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Alkyl Cyanates

XII. On *tert*-Butyl Cyanate, Cyclohexyl Cyanate, Aralkyl Cyanates, and Tetramethylene Dicyanate

KAI ARNE JENSEN, ARNE HOLM and JACOB WOLFF-JENSEN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark

tert-Butyl cyanate has been prepared *via* 5-*tert*-butoxy-1,2,3,4-thiatriazole. It is a very unstable compound decomposing with the formation of isobutene and cyanic acid.

Cyclohexyl cyanate was obtained from the reaction of *O*-cyclohexyl thiocarbamate and mercury(II) oxide. It decomposes into cyclohexene and cyanic acid when heated.

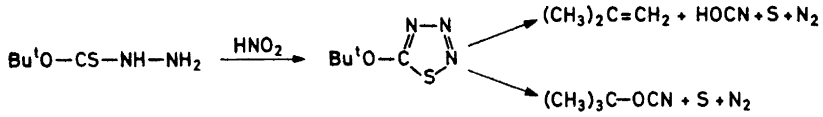
According to the infrared spectra of the crude decomposition products, isolated at low temperature, of 5-benzyloxy-1,2,3,4-thiatriazole and 5-phenethyloxy-1,2,3,4-thiatriazole, benzyl cyanate and phenethyl cyanate were formed. However, they were too unstable to be purified, being transformed into the corresponding isocyanates and isocyanurates at room temperature.

5,5′-(Tetramethylenedioxy)di-1,2,3,4-thiatriazole decomposes in the usual way in solution with the formation of nitrogen and sulfur. The presence of the corresponding dicyanate in the solution could be proved by infrared spectroscopic measurements and by the isolation of *O*,*O*′-tetramethylene bis(thiocarbamate) from the reaction of the thiatriazole with hydrogen sulfide. However, the dicyanate could not be isolated but formed an isoluble high polymer on removal of the solvent.

In our previous publications [1–3] the preparation of several alkyl cyanates has been described. However, an important representative, *tert*-butyl cyanate, could not be obtained by the ordinary route, *viz.* [(alkoxythiocarbonyl)thio]acetic acid ⟶ alkoxythiocarbonylhydrazine ⟶ 5-alkoxy-1,2,3,4-thiatriazole ⟶ alkyl cyanate, because it proved impossible to prepare [(*tert*-butoxythiocarbonyl)thio]acetic acid. Also, several attempts to prepare *tert*-butyl cyanate from *tert*-butyl iodide and silver cyanate were unsuccessful for even at −80°C only cyanic acid and isobutene were formed.

tert-Butoxythiocarbonylhydrazine has now been prepared in another way [4] and was found to form 5-*tert*-butoxy-1,2,3,4-thiatriazole (I) by the normal reaction with nitrous acid. This alkoxythiatriazole decomposes only slowly

in ether solution at room temperature giving isobutene and cyanic acid, whereas the thiatriazoles bearing isomeric butoxyl groups are less stable and furnish the corresponding butyl cyanates in high yields under the same conditions. When the thiatriazole (I) was heated in petroleum ether to about 45°C, however, decomposition into *tert*-butyl cyanate (II) took place smoothly and the cyanate was stable enough in this solvent to allow isolation.



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tert-Butyl cyanate is a colourless liquid at room temperature but is extremely unstable, decomposing to isobutene and cyanic acid, which in turn polymerises to cyanuric acid. In solvents other than alkanes the decomposition takes place rather rapidly. Thus a 5 % solution in carbon tetrachloride reacted completely in the course of 5 h, giving isobutene and cyanic acid. *tert*-Butyl isocyanate is formed from *tert*-butyl iodide and silver cyanate, together with the cyanate, and from 5-*tert*-butoxy-1,2,3,4-thiatriazole. Whether the isocyanate is formed by rearrangement of the cyanate or directly from *tert*-butyl iodide or the alkoxythiatriazole is under investigation. The infrared spectrum of the freshly prepared carbon tetrachloride solution of *tert*-butyl cyanate exhibited strong absorptions at 2251 ± 5 cm^{-1} and 1106 ± 2 cm^{-1} in 1:1 ratio, which is characteristic of alkyl cyanates.[5] When 5-*tert*-butoxy-1,2,3,4-thiatriazole was decomposed in petroleum ether in the presence of hydrogen sulfide, *O-tert*-butyl thiocarbamate could be isolated in 51 % yield, proving that the decomposition product is in fact *tert*-butyl cyanate.

