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> LETTERS TO THE EDITOR

Reactions of 1,1-Dimethyl-2,2-bis(trimethylsilyl)hydrazine with Alcohols and Ketones: A New Route to Trimethylsilyl Enol Ethers

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Proceeding with studies on the reactivity of organosilicon derivatives of 1,1-dimethylhydrazine [1, 2], we examined the reactions of 1,1-bis(trimethyl-silyl)-2,2-dimethylhydrazine \mathbf{I} with alcohols and enolizing ketones. The reaction of \mathbf{I} with excess methanol leads to the cleavage of both N–Si bonds according to the following scheme:

 $Me_2NN(SiMe_3)_2 + 2HOMe \rightarrow Me_2NNH_2 + 2Me_3SiOMe.$

Hydrazine I did not react with acetophenone in THF and methylene chloride in a sealed ampule at 90°C during a period of 20 h even in the presence of the catalytic amounts of cesium fluoride or KCN/18-crown-6 complex. However, on adding an equimolar amount of methyl iodide into the above mixture, 1-phenyl-1-(trimethylsiloxy)ethene II readily formed in 98% yield. The second reaction product was the crystalline precipitate of 1,1,1-trimethyl-2-trimethyl-silylhydrazinium iodide. Phenyl isopropyl ketone and methyl *tert*-butyl ketone react with I similarly in the presence of methyl iodide to form the corresponding trimethylsilyl enol ethers III and IV in 72% and 86% yields, respectively.

 $\begin{array}{rl} \mathrm{Me_2NN}(\mathrm{SiMe_3})_2 + \mathrm{RCOCHR'_2} + \mathrm{MeI} \\ \longrightarrow & \mathrm{R}(\mathrm{Me_3SiO})\mathrm{C=CR'_2} + [\mathrm{Me_3NHSiMe_3}]^+\mathrm{I^-}, \\ \mathrm{R} = \mathrm{Ph}, \ \mathrm{R'} = \mathrm{H} \ (\mathrm{II}), \ \mathrm{Me} \ (\mathrm{III}); \ \mathrm{R} = t\text{-Bu}, \ \mathrm{R'} = \mathrm{H} \ (\mathrm{IV}). \end{array}$

The easiness of the process and the high yields of trimethylsilyl enol ethers allowed this reaction to be recommended as a preparative route to these compounds. It is interesting that, in the absence of ketones, hydrazine I does not react with methyl iodide even at prolonged heating.

Reaction of 1,1-dimethyl-2,2-bis(trimethylsilyl)hydrazine I with methanol. A solution of 4.08 g of hydrazine I in 5 ml of absolute methanol was placed in an evacuated glass ampule and heated for 5 h at 95°C. A GLC analysis using references showed that the reaction mixture contained dimethylhydrazine, trimethylmethoxysilane, and an excess of methanol, with compound I being completely consumed.

Reaction of 1,1-bis(trimethylsilyl)-2,2-dimethylhydrazine I with acetophenone. A solution of 4.08 g of I and 2.4 g of acetophenone in 20 ml of absolute THF was stirred in an evacuated glass ampule with a magnetic stirrer for 20 h at 90°C. Distillation of the reaction mixture in a vacuum gave the starting compounds in quantitative yields. Similar results were obtained on adding 1.6 g of CsF or 0.5 g of KCN/18crown-6 complex to the reaction mixture.

Reaction of I with acetophenone and methyl iodide. A solution of 6.0 g of **I**, 3.5 g of acetophenone, and 10 ml of methyl iodide in 20 ml of dry methylene chloride was heated for 20 h at 90°C in an ampule. The precipitate was filtered off and washed with two 10-ml portions of methylene chloride. Distillation of the combined filtrates gave 5.5 g (98%) of Ph(Me₃SiO)CH=CH₂, bp 75°C (5 mm Hg), n_D^{20} 1.5040. Published data [3]: bp 53–54°C (1 mm Hg), n_D^{20} 1.5040.

According to GCL data, the product is highly pure, and its retention time agrees with that of the specially prepared reference.

The precipitate (slightly yellowish crystals) is 1,1,1-trimethyl-2-trimethylsilylhydrazinium iodide $[Me_3NNHSiMe_3]^+I^-$, yield 6.4 g (81%), mp 158°C. ¹H NMR spectrum (CD₃CN, TMS), δ , ppm: 0.313 s (9H, SiMe₃); 3.50 s [9H, N⁺Me₃]; 5.86 s (1H, NH). ²⁹Si NMR spectrum (CD₃CN, TMS), δ_{Si} , ppm: 8.86.

Reaction of I with phenyl isopropyl ketone and methyl iodide. A solution of 3.0 g of **I**, 2.02 g of phenyl isopropyl ketone, and 2.5 g of methyl iodide in 20 ml of absolute methylene chloride was heated for 100 h at 95°C. The precipitate was filtered off, and the filtrate was distilled in a vacuum to give 2.16 g (72%) of Ph(Me₃SiO)C=CMe₂ **III**, bp 60–62°C (0.5 mm Hg), n_D^{20} 1.4936. ¹H NMR spectrum, δ , ppm: 0.01 s (9H, SiMe₃), 1.86 s, 1.79 s (6H, =CMe₂); 7.31 m (5H, C₆H₅).

Reaction of I with *tert*-butyl methyl ketone and methyl iodide. A solution of 4.08 g of hydrazine I, 2.0 g of *tert*-butyl methyl ketone, and 5.0 g of methyl iodide in 10 ml of absolute methylene chloride was heated for 15 h at 95°C. The precipitate was filtered off, and the filtrate was distilled in a vacuum to give 2.96 g (86%) of *t*-Bu(Me₃SiO)C=CH₂, bp 69–70°C (70 mm Hg), n_D^{20} 1.4159. ¹H NMR spectrum, δ , ppm: 0.21 s (9H, SiMe₃), 1.05 s (9H, CMe₃), 3.92 d, 4.08 d (2H, =CH₂, ²J_{HH} 1.29 Hz).

Reaction of I with methyl iodide. A solution of 4.08 g of **I** and 5.0 g of methyl iodide in 10 ml of absolute THF was heated for 50 h at 95°C. No formation of the salt was observed, and, according to GLC data, the reaction mixture contained only the starting substances which were quantitatively recovered by distillation.

The ¹H and ²⁹Si NMR spectra were recorded on a Bruker DPX-400 spectrometer against internal TMS

from 10–20% solutions of the compounds in CDCl_3 or CD_3CN . The chemical shifts were measured with an accuracy of 0.01 ppm and are presented in the δ scale.

The GLC studies were carried out on a Tsvet-500 chromatograph equipped with a catharometer and 3000×4 -mm glass columns packed with Inerton-Super (0.125–0.150 mm granulation) impregnated with 10% PMS-1000.

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