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Reactions of *N*-Bromohexamethyldisilazane with Triorganylsilanes

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Abstract—Reactions of *N*-bromohexamethyldisilazane $(Me_3Si)_2NBr$ with Si–H compounds of the general formula RR'_2SiH yield up to 90% of unsymmetrical disilazanes $(Me_3Si)_2NSiRR'_2$ and bromotrimethylsilane. An unexpected solvent effect on the reaction conditions is revealed: In benzene the products are formed already on mixing, whereas in cyclohexane, under UV irradiation only.

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N-Bromohexamethyldisilazane $(Me_3Si)_2NBr$ is a promising reagent for free-radical bromination of organic and organoelement compounds. With $(Me_3Si)_2NBr$, unlike what is observed with most brominating agents, abstraction of hydrogen from substrates involves the nitrogen-centered hexamethyldisilazanyl radical, rather than the bromine radical, which alters the selectivity of the whole process [1].

The reactivity of $(Me_3Si)_2NBr$ was poorly studied so far because of the lack of reliable methods of its synthesis. We recently developed a procedure for the preparative synthesis of $(Me_3Si)_2NBr$ in up to 80% yield, based on photoinduced reaction of *N*-bromosuccinimide with hexamethyldisilazane in carbon tetrachloride [2]. To reveal the synthetic potential of $(Me_3Si)_2NBr$, we studied its reactions with triorganylsilanes, tetramethyldisiloxane, and tetramethyldisilazane under UV irradiation. The reactions unexpectedly gave unsymmetrical hexaorganyldisilazanes **I**–**VI** in yields of up to 83% and bromotrimethylsilane in quantitative yield.

$$(Me_3Si)_2NBr + RR'_2SiH \xrightarrow{h\nu} Me_3SiNHSiRR'_2 + Me_3SiBr,$$

RR'_2 = $MePh_2$ (**I**); Me_2Ph (**II**); Ph_3 (**III**); $(EtO)_3$ (**IV**); $HMe_2SiOSiMe_2$ (**V**); $HMe_2SiNHSiMe_2$ (**VI**).

The reactions were performed under UV irradiation of the reagent mixture without solvent in a preliminarily evacuated glass ampule or by stirring a solution of both the components in benzene or cyclohexane. The reaction in benzene proceeds without irradiation, it starts with heat evolution and is complete within 15–30 min. The reaction in cyclohexane occurs under UV irradiation only. The simplicity and sufficiently high yields of the final products allows this procedure to be recommended for the preparative synthesis of unsymmetrical disilazanes.

EXPERIMENTAL

General procedure. Equimolar mixture of triorganylsilane and $(Me_3Si)_2NBr$ was placed in a thoroughly dried ampoule. The mixture was degassed by the freezing–thowing procedure and then irradiated for 10 h with UV light (DRG-400 lamp). The reaction products were isolated by vacuum distillation and identified by ^1H NMR spectroscopy at 400 MHz (Bruker spectrometer DPX-400).

1,1,1,3-Tetramethyl-3,3-diphenyldisilazane (I), bp 163°C (9 mm Hg), n_D^{20} 1.5435, yield 83%. ^1H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 0.02 s (9H, $SiMe_3$), 0.61 s (3H, SiMe), 7.64–7.19 m (10H, $SiPh_2$).

1,1,1,3,3-Pentamethyl-3-phenyldisilazane (II), bp 87°C (2 mm Hg), n_D^{20} 1.4861, yield 46.6%. ^1H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 0.15 s (9H, $SiMe_3$), 0.45 s (6H, $SiMe_2$), 7.47–7.45 m (5H, SiPh).

1,1,1-Trimethyl-3,3,3-triphenyldisilazane (III), bp 187°C (1 mm Hg), n_D^{20} 1.5823, yield 69.2%. ^{1}H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 0.10 s (9H, $SiMe_3$), 0.93 s (1H, NH), 7.68–7.31 m (15H, $SiPh_3$).

1,1,1-Triethoxy-3,3,3-trimethyldisilazane (IV), bp 68°C (2 mm Hg), n_D^{20} 1.4078, yield 51.7%. ^{1}H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 0.10 s (9H, $SiMe_3$), 1.21–1.18 t (9H, $CH_3–CH_2–$), 3.80–3.75 m (6H, $–CH_2–O–$).

1,1,1,3,3-Pentamethyl-3-(dimethylsiloxy)disilazane (V), bp 46°C (12 mm Hg), n_D^{20} 1.4185, yield 43.9%. ^{1}H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 0.02 d (9H, $SiMe_3$), 0.13 s (6H, $SiMe_2$), 0.09 s (6H, $SiMe_2$), 2.49 s (1H, NH).

1,1,1,3,3-Pentamethyl-3-(dimethylsilylamino)disilazane (VI), bp 92°C (2 mm Hg), n_D^{20} 1.4566, yield 51.9%. ^{1}H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 0.25 s (9H, $SiMe_3$), 0.10 s (6H, $SiMe_2$), 0.36 s (6H, $SiMe_2$), 4.53–4.49 m (1H, SiH).

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