Trimethylsilanecarbonitrile Oxide

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The reaction between silver fulminate and substituted chlorosilanes has been reported to produce triphenylsilanecarbonitrile oxide from chlorotriphenylsilane and unidentified products from chlorotrimethylsilane[1]. On the contrary, in our hands, the reported reaction appeared to be difficult with chlorotriphenylsilane whereas trimethylsilanecarbonitrile oxide (3) was easily isolated. The preparation of the nitrile oxide 3 was then improved by reacting bromotrimethylsilane (2) with the less dangerous mercury fulminate (1).

The pure compound **3** is a stable, colourless oil at room temperature and can be stored in sealed tubes; after two days heating at 70 °C, it is converted in part to trimethylsilyl isocyanate (**4**), $\nu_{N=C=O} = 2280$ cm^{-1} (in chloroform; Ref.[2], $\nu = 2282$ cm^{-1}), ^{29}Si-N.M.R.: $\delta = 4.4$ ppm (in deuteriochloroform; Ref.[3], $\delta = 7.4$ ppm) according to the well-known behaviour of nitrile oxides[4].

Owing to its high sensitivity to moisture, the silylated nitrile oxide **3** must be handled in dry-box; a reaction with water without solvent led to violent decomposition, but under milder conditions hexamethyldisiloxane (**6**) and "metafulminuric acid" (**5**)[5] were identified as the main products, thus indicating a primary hydrolysis to trimethylsilanol and fulminic acid.

The nitrile oxide **3** behaves as a 1,3-dipole: on cycloaddition with methyl methacrylate one regioisomer **7** is obtained, which in turn is hydrolysed to the cyanoester **8**. The structure of this product, and hence that of the cycloadduct **7**, is supported by the signal at $m/z = 103$ observed in the mass spec-

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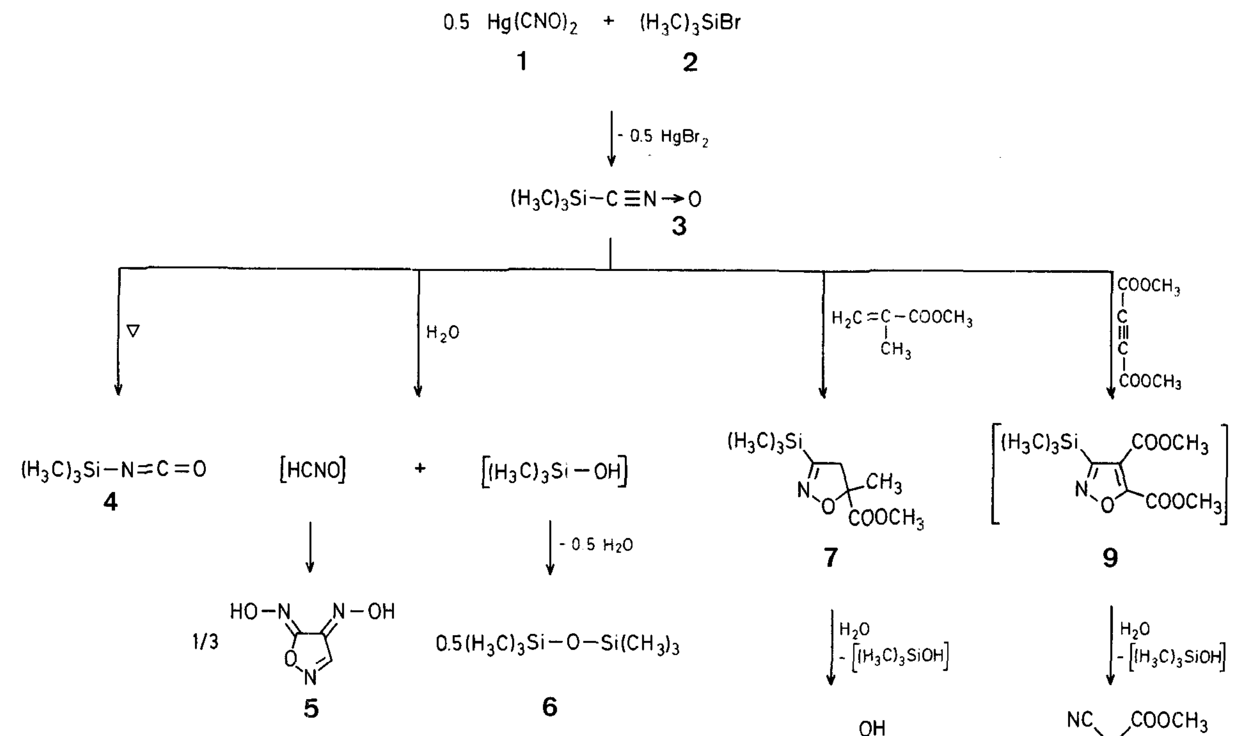

