H, m, Ph), 7.32 (5 H, br s, benzylic Ph), 7.39 (1 H, d, *J* 8.30 Hz, 5-H), 7.57 (1 H, d, *J* 1.00 Hz, het. 2-H), and 7.86 (1 H, d, *J* 8.30 Hz, 4-H); *m/z* 404 (M^+), 376 ($M^+ - C_2H_4$), 285 ($M^+ - C_2H_4 - C_7H_7$), and 253 (285 – S, base).

7-*Benzyl*-6-*phenyl*-3-(1,3-*dithian*-2-*yl*)*benzo*[b]*thiophene* (**10b**).—Following the same procedure as above, compound (**6**) (0.75 g; 2.28×10^{-3}M), TsOH (0.44 g; 2.28×10^{-3}), and propane-1,3-dithiol (1.20 ml; 12×10^{-3}M) in refluxing toluene (20 ml) gave *compound* (**10b**) (0.05 g, 5%), m.p. 170 °C (Found: C, 70.35; H, 5.3; S, 22.9. $C_{25}H_{22}S_3$ requires C, 71.72; H, 5.29; S, 22.98%); $\nu_{max.}$ 1 600 (C=C), 1 495, 1 462, 1 455, and 700 cm^{-1}; δ *ca.* 3.00 [6 H, m, $S(CH_2)_3S$], 4.25 (2 H, s, CH_2), 5.61 (1 H, d, *J* 1.00 Hz, 2-H), 7.00—7.30 (10 H, m, arom.), 7.39 (1 H, d, *J* 8.30 Hz, 5-H), 7.54 (1 H, d, *J* 1.00 Hz, het. 2-H), and 8.00 (1 H, d, *J* 8.30 Hz, 4-H); *m/z* 418 (M^+), 334 [$M^+ - S(CH_2)_3$], and 253 (344 – C_7H_7, base).

7-*Benzyl*-3-*formyl*-6-*phenylbenzo*[b]*thiophene* (**11**).—A suspension of compound (**10b**) (2.00 g; 5×10^{-3}M), SiO_2 (2.00 g) in H_2O (2 ml) and CH_2Cl_2 (60 ml) was treated, under vigorous stirring, with a solution of sulphuryl chloride (3 ml) in CH_2Cl_2 (40 ml). After 10 min the mixture was filtered, treated with anhydrous K_2CO_3, and evaporated. The oily residue was chromatographed on SiO_2 (CH_2Cl_2–C_6H_{14}, 2:1) giving *compound* (**11**) as a colourless solid (1.02 g, 62%), m.p. 136 °C (Found: C, 80.4; H, 5.0; O, 4.8; S, 9.4. $C_{22}H_{16}OS$ requires C, 80.45; H, 4.91; O, 4.87; S, 9.76%); $\nu_{max.}$ 1 675 (C=O), 1 600, 1 589 (C=C), 1 497, 1 463, 1 455, 1 441, and 1 376 cm^{-1}; δ 4.30 (2 H, s, CH_2), 7.00—7.30 (5 H, m, Ph), 7.34 (5 H, br s, benzylic Ph), 7.49 (1 H, d, *J* 8.40 Hz, 5-H), 8.23 (1 H, s, 2-H), 8.61 (1 H, d, *J* 8.40 Hz, 4-H), and 10.11 (1 H, s, CHO); *m/z* 328 (M^+, base).

[aldehyde-4-$^2H_2$]-7-*Benzyl*-3-*formyl*-6-*phenylbenzo*[b]*thiophene* [aldehyde-4-$^2H_2$]-(**11**).—Compound [3b,7-$^2H_2$]-(**6**) (0.66 g; 2×10^{-3}M), TsOH (0.38 g; 2×10^{-3}M), and ethane-1,2-dithiol (0.85 ml; 10×10^{-3}M) in anhydrous toluene (40 ml) were treated in the same way as (**6**). The crude dithiolane (0.32 g) was stirred with SiO_2 (0.30 g) and H_2O (0.3 ml) in CH_2Cl_2 (10 ml). Sulphuryl chloride (0.3 ml) in CH_2Cl_2 (20 ml) was then added. Pure *compound* [*aldehyde*-4-$^2H_2$]-(**11**) was obtained (0.9 g, 15%), m.p. 133 °C; δ 4.30 (2 H, s, CH_2), 7.00—7.30 (5 H, m, Ph), 7.34 (5

* For details of the Supplementary Publications Scheme see Instructions for Authors (1985) in *J. Chem. Soc., Perkin Trans. 1*, 1985, Issue 1.

† To prevent D/H exchange during the reaction.

H, br s, benzylic Ph), 7.49 (1 H, s, 5-H), and 8.24 (1 H, s, 2-H); *m/z* 330 (M^+, base).

[5-^{2}H]-7-*Benzyl*-3-*formyl*-6-*phenylbenzo*[b]*thiophene* [5-^{2}H]-(**11**).—From [4,4-^{2}H]-(**6**), the same quantities of reactants as above led to [5-^{2}H]-(**11**) (0.88 g, 14%), m.p. 133 °C; δ 4.30 (2 H, s, CH_2), 7.00—7.30 (5 H, m, Ph), 7.34 (5 H, br s, benzylic Ph), 8.24 (1 H, s, 2-H), 8.61 (1 H, s, 4-H), and 10.11 (1 H, s, CHO); *m/z* 329 (M^+, base).

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