Alkyl Cyanates

XIV. Isomerization of Allylic Cyanates and Allylic Thionoderivatives
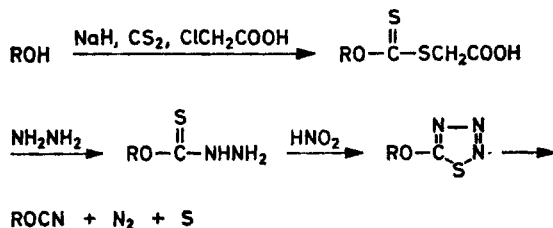
CARSTEN CHRISTOPHERSEN and ARNE HOLM

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

5-(2-Alkenyloxy)-1,2,3,4-thiatriazoles decompose in solution with formation of nitrogen, sulfur, and 2-alkenyl isocyanates. Alkenyl cyanates were not isolated. O-(2-Alkenyl) thiocarbamates react with silver(I) oxide likewise to give 2-alkenyl isocyanates. These results are explained by assuming a primary formation of 2-alkenyl cyanate followed by rapid isomerization to 2-alkenyl isocyanate *via* a cyclic transition state. The thiatriazoles are formed from compounds of the general type $RO-C(=S)-X$ where R is allylic. These compounds are also labile, undergoing isomerization to $RS-C(=O)-X$ *via* a cyclic transition state. This reaction was observed in the temperature range 0°C to 140°C, and the rate of isomerization was found to be dependent on X. With different X the approximate order of stability is: $-S^- \gg -NHNH_2 \sim -NH_2 > -S$-alkyl$> -SCH_2COOH \sim -SCH_2COOEt \sim 4\text{-}ClC_6H_4O - \sim -NHNH_3^+$.

T he method generally used in the preparation of aliphatic cyanates is conversion of an alcohol *via* the corresponding [(alkoxythiocarbonyl)thio]acetic acid and alkoxythiocarbonylhydrazine to the 5-alkoxy-1,2,3,4-thiatriazole, which decomposes at room temperature giving alkyl cyanate.[1]

It has now been found that allyl alcohol also reacts in this manner giving a satisfactory yield of [(allyloxythiocarbonyl)thio]acetic acid (I). However,

$$ROH \xrightarrow{\text{NaH, CS}_2,\ \text{ClCH}_2\text{COOH}} RO-\overset{\overset{\text{S}}{\|}}{C}-SCH_2COOH$$

$$\xrightarrow{\text{NH}_2\text{NH}_2} RO-\overset{\overset{\text{S}}{\|}}{C}-NHNH_2 \xrightarrow{\text{HNO}_2} RO-\overset{\overset{\text{N}-\text{N}}{\|\quad\|}}{\underset{\text{S}}{C}}N\cdot \longrightarrow$$

$$ROCN\ +\ N_2\ +\ S$$

Scheme 1

on heating to approximately 60°C it isomerized in an exothermic reaction yielding {[(allylthio)carbonyl]thio}acetic acid (II):

$$CH_2=CH-CH_2O-\overset{\overset{S}{\|}}{C}-SCH_2COOH \longrightarrow CH_2=CH-CH_2S-\overset{\overset{O}{\|}}{C}-SCH_2COOH$$

I   II

Although the allyloxythiocarbonylhydrazine was also able to isomerize to the corresponding *S*-allyl derivative, the unrearranged product could be converted to 5-allyloxy-1,2,3,4-thiatriazole with due care. At room temperature 5-allyloxy-1,2,3,4-thiatriazole decomposed with the usual formation of sulfur and nitrogen but, instead of the expected allyl cyanate, only allyl isocyanate was isolated. Since both the *O* to *S* and *O* to *N* rearrangements were likely to proceed *via* cyclic transition states we were encouraged to investigate substituted allylic derivatives in order to follow the changes in the allylic system associated with the isomerization. For the sake of convenience the different classes of compounds will be discussed separately.

Thionocarbonates. Allylic rearrangement of thionocarbonates has been described by other authors. Smith,[2] who discovered the isomerization of allylic thionobenzoates, studied the reaction in a variety of solvents. The kinetics were of first order and the products in agreement with those expected from a cyclic transition state. He found that the isomerization occurred only ten times faster in acetic acid than in cyclohexane and attributed this small solvent effect to a small difference in charge separation between ground state and transition state. McMichael[3] measured the secondary α- and γ-deuterium isotope effects on the cyclic intramolecular rearrangement of *O*-allyl thiobenzoate. His results strongly support the conclusions reached by Smith and he concluded that the isotope effects observed were consistent with a transition state which more closely resembled the reactants than the products. Garmaise, Uchiyama and McKay[4] investigated a series of allylic aryl thionocarbonates and found the allylic rearrangement to be so facile that they were unable to isolate the intermediate thionocarbonates:

$$4-Cl-C_6H_4O-\overset{\overset{S}{\|}}{C}-Cl + HO-\overset{\overset{CH_3}{|}}{CH}-CH=CH_2 \longrightarrow$$

$$4-Cl-C_6H_4O-\overset{\overset{O}{\|}}{C}-SCH_2-CH=CH-CH_3$$

In our experiments (I) was isolated as a crystalline substance which could be purified, without isomerization, by recrystallization. On standing at room temperature or on heating, however, isomerization took place. This was demonstrated by infrared (IR) and proton magnetic resonance (NMR) spectroscopy. In carbon tetrachloride compound (I) exhibited two strong bands at 1721 cm^{-1} and 1056 cm^{-1}. The first absorption is due to the carboxylic

C=O group and the second is assigned to the C=S stretching vibration which is normally observed from 1200—1050 cm^{-1}. [5a,6] Compound II showed, in accordance with the proposed structural changes, carbonyl absorptions at 1724 cm^{-1} and 1658 cm^{-1} and absence of the strong absorption at 1056 cm^{-1}. Furthermore, strong absorptions appear about 900 cm^{-1} in the rearranged product and are probably due to skeletal stretching vibrations of the —S—C(=O)—S— system. The C—S stretching vibration normally appears as a weak absorption in the range 700—600 cm^{-1}.[5b] In $(C_4H_9S)_2C=O$, however, the C—S absorption band is raised above the normal limits and appear as a strong absorption at 870 cm^{-1}.[7] The IR spectrum of II obtained in potassium bromide showed doubling of the C=O absorptions and of some of the other bands. This may be due to molecular association or similar well known phenomena.[8]

[(2-Butenyloxythiocarbonyl)thio]acetic acid was prepared in the same way as (I) but was found to contain 15—25 % of the isomerization product {[(1-methylallylthio)carbonyl]thio}acetic acid (Scheme 2 with X = —SCH_2COOH). NMR Spectroscopy was particularly useful in following this isomerization and the other isomerizations described below. Thus, when an O-(2-butenyl) group is converted to an S-(1-methylallyl) group, characteristic changes of the chemical shifts of the CH_2 and CH_3 protons are observed. This is illustrated in Fig. 1 and Fig. 2 for 2-butenyloxythiocarbonylhydrazine and its isomerization product [(1-methylallylthio)carbonyl]hydrazine.

