Cyanosilylation of α-butylthioacrolein

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Cyanosilylation of α-butylthioacrolein with trimethylsilyl cyanide occurs as 1,2-addition. Concurrent rapid dimerization of α-butylthioacrolein occurred both in the presence and in the absence of $H_2PtCl_6 \cdot 6H_2O$ as a catalyst to give 2,5-dibutylthio-2,3-dihydro-4*H*-pyran-2-carbaldehyde, whose cyanosilylation afforded the corresponding cyanohydrin. The latter is prone to retrodiene degradation upon heating.

Key words: α-butylthioacrolein, cyanosilylation, Diels—Alder reaction; substituted dihydropyrans; retro-Diels—Alder reaction.

α-Alkylacroleins have not been studied for a long time because of their instability.[1—4] Recently, we have developed[5] a procedure for the synthesis of these compounds based on the Mannich reaction. The RS group in α-alkylthioacroleins, which exhibits the +M- and −I-effects, may affect differently the conjugated acryl system in heterocyclization reactions. *A priori* it would be expected that these polydentate highly reactive aldehydes will undergo nucleophilic 1,2- or 1,4-addition. However, electrophilic attack on the C=C bond is also possible if these compounds are considered as alkyl α-(formyl)vinyl sulfides. Like selenium analogs,[6,7] α-alkylthioacroleins readily undergo cyclodimerization according to the Diels—Alder reaction but unlike the former, they exist as monomers at room temperature for a rather long period of time.

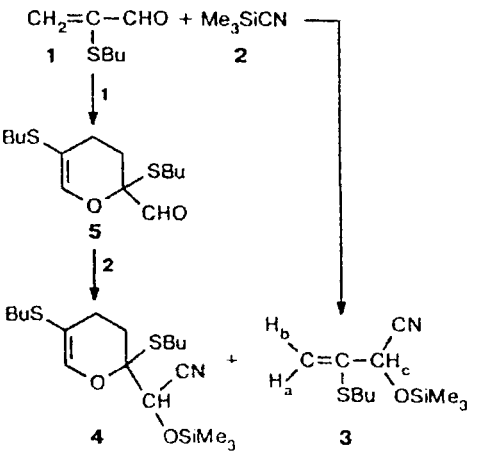
Such scavengers as 2,4-dinitrophenylhydrazine, alkanethiols, and dienophiles, namely, piperylene and hexachlorocyclopentadiene, which have been used to trap the monomeric form of α-alkylthioacroleins at the instant they were formed, appeared to be insufficiently reactive.[4,5,8,9] Reactions with these reagents proceeded too slowly to give final products in low yields (20—30%). As a consequence, dimerization of the initial α-alkylthioacrolein was the predominating competitive process in which the monomer was almost completely consumed.

It is known that the reactions of aldehydes, in particular, alk-2-enals, with Me_3SiCN occur as nucleophilic addition at the carbonyl group (the yields are 80—98%). These reactions were generally carried out in the presence of a Lewis acid[10,11] or $H_2PtCl_6 \cdot 6H_2O$ [12] and even in the absence of a catalyst.[10,13]

With the aim of examining the possibility of the use of trimethylsilyl cyanide (2) as a trap for labile α-alkylthioacroleins, we studied cyanosilylation of α-butylthioacrolein (1) under various conditions. It was expected that by analogy with other cyanosilylated alk-2-enals,[10] 3-alkylthio-2-trimethylsilyloxybut-3-enonitriles, in particular, nitrile 3, would enable regeneration of the initial carbonyl compound. In addition, these adducts can be used for preparing sulfur-containing 2-hydroxycarboxylic acids and other compounds analogous to those prepared by cyanosilylation of alkenals.[14—16]

The reaction of α-butylthioacrolein 1 with a small excess of silyl cyanide 2 in the absence of a catalyst at room temperature yielded (2,5-dibutylthio-2,3-dihydro-4*H*-pyran-2-yl)-(trimethylsilyloxy)acetonitrile (4) (~40%) and 2,5-dibutylthio-2,3-dihydro-4*H*-pyran-2-carbaldehyde (5) (~40%) (Scheme 1).

Scheme 1



Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 7, pp. 1418—1420, July, 1998.

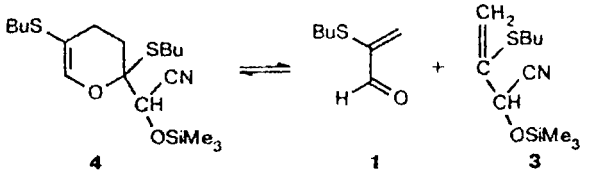
Apparently, adduct **4** resulted from cyanosilylation of cyclodimer **5**. Compound **4** is a 1 : 1 mixture of two diastereisomers. The ^{1}H NMR spectrum of the mixture shows doubled signals of the protons of the trimethylsilyl group and of the methine proton and a broadened signal of the olefin proton.

