

Electrocyclic Rearrangement of a Strained Cyclic β -Carbonyl Sulfonium Ylide

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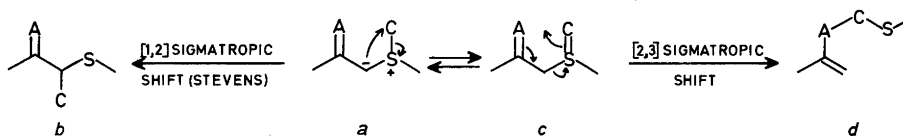
The β -carbonyl sulfonium ylide generated from *syn*-15-methyl-5,6,12,13-tetrahydro-5,13:6,12-bisepithiodibenzo[*a,f*]cyclodecene-7,14-dione fluoroborate suffers a [2,3]sigmatropic shift to the cyclic enol ether *syn*-5,12-dihydro-5,14-(epithiomethylenoxy)-6,12-epithiodibenzo[*a,f*]cyclodecen-7(6*H*)-one. X-Ray crystallographic data are briefly discussed.

The 1,2-shift of the Stevens rearrangement in sulfonium ylides is a useful method for carbon-carbon bond formation.¹ Thus in a double Stevens rearrangement syntheses of strained [2,2]cyclophanes can be realised from ylides of [3,3]cyclophane bis-sulfonium salts.² In allyl sulfonium ylides the reaction takes another course, however, in that a thermal orbital symmetry-allowed [2,3]sigmatropic rearrangement occurs with the generation of homoallylic sulfides, an important method for carbon-carbon bond formation.³ The terminal carbon atom of the allylic group can be replaced by a heteroatom, (Scheme 1); thus the carbonyl functionality may in some cases participate in the electrocyclic reaction yielding enol ethers.^{4,5}

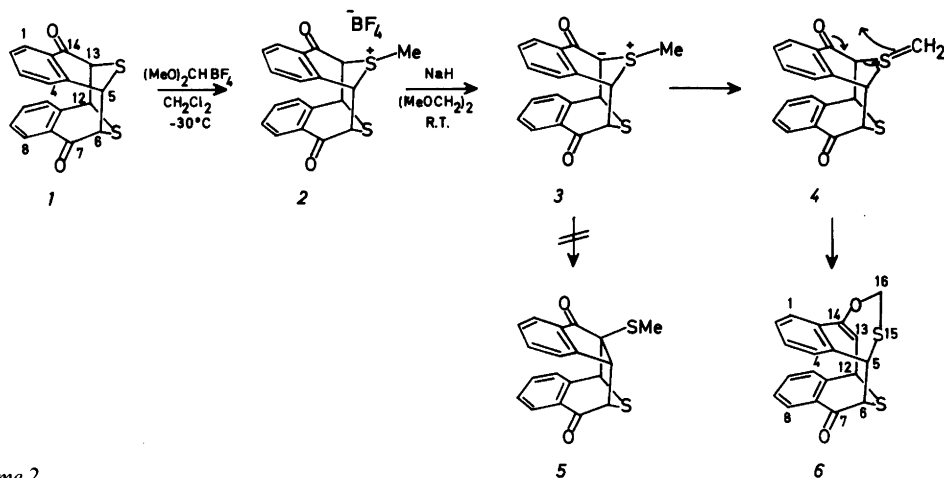
In the methylsulfonium ylide 3, which is prepared from *syn*-5,6,12,13-tetrahydro-5,13:6,12-bisepithiodibenzo[*a,f*]cyclodecene-7,14-dione⁶ 1, an electrocyclic rearrangement was to be expected rather than a 1,2-Stevens shift with ring contraction to

5.⁵ In the absence of a carbanionic bridgehead, cyclic β -carbonyl sulfonium ylides appear to be quite stable.^{7,8} In particular, the ylide of 2-methylisothiochroman-4-one, which corresponds to the ylide-half of 3, was isolated from the sulfonium salt after treatment with aqueous sodium hydroxide, or after treatment with sodium hydride in dry THF.⁷ On photolysis, however, ring contraction to the expected primary indanone derivative occurred.⁹

The reaction sequence in Scheme 2 was initiated by *S*-methylation of 1 which is the major stereoisomer formed by dimerisation of 2-benzothio-pyrylium-4-olate.⁶ Dimethoxycarbonium fluoroborate is an effective methylating agent;¹⁰ its use in methylene chloride led to precipitation of the monomethylated sulfonium salt 2, the proton signals for the methyl group being at δ 3.01. In a solvent mixture of methylene chloride and acetonitrile (1:2), where the monomethylated salt is soluble, a partially dimethylated product was obtained. The nature of the dimethylated product was not investigated. The molecular ion *m/e* 324 in the mass spectrum from 2 is consistent with demethylation before evaporation. The demethylation is attributed to nucleophilic attack by fluoride ions which presumably are generated together with boron trifluoride from the fluoroborate ions on heating.¹¹



Scheme 1.



