

The synthesis of compound 2 and of the *cis* endo isomer 3 has been accomplished as follows:

3-Exoamino-2-endohydroxybornane. 2-Endo-hydroxy-3-hydroxyiminobornane* (1) [m.p. 174–176°; $[\alpha]_D^{25} +181.5^\circ$ (c 0.96; ethanol); *m/e* 183 (M^+) ($C_{10}H_{17}NO_2$); Found: C 65.6; H 9.4; N 7.5. $C_{10}H_{17}NO_2$ requires C 65.5; H 9.4; N 7.6], was reduced with Na-amalgam (2%) in water at 70° for 4 h. Carbon dioxide was passed through the solution during the reaction. After working up the reaction mixture the acid soluble fraction gave an amino alcohol mixture in 82% yield containing (NMR) 2 and 3 in a ratio of ca. 3:1. Steam distillation



1. $RR_1 = NOH$
2. $R = NH_2, R_1 = H$
3. $R = H, R_1 = NH_2$

removed the *cis* isomer (3) and after addition of dilute NaOH and subsequent ether extraction the residue afforded the *trans* isomer (2). [M.p. 216–218° (recrystallized from hexane); *m/e* 169 (M^+) ($C_{10}H_{19}NO$); NMR ($CDCl_3 + D_2O$) δ (ppm, TMS): 3.78 (br d $J = 3.5$ Hz, 1 H, $CH-OH$), 2.51 (br d $J = 3.5$ Hz, 1 H, $CH-NH_2$), 1.02 (s, 3 H, CH_3), 0.87 (s, 6 H, CH_2 , CH_3). *Hydrobromide*: [M.p. 298°; $[\alpha]_D^{25} +21.8^\circ$ (c 0.62; ethanol). Found: C 48.1; H 7.9; Br 32.2; N 5.6. $C_{10}H_{20}BrNO$ requires C 48.0; H 8.1; Br 31.9; N 5.6].

3-Endoamino-2-endohydroxybornane. The *cis* isomer (3) was obtained from the distillate by the same procedure and gave NMR data in complete agreement with those published¹ [m.p. 170–172° (lit.² 170–171°)].

1. Becket, A. H., Ngiam Tong Lan and McDonough, G. R. *Tetrahedron* **25** (1969) 5689.
2. Chittenden, R. A. and Cooper, G. H. *J. Chem. Soc. C* **1970** 49.
3. Thorén, S. *Acta Chem. Scand.* **24** (1970) 93, and references cited therein.

Received June 5, 1970.

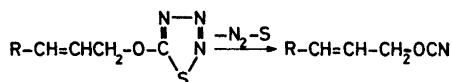
* The parent ketol was prepared from (+)-camphor; see Ref. 3. Melting points are uncorrected.

Formation of 1-Methylallyl and 2-Butenyl Isocyanate from Crotyl Bromide and Silver Cyanate

CARSTEN CHRISTOPHERSEN and ARNE HOLM

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

In a previous paper, attempts to prepare 2-alkenyl cyanates from 5-(2-alkenyl-oxy)-1,2,3,4-thiazotriazoles were described.¹ Although alkyl cyanates are formed when 5-alkoxy-1,2,3,4-thiazotriazoles decompose at room temperature, only isocyanates were isolated from the 5-(2-alkenyl-oxy)-1,2,3,4-thiazotriazoles:



rapid isomerisation $\rightarrow CH_2=CH-CH(R)-N=C=O$

The 2-alkenyl isocyanates were identified by comparison with authentic material, the formation of which, from "crotyl bromide" and silver cyanate, we wish to report here.

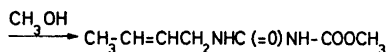
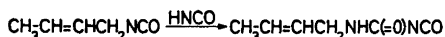
Although 2-butenyl bromide and 1-methylallyl bromide may both be obtained in a pure state, they are converted into an equilibrium mixture on standing at room temperature; thus the compound "crotyl bromide" is reported to consist of approximately 85% 2-butenyl bromide in equilibrium with 15% 1-methylallyl bromide.^{2,3}

In our experiments "crotyl bromide" and silver cyanate in diethylether gave a mixture of the two possible isocyanates in 84% yield. ¹H NMR spectroscopy proved it to comprise 70% 2-butenyl isocyanate and 30% 1-methylallyl isocyanate. The isocyanates were separated by preparative GLC and identified by elemental analysis and by IR and ¹H NMR spectroscopy.

It has been demonstrated that the cyanate ion is ambident,⁴ and it may therefore be assumed that some 2-butenyl and 1-methylallyl cyanate should be formed in the reaction between "crotyl bromide" and silver cyanate; however neither of these products has been observed. So far, this

result corroborates the hypothesis cited above¹ that 2-alkenyl cyanates rapidly isomerize to the isocyanates.