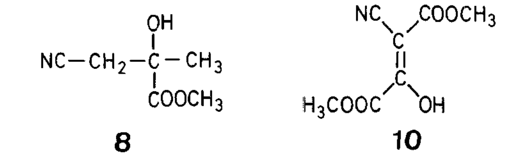

trum and ascribed to the fragment ion $[HO—C(CH_3)COOCH_3]^+$. With dimethyl acetylenedicarboxylate, the expected cycloadduct **9** could not be characterised and the corresponding cyanoester **10** was directly isolated on exposure of the reaction mixture to the atmospheric moisture.

These processes illustrate one of the possible synthetic applications of the title compound **3**, as a reagent for the cyanohydroxylation of unsaturated systems. This method is to be preferred to the known sequence: 1. cycloaddition of fulminic acid, 2. ring-opening with bases[7,8], because: (a) the nitrile oxide **3** is more simply prepared and more stable than fulminic acid; (b) the ring-opening occurs under much milder conditions, no base being required.

I.R. spectra were recorded with a Perkin-Elmer 283 spectrophotometer, ^{1}H-N.M.R. spectra with a Perkin-Elmer R 32 spectrometer (90 MHz), ^{13}C- and ^{29}Si-N.M.R. spectra with a Varian FT-80A spectrometer (respectively, 20 and 15.801 MHz), mass spectra with a Perkin-Elmer 270 mass-spectrometer. N.M.R. shifts (deuteriochloroform solutions unless otherwise stated) are given in ppm from TMS; coupling constants (J) in Hertz. Microanalyses were carried out with a Perkin-Elmer 240 C elemental analyzer.

Trimethylsilanecarbonitrile Oxide (3):

Safety mask and gloves are recommended. Mercury fulminate (**1**; prepared from 17.1 g of mercury nitrate) is transferred into a three-necked flask equipped with magnetic stirrer, condenser, dropping funnel, and gas-inlet tube, containing anhydrous diethyl ether (70 ml). Bromotrimethylsilane[9] (**2**; 10 ml, 76 mmol) is added under nitrogen and stirring is continued for 15 min. The salt is removed by filtration under nitrogen and the clear solution concentrated in vacuo. The residue (solid below 0 °C) is crystallised from light petroleum (70 ml) at −60 °C (white needles) and collected by filtration in a cooled dry-box; yield: >90% (based on **2**); m.p. 15–18 °C.

C_4H_9NOSi	calc.	C 41.71	H 7.87	N 12.16
(115.2)	found	41.04	7.88	13.91[10]

I.R. (CCl_4): $\nu = 2205$ cm^{-1} (C≡N).

^{1}H-N.M.R. ($CDCl_3$): $\delta = 0.2$ ppm.

^{13}C-N.M.R. ($CDCl_3$): $\delta = -1.5$ (q, $^1J_{CH} = 121$ Hz); 36.5 ppm [t, $^1J(^{13}C-^{14}N) = 36$ Hz].

^{29}Si-N.M.R. ($CDCl_3$): $\delta = -9.5$ ppm.

Hydrolysis of the Nitrile Oxide 3:

A 4 molar solution of the nitrile oxide **3** in pure chloroform (2 ml) is stirred with water (1 ml) for 5 min. *Hexamethyldisiloxane* (**6**) is the sole product detected in the organic layer by ^{1}H-N.M.R. ($\delta = 0.3$ ppm) and identified by G.C.-mass spectrometry[11].

A white precipitate is collected from the aqueous layer and identified as *metafulminuric acid* (**5**); yield: 45%, m.p. 115–118 °C (dec., from ether + light petroleum); Ref.[5], m.p. 118 °C (dec.).

^{13}C-N.M.R.-{^{1}H} (CD_3COCD_3): $\delta = 154.0$; 149.2; 131.0 ppm.

5-Methoxycarbonyl-5-methyl-3-trimethylsilyl-4,5-dihydro-1,2-oxazole (7):

A solution of the nitrile oxide **3** (1.15 g, 0.01 mol) and methyl methacrylate (1.06 ml, 0.01 mol) in anhydrous benzene (10 ml) is gently refluxed for 12 h, then concentrated in vacuo. The adduct **7**, almost pure, is obtained as a yellow oil; yield: 90%.