[(1-Methylallyloxythiocarbonyl)thio]acetic acid rearranged to {[(2-butenyl-thio)carbonyl]thio}acetic acid so rapidly that only this compound could be isolated. [(2-Methylallyloxythiocarbonyl)thio]acetic acid could, like the allyl
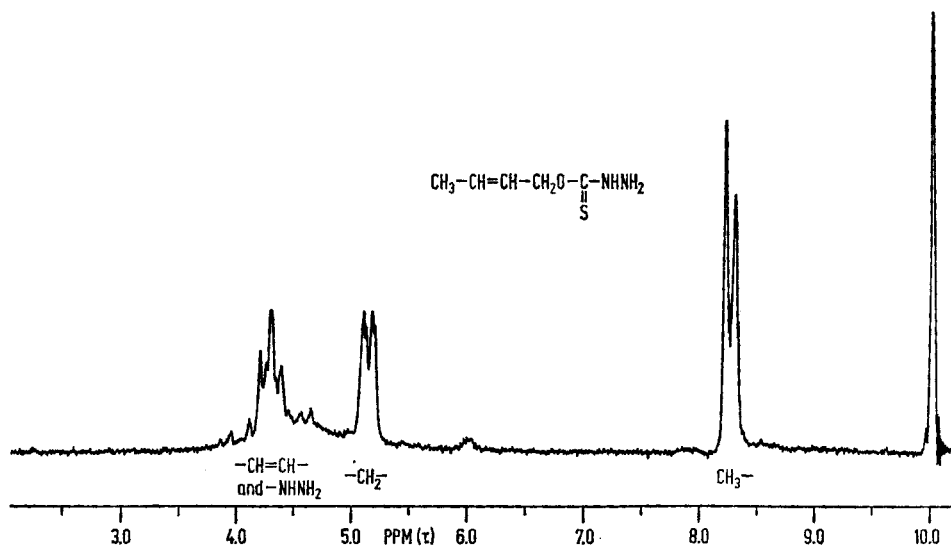
Fig. 1. NMR spectrum of 2-butenyloxythiocarbonylhydrazine.

$$CH_2=CH-CHS-C-NHNH_2$$
$$CH_3 \quad O$$
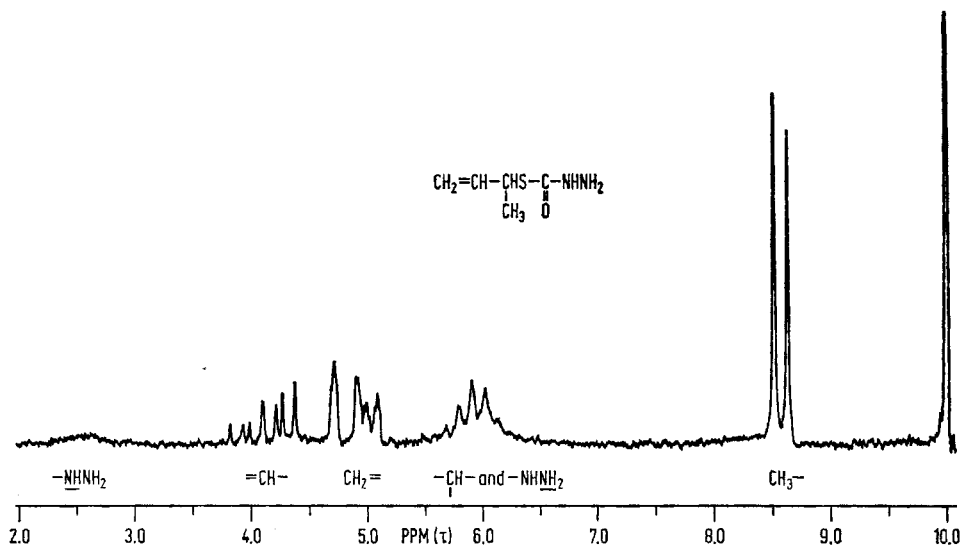
Fig. 2. NMR spectrum of [(1-methylallylthio)carbonyl]hydrazine.

isomer, be isolated in an unrearranged state but isomerized on heating to {[(2-methylallylthio)carbonyl]thio}acetic acid.

[(3-Phenylallyloxythiocarbonyl)thio]acetic acid (III) was isolated as an oil which could not be obtained in a pure state. On standing a crystalline product slowly separated which, according to IR, NMR, and elemental analysis, proved to be the *S*-(3-phenylallyl) isomer (IV). This rearrangement thus probably proceeds *via* a non-cyclic transition state:

$$C_6H_5-CH=CH-CH_2O-\overset{\overset{\displaystyle S}{\|}}{C}-SCH_2COOH \longrightarrow C_6H_5-CH=CH-CH_2S-\overset{\overset{\displaystyle O}{\|}}{C}-SCH_2COOH$$

III   IV
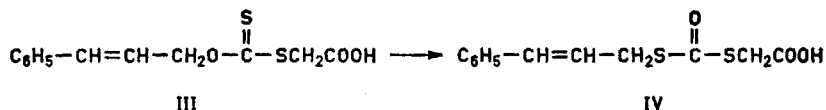
The reaction was not examined further.

Since, as illustrated above, [(2-alkenyloxythiocarbonyl)thio]acetic acids are generally unsuitable for the preparation of allylic cyanates we investigated the possibility of using *O*-alkenyl-*S*-methyl dithiocarbonates ($CH_3SC(=S)O - CH(R^1) - CH = CHR^2$) which have been described by Taguchi *et al.*[9] These esters were more stable than the [(2-alkenyloxythiocarbonyl)thio] acetic acids and could be purified by distillation *in vacuo* at 40°C without isomerization. Taguchi found that they underwent isomerization under these conditions but experimental details are not given. The methyl esters, however, reacted too slowly with hydrazine to be of preparative value.

Alkenyloxythiocarbonylhydrazines. Alkenyloxythiocarbonylhydrazines could be conveniently prepared directly from sodium *O*-alkenyl dithiocarbonates and hydrazine:

$$RO-\overset{\overset{S}{\|}}{C}-SNa + NH_2NH_2 \longrightarrow RO-\overset{\overset{S}{\|}}{C}-NHNH_2 + NaSH$$

The sodium *O*-alkenyl dithiocarbonates are stable towards isomerization at room temperature but are rather easily oxidized by air. Alkenyloxythiocarbonylhydrazines are far more stable towards isomerization than the [(2-alkenyloxythiocarbonyl)thio]acetic acids and were found only to isomerize slowly at room temperature. 3-Phenylallyloxythiocarbonylhydrazine was unchanged after several months at room temperature. On heating to 100°C 1-methylallyloxythiocarbonylhydrazine isomerized to [(2-butenylthio)carbonyl] hydrazine in approximately 4 min whereas the 2-butenyl derivative did not isomerize noticeably under these conditions. On heating to 140°C, however, an exothermic reaction took place with formation of [(1-methylallylthio) carbonyl]hydrazine (Scheme 2 with X = −NHNH$_2$). The isomerization of the 3-phenylallyl derivative and the isomerization products were not examined more closely.

