BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (6), 1871—1872 (1979)

Preparation of 1,3-Bis(4-aminobutyl)-1,3-dimethyl-1,3-diphenyldisiloxane and Siloxane-containing Polyamides

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(Received October 4, 1978)

Synopsis. 1,3-Bis(4-aminobutyl)-1,3-dimethyl-1,3-diphenyldisiloxane has been readily obtained by the reduction of 1,3-bis(3-cyanopropyl)-1,3-dimethyl-1,3-diphenyldisiloxane, the hydrolysate of chloro(3-cyanopropyl)methylphenylsilane. The diamine reacted with abietic acid forming an equimolar crystalline adduct which gave a siloxane-containing polyamide by the conventional salt fusion technique.

Several preparations of compounds with the general formula $[NH_2\text{–}R\text{–}Si(R')(R'')]_2O$, (carbofunctional α,ω-diamino substituted disiloxanes) have been reported.

In the preparation of siloxane-containing α,ω-difunctional oligomeric compounds, 1,3-bis(4-aminobutyl) tetraorganodisiloxanes have been obtained in good yield by the reduction of the corresponding dinitriles by lithium aluminum hydride, followed by alkaline hydrolysis. The tetraorganodisiloxane segments were wholly retained during the procedure.

The preparation of α,ω-diamino compounds has been conducted according to the following scheme:

$$R'R''HSiCl \xrightarrow{CH_2{=}CHCH_2CN,\ H_2PtCl_6}$$

$$ClSi(R')(R'')CH_2CH_2CH_2CN \xrightarrow{H_2O}$$

$$[CNCH_2CH_2CH_2(R')(R'')Si]_2O \xrightarrow{LiAlH_4}$$

$$[NH_2CH_2CH_2CH_2CH_2(R')(R'')Si]_2O$$

All products were well defined spectroscopically and the NMR and IR data were consistent with the assigned structures.

The obtained diamines further underwent polycondensation with organic dibasic acids to give modified polyamides containing disiloxane linkages in the chain backbone.

Experimental

Starting Materials. Dichloromethylsilane (bp 41 °C) and chlorodimethylsilane(bp 36 °C) in purified grades were received from Shin-etsu Chem. Ind. Co.; chloromethylphenylsilane(bp 66—67 °C/15 mmHg) was synthesized from Grignard reagents. 1,3-Dimethyl-1,3-diphenyldisiloxane (bp 90 °C/0.25 mmHg; n_D^{24} 1.5250) was prepared by the acid hydrolysis[2)] of chloromethylphenylsilane (yield 86%). Commercial grade allyl cyanide (bp 119 °C) was purified by distillation immediately prior to use.

3-Cyanopropylchloromethylphenylsilane. A mixture of allyl cyanide (20 g, 0.30 mol), chloromethylphenylsilane (61 g, 0.39 mol), and hexachloroplatinic(IV) acid solution[3)] (300 μl), was sealed in a stainless bomb maintained at 120 °C for 24 h. Fractionation of the resultant products gave 59 g (88%) pure 3-cyanopropylchloromethylphenylsilane (**1**), bp 95—96 °C/0.08 mmHg.

IR (neat): 2225 (ν_{CN}), 1425 (Si–C_6H_5), 1255 (Si–CH_3), 490 (Si–Cl).

NMR (CCl_4): δ=0.65 (3H, s, –CH_3), 1.12 (2H, m, Si–CH_2–), 1.72 (2H, m, C–CH_2–C), 2.23 (2H, t, –CH_2–CN), 7.40 (5H, m, –C_6H_5).

1,3-Bis(3-cyanopropyl)-1,3-dimethyl-1,3-diphenyldisiloxane. Hydrolysis of **1** under refluxing for 1 h, accompanied by conventional treatment gave quantitatively the dimeric product, 1,3-bis(3-cyanopropyl)-1,3-dimethyl-1,3-diphenyldisiloxane (**2**). (bp 193—195 °C/0.05 mmHg, n_D^{20} 1.5298).

