

Short Communications

Alkyl Cyanates

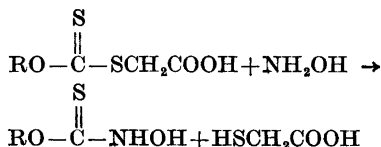
XI. The Decomposition of *O*-Alkyl *N*-(alkyloxycarbonyloxy)thiocarbamates to Alkyl Cyanates

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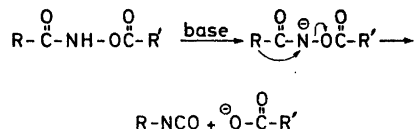
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In earlier papers in this series the spontaneous decomposition of 5-alkoxy-1,2,3,4-thiazoles was shown to give alkyl cyanates in high yield.¹ In connection with studies concerning the mechanism of this process, the Lossen degradation of acylated *O*-alkyl *N*-hydroxythiocarbamates was investigated in the hope of finding a common intermediate in these reactions. The preliminary results given below show that an unusual degradation takes place leading to alkyl cyanates in good yields. This paper deals with the generality of the reaction and its synthetic scope. Mechanistic details will be published elsewhere.²

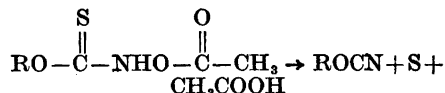
The *O*-alkyl *N*-hydroxythiocarbamates are prepared from ((alkoxythiocarbonyl)-thio) acetic acids and hydroxylamine:



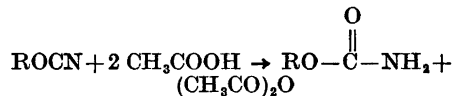
In the Lossen degradation, the next step is acylation of the hydroxamic acid followed by base treatment. Thus generally:



When *O*-alkyl *N*-hydroxythiocarbamates were acetylated, unstable products were formed which could not be isolated due to rapid decomposition at room temperature according to the following scheme:

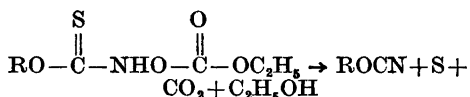


Sulfur was formed almost quantitatively and an alkyl cyanate could be detected immediately. Formation of $\text{RO}-\text{NCS}$ or similar products was not observed. Alkyl cyanate was detected by infrared spectroscopy but the yield was relatively low and the product was contaminated with alkyl carbamate and acetic anhydride due to further reaction between the alkyl cyanate and the acetic acid formed:



This is a well-known reaction.³

When acylated with ethyl chloroformate, a good yield of an alkyl cyanate was obtained:



Although ethanol reacts with alkyl cyanates, this reaction is slow enough to allow isolation of the cyanate. Thus, the following yields were obtained: Butyl, 72 %; isobutyl, 75 %; hexyl, 78 %; nonyl, 67 %; undecyl cyanate, 30 %. The total amount of the cyanate formed is

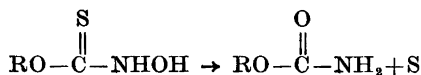
probably higher than the yields indicate since none of the intermediate products could be purified. Also, some cyanate was lost due to side reaction with the ethanol and with water which is present during a certain point of the procedure.

Butyl, isobutyl, and hexyl cyanate were identified by comparison with the infrared spectra of authentic materials. Nonyl and undecyl cyanate which are new compounds, were identified by elemental analysis and spectroscopy. Their infrared spectra exhibited strong absorptions at $2252 \pm 5 \text{ cm}^{-1}$ (nonyl), $2250 \pm 5 \text{ cm}^{-1}$ (undecyl), and $1104 \pm 2 \text{ cm}^{-1}$ (nonyl), $1104 \pm 2 \text{ cm}^{-1}$ (undecyl) which are characteristic of alkyl cyanates due to the cyanate group and to the alkyl C—O vibration, respectively.⁴ The ratio between the 2250 cm^{-1} and 1100 cm^{-1} absorption was, as expected 1:1.⁴

Formation of alkyl cyanates of chain length shorter than butyl was not investigated because the unstable alkyl cyanate would be difficult to separate from the ethanol formed.

The synthesis of alkyl cyanates by this method is considerably faster than from 5-alkoxy-1,2,3,4-thiazoles.