Discussion of the isomerization of allylic thionoderivatives. On grounds of the product formation, described above, and kinetic measurements [2,3] we conclude that compounds of the general type RO−C(=S)−X, where R is allylic, isomerize to RS−C(=O)−X *via* a cyclic transition state:
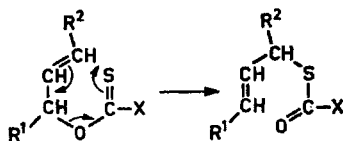
Scheme 2

The compounds which have been investigated are with X = −S-alkyl, −SCH$_2$COOH, −SCH$_2$COOEt, −C$_6$H$_5$,[2] 4-ClC$_6$H$_4$O−,[4] −NH$_2$, −NHNH$_2$, −NHNH$_3{}^+$, and with R = allyl, 1-methylallyl, 2-butenyl, and 2-methylallyl. Compounds with X = −S$^−$ have not been observed to undergo isomerization. [(3-Phenylallyloxythiocarbonyl)thio]acetic acid (X = −SCH$_2$COOH, R = C$_6$H$_5$CH=CH−CH$_2$−) isomerizes to {[(3-phenylallylthio)carbonyl]thio}acetic acid, probably *via* a non-cyclic transition state as described above. Other 3-phenylallyl derivatives presumably isomerize in a similar manner.

The lability of [(2-alkenyloxythiocarbonyl)thio]acetic acids (X = −SCH$_2$COOH) in comparison with *S*-alkyl *O*-alkenyl dithiocarbonates (X = −S-alkyl) suggested that the cyclic isomerization rate is influenced either by inductive effects or by acid catalysis or by both. Smith,[2] however, found from kinetic measurements that the isomerization of allylic thionobenzoates were only little affected by the solvent (CH$_3$COOH, CH$_3$CN, (CH$_3$)$_2$CO, C$_6$H$_5$Cl, (CH$_2$)$_4$O, C$_6$H$_{12}$). We can confirm this on a qualitative basis. Solutions of *S*-methyl *O*-allyl dithiocarbonate in acetonitrile, formic acid, acetic acid, and trideuteriomethanol/conc. hydrochloric acid ratio 5/1 were left for 24 h at room temperature. No appreciable change was found in the NMR spectra. These results suggest that inductive effects are significant. This can also be

compared with the rapid isomerization of O-(1-methylallyl) O-(4-chlorophenyl) thiocarbonate $(X = 4\text{-}ClC_6H_4O-).[4]$ Likewise, the ethyl ester of [(2-butenyl-oxythiocarbonyl)thio]acetic acid $(X = -SCH_2COOEt)$ could be isolated with only a small amount of the isomerization product, but after standing at room temperature for $5\frac{1}{2}$ h, 45 % isomerization had taken place.

These observations suggested that the relatively stable hydrazines should isomerize when converted to hydrazinium salts. This was confirmed by dissolving 2-butenyloxythiocarbonylhydrazine in deuterium oxide by means of a few drops of concentrated hydrochloric acid. The NMR spectrum revealed that complete isomerization had taken place in the course of 40 min. As expected, O-allyl thiocarbamate, $CH_2 = CHCH_2OC(S)NH_2$, prepared from [(2-allyloxythio-carbonyl)thio]acetic acid and ammonia, was also relatively stable. Solutions of $CH_2 = CH - CH_2 - OC(=S) - X$ in carbon tetrachloride (10 %) were kept at 20°C and the NMR spectrum recorded at given intervals. With $X = -SCH_3$ or $-SCH_2COOH$, 3 % and 24 % isomerisation had taken place after 7 days, and 10 % and 75 % isomerisation after 30 days, respectively. With $X = -NH_2$ only $2-3$ % isomerisation was observed in 30 days. With $X = -NHNH_2$ no isomerisation occurred in 30 days.

It is thus apparent that the electron density at the carbonyl group significantly affects the isomerization rate. The compounds $RO - C(=S) - X$, where R is allylic, can be arranged after decreasing stability: $X = 1)$ $-S^-$ $\gg NHNH_2$ $\sim -NH_2$ $> -S\text{-alkyl}$ $>2)$ $-SCH_2COOH \sim -SCH_2COOEt \sim 4\text{-}ClC_6H_4O - \sim -NHNH_3^+$. It is noted that the isomerization rate increases with increasing electron withdrawing power of the substituent X. The classification into two groups has some importance in considering the synthesis of this type of compounds. Thus the compounds in group 1) may be isolated without contamination of the isomerization products whereas the compounds in group 2) may contain an appreciable amount of the isomerization products or may be isolated only as the isomerized products. Despite the lack of exact measurements it seems safe to conclude that the effects of the substituents on the isomerization rate are in accordance with the development of a small positive charge in the transition state at C(1) in the allyl chain:

$$
\begin{array}{c}
\overset{(2)}{} \overset{CH_2}{} \\
\overset{CH}{} \overset{(3)}{} \overset{S}{} \\
\overset{\delta \oplus}{} \overset{CH_2^{(1)}}{} \overset{\|}{} \\
\overset{O}{} C-X
\end{array}
$$
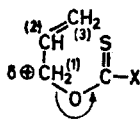
Substitution of a proton in the allyl chain by a methyl group at C(1) should, because of its inductive effect, accelerate the isomerization. A methyl group at C(3) will also stabilize the transition state although to a lesser degree and a methyl group at C(2) should exert only a slight effect on the rate. This is what is observed, and our conclusions are in agreement with those of McMichael[3] and of Smith.[2]

5-(2-Alkenyloxy)-1,2,3,4-thiatriazoles. The alkyl analogues are prepared by adding a sodium nitrite solution to a solution of the alkoxythiocarbonyl-hydrazine in hydrochloric acid (Scheme 1). The rapid isomerization of the 2-alkenyloxythiocarbonylhydrazines in acid necessitates some precautions and

hydrochloric acid was therefore slowly added to a mixture of the hydrazide and sodium nitrite in water. In spite of this precaution NMR spectroscopy revealed the presence of some (2-alkenylthio)carbonyl azide formed from the isomerized hydrazide:

$$CH_3CH=CH-CH_2O-\overset{\overset{\displaystyle S}{\|}}{C}-NHNH_2 \xrightarrow[\text{rapid isomerization}]{H^+}$$