Scheme 2.

When the sulfonium salt 2 was allowed to react with sodium hydride in dry 1,2-dimethoxyethane at room temperature, a major product was formed. The molecular ion in the mass spectrum m/e 338.0432, elemental composition $C_{19}H_{14}O_2S_2$, corresponds to a rearrangement product of the ylide 3. The 1H NMR spectra showed coupled signals at δ 3.95 and 5.07, J 15 Hz corresponding to a methylene group, which was supported by a triplet in the ^{13}C NMR spectra at 71.3 ppm. Four doublets at 30.9, 40.2, 50.9 and 52.2 ppm are ascribed to methine carbons. Of the signals at 190.8 and 207.0 ppm in the carbonyl region, the former corresponds to the signal from the CO carbon atom in 1. The IR

spectrum shows one sharp CO band at 1675 cm^{-1} as in 1. The spectroscopic data are consistent with a

Table 1. Fractional atomic coordinates with estimated standard deviations.

ATOM	X	Y	Z
S15	.49288(3)	.39055(7)	.62529(3)
S18	.61808(4)	.31928(8)	.84137(3)
O17	.67782(11)	.08179(20)	.57790(9)
O	.74953(13)	.73267(23)	.83143(14)
C16	.52190(19)	.23859(34)	.54305(15)
C14	.65150(18)	.13869(28)	.64738(14)
C14A	.71884(15)	.28376(32)	.62034(13)
C4A	.68428(18)	.46623(38)	.62722(13)
C8	.60436(18)	.51453(29)	.67122(14)
C13	.64916(18)	.07928(29)	.72665(14)
C12	.69082(15)	.16107(29)	.81276(14)
C11A	.79489(14)	.24760(29)	.81714(13)
C7A	.81019(16)	.43590(30)	.82066(14)
C7	.73215(17)	.57470(30)	.81122(14)
C6	.63073(16)	.51403(28)	.77515(14)
C4	.73161(18)	.60280(40)	.59221(16)
C3	.80483(21)	.55951(58)	.55143(19)
C2	.83198(20)	.38114(61)	.54629(18)
C1	.78463(18)	.24291(46)	.57925(17)
C8	.90247(20)	.50137(40)	.83015(20)
C9	.97738(20)	.38317(47)	.83486(22)
C10	.96181(19)	.19809(44)	.82995(19)
C11	.87108(18)	.13085(37)	.82137(16)
H161	.5857(15)	.3100(30)	.5835(14)
H162	.4617(15)	.1917(29)	.5112(14)
H8	.6866(14)	.6414(31)	.6589(13)
H13	.6914(15)	.0083(31)	.7304(13)
H12	.7872(14)	.0653(30)	.8569(14)
H6	.5889(18)	.6025(29)	.7907(13)
H4	.7108(18)	.7227(34)	.5975(14)
H3	.8365(15)	.6584(30)	.5278(14)
H2	.8028(16)	.3477(29)	.5193(14)
H1	.8003(15)	.1152(32)	.5715(14)
H8	.9101(18)	.6310(31)	.8332(14)
H9	.9382(18)	.4333(30)	.8406(13)
H10	.8127(16)	.1122(30)	.8312(13)
H11	.8602(15)	.0005(33)	.8199(14)

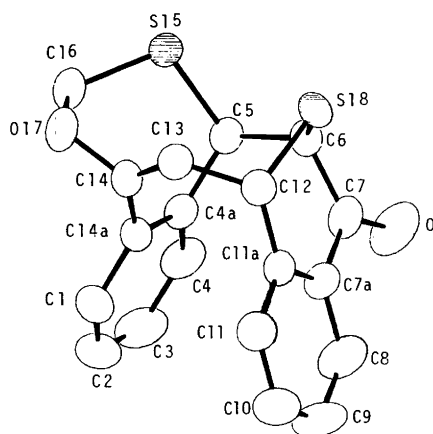


Fig. 1. Molecular geometry with numbering of the atoms.