Cyanosilylation of α-butylthioacrolein **1** in the presence of $H_2PtCl_6 \cdot 6H_2O$, which was carried out at 20 °C for 1 day, afforded cyanosilylated dimer **4** as the major product (58%). The results obtained indicate that the rate of cyclodimerization of α-butylthioacrolein **1** is substantially higher than that of cyanosilylation.

To slow down dimerization of α-butylthioacrolein **1**, cyanosilylation was carried out in hexane with the use of an excess of silyl cyanide **2** (50%) and $H_2PtCl_6 \cdot 6H_2O$ as a catalyst. Under these conditions, 3-butylthio-2-trimethylsilyloxybut-3-enonitrile (**3**) was obtained in the individual form in low yield (~16%). In addition, the fraction that contained a mixture of nitrile **3** and cyclodimer **5** (~1 : 1, ^{1}H NMR spectroscopy) as well as adduct **4** was collected. Repeated distillation gave two major fractions. According to the ^{1}H NMR data, the first fraction was an equimolar mixture of adducts **3** and **5**, and the second fraction was pure adduct **4**. The IR spectrum of nitrile **3** is characterized by a very weak band of the CN group (at 2200 cm^{-1}). When cyanosilylaltion of α-butylthioacrolein **1** was carried out in ether at 5 °C (3 h) with the use of a twofold excess of silyl cyanide **2**, no increase in the yield of nitrile **3** was achieved. According to the ^{1}H NMR data, the ratio of compounds **3** and **4** in the reaction mixture was 1 : 10.

The GLC-MS examination of compound **4**, which is the product of cyanosilylation of cyclodimer **5**, revealed an intense peak at *m/z* 243, which corresponds to nitrile **3**, in addition to a peak at *m/z* 387 (**4** $[M]^+$). The former peak is indicative of the possible thermal retrodiene degradation of adduct **4** (Scheme 2).

Scheme 2



To confirm this suggestion, individual adduct **4**, which has been isolated by molecular rectification (at 150 °C) under high vacuum ($1 \cdot 10^{-3}$ Torr), was heated at 250 °C and 1 Torr. The distillate obtained contained nitrile **3** and α-butylthioacrolein **1** along with adduct **4** in a ratio of 1.5 : 1.5 : 1 (based on the data of ^{1}H NMR spectrum recorded immediately after distillation). The formation of compounds **1** and **3** confirmed that adduct **4** underwent retrodiene degradation. For comparison, retrodiene degradation of 2,3-dihydro-4*H*-pyran-2-carbaldehyde occurred only at 450—500 °C.[17] Profound retrodiene degradation of compound **4** upon heating and a substantially lower amount of nitrile **3** in the fractions obtained by standard vacuum distillation indicate that nitrile **3** can also participate actively in the Diels—Alder reaction as a dienophile. It is the second possible pathway of formation of adduct **4** in the reaction of α-butylthioacrolein **1** with silyl cyanide **2** (see Scheme 2).

Experimental

The ^{1}H NMR spectra were recorded in $CDCl_3$ at room temperature on a JEOL FX-90Q spectrometer operating at 89.95 MHz with HMDS as the internal standard. The mass spectra were obtained on a Hewlett-Packard HP5971A GLC-mass spectrometer equipped with a mass-selective detector and an HP-5890 chromatograph.

α-Butylthioacrolein **1** used in the reactions contained 20% of cyclodimer **5**.

Reaction of Me_3SiCN with α-butylthioacrolein in the presence of the Spier catalyst. Me_3SiCN (6.88 g, 0.069 mol) was rapidly added with intense stirring to a mixture of α-butylthioacrolein **1** (10 g, 0.055 mol), hydroquinone (0.002 g), and a 0.1 *M* solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol (0.03 mL).

