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Alkyl Cyanates

III. Preparation and Properties of Alkyl Cyanates

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In an earlier paper [1] the controlled decomposition of 5-alkoxy-1,2,3,4-thiatriazoles was described as a general method for preparing alkyl cyanates and details were given for ethyl cyanate. In this paper the preparation and properties of methyl cyanate, propyl cyanate, isopropyl cyanate, butyl cyanate, isobutyl cyanate, and *sec*-butyl cyanate are discussed. The cyanates isomerise rapidly to isocyanates which in turn may polymerise to trialkyl cyanurates. They all react with hydrogen sulfide to form *O*-alkyl thiocarbamates (xanthogenamides).

Preparation of ethyl cyanate, a representative of the hitherto unknown class of alkyl cyanates, by spontaneous decomposition of 5-ethoxy-1,2,3,4-thiatriazole has recently been described by Jensen and Holm,[1] and by Martin,[2] and it was reported [1] that other alkyl cyanates could be prepared in a similar way. The following is a more detailed description of the preparation and properties of methyl cyanate and some of its higher homologues.

The cyanates were prepared by keeping an ether solution of the appropriate thiatriazole at room temperature for some time. After removal of sulfur and ether the cyanates were left as colourless, mobile liquids which could be distilled *in vacuo*. Their vapours are lachrymatory but their smell is different from that of the corresponding isocyanates. With the exception of methyl cyanate they are all liquid at −80°C. On gaschromatographic analysis (using a nonpolar column: *Perkin Elmer 0-column*) they showed considerably longer retention times than the isocyanates, which indicates that their boiling points are higher.

On heating propyl, butyl, and isobutyl cyanate to boiling they isomerise to the isocyanates in an exothermal reaction (as described for ethyl cyanate [1]). According to gaschromatographic analysis the only low boiling compounds in the heated products are the isocyanates. These were also identified by transformation into *N*-alkyl-*N'*-phenylureas. No rearrangement in the alkyl chain takes place when the cyanates isomerise to isocyanates.

Contrary to the primary alkyl cyanates, isopropyl cyanate decomposes on heating into propene and cyanic acid, which polymerises to cyanuric acid (identified by its infrared spectrum). Propene was identified by gaschromatography on a benzyl cyanide-silver nitrate column prepared according to Armitage.[3] The gaschromatogram showed only one peak corresponding to propene. An infrared spectrum of the gas also confirmed the presence of propene. Comparison with infrared spectra of propene at known pressures showed that the partial pressure of propene in the gas mixture was 30—40 mm Hg when the total pressure was 43 mm Hg. Accordingly propene constitutes 70—93 % of the volatile products formed from isopropyl cyanate. The infrared spectrum of the gas showed that in addition to propene small amounts of isopropyl isocyanate and unchanged isopropyl cyanate were present. In the same way *sec*-butyl cyanate decomposes on heating, forming cyanuric acid and three or four hydrocarbons which have not yet been finally identified.

As described for ethyl cyanate [1] the alkyl cyanates are rapidly transformed into other products on standing at room temperature. By comparison of the infrared spectra of the reaction products with infrared spectra of alkyl isocyanates, trialkyl cyanurates [4] and trialkyl isocyanurates [5] it was found that the alkyl cyanates are transformed into a mixture of the corresponding alkyl isocyanate and trialkyl isocyanurate. No absorption bands due to trialkyl cyanurates could be identified. However small amounts of trialkyl cyanurate can hardly be excluded by this method and a more refined analysis by means of gas chromatography is in progress. The trimerisation requires certain catalysts. Pure alkyl cyanates are transformed into alkyl isocyanates which in part polymerise. Impure alkyl cyanates, however, form mainly the trimeric product and this reaction may take place explosively.

Undiluted methyl cyanate is extremely labile and is transformed at room temperature into solid trimethyl isocyanurate in a few minutes (explosively if the temperature is allowed to increase). At −30°C the transformation was slower, but after 24 h all had solidified into trimethyl isocyanurate. The isomerisation of methyl cyanate into methyl isocyanate could be followed by gaschromatography at 40°C, because the transformation is slow when the cyanate is diluted. Even with freshly prepared methyl cyanate two peaks are found, presumably caused by the heating during injection into the gaschromatograph resulting in some isomerisation. The second peak assumed to correspond to methyl cyanate is sharp but the front rises unsteadily starting immediately after appearance of the methyl isocyanate peak. This phenomenon is due to the isomerisation of methyl cyanate to methyl isocyanate on the column.

In dilute solutions methyl cyanate is more stable and this circumstance has permitted to perform spectroscopic investigations of this substance (*cf.* the following paper [6]). The infrared spectrum of a 2 % solution of methyl cyanate in carbon tetrachloride begins only after one hour to show visible changes.