[2,3]sigmatropic rearrangement to the cyclic, vinyl ether 6.

Related [2,3]sigmatropic rearrangements require heating and proton-donating solvents.⁵ The ready rearrangement of the ylide from 2 without heating in an aprotic solvent may be rationalised by unfavourable carbanion formation at a bridgehead position (3) which favours a further prototropic shift to the intermediate 4 required for the rearrangement.

The structure of the product has been determined unambiguously by an X-ray crystallographic analysis. Fig. 1 is a schematic drawing of the molecule with numbering of the atoms. Bond lengths and bond angles are given in Table 2. Three of the C—S bonds correspond to normal single bonds,¹² while C5—S15 is somewhat longer. The C5—C6 bond length of 1.574(3) Å is significantly longer than a

normal C—C single bond. The same effect has been observed on the corresponding bonds in the sandwich-like starting material 1,¹³ and corresponding dimerisation products from 5-methylthiopyrylium-3-olate where the bond lengths were 1.577(5), 1.569(5) and 1.573(3) Å, respectively.¹⁴ All other bond distances and angles have normal values within error limits.

EXPERIMENTAL

syn-15-Methyl-5,6,12,13-tetrahydro-5,13:6,12-bisepithiodibenzo[a,f]cyclodecene-7,14-dione fluoroborate. 2. A solution of *syn-5,6,12,13-tetrahydro-5,13:6,12-bisepithiodibenzo[a,f]cyclodecene-7,14-dione* (1.4 g, 4.3 mmol) in anhydrous dichloromethane (40 ml) was added dropwise to dimethoxy-

Table 2. Bond distances and bond angles.

DISTANCE		(Å)	DISTANCE		(Å)
S15 = C16	1.810(2)		S15 = C5	1.851(2)	
S18 = C12	1.824(2)		S18 = C6	1.808(2)	
O17 = C16	1.437(3)		O17 = C14	1.402(3)	
O = C7	1.208(3)		C14 = C14A	1.480(3)	
C14 = C13	1.312(3)		C14A = C4A	1.398(3)	
C14A = C1	1.389(3)		C4A = C5	1.506(3)	
C4A = C4	1.305(3)		C5 = C6	1.574(3)	
C13 = C12	1.496(3)		C12 = C11A	1.509(3)	
C11A = C7A	1.393(3)		C11A = C11	1.386(3)	
C7A = C7	1.499(3)		C7A = C8	1.393(3)	
C7 = C6	1.515(3)		C4 = C3	1.384(4)	
C3 = C2	1.368(5)		C2 = C1	1.379(4)	
C8 = C9	1.374(4)		C9 = C10	1.370(4)	
C10 = C11	1.378(4)				

ANGLE		(°)	ANGLE		(°)
S15 = C16 = O16	115.0(2)		C16 = S15 = C5	104.7(1)	
S15 = C5 = C4A	113.6(2)		S15 = C5 = C6	112.9(1)	
S18 = C6 = C5	123.5(1)		S18 = C12 = C13	104.6(1)	
S18 = C12 = C11A	113.0(1)		C12 = S18 = C6	99.7(1)	
S18 = C6 = C7	105.6(1)		C16 = O17 = C14	108.8(2)	
O17 = C14 = C14A	112.5(2)		O17 = C14 = C13	116.9(2)	
O = C7 = C7A	120.8(2)		O = C7 = C6	120.3(2)	
C14 = C14A = C4A	118.4(2)		C14A = C14 = C13	129.6(2)	
C14 = C14A = C1	121.8(2)		C14 = C13 = C12	126.9(2)	
C14A = C4A = C5	120.6(2)		C14A = C4A = C4	119.4(2)	
C4A = C14A = C1	119.4(2)		C14A = C1 = C2	120.4(3)	
C4A = C8 = C6	115.3(2)		C5 = C4A = C4	120.1(2)	
C4A = C4 = C3	120.4(3)		C5 = C6 = C7	112.0(2)	
C13 = C12 = C11A	117.6(2)		C12 = C11A = C7A	123.7(2)	
C12 = C11A = C11	117.2(2)		C11A = C7A = C7	123.5(2)	
C11A = C7A = C8	119.1(2)		C7A = C11A = C11	119.0(2)	
C11A = C11 = C10	121.1(3)		C7A = C7 = C6	118.9(2)	
C7 = C7A = C8	117.3(2)		C7A = C8 = C9	120.9(3)	
C4 = C3 = C2	120.1(3)		C3 = C2 = C1	120.3(3)	
C8 = C9 = C10	120.0(3)		C9 = C10 = C11	119.9(3)	