The reaction was exothermal. The mixture was stirred for 45 min, and the low-boiling compounds were removed *in vacuo* under an atmosphere of argon. Distillation gave adduct **4** in a yield of 6.81 g (57.9%), b.p. 188—189 °C (1 Torr); n_D^{20} 1.4935. Found (%): C, 54.90; H, 9.08; S, 16.76. $C_{18}H_{33}NO_2S_2Si$. Calculated (%): C, 55.77; H, 8.58; S, 16.54. IR, ν/cm^{-1}: 1585, 1610 (C=C); 2200 (C≡N). ^{1}H NMR, δ: 0.2 and 0.24 (both s, 9 H, $SiMe_3$); 0.89 (t, 6 H, C<u>CH</u>$_3$CH$_2$—); 1.48 (m, 8 H, Me—<u>CH</u>$_2$—C<u>H</u>$_2$); 2.06 (m, 4 H, 3,4-CH_2); 2.54 (m, 4 H, CH_2S); 4.54 and 4.65 (both s, 1 H, CHCN); 6.56 (s, 1 H, HC=). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 387 $[M]^+$ (16), 298 $[M-SC_4H_9]^+$ or $[M-OSiMe_3]^+$ (38), 243 $[M-CH_2=C(SC_4H_9)CHO]^+$ (19), 208 (18), 187 (15), 145 (15), 115 $[CH_2=C(SC_4H_9)]^+$ (53), 73 $[SiMe_3]^+$ (100).

Reaction of MeSiCN with α-butylthioacrolein without a catalyst. α-Butylthioacrolein **1** (10 g, 0.55 mmol) was rapidly added to a mixture of Me_3SiCN (6.8 g, 0.069 mol) and hydroquinone (0.002 g). The temperature increased spontaneously by 8 °C. The reaction mixture was stirred for 2 h. Distillation *in vacuo* under an atmosphere of argon gave a fraction with b.p. 130—140 °C (1 Torr), n_D^{20} 1.5045, which contained predominantly cyclodimer **5** (3.86 g, 38.6%) (*cf.* Ref. 3) and adduct **4** (6.15 g, 40%), b.p. 182—203 °C (1 Torr), n_D^{20} 1.4930.

Addition of Me_3SiCN to α-butylthioacrolein in hexane. Me_3SiCN (7.8 g, 0.079 mol) to which the Spier catalyst has been preliminarily added was mixed with intense stirring with a solution of hydroquinone (0.002 g) and freshly distilled α-butylthioacrolein **1** (10 g, 0.055 mol) in hexane (100 mL). The reaction mixture was stirred for 5 h. Distillation under an atmosphere of argon gave nitrile **3** in a yield of 2.08 g (15.5%), b.p. 120—130 °C (1 Torr), n_D^{18} 1.4700. Found (%): C, 53.50; H, 9.14; S, 13.47. $C_{11}H_{21}NOSSi$. Calculated (%): C, 54.27; H, 8.70; S, 13.17. ^{1}H NMR, δ: 0.22 (s, 9 H, $SiMe_3$); 0.91 (t, 3 H, Me); 1.56 (m, 4 H, CH_2CH_2); 2.76 (m, 2 H, CH_2S); 4.93 (s, 1 H, H_a); 5.11 (s, 1 H, H_b); 5.66 (s, 1 H, H_c). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 243 $[M]^+$ (14), 228 $[M-CH_3]^+$ (5), 187 (5).

172 (5), 156 (13), 145 $[M-OSi(CH_3)_3-C_4H_8]^+$ (100), 115 $[CH_2=C(SC_4H_9)]^+$ (36), 84 (20), 75 (28), 73 $[Si(CH_3)_3]^+$ (82). In addition, a fraction with b.p. 148—173 °C (1 Torr), n_D^{18} 1.4995, was collected in a yield of 10.6 g. The fraction contained adducts **3**, **5**, and **4**. Repeated distillation of this fraction afforded a fraction (1.5 g) with b.p. 105—110 °C (2 Torr), $n_D^{20.5}$ 1.4770, which, according to the data of ^{1}H NMR spectroscopy, contained an equimolar mixture of **3** and **5**. In addition, a fraction with b.p. 202—204 °C (2 Torr), n_D^{21} 1.5000, was isolated in a yield of 5.0 g. The latter fraction contained adduct **4** (^{1}H NMR data).

Retro-Diels—Alder reaction of adduct 4. Molecular distillation carried out at $1 \cdot 10^{-3}$ Torr and 150 °C gave spectrally pure (^{1}H NMR data) adduct **4** with n_D^{22} 1.4965. Found (%): C, 54.67; H, 8.52; N, 3.41. $C_{18}H_{33}NO_2S_2Si$. Calculated (%): C, 55.77; H, 8.58; N, 3.61. Vacuum distillation of this compound at the boiling temperature of 130—200 °C (1 Torr) (the temperature of the bath was 250 °C) afforded a distillate that contained (immediately after distillation) a mixture of compounds **4**, **1**, and **3** in a ratio of 1 : 1.5 : 1.5 (according to the ^{1}H NMR data).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 97-03-33132a).

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Received January 12, 1998