$$CH_2=CH-\underset{\underset{\displaystyle CH_3}{|}}{CHS}-\overset{\overset{\displaystyle O}{\|}}{C}-NHNH_3^+ \xrightarrow{HNO_2} CH_2=CH-\underset{\underset{\displaystyle CH_3}{|}}{CHS}-\overset{\overset{\displaystyle O}{\|}}{C}-N_3$$
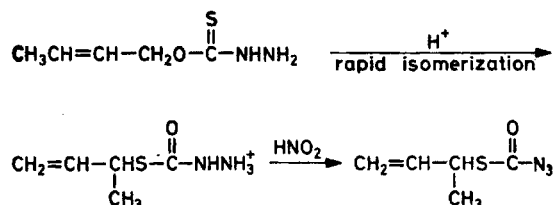
Generally the amount of azide formed did not exceed 10 % of the total amount of alkenyloxythiocarbonylhydrazine, but exact data are not known at present. Since the presence of this azide could interfere with the analysis of the decomposition products of the alkenyloxythiatriazoles a preliminary investigation of the properties of these azides was undertaken. They were found to decompose rapidly in ether solution, even at 0°C, with the formation of nitrogen. This high rate is not due to the presence of a double bond in allylic position since it was also found that (propylthio)carbonyl azide decomposed rapidly. Lwowsky,[11] in particular, has undertaken investigations of the decomposition of the corresponding ethoxycarbonyl azide. It was found that a nitrene was formed:

$$RO-\overset{\overset{\displaystyle O}{\|}}{C}-N_3 \longrightarrow RO-\overset{\overset{\displaystyle O}{\|}}{C}-\ddot{N} + N_2$$

Whether the decomposition of (alkythio)carbonyl azide takes place with the formation of a nitrene or not is not known at present but the essential fact in this respect is that an alkyl cyanate or an alkyl isocyanate is not formed. This was shown by means of comparative gas chromatography. An investigation of the reaction is in progress in this laboratory.

Except for the 3-phenylallyl derivative the alkenyloxythiatriazoles were not isolated due to the instability of these compounds but ether solutions were used directly for the further preparation of alkenyl cyanates. The 3-phenylallyl isomer was sufficiently stable to be isolated and was investigated by means of NMR spectroscopy; the chemical shifts found are in accordance with the assumed structure.

Isomerization of 2-alkenyl cyanates to 2-alkenyl isocyanates. Alkoxythiatriazoles decompose completely in the course of approximately 16 h[1] at room temperature with the formation of alkyl cyanates in good yields (see Scheme 1). When allyloxy-, 1-methylallyloxy-, 2-butenyloxy-, and 3-phenylallyloxythiatriazole decomposed at room temperature in ether, the normal evolution of nitrogen and precipitation of sulfur was observed. Infrared spectroscopy on the isolated products showed, however, that the substances formed were isocyanates and not cyanates. It was not possible to show the presence

of alkenyl cyanate in any stage of the decomposition although cyanates may easily be detected due to a strong $C-O$ absorption around 1100 cm^{-1}.[12]

In an earlier paper one of us showed that alkyl cyanates are formed in the reaction between O-alkyl thiocarbamate and silver(I) oxide at 0°C in ether or carbon tetrachloride:[18]

$$RO-\overset{\overset{S}{\|}}{C}-NH_2 + Ag_2O \longrightarrow ROCN + Ag_2S + H_2O$$

This reaction is very fast, being completed in 5 – 10 min. Allyloxythiocarbonyl-amine, prepared from [(allyloxythiocarbonyl)thio]acetic acid and ammonia, was submitted to this treatment, allowing a reaction time of 5 min in carbon tetrachloride. The solution was rapidly distilled in high vacuum at 0°C and the infrared spectrum of the distillate recorded immediately. Even under these conditions the presence of a cyanate could not be shown. On the contrary, a very intense absorption at 2250 cm^{-1} showed that the product formed was the isocyanate. There is no obvious reason to believe that a cyanate should not have been present as an intermediate in this reaction, but its isomerization rate is obviously very high, far exceeding that of the saturated aliphatic cyanates. Thus, a 2 % methyl cyanate solution in ether can be kept at room temperature for about 1 h with only little isomerization and isobutyl cyanate was heated to ca. 130° for 8 min before isomerization to isobutyl isocyanate was nearly complete.[1] This difference in isomerization rate suggests an isomerization mechanism for 2-alkenyl cyanates different from that of the alkyl cyanates. One of the possible mechanisms is an allylic rearrangement via ionization:

$$CH_2=CH-CH_2OCN \rightleftharpoons \left[CH_2=CH-CH_2^+ + OCN^- \right]$$

$$\longrightarrow CH_2=CH-CH_2-N=C=O$$
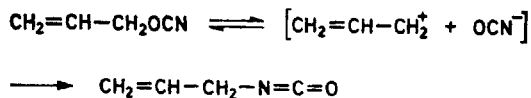
This mechanism necessitates formation of the same isomers from 1-methylallyl and 2-butenyl cyanate although not necessarily in the same amount.[14] By means of gas chromatography[17] it was found that 1-methylallyl cyanate (from 5-(1-methylallyloxy)-1,2,3,4-thiatriazole) yielded exclusively 2-butenyl iso-cyanate and that 2-butenyl cyanate (from 5-(2-butenyloxy)-1,2,3,4-thiatriazole) exclusively gave 1-methylallyl isocyanate. These results are consistent with a six-membered cyclic transition state and are not compatible with a preliminary ionization or a radical mechanism. The cyclic mechanism is so energetically favourable that even the isomerization of 3-phenylallyl cyanate proceeds via this transition state with formation of 1-phenylallyl isocyanate:

$$\longrightarrow CH_2=CH-\overset{\overset{R}{|}}{C}H-N=C=O$$
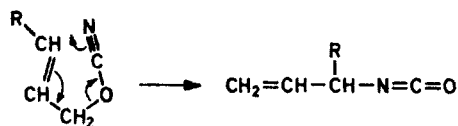
If the reaction had taken place *via* an ionic mechanism 3-phenylallyl isocyanate would have been the result.

The cyclic mechanism is analogous to the isomerization mechanism found for alkenyl thiocyanates investigated by Smith and Emerson.[15] On the basis of kinetic data and the nature of products formed they concluded that 2-alkenyl thiocyanates isomerizes *via* a six-membered transition state. However, 3-phenylallyl thiocyanate was observed to isomerize to 3-phenylallyl isothiocyanate and in this case the reaction also exhibited salt effects showing that the isomerization takes place *via* an ionic mechanism.

It should be pointed out that the present data do not exclude that decomposition of allylic oxythiatriazoles takes place *via* attack on the nitrogen at the 4-position although there is neither chemical nor spectroscopic evidence for such a step and it therefore seems rather unlikely:

$$CH_2=CH-CH_2-N=C=O \; + \; N_2 \; + \; S$$
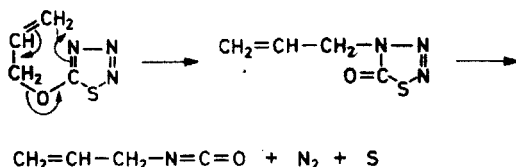
This pathway will give the same isocyanates as found in the experiments described above. Allylic rearrangements of similar type are known.[16] Attempts will be made to investigate this reaction further but at present 4-alkyl-1,2,3,4-thiatriazoline-5-ones are not known.

