Dichotomous Thermolysis of 9,10-Dihydro-11-thia-9,10-ethanoanthracene 11,11-Dioxides: a Novel Synthesis of 5*H*-Dibenzo[*a*,*b*]cycloheptenes

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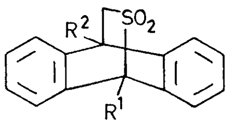
Summary 9,10-Dihydro-11-thia-9,10-ethanoanthracene 11,11-dioxides (**1**) on thermolysis eject sulphur dioxide and undergo rearrangements either to 9-methylanthracenes at low temperatures or at high temperatures to 5*H*-dibenzo[*a*,*d*]cycloheptenes (**2**), which have been shown to undergo slow ring inversion.

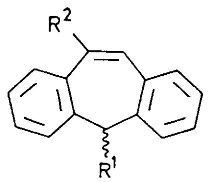
The thermolysis of cyclic sulphones is a well studied reaction which can lead to ring contraction,[1] ring expansion,[2] or fragmentation.[3] In continuing our studies of these processes we prepared the compounds (**1**).[4]†

Contrary to precedent[3] the thermal decomposition of the sulphones (**1**) proceeded by loss of sulphur dioxide and rearrangement. The course of the rearrangement is temperature dependent. Thermolysis of (**1a**) at 300 °C in a sealed tube evacuated to 0·5 mmHg gave only 9-methyl-



(1)

a, $R^1 = R^2 = H$
b, $R^1 = Me, R^2 = H$
c, $R^1 = R^2 = Me$



(2)

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† All new compounds have the correct analyses and the expected spectral data.

anthracene (quantitative), whereas flash vacuum thermolysis at 560 °C and 0·003 mmHg gave 5*H*-dibenzo[*a*,*d*]cycloheptene[5] (**2a**, 89%). Compound (**2a**) was not produced from 9-methylanthracene under our flash thermolysis conditions. Thermal decomposition of the sulphone (**1b**) also shows a temperature dependence, giving 9,10-dimethylanthracene and (**2b**) (97%) at 300 °C and 0·5 mmHg and 610 °C and 0·004 mmHg, respectively. At 300 °C the sulphone (**1c**) is relatively inert and does not form an anthracene, indicating that the lower temperature rearrangement is blocked by the extra methyl group, but rearranges with loss of sulphur dioxide into (**2c**) which is also the quantitative product of the flash thermolysis of (**1c**).

TABLE

Compound	Coalescence temperature[a] T_c/K ($\pm$5)	Inversion barrier ΔG^*/kJ mol^{-1} ($\pm$1)
(**2a**)	188[b]	38·5
(**2b**)	348[b]	72·5[d]
(**2c**)	401[c]	83·8[d]

[a] ^{1}H n.m.r. spectra determined (at 100 MHz) between τ 0·00 and τ 5·00 for *ca.* 0·5 M solutions in *o*-$C_6H_4Cl_2$. [b] τ (293 K) 6·01 (q, 0·58H, *J* 7·0 Hz), 6·73 (q, 0·42H, *J* 7·0 Hz), 8·36 (d, 1·26H, *J* 7·0 Hz), and 8·80 (d, 1·74H, *J* 7·0 Hz); τ (414 K) 6·22 (q, 1H, *J* 7·0 Hz), and 8·54 (d, 3H, *J* 7·0 Hz). [c] τ (294 K) 6·05 (q, 0·26H, *J* 7·0 Hz), 6·71 (q, 0·74H, *J* 7·0 Hz), 7·74 (m, 3H), 8·39 (d, 2·07H, *J* 7·0 Hz), and 8·77 (d, 0·93H, *J* 7·0 Hz); τ (452 K), 6·27 (q, 1H, *J* 7·0 Hz), 7·65 (d, 3H, *J* 7·0 Hz), and 8·44 (d, 3H, *J* 7·0 Hz). [d] As the conformers are not equally populated, there are two distinct G^* values, one for each conformer. The estimate is of the lower value (H. Shanan–Atidi and K. H. Bar-Eli, *J. Phys. Chem.*, 1970, **74**, 961).

Compounds (**2**) are known to be conformationally mobile,[6] existing as interconverting tubs. There is little information available about the influence of substituents on the ease of this interconversion. We now report that even a methyl group can produce a considerable stiffening of the seven-membered ring; (**2b**) and (**2c**) undergo ring inversion slowly on the n.m.r. time-scale at room temperature. In both cases the ^{1}H n.m.r. spectra were observed as the superimposed spectra of the two invertomers, which collapsed to time-averaged spectra at higher temperatures.

The high inversion barriers (Table) can be attributed primarily to non-bonded interactions between the 5-methyl group (R^1 in **2**) and the neighbouring *peri*-hydrogens of the benzo-rings.

The thermal fragmentation of the sulphones (**1**) is probably a diradical process; related homo-[5] and heterolytic[7] ring expansions have been reported, but the sequence of bond breaking and rearrangement and the cause of the temperature dependence of the reaction course is not clear.

We thank the S.R.C. for a Fellowship.

(*Received*, 8*th October* 1976; *Com.* 1144.)

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