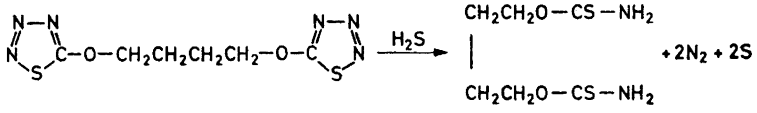
Numerous attempts were made to prepare benzyl and phenethyl cyanates by decomposition of the corresponding thiatriazoles. While infrared spectroscopic measurements on the crude products, isolated at low temperature, indicate that the cyanates were in fact formed, they were too unstable to be purified.*

Isomerisation to the corresponding isocyanates took place even at low temperature and the isocyanates in turn polymerised to isocyanurates. This is an exothermic reaction (*cf.* Ref. 6), which in some cases occurred almost explosively when the reaction mixture was warmed above 0°C.

In attempts to prepare cyclohexyl cyanate by the usual route difficulties were encountered in obtaining a pure product from cyclohexyloxythiocarbonylhydrazine *via* 5-cyclohexyloxy-1,2,3,4-thiatriazole. However, cyclohexyl cyanate could be obtained pure from the reaction of *O*-cyclohexyl thiocarbamate and mercury(II) oxide, according to another of the general methods for the preparation of alkyl cyanates.[7] Cyclohexyl cyanate could be distilled *in vacuo* but on heating decomposed easily into cyclohexene and cyanic acid.

* The crude product formed by decomposition of phenethyloxythiatriazole has been claimed in a German patent [9] to be phenethyl cyanate. However, according to our experience this product may have contained little or no cyanate.

Finally, attempts were made to prepare an alkylene dicyanate. 5,5'-(Tetramethylenedioxy)di-1,2,3,4-thiatriazole (VIII) was obtained in good yield from butane-1,4-diol *via* the alkoxythiocarbonylhydrazine. It decomposed in chloroform solution at room temperature with the elimination of sulfur and nitrogen, and infrared spectra of the solution indicated that a cyanate was formed. This conclusion was substantiated by the isolation of *O,O'*-tetramethylene bis(thiocarbamate) (IX) when the decomposition occurred in the presence of hydrogen sulfide. However, on removal of the solvent from solutions containing the cyanate polymerisation occurred with the formation of a hard, glassy, insoluble mass.



VIII IX

In connection with these studies it has also been shown that the method we have used in the most cases to prepare alkyl cyanates is also applicable to the preparation of aryl cyanates. Phenyl cyanate, prepared earlier by Martin [8] from *O*-phenyl chlorothioformate *via* 5-phenoxy-1,2,3,4-thiatriazole, was obtained in very good yield from phenoxythiocarbonylhydrazine.[4]

EXPERIMENTAL

5-tert-Butoxy-1,2,3,4-thiatriazole (I). Solutions of 4.0 g of *tert*-butoxythiocarbonylhydrazine [4] in 40 ml of ether and 2.4 g of sodium nitrite in 100 ml of water were mixed and cooled to 0°C. Hydrochloric acid (1 N; *ca.* 33 ml) was added dropwise under vigorous stirring during 45 min until the starch-iodide test for nitrous acid was positive. The ether phase was separated and the water phase extracted twice with 60 ml portions of ether. The combined extracts were washed with 20 ml of aqueous sodium hydrogen carbonate (2 M) and then with 30 ml of saturated sodium chloride. After drying over magnesium sulfate, the solvent was removed *in vacuo* to leave the thiatriazole as a colourless oil. Yield 3.21 g (75 %). It could be recrystallized from pentane at low temperature, though the product was not of high purity. (Found: C 37.1; H 5.6; N 27.7; S 18.9. Calc. for $C_5H_9N_3OS$: C 37.7; H 5.7; N 26.4; S 20.1). It could be distilled with only slight decomposition at 40—43°C and 0.1 mm Hg; however, a purer product was not obtained in this way either. The compound may be stored for months at —30° but decomposes rapidly at room temperature.