The transformation rates of the higher alkyl cyanates decrease with increasing molecular weight. It was thus found, by aid of gaschromatography, that on boiling butyl cyanate for 30 sec a mixture of 15 % isocyanate and 85 % cyanate was formed. Boiling for about one min resulted in a 40 %

transformation and boiling for two and a half min in a 100 % transformation of the cyanate into isocyanate, whereas ethyl cyanate, as described earlier,[1] was isomerised completely during 20—30 sec. Isobutyl cyanate, when pure, isomerised completely only after about 8 min.

On gaschromatographic analyses propyl, butyl, and isobutyl cyanate show only one peak, however with some tailing. The products were free from isomers and no isomerisation took place during the analyses. As mentioned above, isopropyl and *sec*-butyl cyanate decompose on heating and this circumstance has precluded a gaschromatographic analysis of them.

An NMR-spectroscopic investigation of ethyl, propyl, isopropyl, butyl, isobutyl and *sec*-butyl cyanate has also been performed. The cyanates were found to contain less than one percent of the corresponding isocyanates (*cf.* the following paper [6]).

The presence of the R-OCN grouping in ethyl cyanate was shown by the formation of *O*-ethyl thiocarbamate (ethylxanthogenamide) on reaction with hydrogen sulfide.[1] It has been found that the higher alkyl cyanates react in the same way. The reaction was very slow with butyl and isobutyl cyanate but could be accelerated on addition of pyridine. The identity of the reaction products with authentic samples of *O*-alkyl thiocarbamates was shown by comparison of their infrared spectra.

Details of the gaschromatographic analyses of alkyl cyanates will be published in another paper.

EXPERIMENTAL

5-Alkoxy-1,2,3,4-thiatriazoles. The method described [7] for the preparation of 5-ethoxy-1,2,3,4-thiatriazole was used also for the preparation of the higher homologues, only with some slight modifications: The alkoxythiocarbonylhydrazine [8] (0.1 mole) was dissolved in 0.5 N* hydrochloric acid (250 ml), and a solution of sodium nitrite (6.9 g) in water (75 ml) was added with stirring and cooling, the temperature being kept between $-2°$ and $+3°$C. The addition of the sodium nitrite solution was stopped as soon as a test with potassium iodide-starch paper showed positive HNO_2 reaction. The cold solution was extracted three times with 100 ml of ether each time and the ether solution was washed twice with 25 ml of water. After drying over sodium sulfate at 0° the solution was filtered and evaporated *in vacuo* at 10°C.

In the case of 5-methoxy-1,2,3,4-thiatriazole the washing of the ether solution was omitted, because the compound is rather soluble in water. Instead a purification was attained by dissolving the crude 5-methoxy-1,2,3,4-thiatriazole in dry ether (30 ml to 4.8 g of the thiatriazole) and cooling of the solution in a "dry ice"-acetone mixture. The thiatriazole separated as colourless crystals, melting below room temperature, which were isolated by centrifugation and recrystallised from 20 ml of ether. However, because of its instability it was not dried in the solid state but was immediately dissolved in 5 ml of dry ether. This solution could be kept at $-30°$C for a few days without decomposition or immediately used for the preparation of methyl cyanate.

The 5-alkoxy-1,2,3,4-thiatriazoles are very labile; to avoid violent exothermic decompositions they should be dissolved in ether immediately after isolation. This applies especially to the 5-methoxy derivative which is very unstable even in solution at room temperature. As mentioned in the first publication the stabilities of the compounds is very dependent on their purity. Therefore the washing with water (propoxy- and butoxy-derivatives) or recrystallisation from ether (methoxy- and ethoxy-derivatives) can not be omitted, although the yields may be diminished by these procedures. The

* The value 0.05 N given in our first paper [1] is due to a misprint.

following yields of 5-alkoxy-1,2,3,4-thiatriazoles were obtained: Methoxy 87 %, ethoxy 96 %, propoxy 86 %, isopropoxy 93 %, butoxy 87 %, *sec*-butoxy 87 %, and isobutoxy 82 %.

Preparation of the alkyl cyanates (except methyl cyanate). The higher alkyl cyanates were prepared exactly as described for ethyl cyanate [1], except that the cyanates were distilled at 1 mm Hg into a receiver kept at −80°C immediately after removal of the ether. The flask was placed in a bath at 30°C in the case of propyl and isopropyl cyanate and at 35°C in the case of butyl, *sec*-butyl and isobutyl cyanate, and the liquid was stirred magnetically during distillation. The cyanates distilled readily and were collected as colourless liquids within 10 min. By this method as much as 8 g of an alkyl cyanate has been prepared in one charge. The yields and analyses are given in Table 1. However, the methoxy compound was too unstable to be analysed; also its refraction index is somewhat uncertain, because isomerisation to the isocyanate takes place already during the measurement. The molecular weights were determined cryoscopically in *ca.* 2×10^{-2} molal solutions in benzene.

With the exception of methyl cyanate the alkyl cyanates isomerise and trimerise at room temperature in a few days, and at −20°C in the course of several weeks. At −80°C they can be kept unchanged for a very long time.

Table 1. Alkyl cyanates, R−O−C≡N.

