Pergamon

Tetrahedron Letters, Vol. 35, No 20, pp. 3281-3284, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 \$6.00+0.00

0040-4039(94)E0579-M

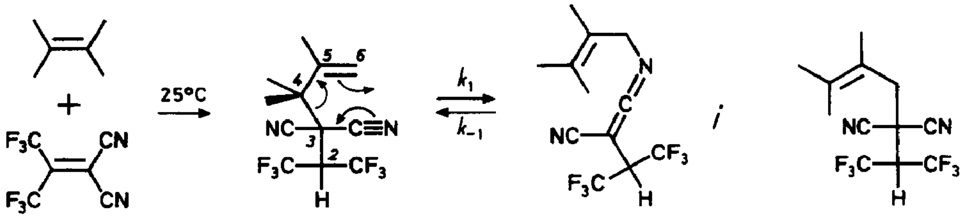
HOMOALLYL CYANIDE AND *N*-ALLYLKETENE IMINE; A [3,3]SIGMATROPIC EQUILIBRIUM

Reinhard Brückner [1] **and Rolf Huisgen***

Institut für Organische Chemie der Universität München
Karlstr. 23, D-80333 München, Germany

Abstract **The γ,δ-unsaturated nitrile 2 equilibrates at room temperature with the *N*-allylketene imine 3. Deuterium labeling established an *intramolecular* rearrangement, and the small influence of solvent polarity on the rate constants is in accordance with a concerted [3,3]sigmatropic shift.**

The *ene reaction* of 2,2-bis(trifluoromethyl)ethylene-1,1-dicarbonitrile (BTF, 1) [2] with 2,3-dimethyl-2-butene furnished 2 [3]. When the conversion in $CDCl_3$ or C_6D_6 at 25°C was monitored by ^1H NMR spectroscopy, 2 turned out to be the primary product which subsequently equilibrated with the isomeric ketene imine 3.

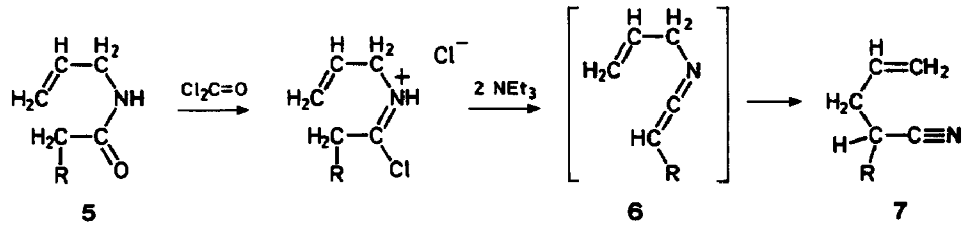


1 **2** **3** **4**

Pure 2 was isolated from the equilibrium mixture (4 d, CH_2Cl_2, 25°C) by distillation at 60°C/10^{-4} torr (84%) and crystallization from pentane at -15°C, mp 65°C (after recryst.)[4]. The ^1H and ^{19}F resonances of 2 were recorded immediately after dissolving in $CDCl_3$. Two vinyl-H at δ_H 5.22 and 5.39, s for 4-$(CH_3)_2$ at 1.57 and 5-CH_3 at 2.04 established the shifted double bond in 2; d at δ_F -61.8 ($J_{F,H}$ = 8.1 Hz) for two CF_3 groups and sept at δ_H 3.64 for 2-H revealed the type of ene product [3] with terminal trifluoromethyl groups.

New resonances appeared in the NMR spectra of 2 on storing the $CDCl_3$ solution, and a 50:50 equilibrium is approached with a half-reaction time of 12.3 h at 25°C. Singlets at δ_H 1.76 for one CH_3, 1.79 for 2 CH_3, and at 4.40 for N-CH_2 indicate 3 as substitution product of 2,3-dimethyl-2-butene; d at δ_F -68.2 and sept at δ_H 3.47 ($J_{H,F}$ = 7.7 Hz) signal the group -$CH(CF_3)_2$. δ(alkenyl-CH_2) occurs at lower field and $\delta(CF_3)$ at higher field than expected for 4 on the basis of δ(4-H_2) 2.9 - 3.1 and $\delta(CF_3)$ in compounds structurally related to 4 [3,5]. The lower solubility of 2 prevented the isolation of 3.