The infrared spectrum of the thiatriazole exhibits absorptions characteristic of the thiatriazole ring [10] (1480s, 1450vs, 1060m, 920m cm^{-1}), the ether grouping (1150vs), and the *tert*-butyl group (1395m, 1370s).

tert-Butyl cyanate (II). The thiatriazole (I) (2.0 g) was dissolved in 200 ml of petroleum ether (b.p. 40—60°C) and heated to 45—48°C for 16 h. The solution was concentrated to about 5 ml *in vacuo* at room temperature and transferred to a distillation apparatus. Most of the solvent was removed at water pump vacuum and the remainder by means of an oil pump without heating. When the pressure reached 0.5 mm Hg the distillation flask was placed in a bath at 20—25°C and the cyanate was distilled with magnetic stirring. The product was collected with liquid air as a solid that melted below room temperature. Yield 0.6 g (48 %). It was too unstable to permit an elemental analysis but was identified by its infrared spectrum, which showed strong absorptions at 2251 cm^{-1} and 1106 cm^{-1}, characteristic of alkyl cyanates.

When the thiatriazole (I) was decomposed in the presence of hydrogen sulfide and pyridine *O-tert*-butyl thiocarbamate (*tert*-butylxanthamide) was formed, which confirmed the formation of *tert*-butyl cyanate in the decomposition.

In CCl_4 solution (5 %) the thiatriazole (I) decomposed with the formation of isobutene, cyanuric acid, and *tert*-butyl isocyanate. The latter was transformed into *tert*-butylurea (identified by comparison with an authenic sample [11]), by addition of ammonia. The isocyanate was further identified by its infrared spectrum after purification by gas chromatography.

O-tert-Butyl thiocarbamate (III). 5-*tert*-Butoxy-1,2,3,4-thiatriazole (0.82 g) was decomposed in ether solution (150 ml, containing 0.2 g of pyridine) at 32°C while a slow stream of hydrogen sulfide was passed through the solution. After 18 h the ether solution was concentrated to 5 ml, filtered from sulfur and evaporated to dryness. The residue was extracted with pentane (5 ml), and the remaining crystalline, colourless substance (yield 0.35 g) was recrystallized from cyclohexane. On heating above 100°C the substance sublimed without melting. (Found: C 45.11; H 8.29; N 10.27; S 24.22. Calc. for $C_5H_{11}NOS$: C 45.03; H 8.27; N 10.53; S 24.03).

5-Benzyloxy-1,2,3,4-thiatriazole (IV). A solution of benzyloxythiocarbonylhydrazine hydrochloride (4 g) in 0.1 N hydrochloric acid (500 ml) was cooled in ice, and a solution of sodium nitrite (1.45 g in 100 ml of water) was added slowly (during *ca.* 1 h) until a positive reaction with starch-iodide paper was obtained. The temperature was kept at 0—2°C during the addition; the solution had to be stirred energetically during the addition of the sodium nitrite in order to obtain a crystalline product, which was filtered off, washed with cold water, and dried *in vacuo* at 0°C over H_2SO_4 (m.p. 30—31°C, yield 86 %). According to analyses and infrared spectrum this was almost pure 5-benzyloxy-1,2,3,4-thiatriazole, $C_8H_7N_3OS$. Attempts to recrystallize it were unsuccessful because of decomposition.

Attempts to prepare benzyl cyanate and phenethyl cyanate. When a solution of the thiatriazole (IV) in ether was kept at room temperature there was a smooth evolution of nitrogen and sulfur separated. However, the oily residue obtained after evaporation of the ether contained no benzyl cyanate, as shown by the absence of an infrared band at *ca.* 1100 cm^{-1}. On attempts to distill the residue at 0.1 mm Hg (bath temperature 30—65°C) only a few percent passed over. This product was shown to be benzyl isocyanate by its infrared spectrum and by transformation into benzylurea (identified by comparison with authentic benzylurea[12—13]), with gaseous ammonia. The semi-solid residue from the distillation yielded on recrystallization from ethanol tribenzyl isocyanurate, m.p. 158—159°C (lit.[13] 157°C).

