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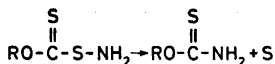
Sulfur Extrusion Reactions

I. On the Decomposition of *S*-(Alkoxythiocarbonyl)thiohydroxylamines

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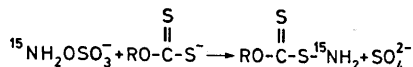
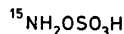
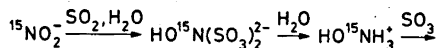
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S-(Alkoxythiocarbonyl)thiohydroxylamines have been prepared from *O*-alkyldithiocarbonates and hydroxylamine-*O*-sulfonate.¹ They are colourless liquids which are stable at low temperature (*e.g.* -30°C), whereas they decompose slowly at room temperature. Within 1–2 weeks the decomposition to *O*-alkyl thiocarbamates and elemental sulfur is complete:¹



As part of an investigation of the mechanism of sulfur elimination from this type of compound, exchange experiments have been carried out using ¹⁵N labelled *S*-(alkoxythiocarbonyl)-thiohydroxylamines, which were prepared from Na¹⁵NO₂ (97.4 % ¹⁵N) *via* the following reaction sequence.^{2,3}

¹⁵N labelled *S*-(isopropoxythiocarbonyl)-thiohydroxylamine was mixed with unlabelled *S*-(ethoxythiocarbonyl)thiohydroxylamine, and allowed to decompose at room temperature over a period of 4 weeks.



Since the mass spectra of *O*-ethyl thiocarbamate and *O*-isopropyl thiocarbamate do not exhibit peaks above *m/e* 100, except those of the molecular ions (which, in both cases, are the base peaks), the distribution of ¹⁵N in the reaction mixture is conveniently followed mass spectrometrically.

After completion of the decomposition, the mass spectral data showed that the ratio $M^+(Ia)/M^+(Ib)$ within the limits of measurements is equal to the ratio $M^+(IIa)/M^+(IIb)$, where M^+ is the relative intensity of the molecular ions, respectively, of *i*-C₃H₇OC(=S)¹⁵NH₂ (Ia), *i*-C₃H₇OC(=S)¹⁴NH₂ (Ib), C₂H₅OC(=S)-¹⁵NH₂ (IIa), and C₂H₅OC(=S)¹⁴NH₂ (IIb). Since the decomposition quantitatively leads to the formation of *O*-alkyl thiocarbamates, the ratios obtained show that ¹⁵N has been distributed equally between the two amides during the sulfur elimination reaction.

Mass spectra of the reaction mixture were also obtained during the decomposition to observe whether the formation of ¹⁵N labelled *O*-ethyl thiocarbamate could have been the result of an exchange within the undecomposed *S*-(alkoxythiocarbonyl)-thiohydroxylamines. However, because of the absence of the relevant ions ((CH₃)₂-CHOC(=S)S¹⁴NH₂ and C₂H₅OC(=S)S-¹⁵NH₂), such an exchange can be excluded with certainty.

Analogous results were obtained from an exchange experiment using ¹⁵N labelled *S*-(methoxythiocarbonyl)thiohydroxylamine and *S*-(ethoxythiocarbonyl)thiohydroxylamine.

Exchange of nitrogen does not take place after decomposition to *O*-alkyl thiocarbamates as shown by mixing ¹⁵N labelled *O*-ethyl thiocarbamate (30 % ¹⁵N) with *O*-isopropyl thiocarbamate. After 4 weeks at room temperature, no nitrogen exchange within the two amides was

observed. Similarly, $\text{CH}_3\text{CH}_2\text{OC}(=\text{S})\text{N}(\text{CH}_2\text{CH}_3)_2$ and $(\text{CH}_3)_2\text{CHOC}(=\text{S})\text{N}(\text{CH}_3)_2$ were heated together for 5 h at 160°C without the formation of any new products.

Finally, *S*-(methoxythiocarbonyl)thiohydroxylamine was decomposed in the presence of ^{15}N labelled *O*-ethylthiocarbamate (30% ^{15}N). Again, formation of ^{15}N labelled *S*-(methoxythiocarbonyl)thiohydroxylamine or ^{15}N labelled *O*-methylthiocarbamate was not observed.

From these experiments we conclude that, at room temperature, the decomposition of *S*-(alkoxythiocarbonyl)thiohydroxylamines is completely intermolecular.

The mass spectra were obtained on a double focusing mass spectrometer, type AEI-MS 902.

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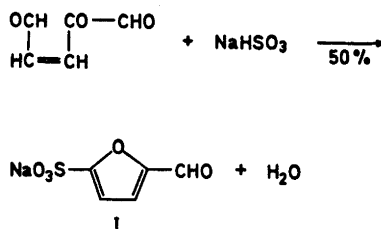
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Synthesis of 5-Formyl-2-furan-sulfonic Acid Sodium Salt from Endialone

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The title compound (I) has previously been prepared by Ivanov and Yankov¹ (cf. also Refs. 2, 3) by sulfonation of furfuraldiacetate with Baumgarten's reagent (sulfur trioxide-pyridine) (yield 37%). It has now been found that I is formed from endialone⁴ (*cis*-oxoglutaconaldehyde) and sodium hydrogen sulfite (cf. Ref. 5). This new synthesis is simpler and cheaper than the sulfonation reaction.



Experimental. Sodium hydrogen sulfite (10.4 g, 0.100 mol) was added to a molar solution of endialone of pH 2.0 and 0°C (100 ml, 0.100 mol), prepared as described previously.⁴ The mixture was stirred at room temperature for 30 min. The resulting clear, slightly yellow solution was heated to 60°C over a period of 30 min and then kept at this temperature for 60 min. About 5 min after the temperature of 60°C had been reached, crystals of a sesquihydrate of I began to separate. The suspension was cooled to 15°C and the crystals isolated by filtration. The wet cake was washed on the filter with ethanol-water (1:1) (20 ml), ethanol (20 ml), and ether (20 ml), and dried (20°C , 15 h). 11.2 g (50%) of I sesquihydrate was obtained, m.p. $> 250^\circ\text{C}$ (decomp.). (Found: C 26.6; H 3.0; S 14.0; ashes from CH-determination 31.9. Calc. for $\text{C}_5\text{H}_4\text{NaO}_5\text{S}$ (225.2): C 26.7; H 2.7; S 14.3; 0.5 Na_2SO_4 31.6). Very rapid Karl Fischer titrations of water gave 12.7% of water (calc. for 1.5 H_2O : 12.0%). Slower titrations showed up to 17.9% of water, indicating formation of water due to acetalization of the aldehyde group during titration.

Drying of the sesquihydrate at 110°C to constant weight gave anhydrous III as a slightly hygroscopic product. (Found: C 30.1; H 1.9; S 15.4; ashes 35.4. Calc. for $\text{C}_5\text{H}_3\text{NaO}_5\text{S}$ (198.1): C 30.3; H 1.5; S 16.2; 0.5 Na_2SO_4 35.9.) The ^1H NMR spectrum of the product agreed with the proposed structure.

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