IR (neat): 2225 (ν_{CN}), 1425 (Si–C_6H_5), 1255 (Si–CH_3), 1055 (Si–O–Si).

NMR (CCl_4): δ=0.33 (6H, s, –CH_3), 0.85 (4H, m, Si–CH_2–), 1.53 (4H, m, C–CH_2–C), 2.10 (4H, t, –CH_2–CN), 7.30 (10H, m, –C_6H_5).

1,3-Bis(4-aminobutyl)tetraorganodisiloxanes. A typical preparation will be given for 1,3-bis(4-aminobutyl)-1,3-dimethyl-1,3-diphenyldisiloxane (**3**):

To a suspension consisting of lithium aluminum hydride (4.3 g, 0.114 mol) and anhydrous ether (230 ml) cooled below 0 °C, a solution of **2** (18.7 g, 0.0476 mol) in anhydrous ether (30 ml) was added dropwise under vigorous stirring for 20 min. The resultant mixture was further stirred for an additional 40 min and water (5 ml). 20% aqueous sodium hydroxide solution (3.5 ml) and water (16 ml) were added in succession. The contents were stirred with continuous cooling to ensure completion of the reaction.

After removal of the inorganic salts formed by filtration, the ethereal layer was dried over anhydrous sodium sulfate and successively fractionated to give 14.9 g (78%) of **3** (bp 182—184 °C/0.1 mmHg; n_D^{20} 1.5312). **1**, **2**, and **3** are new compounds not found in the literature.

The preparation of the intermediate, **2** from the hydrosilylation of 1,3-dimethyl-1,3-diphenyldisiloxane and allyl cyanide in the presence of platinum catalyst was unsuccessful, yielding only a small amount of 3-cyanopropyl-1,3-dimethyl-1,3-diphenyldisiloxane as an addition product.

The use of chlorodimethylsilane in place of chloromethylphenylsilane in the platinum-catalyzed hydrosilylation of allyl cyanide followed by a similar procedure as above, unfailingly yielded the tetramethyl analog, 1,3-bis(4-aminobutyl)tetramethyldisiloxane (**4**), (bp 119—122 °C/0.04 mmHg; n_D^{20} 1.4360).

Compd **3**:

Found: C, 65.78; H, 8.93; N, 6.99; Si, 13.92%. Calcd for $C_{22}H_{36}N_2OSi_2$: C, 65.95; H, 9.06; N, 6.99; Si, 14.02%.

IR (neat): 3350 (ν_{NH}), 1590 (δ_{NH}), 1425 (Si–C_6H_5), 1250 (Si–CH_3), 1055 (Si–O–Si).

NMR (CCl_4): δ=0.28 (6H, s, –CH_3), 0.83 (4H, br, Si–CH_2–), 1.38 (8H, br, C–CH_2–C), 2.60 (4H, br, –CH_2–N), 3.00 (4H, br, –NH_2), 7.30 (10H, m, –C_6H_5).

Compd **4**:

Found: C, 52.22; H, 11.72; N, 9.86; Si, 20.28%. Calcd for $C_{12}H_{32}N_2OSi_2$: C, 52.12; H, 11.66; N, 10.13; Si, 20.31%.

IR (neat): 3340, 3270 (ν_{NH}), 1590 (δ_{NH}), 1250 (Si–CH_3), 1055 (Si–O–Si).

NMR (CCl_4): δ=0.03 (12H, s, –CH_3), 0.48 (4H, m, Si–CH_2–), 1.05 (4H, br, –NH_2), 1.37 (8H, m, C–CH_2–C), 2.62 (4H, t, –CH_2–N).

Polymerization. Compound **3** behaved in a similar manner as the polymethylenediamines towards organic dibasic acids, an example of which will be given as follows:

To a stirred solution of adipic acid (11.0 g, 75.4 mmol) in ethanol (85 ml), a solution of **3** (30.8 g, 77 mmol) in ethanol (60 ml) was added. On standing overnight the solution deposited a fine colorless crystalline mass from which was obtained by recrystallization from ethanol–benzene (1: 1) 31.7 g (77%) of the pure adipic acid salt of **3**, melting at 174—175 °C.