However, when the ether solution obtained by the decomposition of the thiatriazole was evaporated at a temperature not exceeding —25°C, the residue dissolved in CCl_4 (5 %) showed the infrared bands of a cyanate, however, with an intensity ratio larger than 1:1 of the 2250 and 1100 cm^{-1} band, which indicates the presence of some isocyanate. In solution (CCl_4 or CH_2Cl_2) the 1100 cm^{-1} band disappeared in the course of a few hours. When the above mentioned residue was heated to 0°C, an exothermic reaction took place, and according to the infrared spectrum the cyanate disappeared completely.

When hydrogen sulfide was passed through an ether solution (containing a little pyridine) of the decomposing thiatriazole,*O*-benzyl thiocarbamate [14] (benzylxanthamide), m.p. 61—62°C, could be isolated.

These results indicate that benzyl cyanate is formed during the decomposition of benzyloxythiatriazole but is too unstable to be isolated.

Similar results were obtained in attempts to prepare phenethyl cyanate. The thiatriazole (see below) was allowed to decompose in ether solution at room temperature for 18 h, and the ether was evaporated at low temperature. The infrared spectrum of the residue (5 % in CCl_4) exhibited strong bands at 2250 and 1100 cm^{-1}, characteristic of a cyanate. On attempted distillation only a small amount (0.15 g from 4.5 g) passed over at 80°C and 0.1 mm Hg. This was identified as phenethyl isocyanate.[15] The sirupy residue crystallized on standing. It was dissolved in the minimum amount of ethanol at 40°C. When the solution cooled, colourless, needle-shaped crystals separated. Yield 75 % (based on the hydrazide); m.p. 105—106°C after recrystallization from ethanol. According to analyses and infrared spectrum (strong band at 1700 cm^{-1}) this substance was trisphenethyl isocyanurate.

5-Phenethyloxy-1,2,3,4-thiatriazole was prepared from phenethyloxythiocarbonylhydrazine similarly to the preparation of the benzyl derivative. However, the hydrazide, which is very slightly soluble in hydrochloric acid, was dissolved in ether (7 g in 50 ml) and added to the hydrochloric acid, intimate mixing of the two phases being achieved by vigorous stirring. The thiatriazole was not isolated but extracted with ether, and the ether solution was dried with sodium sulfate at 0°C.

Cyclohexyl cyanate (V). *O*-Cyclohexyl thiocarbamate [16] (2 g) was dissolved in 10 ml of ether, magnesium sulfate (4 g) and mercury(II) oxide (5 g) were added, and the mixture was stirred at 0°C for 30 min. The mixture was filtered and the solid extracted with three 5 ml portions of ether. The combined extracts were concentrated *in vacuo* and the cyanate was distilled at about 40°C and 0.1 mm Hg. Yield 57 %. (Found: C 67.10; H 8.93; N 11.60. Calc. for $C_7H_{11}NO$: C 67.20; H 8.88; N 11.20). Cyclohexyl cyanate is a colourless liquid, exhibiting the characteristics of a secondary cyanate. When it was heated at ordinary pressure a colourless liquid with b.p. 82–84°C distilled off; this was identified as cyclohexene by its infrared spectrum. With hydrogen sulfide the cyanate forms *O*-cyclohexyl thiocarbamate.

