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Rapid [3,3] sigmatropic rearrangements of allylic thiono chloroformates

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Abstract

Treatment of allylic alcohols with thiophosgene and pyridine gives thiolo chloroformates directly at room temperature, presumably via very rapid [3,3] sigmatropic rearrangements of thiono chloroformates. Synthesis of allyl thiono chloroformate from allyl alcohol, sodium hydride and thiophosgene at low temperature and warming up to room temperature supports this finding.

Keywords: rearrangements; alcohols; thiocarbonyl; thiocarbamate.

In order to examine thiono–thiolo rearrangement of allylic trimethylhydrazo thiono carbonates we needed to synthesize allylic thionocarbonate **5**. Since no synthesis of these substances has been recorded in the literature,[1] we employed a procedure[2] that we had previously used to prepare diosphenol dimethylamino thiocarbamates. Mixing both 3-buten-2-ol **1** and thiophosgene **2** in equimolar amounts in methylene chloride and adding pyridine dropwise at room temperature resulted in a vigorous reaction (Scheme 1). Consequently without isolation of the intermediate **3**, trimethylhydrazine was added to the mixture. The rearranged thiolo carbamate **6** was obtained, presumably via thiolo chloroformate **4** [liquid, bp 76–78°C/15 mmHg, 78% yield; NMR [60 MHz ^{1}H NMR ($CDCl_3$)] δ: 1.75 (d, J=5 Hz, 3H), 3.63 (d, J=6 Hz, 2H), 5.2–6.2, (m, 2H); IR 1758, 835 cm^{-1}].

To understand the order of events, we needed to isolate the thiono chloroformate **3**. The rearrangement to product **4**, however, was too fast. Therefore, we examined the simple allyl system as a model as described below.

The thiono chloroformate **8** was synthesized using a method previously used to synthesize the corresponding propyl compound[3] by treating allyl alcohol **7** with sodium hydride and thiophosgene at −78°C in diethyl ether for 1 h (Scheme 2). Warming to room temperature and washing with ice-water and brine gave compound **8** (81% yield) with ^{1}H NMR[3–5] [δ: 5.1 (d, J=6, 2H), 5.2–6.5 (m, 3H)] and IR (1268 cm^{-1}). Then the rearrangement of allyl thiono chloroformate **8** to thiolo chloroformate **9**[6] was followed by NMR using *p*-dichlorobenzene as an internal standard. Interestingly, the half-life for this

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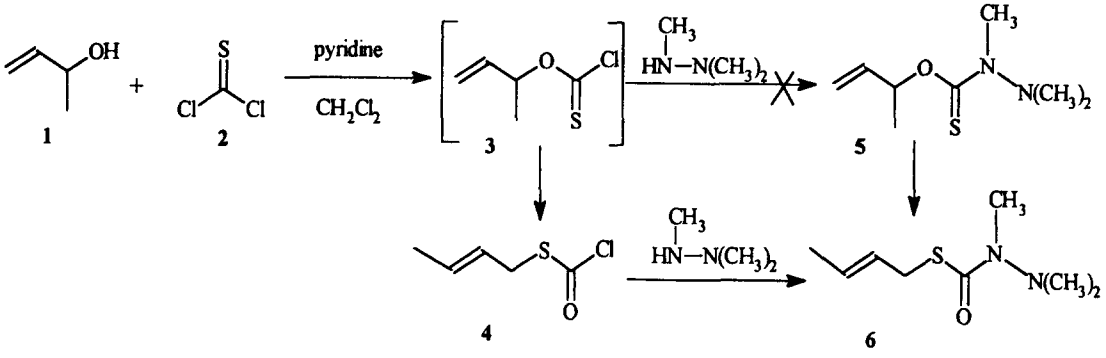
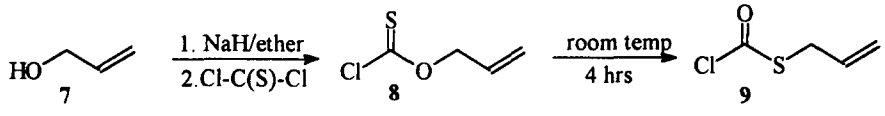
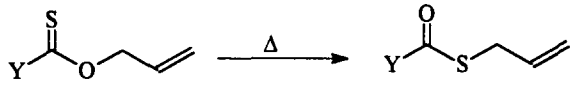


Scheme 1.

transformation was 60 min at room temperature which is much faster than the rearrangement rate of the thiono dimethylamino carbonate derivative of allyl alcohol ($t_{0.5}$=10 340 min at 80.5°C)[7] as shown below (Scheme 3).



