LITERATURE CITED

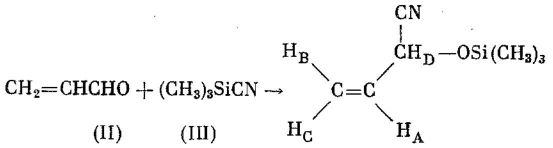
1. Yu. P. Kitaev and B. I. Buzykin, Hydrazones [in Russian], Nauka (1974).
2. M. Lamchen, W. Pugh, and A. M. Stephen. J. Chem. Soc., 2429 (1954).
3. R. C. Aggarwal and S. K. Singh, Bull. Chem. Soc. Jpn., 42, 2878 (1969).
4. F. Minisci, R. Galli, and M. Cecere, Gazz. Chim. Ital., 95, 751 (1965); Ref. Zh. Khim., No. 10Zh221 (1966).
5. F. Gasparini, D. Misiti, and E. Cernia, Inorg. Chim. Acta, 17, L3 (1976); Ref. Zh. Khim., No. 11B564 (1976).
6. H. Kosche, Belgium Patent No. 702458 (1968); Chem. Abstr., 69, P112216 (1968).
7. U. S. A. Patent No. 3208968 (1965); Chem. Abstr., 64, P881 (1966).
8. A. S. Kudryavtsev, Dissertation, Moscow (1964).
9. L. A. Movchan, A. S. Kudryavtsev, and I. A. Savich, Vestn. Mosk. Univ., Ser. Khim., 24, 116 (1969).
10. L. Hanter and I. A. Marriott, J. Chem. Soc., 2000 (1937).
11. H. El-Khadem, M. F. Iskander, and S. E. Zayan, Z. Anorg. Allg. Chem., 330, 109 (1964).
12. L. El-Sayed and M. F. Iskander, J. Inorg. Nucl. Chem., 33, 435 (1971).
13. T. V. Troepol'skaya and E. N. Minin, in: The Chemistry of Hydrazones [in Russian], Nauka (1977), p. 72.
14. L. P. Sysoeva, T. V. Troepol'skaya, B. I. Buzykin, and Yu. P. Kitaev, Zh. Org. Khim., 7, 1525 (1975).
15. M. F. Iskander, L. El-Sayed, and M. A. Lasheen, Inorg. Chim. Acta, 16, 147 (1976).
16. K. S. Balachandran and M. O. George, Tetrahedron, 29, 2119 (1973).
17. W. S. Biradar and B. R. Havinale, Inorg. Chim. Acta, 17, 157 (1976).
18. D. K. Rastogi, S. K. Dua, Shri Prakash, and R. P. Singh, Acta Chim. Acad. Scient. Hung., 87, 63 (1975).
19. N. N. Borisov, R. S. Sagitullin, and A. N. Kost., Khim. Geterotsikl. Soedin., 48 (1972).
20. K. Nakamoto, P. J. McCarty, A. Ruby, and A. E. Martell, J. Am. Chem. Soc., 83, 1066, 1272 (1961).

ISOMERIZATION OF 1-CYANO-1-TRIMETHYLSILOXY-2-PROPENE AND ITS REACTIONS WITH AMINES

M. G. Voronkov, N. A. Keiko,
T. A. Kuznetsova, V. V. Keiko,
E. O. Tsetlina, and V. A. Pestunovich

UDC 542.952.1:547.1'128

In the cyanosilylation of 2-ethoxyacrolein we previously observed the isomerization of 1-cyano-1-trimethylsiloxy-2-ethoxy-2-propene (I) under the effect of an "old" Speier catalyst, as well as in the absence of the catalyst upon heating [1]. In the present investigation we examined the possibility of the isomerization of 1-cyano-1-trimethylsiloxy-2-propene (IV) [2] obtained as a result of the action of trimethylcyanosilane on acrolein in the presence of various catalysts:



(II) (III) (IV)

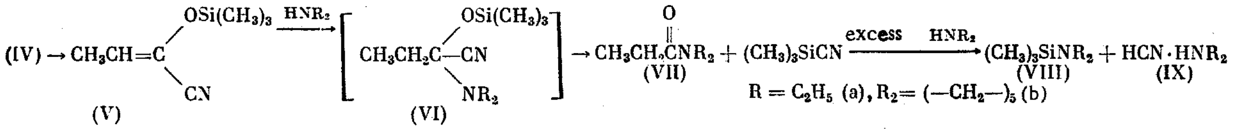
Unlike I, compound IV does not isomerize either upon heating (2 h, 169°C) or under the effect of the Speier catalyst, colloidal nickel, ZnI_2, or pyridine under the same conditions. It has previously been noted that α-heteroatomic β,γ-unsaturated nitriles are capable of prototropic isomerization under the action of amines, on whose structure and nature the rate of the conversion is dependent [3]. In fact, in the case of IV, isomerization is induced by small amounts of piperidine, diethylamine, and triethylamine.