Found: C, 61.61; H, 8.29; N, 5.20; Si, 10.22%. Calcd for $C_{23}H_{46}N_2O_5Si_2$: C, 61.54; H, 8.42; N, 5.13; Si, 10.26%.

IR (neat): 1630, 1540 (NH_3^+), 1580, 1390 (COO^-), 1420 (Si-C_6H_5), 1250 (Si-CH_3), 1055 (Si-O-Si).

X-Ray powder pattern (Cu *K*α/Ni)

d, *k*X: 7.628 6.919 6.707 6.326 4.848 4.770 4.671 4.462 4.291 4.230 4.058 3.802 3.708 3.520 3.440 3.376 3.187 2.950 2.622 2.557

I/I_0 0.63 0.17 0.69 0.54 0.29 0.58 0.42 1.00 0.73 0.44 0.80 0.38 0.19 0.24 0.20 0.20 0.15 0.13 0.11 0.17.

Melt-polymerization of the salt was conducted according to the method of S. B. Speck,[4] and the final beating was conducted at 270 °C under a pressure less than 0.5 mmHg.

The polymer obtained was a pale yellow, transparent, tough solid softening over the range of temperature 100—150 °C to give a sticky highly viscous liquid with high spinnability and insolubility in ordinary organic solvents except for *m*-cresol. The intrinsic viscosity of the polyamide measured at 25 °C in *m*-cresol was [0.46].

IR (neat): 3300 (ν_{NH}), 1640 ($\nu_{C=O}$), 1540 (δ_{NH}), 1425 (Si-C_6H_5), 1255 (Si-CH_3), 1055 (Si-O-Si).

Terephthalic acid and sebacic acid were also found to give similar solids with different softening points when analogously treated.

The authors would like to thank Shin-etsu Chem. Ind. Co. for the supply of the organochlorosilanes.

References

1) a) [R=*m*-C_6H_4; R′,R″=Me] J. C. Bonnet and E. Marechal, *Bull. Soc. Chim. Fr.*, **1972**, 3561; b) (R=*m*,*p*-C_6H_4; R′,R″=Ph) L. W. Breed and J. C. Wiley. Jr., *J. Organomet. Chem.*, **102**, 29 (1975); c) [R=$(CH_2)_2$; R′,R″=Me] L. H. Sommer, N. S. Marans, G. M. Goldberg, J. Rockett, and R. P. Pioch, *J. Am. Chem. Soc.*, **73**, 882 (1951); d) [R=$(CH_2)_3$; R′,R″=Me] J. C. Saam and J. L. Speier, *J. Org. Chem.*, **24**, 119 (1959); T. A. Sladkova and L. Kh. Freidlin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1965**, 1061; *Chem. Abstr.*, **63**, 8395a (1965); e) [R=$(CH_2)_3$; R,R″=Et] T. A. Sladkova and L. Kh. Freidlin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1965**, 1061; *Chem. Abstr.*, **63**, 8395a (1965); f) [R=$(CH_2)_4$; R′,R″=Me; R′=Me, R′=Et; R′,R″=Et] A. D. Petrov, L. Kh. Freidlin, G. I. Kudryavtsev, T. A. Sladkova, V. M. Vdovin, and T. I. Shein, *Doklady Akad. Nauk SSSR*, **129**, 1064 (1959); *Chem. Abstr.*, **54**, 13718 (1960); g) [R=CH_2: R′,R″=Me] J. E. Noll, R. F. Daubert, and J. L. Speier, *J. Am. Chem. Soc.*, **73**, 3871 (1951).

2) M. C. Harvey, W. H. Nebergall, and J. S. Peake, *J. Am. Chem. Soc.*, **79**, 1437 (1957).

3) H_2PtCl_6-$6H_2O$ (1 g) was dissolved in *i*-PrOH (20 ml).

4) S. B. Speck, *J. Org. Chem.*, **18**, 1689 (1953).