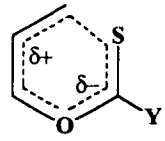
Scheme 2.



Y= -NMe_2 , -SMe

Scheme 3.

There are examples of such rearrangements using thiono dimethylamino-carbonates and xanthates.[8–10] Several catalysts were also reported, such as chromatographic absorbants[11b,12] and transition metals[13] to speed up the rearrangement. It is assumed that the polarized transition state[7] of the rearrangement is **10**, which bears a partial negative charge on O-C-S atoms. Increasing electronegativity for group Y should lower the energy of the transition state and hence speed-up the rate of the rearrangement. This is indeed consistent with our findings. When we used a chlorine (-Cl) atom (as a Y group), which is more electronegative than the nitrogen atom of dimethylamino (-NMe_2) and the sulfur atom of xanthate (-SMe), extremely rapid rearrangement was observed.



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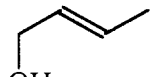
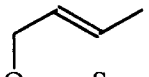
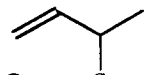
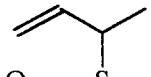
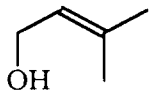
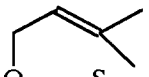
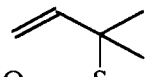
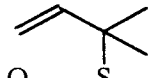
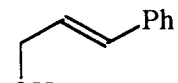
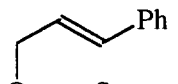
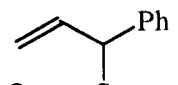
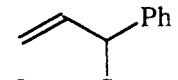
We also examined several starting alcohols, such as crotyl **11**, prenyl **15** and cinnamyl **19** alcohols (Table 1). No thiono choloroformates of these alcohols (**12**, **16**, **20**) were observed after treating them with thiophosgene and pyridine. Pyridine does not appear to play a role as a catalyst in the process of rearrangement since treatment of allylic thiono chloroformates with pyridine give allylic chlorides as reported previously.[1a] These compounds are also present in small amounts along with the rearranged products.

Table 1
Conversion of allylic alcohols to thiolo chloroformates via [3,3] sigmatropic rearrangement of thiono chloroformates

Allylic Alcohols	$CSCl_2$, pyridine → Thiono chloroformates	R.T. → Thiolo chloroformates	$HNMe_2$ → Thiolo dimethylaminoformates
 **11**	 **12**[a]	 **13**[b]	 **14**
 **15**	 **16**[a]	 **17**[c]	 **18**
 **19**	 **20**[a]	 **21**[d]	 **22**

[a]We were unable to isolate **12**, **16** and **20**.

[b]Liquid, 72% yield. NMR [60 MHz ^{1}H NMR ($CDCl_3$)] δ 1.49 (d, *J*=7 Hz, 3H), 4.18 (quintet, *J*=7 Hz, 1H), 5.1-5.6, (m, 2H), 5.6-6.4 (m, 1H); IR 1755, 833 cm^{-1}.

[c]Liquid, 54% yield. NMR δ 1.61 (s, 6H), 5.1-5.6 (m, 2H), 5.9-6.5 (m, 1H); IR 1757, 833 cm^{-1}.

[d]Oil, 77% yield. NMR δ 4.20 (d, *J*=6 Hz, 1H), 5.2-5.6 (m, 2H), 5.8-6.5 (m, 1H), 7.47 (s, 5H); IR 1757, 822 cm^{-1}.

Thiolo chloroformates (**13**, **17**, **21**) were identified by IR and NMR and also by converting them to the known thiolo dimethylaminoformates (**14**, **18**, **22**),[7,9a,11a] which were prepared from **13**, **17**, **21** and aqueous dimethylamine solution.

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