$C_9H_{17}NO_3Si$	calc.	C 50.21	H 7.96	N 6.50
(215.3)	found	50.12	7.82	7.26

^{1}H-N.M.R. ($CDCl_3$): $\delta = 0.17$ (s, 9 H); 1.47 (s, 3 H); 2.76 (d, 1 H, $J = 17$ Hz); 3.44 (d, 1 H, $J = 17$ Hz); 3.67 ppm (s, 3 H).

^{13}C-N.M.R. ($CDCl_3$): $\delta = -2.7$ [$(H_3C)_3Si$, $^1J_{CH} = 120$ Hz]; 22.8 (H_3C—C, $^1J_{CH} = 129$ Hz, $^3J_{CH} = 4.5$ Hz); 50.8 (CH_2, $^1J_{CH} = 135.5$ Hz, $^3J_{CH} = 4$ Hz); 52.3 (H_3CO, $^1J_{CH} = 148$ Hz); 81.8 (C-5); 160.4 (C-3); 172.6 ppm (C=O).

^{29}Si-N.M.R. ($CDCl_3$): $\delta = -6.5$ ppm.

Methyl 2-Hydroxy-2-methyl-4-nitrilobutanoate (8):

The adduct **7**, obtained as above, is magnetically stirred with water (2 ml) at room temperature for 2 h. Chloroform (10 ml) is added, the organic layer is dried with sodium sulphate, and concentrated in vacuo. By Kugelrohr distillation (0.1 torr, 120 °C oven temperature) the pure cyanoester (**8**) is obtained; yield: 1.11 g (78%).

$C_6H_9NO_3$	calc.	C 50.34	H 6.34	N 9.79
(143.1)	found	50.93	6.29	10.20

M.S.: m/e (relative intensity %) = 143 (0.5, M^+); 142 (0.7); 128 (0.4, $M^+ - CH_3$); 112 (0.4, $M^+ - H_3CO$); 103 (4, $M^+ - CH_2CN$); 85 (9); 84

(89, M^{+} − $COOCH_3$); 83 (13); 75 (2); 69 (1.5); 68 (4); 61 (1); 59 (5); 58 (2); 44 (4); 43 (100); 42 (46); 41 (4).

^{1}H-N.M.R. ($CDCl_3$): δ = 1.47 (s, 3H); 2.71 (s, 2H); 3.28 (br s, 1H); 3.80 ppm (s, 3H).

^{13}C-N.M.R. ($CDCl_3$): δ = 25.2 (CH_3, $^{1}J_{CH}$ = 130 Hz; $^{3}J_{CH}$ = 2.7 Hz); 28.8 (CH_2, $^{1}J_{CH}$ = 137.5 Hz, $^{3}J_{CH}$ = 4.9 Hz); 53.2 (q, H_3CO, $^{1}J_{CH}$ = 149 Hz); 71.9 (q, C—OH, $^{2}J_{CH}$ = 4.6 Hz); 115.95 (t, C≡N, $^{2}J_{CH}$ = 9.5 Hz); 173.9 ppm (s, C=O).

Dimethyl 2-Cyano-3-hydroxyfumarate (10):

Dimethyl acetylenedicarboxylate (1.23 ml, 0.01 mol) is added to the nitrile oxide **3** (1.15 g, 0.01 mol) and the mixture is set aside in a stoppered flask until the nitrile oxide is no longer detected by I.R. spectroscopy (2 days). The obtained oil, on exposure to atmospheric moisture, solidifies in a few minutes to give the cyanoester **10**; after washing with a little diethyl ether and drying, yield: 1.53 g (83%); m.p. 106–109 °C; m.p. (from benzene): 111 °C; Ref.[6], m.p. 108 °C.

^{1}H-N.M.R. ($CDCl_3$): δ = 4.00 (s, 6H); 12.4 ppm (br s, 1H).

^{13}C-N.M.R. ($CDCl_3$): δ = 53.7 (q, $COO\underline{C}H_3$, $^{1}J_{CH}$ = 149 Hz); 54.0 (q, $COO\underline{C}H_3$, $^{1}J_{CH}$ = 150 Hz); 159.2 (q, $\underline{C}OOCH_3$, $^{3}J_{CH}$ = 3.8 Hz); 169.9 (q, $\underline{C}OOCH_3$, $^{3}J_{CH}$ = 3.8 Hz); 85.2, 169.1 (2 s, $\underline{C}=\underline{C}$); 111.9 ppm (s, C≡N).

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