Diaryl(acyloxy)sulfonylaminospiro-λ^4-sulfanes. Synthesis, Molecular Structure and Rearrangement

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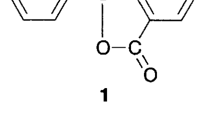
The preparation and the rearrangement of the first diaryl(acyloxy)sulfonylaminospiro-λ^4-sulfane **1** are reported with the molecular structures of **1** and those of the product **2** determined by X-ray diffraction; this work demonstrates that the formation of the rearrangement products (**2** or **4**) depends on the *N*-substituent of the starting spiro-λ^4-sulfane precursor, the sulfoxide **3** or cyclic imide **5**.

Sulfuranes (λ^4-sulfanes) are often considered as reactive intermediates in several reactions of organosulfur compounds with bivalent or tetravalent sulfur where the valency of sulfur either changes to four or remains unchanged.[1] Our studies have centred on the preparation and reaction of λ^4-sulfane type intermediates whose existence in the formation of, or in the acid-catalysed hydrolysis of, *N*-sulfonyl sulfilimines, has been established by kinetic measurements.[2,3] Sulfoxides **3** are suitable precursors, since their structure permits formation of both the spiro-λ^4-sulfane **1** and cyclic sulfilimine **4**, depending on the substituent R at N (R = Me, H or Bu^t). We observe that spiro-λ^4-sulfane **1** is transformed into cyclic imide **2** under conditions of spiro-λ^4-sulfane formation. In addition, we report on the rearrangement of the cyclic imide **5** into the cyclic sulfilimine **4** under the same conditions as for the preparation of **4** from sulfoxide **3** (R = H or Bu^t).

Spiro(3*H*-2,1-benzoxathiol-3-one)-1,1′-3*H*-2-methyl-1,3,2-benzodithiazole-3,3-dioxide **1** was prepared from sulfoxide **3** (R = Me)[4] by either path i or ii (Scheme 1). To obtain the spiro-λ^4-sulfane **1** in optimum yield the reaction mixture was diluted after 10–15 min with dry diethyl ether and cooled to 4 °C, and crystals of **1** were isolated by filtration (86%). With increasing time the amount of the dibenzodithiazocine **2** increases in the reaction mixture (as monitored by ^{1}H NMR or TLC). To obtain **2**, the reaction mixture (path i, Scheme 1) was refluxed for 3 h, then cooled and diluted with dry diethyl ether to yield the crystalline cyclic imide **2** in 89% yield. According to our preliminary experiments, this type of rearrangement can also be carried out in pyridine, AcOH and Ac_2O, or in Ac_2O–pyridine, Ac_2O–AcOH or pyridine–*p*-dimethylaminopyridine mixed solvent systems.

When the starting sulfoxide **3** possesses a hydrogen or *tert*-butyl group in the SO_2NHR moiety instead of Me, the reaction (path iii, Scheme 1, R = H, 100 °C, 5 min; R = Bu^t, 100 °C, 3 h) results in the formation of the benzodithiazole **4** (78%) [mp 327–332 °C (decomp.)]. Compound **5** can also be transformed into the cyclic sulfilimine **4** under the conditions used for the transformation **3** → **4**, or into the cyclic imide **2** by *N*-methylation with diazomethane (path iv, Scheme 1).†

In aqueous solvents spiro-λ^4-sulfane **1** is hydrolysed to the corresponding sulfoxide **3**. When **1** was hydrolysed with ^{18}O-enriched (69 atom%) water, the sulfinyl group of the product was found to contain the same amount of ^{18}O-label as the ^{18}O-enriched water (*cf.* refs. 4, 5). This observation indicates that the nucleophilic attack of water occurs exclusively at the S^{IV} atom of **1**. The cyclic imide **2** shows resistance to attack by water (no reaction at 100 °C for 1 h); however, hydrolysis can be achieved by treatment with sodium hydroxide or hydrochloric acid solutions (1 mol dm^{-3} NaOH, 100 °C, 15 min or 6 mol dm^{-3} HCl, 100 °C, 3 h);



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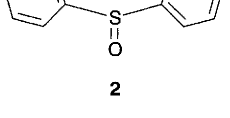

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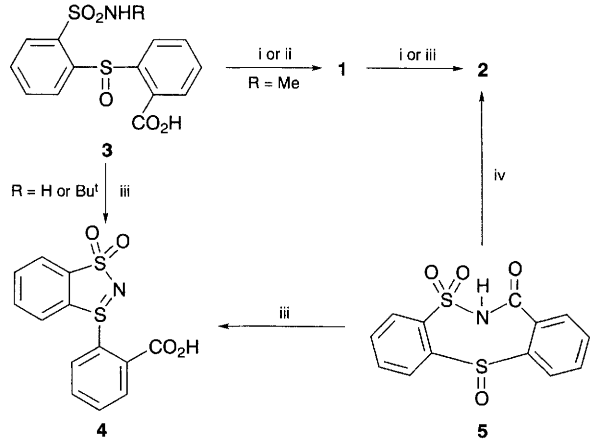
The molecular structures of **1** and **2**, as determined from single-crystal X-ray diffraction‡ are shown in Figs. 1 and 2 with selected interatomic distances and angles.