Only 2-butenyl isocyanate has previously been described.⁶ Berthold treated potassium cyanate in methanol with crotyl bromide and obtained, by distillation, 2-butenyl isocyanate in 16.5 % yield, together with methyl 4-(2-butenyl)allophanate. Products derived from the 1-methylallyl isomer were not reported. To account for the formation of methyl 4-(2-butenyl)allophanate, it was assumed that methyl 2-butenyl ether and hydrobromic acid were formed from the reaction between crotyl bromide and methanol. Further it was proposed that the cyanic acid liberated from the potassium cyanate and hydrobromic acid was capable of reacting with 2-butenyl isocyanate:



However, chemical evidence for the formation of the intermediate carbamoyl isocyanate, and for the formation of the ether, was not given.

When re-investigating this reaction we also obtained methyl 4-(2-butenyl)allophanate but were unable to obtain 2-butenyl isocyanate. A closer investigation of the residue left after distillation of the solvent revealed the presence of four different products. Besides methyl 4-(2-butenyl)allophanate (38 %), methyl carbamate (13 %), methyl allophanate (14 %), and cyanuric acid (6%) were also isolated; this accounts for 71 % of the yield based upon potassium cyanate. Methyl carbamate and methyl allophanate are formed from the well known reactions of one mole of methanol with, respectively, one or two moles of cyanic acid; cyanuric acid is the trimerisation product of cyanic acid.

GLC analysis of the methanol distillate showed the presence of both 1-methylallyl methyl ether and 2-butenyl methyl ether, thus confirming Berthold's assumption. ¹H NMR spectroscopy on the same distillate revealed additional signals from unidentified substances possessing 2-butenyl and 1-methylallyl structures.

Finally, we wish to point out that, although methyl 4-(2-butenyl)allophanate

may be formed according to the above equation, such a reaction has, to the best of our knowledge, not been reported. Since methyl carbamate has been isolated, an alternative explanation is a reaction between methyl carbamate and 2-butenyl isocyanate. Under neutral conditions this reaction is slow, but it is promoted effectively by the presence of acid.⁶ Since it has been assumed that hydrogen bromide is formed during the reaction, such an effective catalyst may be present. However, to distinguish between these two hypotheses a thorough investigation is necessary.

Experimental. The proton magnetic resonance spectra were obtained using a Varian A-60 A instrument (60 Mc/s and with TMS as internal standard), and the infrared spectra on a Perkin-Elmer 337 Grating Infrared Spectrophotometer operated to be accurate to about $\pm 5 \text{ cm}^{-1}$ over 2000 cm^{-1} and $\pm 2 \text{ cm}^{-1}$ below 2000 cm^{-1} . The gas chromatographic separations were performed on a Perkin-Elmer instrument F 21 "Präparativer Gaschromatograph".

Reaction between crotyl bromide and silver cyanate in diethyl ether. Silver cyanate (0.11 mol, 16.5 g) was suspended in dry ether (50 ml) and "crotyl bromide" (commercially available from "Fluka" (purum)) (0.10 mol, 13.5 g) was added dropwise with stirring for a period of 15 min, and the stirring continued for further 2 h. After filtering, ether was removed by distillation at atmospheric pressure to leave 8.5 g of a mixture of 2-butenyl- and 1-methylallyl isocyanate. ¹H NMR spectroscopy revealed that the mixture contained 67 % 2-butenyl isocyanate, 28 % 1-methylallyl isocyanate and 5 % ether; these figures refer to an overall 84 % yield of the isocyanates.

The components may be separated by distillation, but are conveniently obtained pure by preparative gas chromatography. The separations were made on a polypropylene glycol column maintained at 70°C (20 % on Chromosorb A 45-60 mesh, 3/8" × 1.8 m, 400 ml N₂/min, injection port temperature 140°C). The following retention times were observed: Ether 1.2 min, 1-methylallyl isocyanate 5.6 min, and 2-butenyl isocyanate 12.7 min. In each cycle 0.3-0.6 ml of the mixture was injected.

2-Butenyl isocyanate, b.p. 116°C (Found: C 62.05; H 7.22; N 14.52. Calc. for C₅H₇NO: C 61.84; H 7.27; N 14.42). ¹H NMR spectrum (CCl₄) with signals from 8.36 to 8.21 (complex, CH₃), from 6.29 to 6.14 (complex, CH₂), and from 4.76 to 3.94 τ (complex, CH=CH). The IR spectrum (CCl₄) exhibited a very strong

absorption at 2264 cm^{-1} , assigned to the isocyanate group.

1-Methylallyl isocyanate, b.p. 96°C (Found: C 61.40; H 7.26; N 14.40. Calc. for $\text{C}_5\text{H}_7\text{NO}$: C 61.84; H 7.27; N 14.42). ^1H NMR spectrum with signals at 8.65 (doublet, CH_3), 5.90 (quintet with further splitting, CH), and from 5.01 to 3.88 τ (complex, $\text{CH}_2=\text{CH}$). The IR spectrum (CCl_4) exhibited the very strong isocyanate absorption at 2267 cm^{-1} .

