

SHORT
COMMUNICATIONS

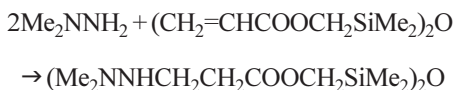
Synthesis of Trimethylsilyl β -(2,2-Dimethylhydrazino)propionate

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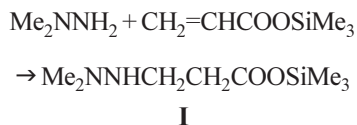
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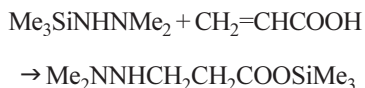
Aliphatic esters of β -(2,2-dimethylhydrazino)propionic acid were synthesized by reaction of 1,1-dimethylhydrazine with the corresponding alkyl acrylates [1, 2]. Methyl acrylate is known to react with 1,1-dimethylhydrazine in polar solvents (water, alcohol), affording a cyclic adduct, 1,1-dimethyldihydro-pyrazol-1-ium-3-olate [1]. In the reaction of an organosilicon acrylate, 1,3-bis(acryloyloxymethyl)-1,1,3,3-tetramethyldisiloxane with 1,1-dimethylhydrazine, product of addition at the double bond is formed in a poor yield (26.6%) [3].



Trimethylsilyl β -(2,2-dimethylhydrazino)propionate (**I**) is a starting compound in the synthesis of Mildranat, which is an efficient cardiotropic drug [4–7]. With the goal of preparing compound **I** we examined the reaction of trimethylsilyl acrylate with 1,1-dimethylhydrazine.



However, heating of an equimolar mixture of the reactants for 4 h at 60°C gave only 24% of ester **I**. We succeeded in obtaining compound **I** in 85% yield by reaction of trimethyl(2,2-dimethylhydrazino)silane with acrylic acid in boiling diethyl ether (reaction time 2 h).



The reaction involves cleavage of the Si–N bond in trimethyl(2,2-dimethylhydrazino)silane with formation of

1,1-dimethylhydrazine and trimethylsilyl acrylate. The subsequent addition of 1,1-dimethylhydrazine at the double bond of trimethylsilyl acrylate leads to the final product in high yield.

Trimethylsilyl acrylate was prepared by reaction of 13.5 g (0.19 mol) of acrylic acid with 43 g (0.27 mol) of hexamethyldisilazane. Yield 22.6 g (84%), bp 35°C (15 mm), $n_{\text{D}}^{20} = 1.4092$; published data [8]: bp 52–54°C (57 mm), $n_{\text{D}}^{20} = 1.4109$.

Trimethylsilyl β -(2,2-dimethylhydrazino)propionate (I**).** (a) A flask was charged with a few crystals of hydroquinone and 14.4 g (0.1 mol) of trimethylsilyl acrylate, and 6 g (0.1 mol) of 1,1-dimethylhydrazine was added dropwise under stirring. The mixture was stirred for 4 h at 60°C. Yield of ester **I** 4.5 g (23.5%), bp 74°C (3 mm), $n_{\text{D}}^{20} = 1.4331$. ^1H NMR spectrum (CDCl_3), δ , ppm: 0.13 s (9H, MeSi), 2.27 s (6H, MeN), 2.36 t (2H, CCH_2), 2.83 t (2H, NCH_2).

(b) Acrylic acid, 99.4 g (1.38 mol), was added dropwise at 7°C to a mixture of 187 g (1.3 mol) of trimethyl(2,2-dimethylhydrazino)silane and 500 ml of dry diethyl ether, and the mixture was heated for 2 h under reflux. Yield of ester **I** 236 g, bp 62–62°C (2 mm), $n_{\text{D}}^{20} = 1.4300$. Found, %: C 47.21; H 9.76; Si 13.81. $\text{C}_8\text{H}_{20}\text{N}_2\text{O}_2\text{Si}$. Calculated, %: C 47.02; H 9.87; Si 13.74.

The ^1H NMR spectra were recorded on a Bruker DPX-400 spectrometer from 10–20% solutions in CDCl_3 using tetramethylsilane as internal reference. The chemical shifts were measured with an accuracy of ± 0.01 ppm.

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