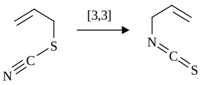
Synthesis of New Vinyl Thiocyanates by Sigmatropic Rearrangement Reactions

Klaus Banert and Anett Müller

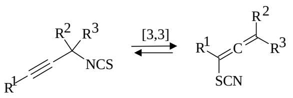
Technische Universität Chemnitz, Institut für Chemie, D-09107 Chemnitz, Germany

The well-known isomerization of allyl thiocyanate **1** to allyl isothiocyanate **2** (mustard oil)[1] is currently interpreted as a [3,3] sigmatropic rearrangement. The formation of a more stable functional group provides the driving force for this irreversible reaction.



1 **2**

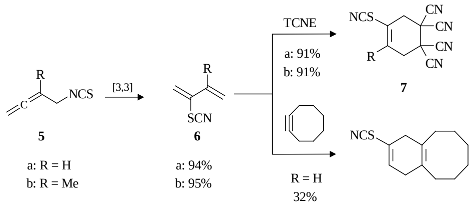
In special cases, the sigmatropic rearrangement can be directed to the thiocyanate. On heating the isothiocyanates **3d**,**e**, equilibria are established favoring allenyl thiocyanates[2] **4d**,**e**. **3f** undergoes a clean irreversible isomerization to give **4f** already at room temperature. For **a, b** and **c** equilibration is on the side of the propargyl precursors **3**. In order to suppress intermolecular secondary reactions, allenyl thiocyanates and novel vinyl thiocyanates are mostly obtained by using flash vacuum pyrolysis.



3 **4**

a: R^1 = Pr, $R^2 = R^3$ = H	**3a** / **4a** = 83 / 17	(77%)
b: R^1 = Me, $R^2 = R^3$ = H	**3b** / **4b** = 78 / 22	(93%)
c: R^1 = CH_2Cl, $R^2 = R^3$ = H	**3c** / **4c** = 55 / 45	(91%)
d: $R^1 = R^2 = R^3$ = H	**3d** / **4d** = 33 / 67	(97%)
e: R^1 = H, $R^2 = R^3$ = Me	**3e** / **4e** = 15 / 85	(ca. 100%)
f : R^1= H, R^2 = Ph, R^3 = H	**3f** / **4f** = 0 /100	(ca. 100%)

Similar irreversible [3,3] sigmatropic rearrangements, for instance **5** → **6,** direct the thiocyanate groups into vinylic positions. Diels-Alder-products **7a**,**b** are subsequently formed in excellent yields by reactions of butadienes **6a**,**b** with tetracyanoethylene (TCNE). On treatment with cyclooctyne, **6a** leads to **8a**.

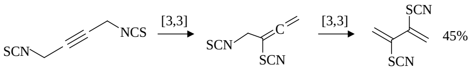


5 **6** **7** **8a**

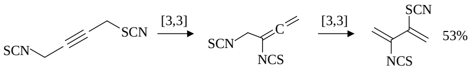
a: R = H
b: R = Me

a: 94%
b: 95%

Diisothiocyanate **9** as well as 2-butyne **12** bearing an isothiocyanate group in 1-position and a thiocyanate group in 4-position react via double [3,3] shifts to the 1,3-butadienes **11** und **14**, respectively. The intermediates **10** und **13** are verified by ^{1}H NMR.

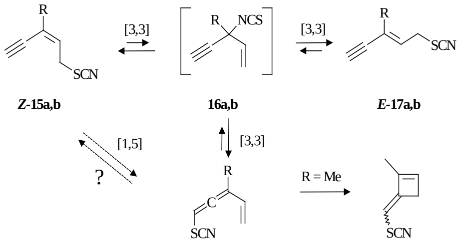


9 **10** **11**



12 **13** **14**

Two different mechanisms can be discussed for reactions **15a** ⇄ **17a** ⇄ **18a** and **15b** ⇄ **17b** ⇄ **18b**. Only *Z*-isomer **15a**,**b** should be able to rearrange to **18a**,**b** via [1,5] shift of the SCN-group for geometric reasons. On the other hand, the *E*-isomer **17a,b** as well as **15a**,**b** can form **18a**,**b** by two subsequent [3,3] migrations. Only **18b** undergoes ring closure reaction to afford **19b**.



***Z*-15a,b** **16a,b** ***E*-17a,b**

18a,b ***E*-19b,*Z*-19b**

a: R = H, **b**: R = Me

Products of flash vacuum pyrolysis of **15a**, **17a**, and **18a**

temper-ature (°C)	starting material	composition of products (%)		
		15a	**17a**	**18a**
250	**15a**	72	13	15
250	**17a**	16	64	20
250	**18a**	5	5	90
400	**15a**	43	21	36
400	**17a**	33	33	33
400	**18a**	31	23	46
yields 65-67%				

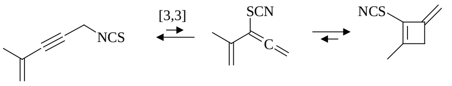
Products of flash vacuum pyrolysis of **15b**

temper-ature (°C)	composition of products			
	15b	**17b**	**18b**	***E*/*Z*-19b**
300	58	9	33	–
400	23	7	23	47*
yields 64-75%				

* mixture of geometric isomers *E*-**19b** and *Z*-**19b**

The obtained results support a mechanism with consecutive [3,3] sigmatropic rearrangements, especially since allenes analogous to **18** can be formed from cyclic thiocyanates, for instance 1-ethynyl-3-thiocyanato-cyclohex-1-ene, which does not permit any [1,5] isomerization.

Rearrangement of enyne **20** leads to **21** and **22**.



20 **21** **22**

temper-ature (°C)	composition of products (%)		
	20	**21**	**22**
300	80	10	10
400	26	5	69
450	30	6	64
yields 75-77%			

---

[1] O. Billeter, *Ber. Dtsch. Chem. Ges*. **1875**, *8*, 462; G. Gehrlich, *Justus Liebigs Ann. Chem*. **1875**, *178*, 80; O. Billeter, *Helv. Chim. Acta* **1925**, *8*, 337.

[2] Earlier methods to synthesize allenyl thiocyanates:
E. Zbiral, *Monatsh. Chem*. **1966**, *97*, 180; E. Zbiral, H. Hengstberger, *Monatsh. Chem*. **1968**, *99*, 412; E. Zbiral, H. Hengstberger, *Justus Liebigs Ann. Chem*. **1969**, *721*, 121; S. Braverman, M. Freund, I. Goldberg, *Tetrahedron Lett.* **1980**, *21*, 3617; S. Braverman, Y. Duar, M. Freund, *Isr. J. Chem*. **1985**, *26*, 108; S. Braverman, M. Freund, *Tetrahedron* **1990**, *46*, 5759. P. W. Austin (Imperial Chemical Industries PLC), *UK Pat. Appl. GB* 2203145A, **1988** *Chem. Abstr*.: **1989**, *110*, P 192250r).