The intermediate *O*-alkyl *N*-hydroxythiocarbamates were also found to be thermally unstable, decomposing to alkyl carbamates and sulfur:



The lower homologues were oils which were too unstable to permit satisfactory analyses. The two highest homologues were solids which could be recrystallized from hexane but were unstable as well. Thus, *O*-nonyl *N*-hydroxythiocarbamate after standing at room temperature for about 15 min decomposed in an exothermic reaction. All *O*-alkyl *N*-hydroxythiocarbamates underwent this reaction when heated to 40–60°C. Alkyl carbamate was isolated in yields from 80 to 94 % by extraction with ether. The products were identified by elemental analysis, m.p., and by comparison with the infrared spectra of authentic samples.

This decomposition could proceed by intermediate formation of alkyl cyanate which in turn reacts with the water formed. A similar pathway has been suggested for the decomposition of *N*-hydroxythioureas.⁵ When *O*-isobutyl *N*-hydroxythiocarbamate

was left at room temperature in ether solution in the presence of magnesium sulfate only isobutyl carbamate was formed. However, when heated in toluene in the presence of phosphorus pentoxide a product was isolated which absorbed in the infrared region at 2250 cm^{-1} , characteristic of alkyl cyanates. On the other hand, when isobutyl carbamate was submitted to the same treatment in toluene isobutyl cyanate or its isomerisation product isobutyl isocyanate was likewise formed. The infrared spectra indicated that other products had also been formed in these reactions. Evidently, a closer examination is necessary to make definite conclusions concerning the decomposition mechanism of *O*-alkyl *N*-hydroxythiocarbamates.

The nuclear magnetic resonance spectra of the *O*-alkyl *N*-hydroxythiocarbamates in carbon tetrachloride showed the following features. The hydrogen resonances of the hydroxylamine group were observed at 1.13 τ and 3.00 τ for both *O*-nonyl and *O*-undecyl *N*-hydroxythiocarbamate in accordance with the postulated structure. These shifts are, however, sensitive to small amounts of water and the lower homologues showed either two very broad bands (one hydrogen each) or a single band (two hydrogens) of varying sharpness and position in the range between 1.1 τ and 3.0 τ . The hydrogens of the isobutyl derivative gave rise to a doublet at 5.72 τ (due to the α -methylene hydrogens), a multiplet at 7.90 τ and a doublet at 9.00 τ , as expected. The α -methylene hydrogens in the other derivatives showed a triplet at approximately 5.5 τ and the rest of the hydrogens between 8.1 and 9.4 τ . Butyl, 5.53 τ ; hexyl, 5.53 τ ; nonyl, 5.55 τ ; undecyl, 5.54 τ .

In the corresponding carbamates in carbontetrachloride signals due to the amino group were observed from 4.68 to 4.82 τ (two hydrogens) and signals due to the α -methylene hydrogens were observed as a triplet at approximately 6.0 τ . The rest of the hydrogens were found between 8.1 and 9.3 τ . Butyl, 6.01 τ ; hexyl, 6.02 τ ; nonyl, 6.01 τ ; undecyl, 6.00 τ . The hydrogens of isobutyl carbamate gave rise to a doublet at 6.21 τ (due to the α -methylene hydrogens), a multiplet at 8.07 τ and a doublet at 9.05 τ . In mixtures of *O*-alkyl *N*-hydroxythiocarbamate and alkyl carbamate the two triplets do not overlap and may be used to follow the conversion of the former to the latter.

Experimental. The nuclear magnetic resonance spectra were obtained with a Varian A-60 A instrument (60 Mc/s and with TMS as internal standard) and the infrared spectra with a Perkin-Elmer 337 Grating Infrared Spectrophotometer.

((Alkoxythiocarbonyl)thio)acetic acids. The preparation of these compounds has been described in another paper.⁵