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 906-909, April, 1978. Original article submitted December 14, 1976.

The structure of the isomer formed, viz., 1-cyano-1-trimethylsiloxy-1-propene (V), is supported by the spectral characteristics, which differ from the data for IV. For example, the IR spectrum of V shows intense absorption bands of the C = C (1647 cm^{-1}) and C ≡ N (2235 cm^{-1}) bonds, which are characteristic of conjugated systems and differ from the very weak corresponding bands for IV (compare [3]), while the band at 3100 (= CH_2) is absent. The parameters of the PMR spectrum of V unambiguously support its structure.

The fact that I [1] undergoes isomerization with greater ease than does IV is apparently due to the + C effect of the OR group, whose concerted influence with the electron-acceptor action of the CN group provides for the appearance of a single conjugated system in 1-cyano-1-trimethylsiloxy-2-ethoxy-1-propene, which is energetically considerably more favorable. The isomerization of IV to V is also accompanied by the formation of a conjugated system, but the geminal substituents have an opposing influence on the polarization of the double bond, and there is apparently no significant gain in energy in the system.

Reactions with an excess of a secondary amine result in further conversions of isomer V to form the corresponding amides of propionic acid and N-substituted aminosilanes. The hydrocyanides of the amines used, as well as free hydrocyanic acid, form in small amounts according to the scheme



The isomerization product, viz., α-trimethylsiloxycrotononitrile (V), probably reacts with the excess of the secondary amine to form an unstable adduct (VI). The dissociation of the latter produces N-substituted amides of propionic acid and trimethylcyanosilane, which undergoes an exchange reaction with the excess of the amine to form VIII and IX. The possibility of an exchange reaction was confirmed by a special synthesis of aminosilanes from cyanosilane. The addition of amines to the double bond of the α-trialkylsiloxycrotononitrile takes place in accordance with the polarization, which is determined by the + C effect of the trialkylsiloxy group. Thus, the effects of the trimethylsiloxy group apparently predominate among the competing effects of the substituents.

In the case of the inadequate freeing of the acrolein from the attendant propanal, the reaction mixture may contain α-trimethylsiloxybutyronitrile, which can be isolated by preparative gas chromatography, in addition to the compounds indicated.

For comparison, we carried out the reaction of I and its isomer with piperidine. The reaction proceeded in analogy to that described for IV. The corresponding amide of α-ethoxypropionic acid (X), N-trimethylsilylpiperidine (VIIIb), and piperidine hydrocyanide (IXb) were isolated.

EXPERIMENTAL

Trimethylcyanosilane was synthesized according to [4], bp 117°C, n_D^{20} 1.3916. All the reagents were distilled in a current of dry nitrogen immediately prior to their introduction into the reaction. The GLC of the reaction products was carried out on a Khrom-3 instrument at 90 and 170°C. The column was 4.6 m× 10 mm, the sorbent was XE-60 on Chromaton N-AW-HMDS (0.25-0.5 mm), and the detector was a katharometer. The IR spectra were obtained on a UR-20 spectrometer in the case of liquid microlayers. The PMR spectra of 10-30% solutions in CCl_4 were recorded on a Tesla BS487B spectrometer (80 MHz) relative to cyclohexane. The chemical shifts (in the τ scale) were measured with an accuracy of ± 0.01 ppm.