Like many polynitriles with neighboring CF_3 groups, **2** does not show a $C\equiv N$ stretching frequency in the IR spectrum (CCl_4). However, the rearranged isomer **3** displays the sharp $C\equiv N$ absorption of a conjugated nitrile at 2218 cm^{-1}, and the band at 2075 cm^{-1} for $C=C=N$ belongs to the most intense of the spectrum. These values correspond to 2210 and 2140 cm^{-1} reported for an α-cyanoketene imine [6]; 2031 and 2019 cm^{-1} were observed in our laboratory for the $C=C=N$ stretching frequency of two cyclic 7-membered, CF_3-substituted ketene imines [7,8]. The trifluoromethyl groups apparently increase the thermal stability of the ketene imine.



In 1965 Brannock and Burpitt [9] converted N-allylcarboxamides **5** into imidoyl chlorides by PCl_5 or phosgene; refluxing with triethylamine in benzene or THF led to nitriles **7**; the ketene imine **6** was a plausible intermediate, although its isolation or spectroscopic analysis were not accomplished. A Claisen-type rearrangement, **6** → **7**, was proposed. Recently Walters et al. [10,11] studied further examples of **5** → **7** in a "one-pot procedure" at room temperature with various reagents, 2 equiv. $(C_6H_5)_3P$ + 2 CCl_4 + 3 $(C_2H_5)_3N$ being the best. The "3-aza Claisen" rearrangement of the supposed ketene imine intermediate **6** proceeded at room temperature whereas the [3,3]sigmatropic equilibration of 1-hexene-5-yne with 1,2,5-hexatriene, the all-carbon analog, requires >300°C [12].

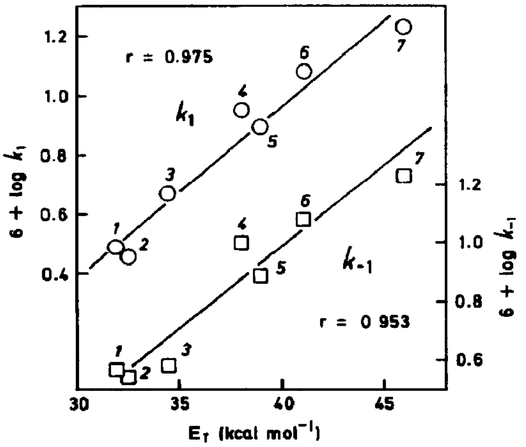
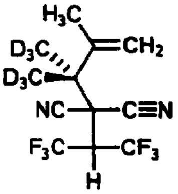


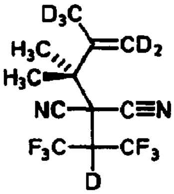
Figure 1. Solvent dependence of the rate constants for the [3,3]sigmatropic rearrangement **2** ⇌ **3** (solvent key in Table 1)

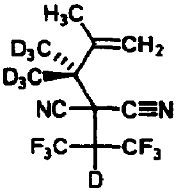
Table 1. Rate Constants at 25°C for the [3,3]Sigmatropic Rearrangement **2** → **3**

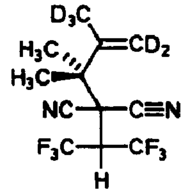
	Solvent	k_1 [$10^{-6}s^{-1}$]	k_{-1} [$10^{-6}s^{-1}$]	% 3 at Equilib.
1	$Cl_2C=Cl_2C$	3.0	3.7	44
2	CCl_4	2.8	3.5	44
3	C_6D_6	4.7	3.8	56
4	o-$C_6H_4Cl_2$	8.9	9.9	47
5	$CDCl_3$	7.8	7.8	50
6	CD_2Cl_2	12	14	47
7	CD_3CN	17	17	50

Pure **2** was equilibrated with **3** in various solvents at 25°C, and the **2**/**3** ratio was monitored by the ^{1}H NMR integrals of the vinylic methyl groups as a function of time [13]; k_1 and k_2 were evaluated with the rate law of reversible first-order reactions [14]. The rate constants (Table 1) increase only by a factor of 6 in going from tetrachloroethylene to acetonitrile indicating a modest increase of charge separation in the activation process, well in accordance with a concerted [3,3]sigmatropic rearrangement. Fairly good linear relations resulted for the plots of log k vs. Reichardt's parameter E_T of solvent polarity [15] (Fig. 1). Interestingly, the equilibrium constant, K = 0.8 - 1.2, does not depend on solvent polarity.