carbonium fluoroborate (2.2 ml) at -30°C . The mixture was allowed to reach room temperature and left overnight. A solid precipitate was formed which was collected, washed well with ethyl acetate and ether, and recrystallised from water; yield 78%, m.p. 280°C (decomp). Anal. $\text{C}_{19}\text{H}_{15}\text{O}_2\text{S}_2\text{BF}_4$: C, H. ^1H NMR (TFA): δ 3.01 (S-Me); the other signals were not resolved. IR (KBr): 1695 cm^{-1} (CO). MS [70 eV; m/e (% rel. int.)]: 324 (18, M for demethylated 2), 291 (42), 260 (23), 231 (25), 162 (59), 134 (100).

syn-5,12-Dihydro-5,14(epithiomethylenoxy)-6,12-epithiodibenzo[a,f]cyclodecen-7(6H)-one 6. The methylsulfonium fluoroborate 2 (0.75 g, 1.8 mmol) and powdered sodium hydride (0.30 g, 12.5 mmol) were added to anhydrous 1,2-dimethoxyethane (50 ml) and the mixture stirred at room temperature for 1 d. The mixture was then poured into ice-water, the organic layer separated and the solvent distilled off at reduced pressure. The residue was redissolved in chloroform, the solution washed with water, dried and the chloroform distilled off. The residue was chromatographed on a silica gel column and the title compound eluted with dichloromethane; yield 53%, m.p. $205-206^{\circ}\text{C}$ (EtOAc). The compound was sensitive to decomposition in contact with the atmosphere; hence it was analysed by high resolution MS. Found for M m/e 338.0432. Calc. for $\text{C}_{19}\text{H}_{14}\text{O}_2\text{S}_2$: m/e 338.0436. ^1H NMR (CDCl_3): δ 3.93 and 5.07 (CH_2 , J 9 Hz), 4.59 (H-6, $J_{5,6}$ 9 Hz), 4.65 (H-5), 4.83 (H-12, $J_{12,13}$ 9 Hz), 6.20 (H-13), 6.5–7.5 (8H, Ph.). ^{13}C NMR [25.14 MHz , CDCl_3]: δ 207.0 (C14), 190.8 (C7), 150.2, 140.2, 137.7 and 132.9 (C4a, C7a, C11a, C14a), 122.2–132.0 (8C-Ph.), 71.3 (C-16, t), 52.2, 50.9, 40.2, 30.9 (C5, C6, C12, d). IR (KBr): 1675 cm^{-1} (CO). MS [70 eV; m/e (% rel. int.)]: 338 (4, M), 292 (16), 291 (45), 263 (13), 261 (9), 260 (10), 259 (26), 204 (37), 202 (25), 176 (25), 163 (52.3), 162 (100).

Crystallographic section. The crystals are monoclinic with cell dimensions $a=14.443(3)\text{ \AA}$, $b=7.307(1)\text{ \AA}$, $c=15.520(2)\text{ \AA}$, $\beta=102.65(1)^{\circ}$, space group $P2_1/c$, and four molecules in the unit cell. 2341 observed reflections were measured (at room temperature) on a four-circle automatic diffractometer. The crystal size was about $(0.2 \times 0.3 \times 0.2)\text{ mm}^3$ and no corrections for absorption or secondary extinction effects were made. The structure was solved by direct methods¹⁵ and refined by full-matrix least squares technique.¹⁶ (All programs used, except those for phase determination, are described in Ref. 16). Anisotropic temperature factors were introduced for S, O, and C atoms. Hydrogen atom positions were calculated. The form factors used were those of Hanson *et al.*,¹⁷ except for hydrogen.¹⁸ Weights in least squares were calculated from the standard deviations in intensities, $\sigma(I)$, taken as

$$\sigma(I) = [C_T + (0.02C_N)^2]^{\frac{1}{2}}$$

where C_T is the total number of counts and C_N the net count. The final R -value was 3.1% ($R_N=3.6\%$) for 2341 observed reflections.

Final fractional coordinates with estimated standard deviations are given in Table 1. (The thermal parameters and a list of observed and calculated structure factors are available from the authors.) Maximum r.m.s. amplitudes for the anisotropic vibrations range from 0.20 to 0.37 \AA . Bond distances and angles may be found in Table 2.

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