Aust. J. Chem., 1981, **34**, 755–7

2,1-Benzisothiazoles. XI*
The Rearrangement of 2,1-Benzisothiazol-3-yl Esters. Autocatalysis of a Sulfur Extrusion by Low-Molecular-Weight Sulfur

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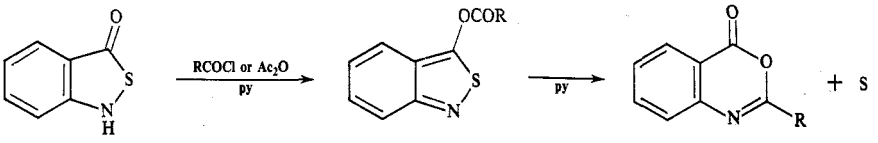
Abstract

The extrusion of sulfur from acyl derivatives of 2,1-benzisothiazol-3(1*H*)-one (1) is autocatalytic. The catalyst is low-molecular-weight sulfur. Addition of cyclohexasulfur (5) to solutions of these acyl derivatives increases the rate of such reactions.

In 1977 we described[1] a novel sulfur extrusion reaction. Addition of benzoyl chloride to 2,1-benzisothiazol-3(1*H*)-one (1) in pyridine affords (Scheme 1) an *O*-benzoyl derivative (2; R = Ph) which can be isolated as a stable solid. When a pyridine solution of this derivative (2; R = Ph) is left overnight at room temperature, sulfur is extruded and the benzoxazinone (3; R = Ph) is formed. We suggested that the *N*-acyl compound (4; R = Ph) was a probable intermediate. An analogous extrusion reaction is observed when (1) is treated with isocyanates.[2]



(1) (2) (3) **Scheme 1**

Most sulfur extrusion reactions require elevated temperatures, and probably for this reason few kinetic studies have been reported. The room-temperature rearrangement of (2) allowed us to make such a study, and we now report an unexpected result.

The rearrangement can be followed by the change in the u.v. absorption spectrum of a solution of the benzoyl derivative (2; R = Ph). Pyridine, on account of its intense u.v. absorption, was unsuitable as a solvent for such kinetic work. Methanol, although transparent to u.v. also proved unsuitable because it slowly reacts with the product (3; R = Ph) forming methyl *N*-benzoylanthranilate and thus complicating the kinetic analysis. In cyclohexane the reaction was very slow with a half-life of several weeks. We eventually found acetonitrile to be suitable, the half-life of the

* Part X, *J. Heterocycl. Chem.*, 1977, **14**, 267.

[1] Davis, M., and Pogany, S. P., *J. Heterocycl. Chem.*, 1977, **14**, 267.
[2] Perronnet, J., and Taliani, L., *J. Heterocycl. Chem.*, 1980, **17**, 673.

benzoyl derivative (2; R = Ph) being about 24 h at room temperature in this solvent The product (3; R = Ph) has an intense u.v. absorption at 298 nm (ε 19800) and the change in the absorbance of samples at this wavelength was measured over a period of time.

Plots of absorbance against time always had a sigmoid shape, characteristic of autocatalytic reactions, but addition of extra benzoxazinone (3; R = Ph) or of solutions of flowers of sulfur (i.e. cyclooctasulfur, S_8) had no effect on the rate. It thus seemed that the catalytic agent might be low-molecular-weight sulfur (S_n, $n < 8$) produced by the extrusion reaction. Of such sulfur modifications only S_6 (cyclohexasulfur) is known as a definite chemical entity; as recently as 1973 it was described in a review lecture[3] as a 'barely considered laboratory curiosity.' Cyclohexasulfur (5) can be prepared by the acid decomposition of thiosulfate ion; it is unstable and is more reactive than cyclooctasulfur.[4]

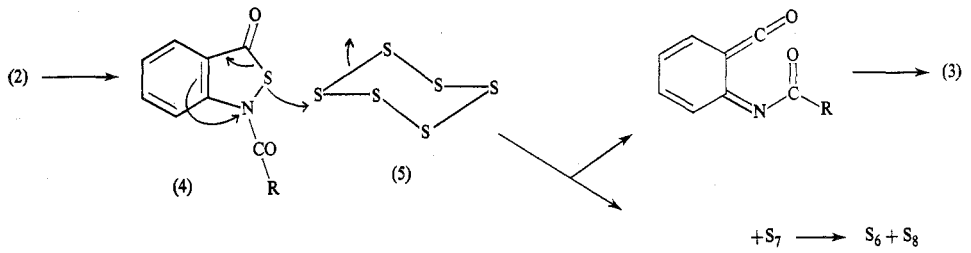
Table 1. Effect of added cyclohexasulfur (5) on the rate of rearrangement of the benzoyl derivative (2; R = Ph) in acetonitrile at 25°