Independent evidence of the six-membered cyclic isomerization of 2-alkenyl cyanates was found from the reaction of silver(I) oxide and O-(2-butenyl) thiocarbamate. This was prepared from [(2-butenyloxythiocarbonyl)thio]acetic acid and ammonia and was treated with silver(I) oxide as already described. In spite of the above mentioned 15 − 25 % isomerization of [(2-butenyloxy-thiocarbonyl)thio]acetic acid a reasonable yield of isocyanate was obtained. Gas chromatography again showed that only 1-methylallyl isocyanate was formed. Unfortunately, several attempts to prepare O-(3-phenylallyl) thiocarbamate have failed.

A completely picture of the isomerization can only be obtained with pertinent kinetic and thermodynamic data. However, it seems at present doubtful whether it will be possible to isolate an allylic cyanate stable enough to allow a detailed investigation.

4-Pentenyl cyanate which is not allylic with respect to the cyanate group was stable, as expected, and could be obtained in high yield from the corresponding 5-(4-pentenyloxy)-1,2,3,4-thiatriazole.

EXPERIMENTAL

spectra were obtained with a Perkin Elmer 337 Grating Infrared Spectrophotometer (± 5 cm^{-1} over 2000 cm^{-1} and ± 2 cm^{-1} below 2000 cm^{-1}). Abbreviations used: br=broad, sh=shoulder, s=strong, m=medium, w=weak. Very weak absorptions have been omitted.

Sodium O-alkenyl dithiocarbonates

Sodium hydride (0.1 mol as a 50 % oil suspension) was suspended in dry ether (100 ml) and the corresponding alcohol (0.1 mol) in ether (100 ml) was added dropwise with stirring over 2 h. The mixture was left overnight with stirring and protected against moisture. Carbon disulfide (0.1 mol) in ether (100 ml) was then added dropwise over a period of 30 min while the reaction mixture was cooled in an ice bath. After 2 h further stirring at room temperature the solid product was isolated by filtration and washed with ether. The following yields of sodium O-alkenyl dithiocarbonates were obtained: *Allyl* 90 %, *2-butenyl* 91 %, *1-methylallyl* 89 %, *2-methylallyl* 82 %, *4-pentenyl* 84 %, and *3-phenylallyl* 92 %. These carbonates do not isomerize on standing but are oxidized on exposure to air and should therefore be stored under nitrogen at low temperature unless used immediately.

Alkenyloxythiocarbonylhydrazines

4-Pentenyloxythiocarbonylhydrazine was prepared from [(4-pentenyloxythiocarbonyl) thio]acetic acid and hydrazine by the method described in another paper.[10] Yield 81 %, isolated as an oil. NMR Spectrum (CDCl$_3$) with signals from 8.39 to 7.67 (c CH$_2$CH$_2$), 5.51 (t CH$_2$O), 5.14—4.76 (m CH$_2$=), and 4.45—3.80 τ (m CH= and NH protons). The other hydrazides were prepared directly from the sodium O-alkenyl dithiocarbonate and hydrazine by the following general procedure: Freshly prepared sodium O-alkenyl dithiocarbonate (0.1 mol) was dissolved in water (100 ml) and hydrazine hydrate (0.1 mol) in water (30 ml) was added. The solution was kept at 3—4°C for 20 h. The hydrazide formed had separated as an oil or crystals and was isolated by filtration or extraction with ether. *Allyl*, 48 % oil which could not be purified by distillation without isomerization. *2-Butenyl*, 51 %, m.p. 41—42°C from ether/hexane. (Found: C 41.20; H 6.91; N 18.99. Calc. for C$_5$H$_{10}$N$_2$OS: C 41.09; H 6.90; N 19.17). NMR Spectrum (CCl$_4$) with signals at 8.25 (d with further splitting, CH$_3$), 5.13 (d CH$_2$) and from 4.61 to 3.84 τ (m CH=CH). *1-Methylallyl*, 40 %, oil. NMR Spectrum (CCl$_4$) with signals at 8.61 (d CH$_3$), and from 4.93 to 3.78 τ (m CH$_2$=CH—CH). *3-Phenylallyl*, 91 %, m.p. 67—68°C from ethanol/water. (Found: C 57.94; H 5.85; N 13.24; S 15.44. Calc. for C$_{10}$H$_{12}$N$_2$OS: C 57.68; H 5.81; N 13.46; S 15.37). NMR Spectrum (CDCl$_3$) with signals at 4.85 (d CH$_2$) from 3.92 to 3.12 (m CH=CH) and 2.65 τ (phenyl protons.) The signals from the hydrazide protons were found at variable positions. A gradual increase in yield of the hydrazides with increasing reaction time was observed but since the products slowly isomerize (and therefore should be stored at low temperature) a reaction time of 20 h was chosen. 1-Methylallyloxythiocarbonylhydrazine was found to contain from 5 to 7 % of the isomerization product, [(2-butenylthio)carbonyl]hydrazine, under these conditions, whereas the allyl and the 2-butenyl derivatives were isolated without isomerization products. The 3-phenylallyl analogue was found to be even more stable towards isomerization and could be stored at room temperature. 4-Pentenyloxythiocarbonylhydrazine was completely stable, as expected. For details of the isomerization of these compounds, see under [(alkenylthio)carbonyl]hydrazines.

[(Alkenylthio)carbonyl]hydrazines

2-Alkenyloxythiocarbonylhydrazines (see above) are slowly converted at room temperature to [(2-alkenylthio)carbonyl]hydrazines. The conversion is conveniently followed by means of NMR spectroscopy. 1-Methylallyloxythiocarbonylhydrazine was 50 % converted to [*(2-butenylthio)carbonyl]hydrazine* after 7 days at room temperature. The 2-butenyloxy derivative was converted at a slower rate and the 3-phenylallyl derivative was not converted to a measurable degree after 30 days at room temperature.

On heating the aliphatic derivatives rapidly isomerized. Thus, 2-butenyloxythiocarbonyl-hydrazine was 15 % isomerized to [(*1-methylallylthio*)carbonyl]hydrazine after 2 min at 140°C. After one further min of heating, an exothermic reaction took place with complete isomerization. The product formed was an oil which did not crystallize on cooling and it was therefore converted to the hydrochloride in ether solution with gaseous hydrogen chloride. M.p. 149—150°C (decomp.) after recrystallization from ethanol/ether. (Found: C 32.69; H 5.95; N 15.22. Calc. for $C_5H_{11}N_2OSCl$: C 32.88; H 6.03; N 15.34). NMR Spectrum (CCl_4) of the free hydrazide with chemical shifts at 8.58 (d CH_3), 5.93 (p CH), 5.14—4.72 (m $CH_2=$), and from 4.40 to 3.85 τ (m=CH). 1-Methylallyloxythiocarbonylhydrazine was 67 % isomerized after heating to 100°C for 4 min. Complete isomerization took place very rapidly at 120°C. After cooling the product solidified and was recrystallized from ether/hexane. M.p. 54.5—55°C. (Found: C 41.15; H 6.88; N 19.31. Calc. for $C_5H_{10}N_2OS$: C 41.09; H 6.90; N 19.17). NMR Spectrum (CCl_4) with signals at 8.32 (d with further splitting, CH_3), 6.54 (d with further splitting, CH_2), and from 4.80 to 3.96 τ (m CH=CH). The possible isomerization of 3-phenylallyloxythiocarbonylhydrazine was not investigated.