Addition of Trimethylcyanosilane to Acrolein in the Presence of an Old Speier Catalyst. A 24.8-g portion of III was added dropwise to a mixture of 14.01 g of II, 0.02 g of hydroquinone, and 0.3 ml of an old Speier catalyst with stirring. After being heated (2 h, 120°C), the mixture contained 92.2% of the 1,2-addition product (IV), according to the GLC data, with bp 69°C (17 mm). Compound IV was isolated by preparative gas chromatography, n_D^{20} 1.4175, d_4^{20} 0.8846. Found: C 53.91; H 8.43; Si 17.99; N 9.01%; MR 44.29. Calculated for $C_7H_{13}SiON$: C 54.14; H 8.43; Si 18.08; N 9.02% MR 44.37. IR spectrum (ν, cm^{-1}): 760 s, 856 v. s, 973 s, 1038 s, 1090 v. s, 1145 s, 1250 v. s, 1352 m, 1423 m, 1643 w, 1695 v. w, 2253 v. w, 2905 m, 2960 v. s, 3100 w. PMR spectrum (τ, ppm): 9.81 (s, CH_3Si), 5.08 (doublet of triplets, CH_D), 4.70 (m, H_C), 4.51 (m, H_B), 4.15 (m, H_A): ${}^3J_{AB}^{trans} = 17.1$, ${}^3J_{AC}^{cis} = 9.2$, ${}^2J_{BC}^{gem} = 1.8$, ${}^3J_{AD} = 4.5$, ${}^4J_{CD} = 1.5$, ${}^4J_{BD} = 1.0$ Hz.

Addition of Trimethylcyanosilane to Acrolein in the Presence of a Freshly Prepared Speier Catalyst. A 12.4-g portion of III was added dropwise to 7 g of II, 0.02 g of hydroquinone, and 0.02 ml of a freshly prepared Speier catalyst with stirring. After being heated (2 h, 106°C), the reaction mixture contained 75.6% IV, according to the GLC data.

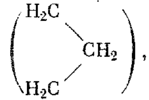
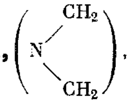
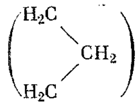
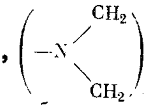
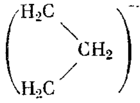
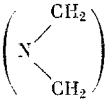
Addition of Trimethylcyanosilane to Acrolein in the Presence of Colloidal Nickel ($NiCl_2$/SiH). A 0.13-g portion of $NiCl_2$ and an 8.6-g portion of triethylsilane were boiled for 2 h until colloidal nickel formed [5]. After cooling, the triethylsilane was decanted, and one third of the $NiCl_2$/SiH was transferred to a reaction flask with II and hydroquinone. Then 12.4 g of III were added dropwise with stirring. After being heated (5 h, 186°C), the reaction mixture contained 71.3% IV according to the GLC data.

When the original acrolein is not adequately freed of propanal, an attendant reaction product with any of the catalysts cited is α-trimethylsiloxybutyronitrile (7-19%) (isolated by preparative gas chromatography), n_D^{20} 1.4078, d_4^{20} 0.8703. Found: C 53.05; H 9.45; Si 17.12; N 9.20%; MR 44.57. Calculated for $C_7H_{15}NOSi$: C 53.45; H 9.16; Si 17.86; N 8.91%; MR 44.84. The IR spectrum does not show a band in the region of the absorption of the C = C bond, and the unconjugated CN group displays very weak absorption (2245 cm^{-1}). PMR spectrum (τ, ppm): 9.85 (s, $SiCH_3$), 9.03 (m, CH_3), 8.34 (m, CH_2), 5.81 (t, CH, $^3J_{CH\,CH_2}$ = 7 Hz).

Isomerization of 1-Cyano-1-trimethylsiloxy-2-propene (IV) in the Presence of Piperidine. A 6.08-g portion of IV, 0.02 g of hydroquinone, and 0.04 ml of piperidine were boiled for 2 h at 171°C. According to the GLC data, partial isomerization took place, and the mixture contained isomer V in a 22.2% concentration. The 1-cyano-1-trimethylsiloxy-1-propene was isolated by preparative gas chromatography.

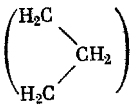
Isomerization of IV in the Presence of Triethylamine. A 5-g portion of IV, 0.02 g of hydroquinone, and 0.2 g of triethylamine were boiled for 6 h at 170°C. Distillation yielded 4.1 g (82.0%) of V, bp 64-65°C (17 mm), n_D^{20} 1.4235, d_4^{20} 0.8811. Found: C 54.20; H 8.84; Si 17.68; N 8.97%; MR 44.92. Calculated for $C_7H_{13}SiON$: C 54.14; H 8.43; Si 18.08; N 9.02%; MR 44.37. IR spectrum (ν, cm^{-1}): 755 s, 855, v. s, 1020 s, 1090 s, 1175 s, 1225 s, 1255 v. s, 1335 s, 1380 m, 1647 s, 2235 s, 2965 v. s. PMR spectrum (τ, ppm): 9.73 (s, CH_2Si), 8.38 (d, CH_3), 4.49 (q, CH, $^3J_{CH\,CH_3}$ = 7.2 Hz).

