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1. Schäffner, A. and Krymey, F. *Z. physiol. Chem.* **255** (1938) 145.
2. Hoffman-Ostenhof, O., Moser, H. and Putz, E. *Experientia* **4** (1948) 352.
3. Hoffman-Ostenhof, O., Moser, H. and Ehrenreich, R. *Monatsh.* **82** (1951) 295.
4. Beerenblum, J. and Chain, E. *Biochem. J.* **32** (1938) 295.
5. Porath, J. *Biochim. Biophys. Acta* **22** (1956) 151.
6. Smithies, O. *Biochem. J.* **61** (1955) 629.
7. Schramm, M. *J. Biol. Chem.* **233** (1958) 1169.
8. Heppel, L., Harkness, D. R. and Hilmoe, R. J. *J. Biol. Chem.* **237** (1962) 841.
9. Kunitz, M. *J. Gen. Physiol.* **35** (1952) 423.
10. Kunitz, M. *J. Am. Chem. Soc.* **73** (1951) 1387.
11. Aavaeva, S., Fölsch, G., Strid, L. and Mellander, O. *Acta Chem. Scand.* **17** (1963) 2718.
12. Fölsch, G. *Acta Chem. Scand.* **12** (1958) 561.

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Alkyl Cyanates

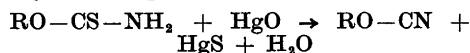
II. A New Route to Alkyl Cyanates

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Alkyl cyanates have recently been prepared by decomposition of 5-alkoxy-1,2,3,4-thiazoles.¹⁻³ Since the properties of these rather unstable compounds are now known it seemed worthwhile to reinvestigate some of the methods which have earlier been tried without success. One of these methods aimed at the removal of hydrogen sulfide from *O*-alkyl thiocarbamates, the reverse reaction of the addition of hydrogen sulfide to alkyl cyanates, which according to our experiences proceeds smoothly.^{1,2}

The reaction between *O*-ethyl thiocarbamate (xanthogenamide) and various metal compounds, such as HgO, Ag₂O, Ag₂CO₃, PbO, TiOH, AgNO₃, and CuSO₄ was studied about one hundred years ago by Debus,⁴ Conrad and Salomon,⁵ and Mulder.⁶ Although, according to these authors, metal sulfides were formed and a sharp smelling substance was recognized no cyanate could be isolated. When performing the reaction between *O*-alkyl thiocarbamates and metal oxides, e.g. mercury(II) oxide, in ether solution at 0°C we have, however, been able to isolate the expected alkyl cyanate, formed according to the equation:



The water formed in the reaction was removed by means of MgSO₄. The alkyl cyanates were found by gas chromatography, infrared spectroscopy, and refractometry to be identical with the products prepared from 5-alkoxy-1,2,3,4-thiazoles.

The reaction was carried out with *O*-ethyl, *O*-propyl, *O*-isopropyl, and *O*-butyl thiocarbamate. The yields varied from 40% to 57% when mercury(II) oxide was used. With Ag₂O as the sulfur removing agent the yields could be raised about 5%. PbO, PbO₂, Cu₂O, and CuO were found to react in a similar way but more slowly than HgO and Ag₂O.

O-Ethyl selenocarbamate, EtO-CSe-NH₂ was found to react very fast with HgO, but the yield of ethyl cyanate was very low (7%).

Attempts to prepare alkyl cyanates from alkyl carbamates (urethans) by means of a dehydrating agent (P₂O₅, dicyclohexylcarbodiimide) were unsuccessful.

The comparatively low yields seem to be due to side reactions or trimerisation since an oily residue is always left when the cyanate is distilled from the reaction mixture; they may, however, also to some extent be due to the circumstance that our preparations were carried out on a rather small scale (about 0.5 g of the cyanates were prepared).

Experimental. Ethyl cyanate: 2 g of *O*-ethyl thiocarbamate were dissolved in 10 ml of dry ether and 4 g of dry magnesium sulfate were added. The solution was cooled at 0°C and 7 g of mercury(II) oxide were added in one portion (1.6 times the calculated amount) with stirring. The stirring was continued for

30 min after which time the solid products were removed by centrifugation. The residue was washed with dry ether (three times 5 ml) and the combined filtrates dried over MgSO_4 (0.5 g). This solution contains some impurities which may cause the cyanate to isomerise vigorously if concentrated at room temperature. The purification was therefore attained by distilling the solution *in vacuo* at 20 mm Hg with only little heating into a receiver kept at -80°C . The receiver was removed and the last amount of the cyanate was distilled at 1 mm Hg. The two distillates were combined. The ether was then removed *in vacuo* without heating and with gentle shaking. When the pressure reached 12 mm Hg the flask was placed in a bath at 20°C for 2–3 min in order to remove the last traces of ether. The residual cyanate was distilled at 1 mm Hg into a receiver kept at -80°C , the distillation flask being kept in a bath at 30°C . Yield 0.54 g (40 %).

If a greater amount of HgO was used (12 g) the yield was raised with some percent. Stirring for 40 min did not change the yield and stirring for 20 min gave a slightly better yield; the time given (30 min) was chosen to ensure removal of the water formed. Elaborate studies may raise the yield further.

The same procedure may be used with silver(I) oxide instead of mercury(II) oxide and the yields are slightly better.

Ethyl cyanate was also prepared from 2 g of *O*-ethyl selenocarbamate in exactly the same manner as described above. Yield 7 %.

Propyl cyanate, isopropyl cyanate, and butyl cyanate were prepared in the same way as ethyl cyanate, except that the purification of the ether solution may be omitted in the case of butyl cyanate because of the higher stability of this compound.³ The filtered solution is then only concentrated and the cyanate is obtained by distilling from a bath at 35°C .

The refraction indexes and infrared spectra of the cyanates prepared in this way were all in accordance with those reported elsewhere^{3,7} for cyanates prepared from 5-alkoxy-1,2,3,4-thiazoles.

O-Ethyl selenocarbamate, $\text{EtO}-\text{CSe}-\text{NH}_2$. 5.2 g of (ethoxyselenocarbonylseleno)acetic acid (selenoxanthogenacetic acid) was suspended in 50 ml of water and 100 ml 2 N aqueous ammonia added slowly with stirring and cooling in ice. The acid went into solution. After standing for 1 h at 0°C the solution was brought to pH 5–6 with 4 N hydrochloric acid, saturated with sodium chloride and extracted with ether. The ether solution was dried with magnesium sulfate and the ether removed *in vacuo*. The residue was an almost colourless oil which solidified on cooling. Yield 1.97 g (68 %). M.p. after recrystallisation from pentane/chloroform $44.5-45^\circ\text{C}$. (Found: C 23.78; H 4.81; N 8.89. Calc. for $\text{C}_3\text{H}_7\text{NOSe}$: C 23.61; H 4.65; N 9.21).

1. Jensen, K. A. and Holm, A. *Acta Chem. Scand.* **18** (1964) 826.
2. Jensen, K. A., Due, M. and Holm, A. *Acta Chem. Scand.* **19** (1965). *To be published.*
3. Martin, D. *Tetrahedron Letters* **39** (1964) 2829.
4. Debus, H. *Ann.* **72** (1849) 1, p. 13.
5. Conrad, R. and Salomon, F. *J. prakt. Chem.* **10** (1874) 28.
6. Mulder, E. *Rec. Trav. Chim.* **3** (1884) 287, p. 306.
7. Groving, N. and Holm, A. *Acta Chem. Scand.* *To be published.*

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