On addition of strong acid isomerization of the 2-alkenyloxythiocarbonylhydrazines took place rapidly. 2-Butenyloxythiocarbonylhydrazine was dissolved in deuterium oxide by means of a few drops of concentrated hydrochloric acid. The solution was placed in an NMR test tube and the spectrum recorded at 40°C at given intervals. 50 % conversion was found after 10 min and 87 % after 30 min.

In accordance with the assumed structure these hydrazides all exhibit carbonyl absorption (about 1690 cm^{-1}) which is absent in the alkenyloxythiocarbonylhydrazines.

[(A l k e n y l o x y t h i o c a r b o n y l) t h i o] a c e t i c   a c i d s

These compounds were prepared according to a method described in a previous paper.[10] Due to the strong tendency to undergo isomerization to {[(alkenylthio)carbonyl] thio}acetic acid some modifications of the procedure were necessary. *Allyl (I):* Freshly prepared sodium *O*-allyl dithiocarbonate (0.557 mol, 86.8 g) was dissolved in water (100 ml) and mixed, while cooling in an ice bath, with a freshly prepared solution of chloroacetic acid (0.557 mol, 52.9 g) neutralized with sodium carbonate in water (75 ml). After standing for 5 h in the refrigerator the mixture was acidified with concentrated hydrochloric acid to pH 3—4 and extracted twice with 50 ml of ether. The ether solution was washed with a saturated sodium chloride solution (15 ml) and dried over magnesium sulfate at 0°C. After evaporation of the ether *in vacuo* at 10°C [(allyloxythiocarbonyl) thio]acetic acid (82 %, 87 g), was left as an oil which crystallized on cooling and scratching. M.p. 51.5—52°C from ether/hexane. (Found: C 37.43; H 4.34 Calc. for $C_6H_8O_3S_2$: C 37.51; H 4.20). NMR Spectrum (CCl_4) with signals at 6.03 (SCH_2), 4.91 (d with further splitting, CH_2O), and from 4.78 to 3.61 τ (m $CH_2=$CH). IR Spectrum (CCl_4, 10 %) 3100w br, 3000w br, 2900w br, 1722s, 1419w, 1291w, 1225m br, 1200sh, 1152w, 1092w, 1061s, 986w, 966w, 932w and 664w cm^{-1}. [*(2-Butenyloxythiocarbonyl)thio*]acetic acid was prepared in the same way but the time of reaction between sodium *O*-(2-butenyl) dithiocarbonate and chloroacetic acid was only 3 h at 0°C. According to IR and NMR spectroscopy [(2-butenyloxythiocarbonyl)thio]acetic acid in different experiments contained 15—25 % of the isomerization product, {[(1-methylallylthio)carbonyl]thio}acetic acid. NMR Spectrum (CCl_4 and corrected for the isomer present) with signals at 8.19 (d CH_3), 6.02 (—SCH_2), 4.96 (d with further splitting, CH_2O) and from 4.51 to 3.72 τ (m CH=CH). The IR spectrum (CCl_4) exhibited the strong characteristic absorptions at 1724, 1230, and 1052 cm^{-1} in accordance with the expected structure but absorptions due to the isomerization product were also present. [*(2-Methylallyloxy-thiocarbonyl)thio*]acetic acid was also prepared with a reaction time of 3 h at 0°C and did not contain isomerization products. Yield 75 %. M.p. 49—50°C from ether/hexane. (Found: C 40.87; H 4.99. Calc. for $C_7H_{10}O_3S_2$: C 40.78; H 4.89). NMR Spectrum (CCl_4) with signals at 8.15 (CH_3), 6.02 (SCH_2COO), 5.00 and 4.93 τ (CH_2O and $CH_2=$ with overlapping signals). IR Spectrum (CCl_4, 10 %) 3080w br, 2980w br, 2920w br, 1723s, 1420m, 1292m, 1225s br, 1195sh, 1175sh, 1061s br, 1075sh, 1030m, 982w, 911m, 668w, 450 cm^{-1}. Under the same conditions sodium *O*-(1-methylallyl) dithiocarbonate and chloroacetic acid yielded only the isomerization product, {[(2-butenyl-thio)carbonyl]thio}acetic acid (see below).

[(4-Pentenyloxythiocarbonyl)thio] acetic acid was prepared according to the method described above for the allyl homologue and was as expected completely stable towards isomerization. Yield 93 %. M.p. 46—47°C from hexane. (Found: C 43.60; H 5.40; S 28.81. Calc. for $C_8H_{12}O_3S_2$: C 43.64; H 5.49; S 29.07). NMR Spectrum (CDCl₃) with signals from 8.38 to 7.60 (m CH_2CH_2), 6.03 (SCH_2COO), 5.37 (t CH_2O), 5.14—4.75 (m $CH_2=$) and from 4.51 to 3.80 τ (m =CH).

[(3-Phenylallyloxythiocarbonyl)thio]acetic acid (III) and {[(3-phenylallylthio)carbonyl]thio}acetic acid (IV)

Sodium *O*-(3-phenylallyl) dithiocarbonate (0.0444 mol) in water (50 ml) was mixed with chloroacetic acid dissolved in water (25 ml) and neutralized with sodium carbonate. The solution was left overnight at 3—4°C. A precipitate was discarded and after addition of concentrated hydrochloric acid to pH 3—4 the solution was extracted with ether (2 times 50 ml). The ether solution was washed with a saturated sodium chloride solution and dried over sodium sulfate. After removal of the ether *in vacuo* an oil was left (3.50 g, 30 %), which did not crystallize on cooling and could not be obtained analytically pure. The NMR spectrum (CCl₄), however, showed characteristic chemical shifts in accordance with the assumed product, [(3-phenylallyloxythiocarbonyl)thio]acetic acid: 6.31 (SCH_2COO) 5.78 (d CH_2O), from 4.23 to 3.55 (m CH=CH) and 2.76 τ (phenyl). On standing at room temperature a yellow crystalline precipitate was formed. M.p. 162—63°C from ethanol. (Found: C 53.82; H 4.60; S 23.88. Calc. for $C_{12}H_{12}O_3S_2$: C 53.73; H 4.51; S 23.86). On comparison with the NMR spectra of 3-phenyl- and 1-phenylallyl alcohol it was deduced that this yellow compound is an isomerization product, {[(*3-phenyl-allylthio*)*carbonyl*]*thio*}*acetic acid*. NMR spectra (CD₃COCD₃): {[(3-Phenylallythio) carbonyl]thio}acetic acid; 6.07, 6.08 (overlapping signals from CH_2S, d, and SCH_2COO, s) from 3.97 to 3.12 (m CH=CH) and 2.62 τ (phenyl with splitting); 3-phenylallyl alcohol; 6.92 (OH), 5.81 (d CH_2), from 4.02 to 3.31 (m CH=CH), and 2.79 τ (phenyl); 1-phenylallyl alcohol; 6.58 (OH), from 5.12 to 4.71 (m CH=CH₂), from 4.38 to 3.84 (m CH), and 2.82 τ (phenyl). The oily filtrate from the yellow precipitate consisted of the original compound but the NMR spectrum revealed additional chemical shifts from 4.98 to 4.56 τ (m) similar to the pattern found from the CH=CH₂ group in 1-phenylallyl alcohol. This indicates that {[*(1-phenylallylthio)carbonyl]thio*}*acetic acid* may also be present, having been formed in a cyclic reaction. The problem was not further investigated, however.