O-Alkyl N-hydroxythiocarbamates. The ((alkoxythiocarbonyl)thio)acetic acid (0.02 mol) was dissolved in 1 N sodium hydroxide (20.0 ml) and after cooling to 0°C hydroxylamine hydrochloride (0.02 mol) dissolved in 1 N sodium hydroxide (19.0 ml) was added. Diethyl ether (50 ml) was added and the mixture was stirred at 0°C for one hour. For preparation of the highest homologues more ether was necessary to keep the products in solution. 2.0 ml 1 N sodium hydroxide was then added and the ether phase was immediately separated from the water phase which was extracted twice with 25 ml of ether. The combined ether extracts were washed twice with 3 ml of water and dried over magnesium sulfate for one hour. On evaporation *in vacuo* at room temperature the following yields were obtained: Butyl, 87 %; isobutyl, 89 %; hexyl, 97 %; nonyl, 93 %; undecyl, 98 %. The nonyl and undecyl derivatives were colourless solids whereas the lower members were oils. Nonyl: M.p. 43–43.5°C from hexane (Found: C 54.90; H 9.74; N 6.26. Calc. for C₁₀H₂₁NO₂S: C 54.77; H 9.65; N 6.39). Undecyl: M.p. 51.5–52°C from hexane. (Found: C 58.30; H 10.11; N 5.72. Calc. for C₁₂H₂₅NO₂S: C 58.27; H 10.19; N 5.66). The oils were too unstable to allow purification for analysis.

When heated slightly over the m.p. or to 40–60°C for the oils, these compounds were transformed into the corresponding alkyl carbamates in a vigorous exothermic reaction. This decomposition may also take place spontaneously after storing at room temperature for some time. Thus a sample of the isobutyl derivative decomposed after about 5 min and a sample of the nonyl derivative decomposed after 15 min. Although some unknown products were formed, the infrared spectra of the unpurified products obtained on extraction with ether were almost identical with the infrared spectra of the products after recrystallisation from hexane. M.p. of the alkyl carbamates are given after recrystallisation, literature values are given in parentheses and yields are of the unpurified products: Butyl, m.p. 50.5–51°C (51.6°C⁷), 81 %. (Found: N 11.81. Calc. for C₅H₁₁NO₂: N 11.96). Isobutyl, m.p. 62–63°C (61°C,⁸ 64–65°C⁷), 94 %. (Found: N 12.02. Calc. for C₅H₁₁NO₂: N 11.96). Hexyl, m.p.

64–65°C (65°C⁷), 93 %. (Found: C 57.84; H 10.35; N 9.90. Calc. for C₇H₁₅NO₂: C 57.90; H 10.41; N 9.65). Nonyl, m.p. 67–68°C (69°C⁷), 92 %. (Found: N 7.28. Calc. for C₁₀H₂₁NO₂: N 7.48). Undecyl, m.p. 74–75°C, 94 %. (Found: N 6.88. Calc. for C₁₂H₂₅NO₂: N 6.51).

Alkyl cyanates. Immediately after isolation the *O*-alkyl *N*-hydroxythiocarbamate (0.01 mol) was dissolved in ether (50 ml) and ethyl chloroformate (0.01 mol) was added. After cooling to 0°C triethyl amine (0.01 mol) in ether (50 ml) was added over a period of 3 min. After stirring for 4 additional minutes 50 ml of water was added and the ether phase was isolated. Already at this point some sulfur had separated due to the decomposition to cyanate. The water layer was extracted twice with 15 ml of ether and the combined extracts washed twice with 5 ml of water. After drying over magnesium sulfate for 30 min the ether was removed *in vacuo* with a water pump. During evaporation sulfur separated and the cyanate was left as an oil. This was extracted with a little ether and the solvent evaporated. At this point decomposition was almost complete and the pure alkyl cyanate was isolated by distillation at 10⁻² mm Hg from a water bath at 30–40°C for the lower alkyl cyanates and at 60–70°C for nonyl and undecyl cyanate. The acylated *O*-nonyl and *O*-undecyl *N*-hydroxythiocarbamates are more stable than the lower homologues and were heated at 40°C in water pump vacuum for about 5 min to ensure decomposition. It should be pointed out that alkyl cyanates are thermally unstable although the higher homologues are far more stable than the lower ones. Yields after distillation: Butyl, 72 %; isobutyl, 75 %; hexyl, 79 %; nonyl, 67 %; undecyl, 30 %. The two cyanates with the highest molecular weight were distilled twice in a short path distillation apparatus before elemental analyses although the infrared spectrum of the first distillate was almost identical with that of the second distillate. The distillation was stopped when a semisolid material appeared in the receiver. The low yield of undecyl cyanate is probably due to difficulties in obtaining complete decomposition before distillation which results in side reactions with undecomposed material and alkyl cyanate at the elevated temperature. Codistillation of some undecomposed material may also account for the not quite satisfactory elemental analyses obtained. (Found: C 70.00; H 11.20; N 7.88. Calc. for C₁₀H₁₉NO (nonyl cyanate): C 70.96; H 11.32; N 8.28. Found: C 71.45; H 11.49; N 6.46. Calc. for C₁₂H₂₃NO (undecyl cyanate): C 73.04; H 11.75; N 7.10).