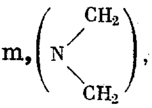
Isomerization of IV in the Presence of Diethylamine. A 3.5-g portion of IV, 0.02 g of hydroquinone, and 1.6 g (0.022 mole) of diethylamine were boiled for 2 h at 106°C. According to the GLC data, the concentration of V in the mixture was 66.8%.

Reaction of IV with Piperidine. A 20.44-g portion (0.24 mole) of piperidine was added with stirring to 18.6 g (0.12 mole) of IV and 0.02 g of hydroquinone. An increase in the temperature of the reaction mixture was observed. After heating (2 h, 94°C), the following compounds were isolated and characterized: 1. N-Cyclopentamethylenepropionamide (VIIb), 14.95 g (88.4%), bp 74.5°C (1 mm), n_D^{20} 1.4790, d_4^{20} 0.9808. Found: C 68.70; H 10.70; N 9.94%, MR 40.84. Calculated for $C_8H_{15}NO$: C 68.04; H 10.70; N 9.91%; MR 40.95. IR spectrum (ν, cm^{-1}): 815 w, 850 m, 895 w, 1018 s, 1070 s, 1142 s, 1225 v. s, 1255 s, 1375 m, 1440 v. s, 1475 v. s, 1645 v. s, 2860 v. s, 2940 v. s, 2980 v. s. PMR spectrum (τ, ppm): 9.00 (t, $CH_3CC{=}O$), 8.44 (m, , 7.75 (q, $CH_2C{=}O$), 6.61 (m, , $^3J_{CH_3CH_2}$ = 7.0 Hz). 2. Piperidine hydrocyanide (IXb), unstable colorless crystals, which readily sublime. Found: C 64.05; H 10.66; N 25.10%. Calculated for $C_6H_{12}N_2$: C 64.24; H 10.78; N 24.97%. IR spectrum (ν, cm^{-1}): 860 m, 930 m, 947 m, 1030 s, 1080 m, 1160 m, 1280 w, 1390 m, 1435 s, 1464 s, 1690 s, 2090 w, 2155 w, 2425 s, 2523 v. s, 2638 s, 2745 s, 2815 m. PMR spectrum (τ, ppm): 8.51 (m, , 7.31 (m,  7.02 (common singlet, (HCN·HN<), The position of the last signal is sensitive to dilution and changes in the temperature, making it possible to evaluate the weakly expressed salt formation. The weak-field signal characteristic of HC = N in the alternative formamide structure is not present in the spectrum. 3. An 8-ml fraction with n_D^{20} 1.4380, in which the presence of N-trimethylsilylpiperidine was established by comparison with a standard with the aid of GLC and PMR. PMR spectrum (τ, ppm): 9.98 [s, $(CH_3)_3Si$], 8.58 (m, 7.22 (m .

Reaction of IV with Diethylamine. A 12.14-g portion (0.16 mole) of diethylamine was added with stirring to a mixture of 12.89 g (0.08 mole) of IV and 0.02 g of hydroquinone. A strong increase in the temperature of the reaction was observed. After heating (2 h, 87°C), the following compounds were isolated by distillation and characterized: 1. N-Diethylpropionamide (VIIa), 5.85 g (51.72%), bp 88.5-89°C (19 mm), n_D^{20} 1.4425, d_4^{20} 0.8961. Found: C 63.80; H 11.78; H 12.63%; MR 38.18. Calculated for $C_7H_{15}NO$: C 65.07; H 11.7; N 12.38%;

MR 38.35. IR spectrum (ν, cm^{-1}): 795 m, 895 m, 1100 s, 1150 s, 1220 s, 1250 v. s, 1383 s, 1432 v. s, 1465 v. s, 1647 v. s, 2355 w, 2935 v. s, 2975 v. s. PMR spectrum (τ, ppm): 8.97 (t, $NCCH_3$, $^3J_{NCH_2CH_3} = 6$ Hz), 8.87 (t, CH_3COO), $^3J_{CH_2CH_3} = 6$ Hz), 7.74 (q, CH_2CO), 6.69 (q, NCH_2). 2. Diethylamine hydrocyanide (IXa), unstable colorless crystals, which turn brown and decompose when brought into contact with the air. IR spectrum (ν, cm^{-1}): 1030 w, 1050 s, 1145 s, 1180 s, 1260 s, 1320 m, 1370 s, 1450 s, 1615 m, 2075 m, 2820 v. s. PMR spectrum (τ, ppm): 8.97 (t, CH_3), 7.88 (s, $(HCN\cdot HN\langle)$, 7.43 (q, CH_2N, $^3J_{CH_2CH_2} = 7.0$ Hz). 3. The presence of N-trimethylsilyldiethylamine (VIIIa) was determined by comparison with a known sample with the aid of GLC.

