2,1-Benzisothiazoles. X. (1). Acylation of 2,1-Benzisothiazolin-3-one. A Remarkable Sulfur Extrusion With Ring Expansion.

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Acylation of 2,1-benzisothiazolin-3-ones (**1**) in pyridine gives *O*-acyl derivatives initially; these rapidly extrude sulfur and form substituted 3,1-benzoxazinones (**4**).

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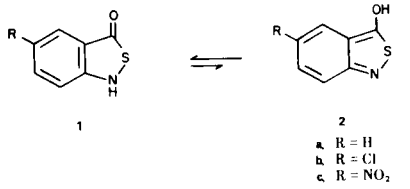
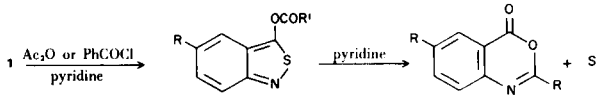
We have shown previously (2) that the keto form 2,1-benzisothiazolin-3-one (**1**) is the preferred tautomer in the equilibrium between **1** and its enol **2**, and that alkylation of the anion of **1** gives *N*-alkylated products.



1 **2**

a. R = H
b. R = Cl
c. R = NO_2

We now find that acylation of **1** in pyridine solution affords *O*-acylated derivatives (**3**) which then extrude sulfur and rearrange to benzoxazinones (**4**).

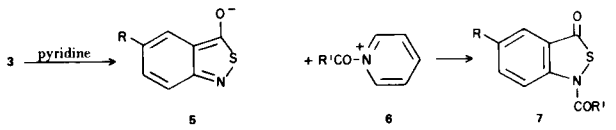


3 **4**

The rearrangement of the *O*-acetyl derivatives (**3**); R′ = CH_3) can be conveniently followed by nmr. On addition of acetic anhydride to a pyridine solution of **1**, the methyl group signal of the *O*-acetyl derivative immediately appears at 2.33 δ; within a few seconds a second peak at 2.21 δ appears and increases in intensity as the 2.33 δ peak decays. This 2.21 δ peak is due to a benzoxazinone (**4**). The half-lives of the *O*-acetyl derivatives **3a**, **3b** and **3c** in pyridine are about 20 minutes, 6 minutes, and 90 seconds, respectively, at the probe temperature of 37°.

The *O*-benzoyl derivatives (**3**, R′ = Ph) rearrange in a similar fashion, but more slowly, and it is possible to isolate the *O*-benzoyl derivative **1a** (R′ = Ph). This is stable in the absence of base, but on being dissolved in pyridine and set aside overnight it deposits a mixture of sulfur and the benzoxazinone (**4a**, R′ = Ph). Heating of the compound to 250-300° for a few minutes in the absence of pyridine brings about the same reaction.

We suggest that the room temperature rearrangement of **3** begins by a solvent-induced ionization followed by



5 **6** **7**

slow *N*-acylation of anion (**5**) to an *N*-acyl derivative **7** in which the S-N bond is so weakened that sulfur extrusion, and subsequent recyclisation to benzoxazinone (**4**), occurs readily.

Acylation of the 2,1-benzisothiazolin-3-ones (**1**) in the presence of excess aqueous base produces salts of *N*-acylanthranilic acids, as might be expected from the known hydrolysis of benzoxazinones (**4**).

EXPERIMENTAL

2,1-Benzisothiazolin-3-one (**1a**) and 5-Chloro-2,1-benzisothiazolin-3-one (**1b**).

These compounds were prepared as described previously (2).

5-Nitro-2,1-benzisothiazolin-3-one (**1c**).

This compound was prepared from 5-nitroisatoic anhydride by a similar procedure (3) and formed yellow leaflets (from acetic acid), m.p. 214-216°.

Anal. Calcd. for $C_7H_4N_2O_3S$: C, 42.85; H, 2.06; N, 14.28. Found: C, 42.88; H, 2.12; N, 14.40.

2,1-Benzisothiazol-3-yl Benzoate (**3a**, R′ = Ph).

This compound was prepared by adding benzoyl chloride (0.3 g., 2 mmoles) to a solution of 2,1-benzisothiazolin-3-one (**1a**) (0.3 g., 2 mmoles) in dry pyridine (3 ml.). After 10 minutes the mixture was diluted with water (20 ml.) and the crude *O*-benzoate

collected and recrystallised from methanol. It formed colorless needles (0.3 g., 59%) m.p. 104°; ir: ν(C=O) 1710 cm^{-1}; λ max 238 nm (ϵ max 26,400), 274 (15,600), 284 (17,200), 296 (15,200), 320 (11,200) and 336 (8,000). The bands at 284, 296 and 336 nm are characteristic of *o*-quinonoid 2,1-benzisothiazoles (2).

Anal. Calcd. for $C_{14}H_9NO_2S$: C, 65.86; H, 3.56; N, 5.49. Found: C, 65.91; H, 3.56; N, 5.44.

If the initial pyridine solution was allowed to stand overnight then sulfur was deposited together with 2-phenyl-3,1-benzoxazinone (**4a**; R′ = Ph), m.p. and mixed m.p. 123° (lit. (4) 123°). A similar reaction occurred when isolated *O*-benzoate (**3a**, R = Ph) was redissolved in pyridine. The other 2,1-benzisothiazolin-3-ones (**1b** and **1c**) gave the corresponding benzoxazinones **3b** and **3c** in similar fashion (**3b**, m.p. 196° [lit. (5) 196°]; **3c**, m.p. 169° [lit. (6) 168°]).

Nmr Studies.

A solution of the 2,1-benzisothiazolin-3-one (1 mmole) in dry pyridine (2 ml.) containing TMS (1%) was treated with acetic anhydride (102 mg., 1 mmole). A sample of the mixture was at once put into an nmr tube and the methyl group resonances at 2.1-2.4 δ scanned repeatedly. The nmr samples, when left overnight, deposited sulfur. In the case of the 5-nitro compound, crystalline 2-methyl-5-nitro-3,1-benzoxazinone (**4c**, R′ = CH_3), m.p. and mixed m.p. 160° (lit. (7) 161-162°) was obtained.

REFERENCES AND NOTES

(1) Part IX, M. Davis, E. Homfeld, J. McVicars and S. Pogany, *Aust. J. Chem.*, **28**, 2051 (1975).

(2) M. Davis, L. W. Deady, E. Homfeld and S. Pogany, *ibid.*, **28**, 129 (1975).

(3) A. H. Albert, R. K. Robins and D. E. O'Brien, *J. Heterocyclic Chem.*, **10**, 413 (1973).

(4) D. I. Bain and R. K. Smalley, *J. Chem. Soc. (C)*, 1593 (1968).

(5) L. Legrand, *Bull. Soc. Chim. France*, 337 (1960).

(6) L. A. Errede, U. S. Patent 3,357,977; *Chem. Abstr.*, **68**, 40326w (1968).

(7) M. T. Bogert and E. P. Cook, *J. Am. Chem. Soc.*, **28**, 1451 (1906).