Butyl, isobutyl, and hexyl cyanate have been prepared earlier^{1,10} and were identified by comparison of their infrared spectra with authentic materials.

Nonyl and undecyl cyanate are non-lachrymatory, pleasantly smelling liquids, in contrast to the lower members.

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Note on $[\text{Ni}(\text{en})_2][\text{AgX}_2]_2$ (X = Br and I)

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It has been observed that in some cases small differences in chemical structure are responsible for a change in configuration. Thus, the nickel(II) salicylaldoxime complex is yellow and diamagnetic in benzene solution and in the solid state, and has been shown to be planar by X-ray analysis,¹ but its solution in pyridine is

blue and paramagnetic. Similarly, two series of bis(ethylenediamine)nickel(II) complexes are known.² One, exemplified by the salt $[\text{Ni}(\text{en})_2][\text{AgBr}_2]_2$, consists of orange and diamagnetic compounds, the other, exemplified by $[\text{Ni}(\text{en})_2]\text{SO}_4$, of blue and paramagnetic ones. Sone and Kato³ have observed that the blue-violet colour of an alcoholic solution of $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ becomes yellowish with rise in temperature and the same type of thermochromism was also found in its aqueous solution containing NaClO_4 . They claim, from spectrophotometric studies, that there exists a dehydration equilibrium of the complex ion, in which the yellow planar complex $[\text{Ni}(\text{en})_2]^{2+}$ is produced in the solution from the octahedral $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ complex. Brown and Lingafelter⁴ have determined the crystal structure of the blue-violet $[\text{Ni}(\text{en})_2(\text{NCS})_2]$ and have found a nearly regular octahedral configuration contrary to the tetrahedral arrangement proposed by Pauling.⁵ In the present work attention has been focused upon the orange coloured type of $[\text{Ni}(\text{en})_2]^{2+}$ complexes. This note reports on the preparation and crystal data for $[\text{Ni}(\text{en})_2][\text{AgBr}_2]_2$ and $[\text{Ni}(\text{en})_2][\text{AgI}_2]_2$.

Preparation and analysis. The method used by Harris⁶ in his preparation of $[\text{Ni}(\text{en})_2][\text{AgI}Br]_2$ has been modified for the preparation of $[\text{Ni}(\text{en})_2][\text{AgBr}_2]_2$ and $[\text{Ni}(\text{en})_2][\text{AgI}_2]_2$ in order to avoid the inconvenience of coprecipitation of NH_4Br and NH_4I , respectively.

$[\text{Ni}(\text{en})_2][\text{AgBr}_2]_2$: To a hot solution of 60 g NH_4Br and 1.88 g AgBr (0.01 mole) in 100 ml water was added a hot solution of 2.15 g $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]Br_2$ and 5 g NH_4Br in 12.5 ml. On cooling, beautiful, well-developed, orange crystals of $[\text{Ni}(\text{en})_2][\text{AgBr}_2]_2$ separated out. These were dried between filter papers and washed with alcohol and acetone (Yield: 1.4 g).

Nickel was determined as nickel dimethylglyoxime, ethylenediamine by the Kjeldahl method, silver as silver bromide and bromide as silver bromide. (Found: Ni 8.28; Ag 29.96; Br 44.80; en 16.83. Calc. for $[\text{Ni}(\text{en})_2][\text{AgBr}_2]_2$: Ni 8.22; Ag 30.20; Br 44.75; en 16.83).

$[\text{Ni}(\text{en})_2][\text{AgI}_2]_2$ was prepared and analyzed in a similar way.

Unit cell dimensions were calculated by a least-squares procedure on the observed $\sin^2\theta$ values, obtained from Guinier photographs taken with $\text{CuK}\alpha$ radiation. Single crystal data have been collected by the Weissenberg method for $[\text{Ni}(\text{en})_2][\text{AgBr}_2]_2$ and by a single-crystal automatic diffractometer (PAILRED) for $[\text{Ni}(\text{en})_2][\text{AgI}_2]_2$.