Ethyl [(alkenyloxythiocarbonyl)thio]acetate and ethyl {[(alkenylthio)carbonyl]thio}acetate

Sodium *O*-(2-butenyl) dithiocarbonate (0.1 mol, 17.0 g) was dissolved in ice-cold acetone (80 ml) and ethyl bromoacetate (0.1 mol, 16.7 g) was added dropwise over 10 min at 0°C. After standing for 1½ h at 0°C the mixture was filtered and the filtrate concentrated *in vacuo* at 10°C. Yield of oil left, 18.5 g, 79 %. The oil was not obtained analytically pure but the NMR spectrum (CDCl₃) confirmed its identity with ethyl *[(2-butenyloxythiocarbonyl)thio]acetate:* 8.70 (t CH_3 from the ethyl group), 8.23 (d with further splitting, CH_3), 6.07 (SCH_2COO), 5.78 (q CH_2 from the ethyl group), 4.97 (d with further splitting, CH_2), and from 4.53 to 3.73 τ (m CH=CH). Its isomerization product was absent in the spectrum. On distillation *in vacuo* (95—100°/0.25—0.5 mm Hg) it isomerized completely to ethyl {[*(1-methylallylthio)carbonyl]thio*}*acetate* and although it did not yield satisfactory elemental analysis, its NMR spectrum (CDCl₃) was in accordance with the assumed structure: 8.71 (t CH_3 from the ethyl group), 8.56 (d CH_3), 5.78 (q CH_2 from the ethyl group), 5.64 (p, CH), from 4.99 to 4.59 (m $CH_2=$), and from 4.33 to 3.77 τ (m =CH). Ethyl *[(allyloxythiocarbonyl)thio] acetate* prepared in this way was isolated as an oil in 90 % yield. According to its NMR spectrum it was free of the isomerization product.

{[(Alkenylthio)carbonyl]thio}acetic acids

When [(allyloxythiocarbonyl)thio]acetic acid (I) was left at room temperature for some days, appreciable isomerization had occurred. In carbon tetrachloride solution (10 %) at room temperature approximately 15 % isomerization had taken place after 4 days, 24 % after 7 days, and 75 % after 30 days. On heating to approximately 60°C an exothermic reaction took place and isomerization to {[(allylthio)carbonyl]thio}acetic acid (II) was completed within a few minutes. A pure product was obtained by recrystallization from hexane. M.p. 68—68.5°C. (Found C 37.35; H 4.20. Calc. for $C_6H_8O_3S_2$: C 37.51; H 4.20). NMR Spectrum (CDCl$_3$) with signals at 6.27 (d with further splitting, CH$_2$ from the allyl group), 6.13 (SCH$_2$COO), and from 4.87 to 3.70 τ (m CH$_2$=CH). IR Spectrum (CCl$_4$, 10 %), 3086w br, 3000w br, 2920w br, 2670w, 2570w, 1724s, 1658s, 1423m, 1299m, 1231w, 1199m, 984w, 924s, 894s, 875s, 667w, 460w cm^{-1}. [(2-Butenyloxythiocarbonyl)thio]acetic acid was obtained in a partly isomerized state (from 15 to 25 %, see above) and complete isomerization took place on standing for a few hours at room temperature. The isomerization product, {[(1-methylallylthio)carbonyl]thio}acetic acid, was obtained as an oil which could be purified by distillation in a short path distillation apparatus. (Found: C 41.06; H 5.05; S 31.20. Calc. for $C_7H_{10}O_3S_2$: C 40.78; H 4.89; S 31.05). NMR Spectrum (CCl$_4$) with signals at 8.52 (d CH$_3$), 6.22 (SCH$_2$COO), 5.66 (p CH) from 5.00 to 4.60 (m CH$_2$=), and from 4.34 to 3.77 τ (m =CH). IR Spectrum (CCl$_4$, 10 %) 3089w br, 2980w br, 2930w br, 2670w, 2568w, 1724s, 1658s, 1456w, 1420m, 1378w, 1298m, 1201m, 1160w, 1140w, 993w, 983w, 925s, 895s, 872s, 859s, 671w, 460w cm^{-1}. [(1-Methylallyloxythiocarbonyl)thio]acetic acid isomerized too rapidly to be isolated and only the isomerization product, {[(2-butenylthio)carbonyl]thio}acetic acid was obtained. M.p. 74.5—75.5°C from ether/hexane. (Found: C 40.60; H 4.97; S 30.91. Calc. for $C_7H_{10}O_3S_2$: C 40.78; H 4.89; S 31.05). NMR Spectrum (CDCl$_3$) with signals at 8.32 (d with further splitting, CH$_3$), 6.35 (d with further splitting, CH$_2$S), 6.18 (SCH$_2$COO) and from 4.80 to 3.95 τ (m CH=CH). IR Spectrum (CCl$_4$, 10 %), 3085sh, 3031m br, 2919m br, 1724s, 1655s, 1419m, 1294m, 1228w, 1199m, 963m, 928sh, 915sh, 896s, 872s, 858sh, 670w, 460w cm^{-1}

5-(3-Phenylallyloxy)-1,2,3,4-thiatriazole

3-Phenylallyloxythiocarbonylhydrazine (0.01 mol, 2.08 g) and sodium nitrite (0.01 mol, 0.69 g) were dissolved in a mixture of 50 ml of ether and 50 ml of water. Under vigorous stirring and cooling in an ice-bath, 1 N hydrochloric acid was added dropwise until a test for nitrous acid with starch-iodide was positive. After 10 min of further stirring the phases were separated and the water phase was extracted with 25 ml of ether. The combined ether extracts were dried over magnesium sulfate and 5-(3-phenylallyloxy)-1,2,3,4-thiatriazole was left as a yellowish crystalline residue on evaporation in vacuo at 5°C. The yield was quantitative.

Due to the instability of this compound, elemental analysis could not be performed but the infrared spectrum (CHCl$_3$) did not exhibit carbonyl absorption, thus proving that rearrangement had not taken place during the synthesis of this compound and its precursors. NMR Spectrum (CDCl$_3$) with signals at 4.78 (d CH$_2$), from 3.85 to 2.97 (m CH=CH), and 2.64 τ (phenyl, with further splitting).