$10^5 \times$ concn (M) of benzoyl derivative	4·1	7·5	7·5	7·5
$10^5 \times$ concn (M) of S_6	0	0·9	1·9	3·7
Time for 75% reaction (min)	3000	2·5	2·0	1·2

Table 2. Effect of added cyclohexasulfur (5) on the rate of rearrangement of product of acetylation of (1) in pyridine at 37°

The concentration of (1) and of Ac_2O was 0·25 M in each experiment

Concentration of S_6 (M)	0	0·01	0·05	0·09
Time for 50% reaction (min)	19·5	5	4	2



Scheme 2

We found that addition of cyclohexasulfur (5), even at relatively low concentration, to a solution of the benzoyl derivative (2; R = Ph) produced a dramatic, thousandfold or more, acceleration of the rate of the extrusion reaction (Table 1).

In our earlier report[1] we described how the acetylation of (1) in pyridine and the subsequent rearrangement of the initial product (2; R = Me) could be followed by repetitive-scan ^1H n.m.r. of the methyl group protons. Although this is a less accurate method, and the time scale of the uncatalysed reaction is much less, the rate curves are also sigmoid. The reaction is accelerated, though to a lesser degree, by addition of cyclohexasulfur (Table 2).

[3] Schmidt, M., *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 445.
[4] Bartlett, P. D., Cox, E. F., and Davis, R. E., *J. Am. Chem. Soc.*, 1961, **83**, 103.

The mechanism of the catalysis by cyclohexasulfur is unclear. Perhaps the cyclohexasulfur assists the extrusion of sulfur from the *N*-acyl compound (4) by an electrocyclic process as indicated; the transient S_7 would very likely disproportionate to S_6 and S_8. In effect some or all of the free energy difference between S_6 and S_8 would have been applied to the rearrangement of the intermediate *N*-acyl compound (4) (Scheme 2).

Experimental

^{1}H n.m.r. spectra were recorded on a Perkin–Elmer R32 instrument with $SiMe_4$ as internal standard. Ultraviolet absorption spectra were recorded on a Varian Techtron 635 instrument. Melting points are uncorrected and were obtained with a Büchi apparatus.

*2,1-Benzisothiazol-3(1*H*)-one (1)*

This was prepared from isatoic anhydride as described by Albert *et al.*[5]

2,1-Benzisothiazol-3-yl Benzoate (2; R = Ph)

This was prepared by the benzoylation of (1) as previously described;[1] we have however since found that it is slowly decomposed by methanol, even in the cold. Rapid recrystallization from chloroform/light petroleum (b.p. 40–60°) is preferable and affords a product of m.p. 108–109°. U.v. (MeCN): λ_{max} 261 (ε 5200), 271 (6900), 335 nm (7400).

Cyclohexasulfur (5)

This was prepared as described by Bartlett *et al.*[4] Cyclohexasulfur changes rapidly and unpredictably to cyclooctasulfur; the stated concentrations in Tables 1 and 2 are approximate only. Solutions in cyclohexane were kept at 4° and used as quickly as possible.

Measurement of Rate of Reaction by Ultraviolet Absorption

The benzoyl derivative (2; R = Ph) was dissolved in dry, redistilled acetonitrile to give a solution of known concentration ($7{\cdot}5 \times 10^{-5}$ M in most runs). An appropriate volume of cyclohexasulfur in acetonitrile solution was added and the absorbance of the mixture at 298 nm was followed for the next 10 min. In the absence of cyclohexasulfur the absorbance was followed for at least 2 days.

Reactions to which 2-phenyl-4*H*-3,1-benzoxazinone[6] or cyclooctasulfur had been added were also followed, but the presence of these substances, in concentrations similar to that of the benzoyl derivative, had no significant effect on the rate.

^{1}H n.m.r. was used to follow the rate of acetylation and rearrangement of 2,1-benzisothiazol-3(1*H*)-one in the absence and presence of cyclohexasulfur, by a method similar to that described previously.[1]

Manuscript received 27 November 1980

[5] Albert, A. H., Robins, R. K., and O'Brien, D. E., *J. Heterocycl. Chem.*, 1973, **10**, 413.
[6] Bain, D. I., and Smalley, R. K., *J. Chem. Soc. C*, 1968, 1593.