Scheme 1 *Reagents and conditions*: i, Ac_2O–pyridine, 20 °C; ii, $(CF_3CO)_2O$–DMF, 0–5 °C; iii, Ac_2O–pyridine, 100 °C or reflux; iv, CH_2N_2–diethyl ether

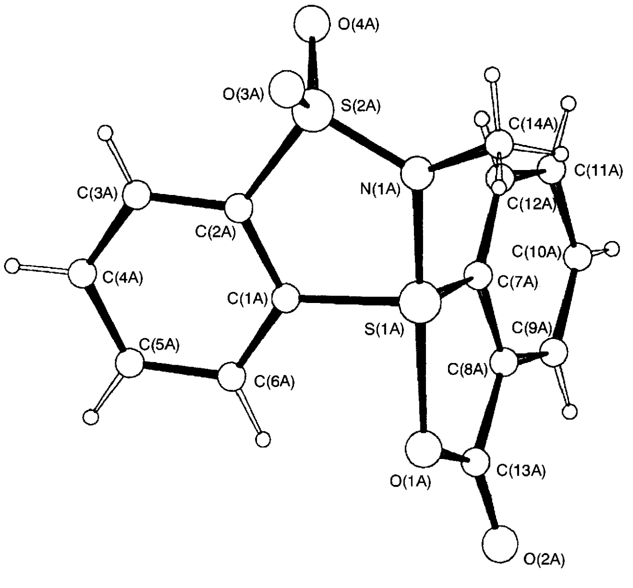


Fig. 1 Perspective view of molecule A of **1** with numbering scheme for non-hydrogen atoms. Selected interatomic distances (Å) and angles (°) for both symmetry independent molecules A and B: S(1)–N(1) 1.7885(2), 1.745(1), S(1)–C(1) 1.811(2), 1.806(2), S(1)–C(7) 1.808(2), 1.807(2), S(1)–O(1) 2.010(2), 2.047(1), C(13)–O(1) 1.305(2), 1.282(2), C(13)–O(2) 1.217(3), 1.223(2), S(2)–N(1) 1.615(2), 1.618(2), S(2)–O(3) 1.433(2), 1.429(1), S(2)–O(4) 1.429(2), 1.433(2), S(2)–C(2) 1.748(3), 1.741(2), O(1)–S(1)–N(1) 178.4(1), 178.1(1), C(1)–S(1)–C(7) 104.2(1), 106.0(1), S(1)–N(1)–S(2) 120.8(2), 121.8(2).

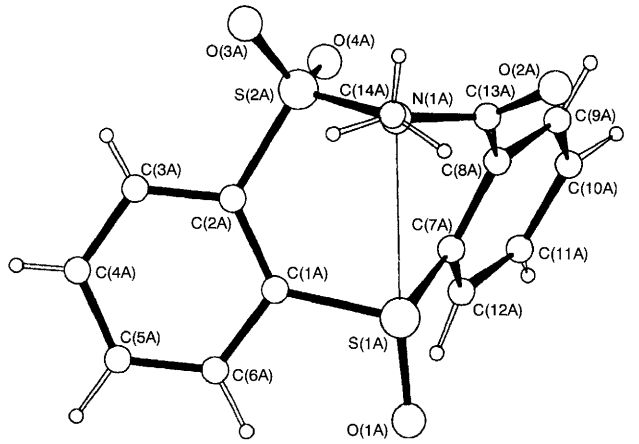


Fig. 2 Perspective view of molecule A of **2** with numbering scheme for non-hydrogen atoms. Selected interatomic distances (Å) and angles (°) for both symmetry independent molecules A and B: S(1)···N(1) 2.896(2), 2.929(1), S(1)–C(1) 1.809(3), 1.825(2), S(1)–C(7) 1.800(2), 1.803(2), S(1)–O(1) 1.485(2), 1.480(1), C(13)–N(1) 1.416(3), 1.413(2), C(13)–O(2) 1.207(2), 1.207(3), S(2)–N(1) 1.648(2), 1.651(2), S(2)–O(3) 1.422(2), 1.426(1), S(2)–O(4) 1.423(1), 1.426(2), S(2)–C(2) 1.769(3), 1.757(2), O(1)–S(1)···N(1) 176.1(1), 175.7(1), C(1)–S(1)–C(7) 102.0(2), 101.5(1), S(1)···N(1)–S(2) 95.3(1), 94.2(1).