(Tetramethylenedioxy)di[(thiocarbonylthio)acetic acid], $(-CH_2CH_2O-CS-SCH_2CO_2H)_2$ (VI). To a suspension of sodium hydride (26.4 g) in dimethyl sulfoxide (1500 ml) butane-1,4-diol (45 g) was added slowly with stirring. The mixture was heated to 75°C and stirred for 3 days. It was essential that the solution should assume a dark red-brown colour at this stage; if the colour failed to appear another 5 g of sodium hydride was added. After cooling of the solution the liquid was decanted from the sodium salt of the diol, the salt was taken up in dry ether (1000 ml), and carbon disulfide (76 g) was added dropwise to the vigorously stirred, cooled suspension at such a rate that the temperature was kept at 25–30°C. After the addition the solution was stirred for 6 h. Most of the ether was removed by decantation and the rest by evacuation of the flask. The salt was dissolved in water (300 ml), a neutralized solution of chloroacetic acid (95 g) in water (400 ml) was added, and the mixture was left for 24 h and filtered. Dilute hydrochloric acid was added slowly to the well stirred solution. When (VI) began to separate, the acid was added very slowly until crystallization began, then more rapidly until the solution was strongly acid (pH < 1). The solid was filtered off, washed with cold water and dried in a desiccator. Yield of crude (brownish-yellow) product 138 g (77 %). This was sufficiently pure for the following preparation but could be recrystallized from methanol-water (with active carbon). (Found: C 33.2; H 4.2; S 35.6, Calc. for $C_{10}H_{14}O_6S_4$: C 33.5; H 3.9; S 35.8. Eqw.wt. by titration 180, calc. 179).

(Tetramethylenedioxy)di(thiocarbonylhydrazine), $(-CH_2CH_2O-CS-NHNH_2)_2$ (VII). The acid (VI) (3.58 g) was dissolved in water by addition of the equivalent amount of sodium hydrogen carbonate. The filtered solution was cooled to 0°C and added dropwise to a solution of hydrazine hydrate (5 g) in water (40 ml) while the temperature was kept at *ca.* 20°C. The hydrazide separated as a colourless crystalline precipitate, which was filtered off, washed with cold water, and dried in a desiccator, Yield 2.2 g. M.p. 158–160°C (decomp.) after recrystallization from ethanol. (Found: C 30.38; H 6.07; N 23.30; S 26.65. Calc. for $C_6H_{14}N_4O_2S_2$: C 30.13; H 5.88; N 23.53; S 26.90).

5,5'-(Tetramethylenedioxy)di-1,2,3,4-thiatriazole (VIII). The hydrazide (VII) (2 g) was dissolved in 2 N hydrochloric acid and converted into the thiatriazole by addition of sodium nitrite. The thiatriazole separated as an almost white solid, which was filtered off, washed with water, and dried in a desiccator at 0°C. Yield 2.12 g (97 %). On heating it deflagrates at *ca.* 80°C (Kofler stage). The product is insoluble in ether, carbon tetrachloride, or carbon disulfide, but soluble in methylene chloride or chloroform. It decomposes rapidly, both in solution and in suspension (*e.g.* in ether) with the formation of sulfur. In the solid state it is rather stable at room temperature but starts to decompose at *ca.* 50°C. It could be recrystallized from methylene chloride. (Found: N 31.7. Calc. for $C_6H_8N_6O_2S_2$: N 32.3. No other analyses were performed because of the explosive decomposition of the substance on being heated).

O,O'-Tetramethylene bis(thiocarbamate), $(-CH_2CH_2O-CS-NH_2)_2$ (IX).. VIII (1 g) was dissolved in pure, dry methylene chloride (100 ml). A few drops of pyridine were added and hydrogen sulfide was led into the solution at room temperature for 18 h. The solution was evaporated to dryness and extracted with carbon disulfide to remove the sulfur formed. The residue was recrystallized from ethanol. Yield 0.51 g (64 %).

M.p. 174–175°C. (Found: C 34.88; H 5.88; S 30.50. Calc. for $C_6H_{12}N_2O_2S_2$: C 34.6; H 5.81; S 30.80).

Attempts to prepare tetramethylene dicyanate. Solutions of the thiatriazole(VIII) in chloroform or methylene chloride (*ca.* 5 %) decomposed in the course of 18 h at room temperature. The solutions showed infrared bands at 2250 cm^{-1} and 1100 cm^{-1} with the intensity ratio 1:1, characteristic of a cyanate, but a strong band at 1700 cm^{-1} indicated beginning polymerisation. On evaporation an oil was left, which in the course of one day became hard and glassy. It was insoluble even in dimethyl sulfoxide, acetone or conc. sulfuric acid and did not melt below 300°C.

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