R	Yield, %	Formula	Analyses (C,H,N)		Mol. w.		n_D^{25}
			Calc.	Found	Calc.	Found	
Methyl	17	C_2H_3NO					(1.3675)
Ethyl [1]	91	C_3H_5NO	50.85; 7.18; 19.72	50.69; 7.09; 19.71	71.0	73	1.3768
Propyl	82	C_4H_7NO	56.45; 8.29	56.50; 8.52	85.0	82	1.3908
Isopropyl	77	C_4H_7NO	56.45; 8.29; 16.46	56.40; 8.24; 16.50	85.0	89	1.3868
Butyl	78	C_5H_9NO	60.60; 9.13	60.70; 8.98	99.2	98	1.4010
Isobutyl	73	C_5H_9NO	60.60; 9.13	60.30; 9.15	99.2	97	1.3975
sec-Butyl	77	C_5H_9NO	60.60; 9.13	60.90; 9.32	99.2	101	1.3988

Methyl cyanate. A solution (20 %) of 5-methoxy-1,2,3,4-thiatriazole in ether was kept for 3 h at 20−25°C, after which time the nitrogen evolution had practically stopped. The solution was distilled into a receiver cooled in a "dry ice"-acetone mixture. The ether was removed from the solution without heating by evaporation *in vacuo* until the pressure had diminished to 12 mm Hg, and the last traces of ether were removed by placing the flask in a bath at 5°C for 30 sec and shaking. The residue was immediately distilled at 1 mm Hg, the flask being kept in a bath at 5°C and the receiver being cooled in "dry ice"-acetone. The methyl cyanate prepared in this way was shown by gas chromatography to be free from ether. It is crystalline at −80°C but melts below −30°C. It is very labile and cannot be kept at room temperature, even for a few minutes, without decomposing. At −80°C it can be kept for some hours. Because of the rapid decomposition the yield was low (17 %) and no analyses could be performed.

Isomerisation of propyl cyanate, butyl cyanate, and isobutyl cyanate. About 1 g of the alkyl cyanate was heated until an exothermic reaction took place which caused the liquid to start boiling. The boiling was continued for 2−8 min with only little heating. During the boiling the temperature fell. The boiling started at 107°, 135°, and 133°C for propyl cyanate, butyl cyanate, and isobutyl cyanate, respectively, but it is probable that considerable isomerisation had taken place before boiling started. The corresponding isocyanates boil at 88°, 114−116°, and 106°C. Gaschromatographic analyses of the reaction products showed that the alkyl cyanate had disappeared completely, the only low boiling products being the isocyanates.

The reaction products were mixed with excess aniline and the N-alkyl-N′-phenylureas recrystallised from heptane/ether.

The following data were found for the propyl, butyl, and isobutyl derivatives, respectively:

Alkyl	N %		M.p., °C		Yield, %
	Found	Calc.	Found	Lit.	
Propyl	15.95	15.72	116–116.5	116[9]	68
Buty	14.54	14.57	130–131	130[9]	52
Isobutyl	14.63	14.57	151–151.5	147[9] 158[10]	72

The identity of these products was proved by comparison of their infrared spectra with authentic samples of N-alkyl-N′-phenylureas, prepared from phenyl isocyanate and the appropriate amine. Accordingly no rearrangement of the alkyl group takes place during the isomerisation. The m.p. of *N*-isobutyl-*N′*-phenylurea prepared in this way was also found to be 151–151.5°C, so that both values given in the literature seem to be erroneous.

The reaction between alkyl cyanates and hydrogen sulfide. The preparation of xanthogenamides from alkyl cyanates were performed essentially as described for ethyl cyanate,[1] however, at room temperature instead of 0° and with solutions of 0.5 g of the alkyl cyanate in 40 ml of ether. Further it was found necessary to add a few drops of pyridine as catalyst to induce the reaction of butyl cyanate or isobutyl cyanate with hydrogen sulfide.

All the *O*-alkyl thiocarbamates (xanthogenamides) were first isolated as oils. However, the isopropyl and isobutyl derivatives crystallised on rubbing and the propyl derivative crystallised from hexane. The *O*-butyl and *O-sec*-butyl thiocarbamates crystallised after distillation. The following yields of crude products were obtained: propyl 31 %, isopropyl 47 %, butyl 56 %, isobutyl 84 %, and *sec*-butyl 94 %. The identity of the products was controlled by analyses and by comparison of their infrared spectra with infrared spectra of *O*-alkyl thiocarbamates prepared from (alkoxythiocarbonylthio)acetic acids[8] and ammonia. With the exception of *O-sec*-butyl thiocarbamate all these thiocarbamates had been prepared previously[11] and the melting points given in the literature were confirmed. *O-sec*-Butyl thiocarbamate was obtained by the above mentioned method. After distillation and recrystallisation from ether/hexane the melting point was 39–39.5°C. (Found: C 45.30; H 8.28; N 10.33. Calc. for $C_5H_{11}NOS$: C 45.10; H 8.33; N 10.52).

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