The molecular structures of **1** and **2** show slightly distorted trigonal-bipyramidal geometry about the sulfur(IV) atom (with regard to the O=S···N array in **2**) similarly to the diarylacyloxycarbonylamino,[6] diarylbiscarbonylamino-,[7] and diaryldiacyloxyspiro-λ^4-sulfanes.[8] In **1** the S^{IV}–N distances (1.79, 1.75 Å in molecules A and B) are near to the sum of the covalent radii[9] (1.74 Å), showing, however, considerable elongation compared to the corresponding distances in the analogous diarylacyloxycarbonylaminospiro-λ^4-sulfanes[6] (1.71–1.74 Å), while the S^{IV}–O interatomic distances in **1** (2.01, 2.05 Å) are considerably shorter than for diarylacyloxycarbonylaminospiro-λ^4-sulfanes[6] (2.15–2.25 Å) and approach the hypervalent S^{IV}–O bond lengths (1.84–1.87 Å) found in diaryldiacyloxyspiro-λ^4-sulfanes.[8] In **2**, close contacts of 2.90 and 2.93 Å occur between S and N (sum of van der Waals radii[9] 3.35 Å) which controls the conformation of the eight-membered ring of **2** (*cf.* ref. 10).

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Footnotes

† All new products gave satisfactory microanalysis. The syntheses of **3** and **5** were based on classical methodologies (*cf.* ref. 4); the precursor sulfide for **5** was prepared from 2-(2-aminosulfonylphenylthio)benzoic acid[4] by cyclization with TsCl in pyridine. The structure of the cyclic sulfilimine **4** was verified by X-ray structure determination of its methyl ester obtained from **4** by methylation with diazomethane, and will be published elsewhere.

Selected spectroscopic data: IR[ν(C=O)/cm^{-1} KBr]: for **1** 1672vs; for **2** 1711vs, 1700vs; for **3**(R = Bu^t) 1685vs; for **4** 1685vs; for **5** 1702vs; ν(S=O)/cm^{-1} (KBr): for **2** 1075s; for **3**(R = Bu^t) 1006s; for **5** 1022s. ^{1}H NMR (60 MHz): for **1** {[$^2H_7$]DMF–$(CF_3CO)_2O$, 5 : 2 (*v*/*v*)}, δ 3.65 (s, Me); for **2** ([$^2H_7$]DMF), δ 3.44 (s, Me); for **3**(R = Me), ([$^2H_7$]DMF), δ 2.6 (d, *J* = 5 Hz, Me); for **3**(R = Bu^t) {[$^2H_5$]pyridine}, δ 1.35 (d, *J* = 3 Hz, Bu^t).

‡ X-Ray quality single crystals of **1** (mp 225–230 °C) were grown from Ac_2O–pyridine by addition of dry diethyl ether, and of **2** (mp 187–188 °C) by crystallisation from aqueous acetone.

Crystal data for **1**: $C_{14}H_{11}NO_4S_2$, $M = 321.37$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.045(3)$, $b = 11.127(3)$, $c = 14.929(2)$ Å, $\alpha = 107.71(2)$, $\beta = 92.61(2)$, $\gamma = 105.10(2)°$, $V = 1369.2(7)$ Å^3, $Z = 4$ (two molecules in the asymmetric unit), $D_c = 1.559$ g cm^{-3}, monochromated Cu-Kα radiation, $\lambda = 1.54184$ Å, $\mu = 36.2$ cm^{-1}. Data were collected on an Enraf-Nonius CAD-4 diffractomer in the range $1.5 < \theta < 75.0°$. The structure was determined by direct methods and refined by full-matrix least-squares analysis. All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were introduced in idealised positions and added to the structure-factor calculations. Their isotropic thermal parameters were fixed as $B_{iH} = (B_{iC} + 1)$ Å^2. The final residuals were $R = 0.049$, $R_w = 0.075$ for 4284 reflections with $I > 3\sigma(I)$ and for 5641 unique reflections $R_{tot} = 0.088$.

For **2**: $C_{14}H_{11}NO_4S_2$, $M = 321.37$, monoclinic, space group $P2_1/c$ (no. 14), $a = 14.588(1)$, $b = 6.817(1)$, $c = 27.829(5)$ Å, $\beta = 100.07(1)°$, $V = 2724.9(7)$ Å^3, $Z = 8$, (two molecules in the asymmetric unit), $D_c = 1.567$ g cm^{-3}, monochromated Cu-Kα radiation, $\lambda = 1.54184$ Å, $\mu = 36.3$ cm^{-1}. Data collection as for **1** giving residuals $R = 0.034$, $R_w = 0.050$ for 3568 reflections with $I > 3\sigma(I)$ and for 4023 unique reflections $R_{tot} = 0.062$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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