8


9


10


11

Although the isomerization **2** → **3** is hardly conceivable as a process involving a dissociation or ionization, we probed the *intramolecular* course by reacting $(D_3C)_2C=C(CH_3)_2$ [16] with **1**. The ene product, isolated after 4 d as described above, contained **8** and **9** in the ratio 82:18, corresponding to $(k_H/k_D)_{intra}$ = 4.5 at 25°C. After several d of equilibration with the ketene imine isomer, the MS analysis of the isolated deuterated **2** showed only M$^+$ 304 (6 D incorporated) with m/z = 305 only negligibly deviating from the ^{13}C isotope peak. A crossing over of fragments resulting from **8** and **9** should have led to some **10** (D_7) and **11** (D_5).

Why are **2** and **3** at nearly the same free energy level in contrast to the irreversible rearrangement **6** → **7** ? The 3,4-bond of **2** signalizes a hexasubstituted ethane; strain relief by breaking this bond may play a role.

ACKNOWLEDGMENT

We express our gratitude to the *Fonds der Chemischen Industrie*, Frankfurt, for supporting the research projects of this and the following communication. We thank Mr. *H. Huber* for his competent help in the spectroscopic measurements and Mr. *H. Schulz*, and Mrs. *M. Schwarz* for the microanalyses.

REFERENCES AND NOTES

Dedicated to Professor Wolfgang Steglich, München, on the occasion of his 60th birthday.

1. New address: Institut für Organische Chemie der Universität, Tammannstr. 2, 37077 Göttingen.
2. Middleton, W. J. *J.Org.Chem.* **1965**, *30*, 1402-1407.
3. Huisgen, R.; Brückner, R. *J.Org.Chem.* **1991**, *56*, 1679-1681.
4. Satisfactory elemental analyses have been obtained for all new compounds.

5. Brückner, R. Ph.D. Thesis, Univ. of Munich, 1984.
6. Abel, E. W.; Crow, J. P.; Wingfield, J. N., *J.Chem.Soc., Dalton Trans.* **1972**, 787-790.
7. Huisgen, R.; Langhals, E.; Mloston, G.; Oshima, T. *Heterocycles* **1989**, *29*, 2069-2074.
8. Huisgen, R.; Langhals, E.; Nöth, H. *J.Org.Chem.* **1990**, *55*, 1412-1414.
9. Brannock, K. C.; Burpitt, R. D. *J.Org.Chem.* **1965**, *30*, 2564-2565.
10. Walters, M. A.; McDonough, C. S.; Brown, P. S.; Hoem, A. B. *Tetrahedron Lett.* **1991**, *34*, 179-182.
11. Walters, M. A.; Hoem, A. B.; Arcand, H. R.; Hegeman, A. D.; McDonough, C. S. *Tetrahedron Lett.* **1993**, *34*, 1453-1456.
12. Huntsman, W. D., In *The Chemistry of Ketenes, Allenes, and Related Compounds*; S. Patai, Ed.; John Wiley and Sons, Inc.: New York 1980, pp 521, 603.
13. 0.18 - 0.22 mmol of **2** and 0.4 - 0.6 g solvent were weighed into the NMR tube. For each concentration measurement the sum of the NMR integrals was divided into the shares of **2** and **3**. Per run 8 - 17 analyses were taken within 13 - 18 hr, dependent on the solvent. Because the equilibrium is not reached in this time, we varied provisional values for A_e (nitrile **2**) at equilibrium in

$$k_1t = \frac{A_o - A_e}{A_o} \ln \frac{A_o - A_e}{A_t - A_e}$$

until the plots for this expression vs. time were linear. This dynamic determination of A_e and K is superior to the static one.
14. Huisgen, R. *Ausführung kinetischer Versuche*; In Methoden der organischen Chemie (Houben-Weyl), 4th ed.; Müller, E., Ed.; G. Thieme, Stuttgart 1955: Vol. 3/1, pp 101-162.
15. Reichardt, C. *Angew.Chem. Int.Ed.Engl.* **1979**, *18*, 98-110.
16. Prepared from isobutyric acid dianion with [D_6]acetone (24%), formation of ß-lactone with TsOH (64%), and thermolysis at 180-230°C (83%).

(*Received in Germany* 9 *March* 1994; *accepted* 18 *March* 1994)