It should be noted that the boiling point found for 2-butenyl isocyanate, 116°C , is considerably higher than recorded by Berthold, 93°C .⁵

Reaction between crotyl bromide and potassium cyanate in methanol. Potassium cyanate (1 mol) and "crotyl bromide" (1 mol) were left in methanol overnight after which, following Berthold,⁵ the mixture was distilled to remove the alcohol. The methanol distillate was analysed gas chromatographically and found to contain 2-butenyl methyl ether and 1-methylallyl methyl ether, identified by comparison with an authentic mixture of these ethers. (This mixture was prepared from crotyl bromide and sodium methoxide in methanol). The semi-solid left from the methanol distillation was extracted with 300 ml of ether (extract I), and then with 200 ml of water ($40-50^\circ\text{C}$) to remove potassium bromide. A colourless solid, corresponding by elemental analysis to ca. $\text{C}_6\text{H}_8\text{N}_2\text{O}_2\text{K}$ was left (11.7 g; yield 20 %, based upon potassium cyanate). A product free of potassium was obtained on dissolving in hot water, adding hydrochloric acid until distinctly acid, and cooling rapidly. A white solid was obtained (70 % yield) which, after recrystallization from water, gave the analysis $\text{C}_9\text{H}_{12}\text{N}_2\text{O}_2$ (Found: C 28.75; H 3.23; N 29.75. Calc. for $\text{C}_9\text{H}_{12}\text{N}_2\text{O}_2$: C 28.73; H 3.22; N 29.76). Heating this substance to approximately 150°C gave rise to two components, one of which sublimed. Comparison of the IR spectra of these products with those of authentic samples identified the sublimate as methyl allophanate and the residue as cyanuric acid. Analysis proved that one mole of $\text{C}_9\text{H}_{12}\text{N}_2\text{O}_2$ gave rise to one mole of methyl allophanate and two moles of cyanuric acid on heating. The IR spectrum of $\text{C}_9\text{H}_{12}\text{N}_2\text{O}_2$ showed the superimposed absorption bands of methyl allophanate and cyanuric acid. Repeated recrystallization, however, resulted only in the isolation of cyanuric acid,

furthermore, we did not succeed in preparing a molecular complex with the composition $\text{C}_9\text{H}_{12}\text{N}_2\text{O}_2$ from the authentic materials. The isolation of a product corresponding to $\text{C}_9\text{H}_{12}\text{N}_2\text{O}_2$ therefore seems to be coincidental. Ether extract I was evaporated to dryness leaving a semisolid product. On distillation at 90°C and 0.5 mm Hg, methyl carbamate (10.0 g, 13 %) was obtained, and methyl 4-(2-butenyl)allophanate (32.7 g, 38 % based upon potassium cyanate) was left in the distillation flask. These substances were identified by comparing their IR spectra and melting points with those of authentic materials.

N-(2-Butenyl)-N'-phenyl urea. 2-Butenyl isocyanate (0.01 mol, 0.97 g) was added to aniline (0.0108 mol, 1.0 g) in benzene (10 ml) and refluxed for 15 min. Hexane (30 ml) was added and after cooling the precipitate was isolated by filtration and washed twice with 15 ml of 1:3 benzene:hexane followed by hexane. Yield 97 %, m.p. $129.5-30^\circ\text{C}$ from an 1:1 ethanol:water mixture. (Found: C 69.82; H 7.49; N 14.77. Calc. for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}$: C 69.44; H 7.42; N 14.73). The ^1H NMR spectrum confirmed the assumed structure.

N-(Methylallyl)-N'-phenyl urea. This substance was prepared in the same way as *N*-(2-butenyl)-*N'*-phenyl urea, except that it was isolated by evaporation of the benzene solution and then washed with 25 ml of 1:5 benzene:hexane. Yield 92 %, m.p. $151-52^\circ\text{C}$ from an 1:1 ethanol:water mixture. (Found: C 69.70; H 7.38; N 14.71. Calc. for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}$: C 69.44; H 7.42; N 14.73). The ^1H NMR spectrum confirmed the assumed structure.

1. Christophersen, C. and Holm, A. *Acta Chem. Scand.* **24** (1970) 1512.
2. a) England, B. D. *J. Chem. Soc.* **1955** 1615; b) Kharasch, M. S., Margolis, E. T. and Mayo, F. R. *J. Org. Chem.* **1** (1937) 393; c) Winstein, S. and Young, W. G. *J. Am. Chem. Soc.* **58** (1936) 104.
3. DeWolfe, R. H. and Young, W. G. *Chem. Rev.* **56** (1956) 753.
4. Holm, A. and Wentrup, C. *Acta Chem. Scand.* **20** (1966) 2123.
5. Berthold, R. *Chem. Ber.* **90** (1957) 2743.
6. Blohm, H. W. and Becker, E. I. *Chem. Rev.* **51** (1952) 471.

Received May 28, 1970.