The spontaneous decomposition of 5-(3-phenylallyloxy)-1,2,3,4-thiatriazole

The thiatriazole (0.01 mol, 2.19 g) was dissolved in ether (15 ml) and left at room temperature for 16 h or until the nitrogen evolution had ceased. The solution was decanted from the precipitated sulfur and the solution was evaporated to dryness in vacuo. The oil left, 1.75 g (theoretical yield of phenylallyl cyanate, 1.60 g), contained some sulfur and was purified by distillation in high vacuum. The product obtained was an oil. (Found: C 75.60; H 5.84; N 8.62. Calc. for $C_{10}H_9NO$: C 75.45; H 5.70; N 8.80). In the IR spectrum (CHCl$_3$) the characteristic absorption of alkyl cyanates at 1100 cm^{-1} was absent and, instead, the very strong absorption at 2261 cm^{-1} showed the compound to be an isocyanate. In the NMR spectrum (CDCl$_3$) chemical shifts were found from 4.93 to

4.52 (m $CH=CH_2$), from 4.29 to 3.76 (m CH), and at 2.68 τ (phenyl). By comparison with the NMR spectra of 1-phenyl- and 3-phenylallyl alcohol (see [(3-phenylallyloxy-thiocarbonyl)thio]acetic acid) the structure of the isocyanate was established as *1-phenylallyl isocyanate*. It should be mentioned that the presence of cyanate could not be traced even in the undistilled material.

The spontaneous decomposition of 5-(2 butenyloxy)- and 5-(1-methylallyloxy)-1,2,3,4-thiatriazole

The thiatriazoles were prepared from the corresponding hydrazides by the following procedure: Alkenyloxythiocarbonylhydrazine (0.01 mol) and sodium nitrite (1.0 g) were dissolved in a mixture of 10 ml of water and 20 ml of ether. After cooling to 0°C, 1 N HCl was added dropwise under vigorous stirring for a period of 30 min until a test for nitrous acid with iodide-starch was positive. The phases were separated and the ether phase washed with water. After drying over magnesium sulfate the solution was left at room temperature to allow spontaneous decomposition to sulfur, nitrogen, and alkenyl cyanate to take place.[1] After the nitrogen evolution had ceased (the decomposition of the alkenyl derivatives are somewhat faster than the decomposition of the alkyl derivatives which takes approximately 16 h[1]) the ether was removed *in vacuo* at 0°C and the liquid left purified by vacuum distillation. 2-Butenyloxythiatriazole yielded 0.6 g of liquid and 1-methylallyloxythiatriazole yielded 0.5 g of liquid. The IR spectra of both substances revealed an intense absorption about 2250 cm^{-1} strongly suggesting the presence of an isocyanate group. Absorption about 1100 cm^{-1}, which is characteristic of cyanates[12] was completely absent. The 2-butenyl derivative was found by means of NMR spectroscopy to have changed to a 1-methylallyl derivative and 1-methylallyl was changed to 2-butenyl. Both compounds were submitted to gas chromatography which on comparison with authentic material[17] confirmed that 2-butenyloxythiatriazole had given *1-methylallyl isocyanate* without 2-butenyl isocyanate (at least less than 0.5 %) and that 1-methylallyloxythiatriazole had given *2-butenyl isocyanate* without 1-methyl-allyl isocyanate (at least less than 0.5 %).

Although the intermediate thiatriazole could not be isolated, it could be analyzed in solution by means of NMR spectroscopy. It is fair to assume some contamination of the thiatriazole with (alkenylthio)carbonyl azide formed from [(alkenylthio)carbonyl] hydrazine. (As mentioned above, 2-alkenyloxythiocarbonylhydrazine isomerizes readily in acid solution to [(2-alkenylthio)carbonyl]hydrazine). With the precautions described above, the rearrangement product formed seems, however, not to exceed 10 %. Thus, 2-butenyloxythiatriazole was prepared with carbon tetrachloride as solvent and submitted to NMR spectroscopy at 0°C. Chemical shifts were found at 8.17 (d CH_3), 4.96 (d CH_2), and from 4.46 to 3.61 τ (m $CH=CH$) establishing the expected 2-butenyl side chain of the thiatriazole. A doublet at 8.60 τ was integrated to 6 % of the signal at 8.17 τ. This signal may be due to the azide referred to but may also be due to 1-methylallyl isocyanate, since it is close to the position for this compound (8.63 τ, CCl_4).

4-Pentenyl cyanate

This compound was prepared from 4-pentenyloxythiocarbonylhydrazine by the general method described previously for alkyl cyanates.[1] It was isolated as a colourless oil and purified by high vacuum distillation. Yield, 44 %. (Found: C 64.54; H 8.21; N 12.41. Calc. for C_6H_9NO: C 64.84; H 8.16; N 12.60). The IR spectrum exhibited strong bands at 2251 and at 1108 cm^{-1} in the ratio 1:1 which is characteristic of alkyl cyanates.[12] The absorptions are due to the cyanate group and to the C−O vibration, respectively. The cyanate, as expected, proved stable towards isomerization *via* a cyclic reaction.

O-Allyl thiocarbamate

[(Allyloxythiocarbonyl)thio]acetic acid (0.0265 mol, 5.1 g) was dissolved in ether (25 ml) and 2 N aqueous ammonia (30 ml) was added. The mixture was stirred vigorously at 0°C for 1 h, after which sodium chloride was added to saturation and the phases separated. The water layer was extracted with 25 ml of ether and the combined ether extracts dried over anhydrous magnesium sulfate. On evaporation of the ether *in vacuo* an oil was left (1.35 g, 44 %), which crystallized on cooling and could be recrystallized from ether/hexane. M.p. 34.5—35°C. (Found: C 40.60; H 6.03; N 11.65. Calc. for C_4H_7NOS: C 41.02; H 6.03; N 11.96). According to the NMR spectrum, it was free of the isomerization product. After 14 days at room temperature in carbon tetrachloride (10 %), very little isomerization had taken place (2—3 %). On heating, however, isomerization takes place readily.

Reaction between O-allyl thiocarbamate and silver(I) oxide

Allyloxythiocarbonylamine (0.75 g) was dissolved in carbon tetrachloride (10 ml) and anhydrous magnesium sulfate (1 g) was added. After cooling to 0°C silver(I) oxide (2 g) was added to the mixture under vigorous stirring. After stirring for 5 min the solid materials were removed by centrifugation and the remaining solution was distilled in high vacuum at 0°C as rapidly as possible. The infrared spectrum of the distillate was recorded immediately after the distillation. The absorption at 1100 cm^{-1} due to C—O and characteristic of alkyl cyanates was absent in the spectrum. Instead, a very intense absorption at 2250 cm^{-1} showed that of the two isomers only *allyl isocyanate* was present. Comparison with authentic material revealed its identity.

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