Reaction of 1-Cyano-1-trimethylsiloxy-2-ethoxy-2-propene (I) with Piperidine. An 8.52-g portion (0.1 mole) of piperidine was rapidly added to 7.8 g (0.04 mole) of I, which was synthesized according to [1], and 0.02 g of hydroquinone. The following compounds were isolated and characterized after heating (2 h, 116°C) and distillation: 1. N-Cyclopentamethylene-2-ethoxypropionamide (X), 7.02 g (96.82%), bp 78.5°C (1.5 mm), n_D^{20} 1.4720, d_4^{20} 0.9959. Found: C 64.12; H 10.04; N 7.41%; MR 52.09. Calculated for $C_{10}H_{19}NO_2$: C 64.82; H 10.33; N 7.56%; MR 52.03. IR spectrum (ν, cm^{-1}): 852 m, 950 m, 1008 m, 1115 v. s, 1165 s, 1230 s, 1245 s, 1365 s, 1445 v. s, 1640 v. s, 2855 v. s, 2930 v. s, 2972 v. s. PMR spectrum (τ, ppm): 8.83 (t, $OCCH_3$), 8.69 (d, CH_3COO), 8.44 (m, 

, 6.62 (q, OCH_2), 6.49 (m, 

, 5.87 (q, CH); $^3J_{CH_2CH_3} = 7.2$, $^3J_{OCH_2CH_3} = 7.2$ Hz. 2. N-trimethylsilylpiperidine (VIIIb), 2.01 g (32.68%), bp 158°C, n_D^{20} 1.4418, d_4^{20} 0.8370 (compare the data in [6]). 3. Colorless unstable crystals of piperidine hydrocyanide were sublimed into a trap during the vacuum distillation.

Reaction of 1-Cyano-1-trimethylsiloxy-2-ethoxy-1-propene (XI) with Piperidine. An 8.09-g portion (0.1 mole) of piperidine was rapidly added to 9.46 g (0.05 mole) of XI, which was synthesized according to [1], and 0.02 g of hydroquinone. Heating (2 h, 116°C) and distillation yielded 5.22 g (53.3%) of X and 2.65 g (41.53%) of VIIIb Crystals of piperidine hydrocyanide were collected in a trap.

CONCLUSIONS

1. Cyanosilylated acrolein and 2-ethoxyacrolein isomerize in the presence of secondary amines and react with an excess of the latter to form derivatives of propionamide and N-substituted aminosilanes.

2. Unlike 1-cyano-1-trimethylsiloxy-2-ethoxy-2-propene, 1-cyano-1-trimethylsiloxy-2-propene is thermally stable and does not isomerize under the action of the Speier catalyst, colloidal nickel, ZnI_2, or pyridine.

LITERATURE CITED

1. M. G. Voronkov, N. A. Keiko, T. A. Kuznetsova, E. O. Tsetlina, V. A. Pestunovich, and V. K. Roman, Izv. Akad. Nauk SSSR, Ser. Khim., 403 (1977).
2. D. A. Evans, L. K. Trulsdak, and G. L. Carroll, J. Chem. Soc. Chem. Communs., 55 (1973).
3. N. A. Keiko, T. N. Mamashvili, I. D. Kalikhman, and M. G. Voronkov, Izv. Akad. Nauk SSSR, Ser. Khim., 2122 (1973).
4. M. G. Voronkov, V. K. Roman, and E. A. Maletina, in: Chemistry of Heteroorganic Compounds [in Russian], Nauka, Leningrad (1976), p. 49.
5. N. F. Frolov, R. A. Bogatkin, Z. I. Sergeeva, and M. G. Voronkov, Zh. Obshch. Khim., 32, 2651 (1962).
6. L. Birkofer, P. Richter, and A. Ritter, Chem. Ber., 93, 2804 (1960); R. Fessenden and D. T. Crowe, J. Org. Chem., 26, 4638 (1961).