New 3-Isocyanatopropylsilanes

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Five 3-isocyanatopropylsilanes were prepared by the addition of silicon hydrides to allyl isocyanate. Physical properties, infrared and nuclear magnetic resonance data are recorded. One of the organosilicon hydrides is described for the first time as are the properties of dimethylsilanol acetate. Chlorodimethyl(3-isocyanatopropyl)silane was converted to the new compound, 1,3-bis(3′-isocyanatopropyl)-1,1,3,3-tetramethyldisiloxane, and to 1,3-bis(3′-aminopropyl)-1,1,3,3-tetramethyldisiloxane.

Previous reports (*2*, *6*) evince interest in organosilicon compounds containing a carbon-bound isocyanate group. Five new 3-isocyanatopropylsilanes are reported here with their physical properties and spectral data. In addition, the chemistry of one of these, chlorodimethyl (3-isocyanatopropyl)silane, is explored.

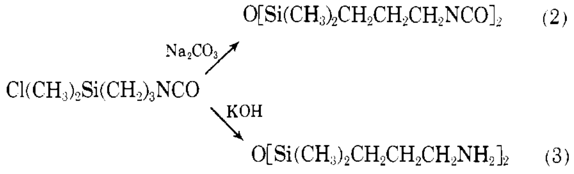
The preparative method (Reaction 1) is that of Speier et al. (*7*) with a minor modification in the catalyst (*1*).

$$RR'(CH_3)SiH + CH_2{=}CHCH_2NCO \xrightarrow{[PtCl_2(C_2H_4)]_2} RR'(CH_3)SiCH_2CH_2CH_2NCO \quad (1)$$

The properties of the products obtained by these additions of silicon hydrides to allyl isocyanate are shown in Table I. The nmr data (Table II) indicate that the silicon adds terminally in these additions as is the case in many other hydrosilations. Structure assignments are also confirmed by the ir data (Table III).

. One of the silicon hydrides, 2-butanone *O,O′*-(methylsilylidene)dioxime, is new. Although dimethylsilanol acetate is mentioned elsewhere (*3*), some of its properties and preparation are documented here because of their absence from the literature. Methylsilanediol diacetate was prepared by the method of Schluyten and coworkers (*4*). The remaining two hydrides, chlorodimethylsilane and dichloromethylsilane, are well-known materials.

These 3-isocyanatopropylsilanes all contain a reactive site on silicon in addition to the well-known reactivity of the isocyanate group. This duplicity is illustrated by the stepwise conversion of Compound I, chlorodimethyl(3-isocyanatopropyl)silane. Hydrolysis in mild base leads to the previously unreported bis(3-isocyanatopropyl)disiloxane, Reaction 2, while hydrolysis in strong base gives the bis(3-aminopropyl)disiloxane, Reaction 3:



$$Cl(CH_3)_2Si(CH_2)_3NCO \xrightarrow{Na_2CO_3} O[Si(CH_3)_2CH_2CH_2CH_2NCO]_2 \quad (2)$$

$$Cl(CH_3)_2Si(CH_2)_3NCO \xrightarrow{KOH} O[Si(CH_3)_2CH_2CH_2CH_2NH_2]_2 \quad (3)$$

Experimental

Boiling points are uncorrected. Microanalyses are from Galbraith Laboratories. Bichloromethylsilane and chlorodimethylsilane are General Electric Co. products.

General procedure for preparation of 3-isocyanatopropylsilanes, Compounds I–V. A mixture of 0.1 mole of allyl isocyanate (Chemetron Corp.) and 2 drops of a dilute solution of chloroplatinic acid hexahydrate in octanol-1 (3% Pt) was prepared under dry nitrogen. Alternately, the catalyst was about 0.05 gram of $[PtCl_2(C_2H_4)]_2$. Then 0.1

Table II. Nmr Absorption Data for Some 3-Isocyanatopropylsilanes[a]

Compound	Protons	Chemical shift	Multiplicity[b]	Relative intensity Found	Relative intensity Theory
I	$SiCH_3$	0.43	S	not measured	
	$SiCH_2$—	0.85	C		
	—CCH_2C—	1.7	C		
	—CH_2NCO	3.3	T		
II	$SiCH_3$	0.79	S	1.00	1.00
	$SiCH_2$—	1.2	C	0.70	0.67
	—CCH_2C—	1.8	C	0.80	0.67
	—CH_2NCO	3.4	T	0.70	0.67
IV	$SiCH_3$	0.25	S	1.00	1.00
	$SiCH_2$—	0.78	C	0.35	0.33
	—CCH_2C	1.7	C	0.37	0.33
	CH_3COO—	2.0	S	0.50	0.50
	—CH_2NCO	3.2	T	0.30	0.33

[a] All shift values are δ in ppm relative to tetramethylsilane at zero. Samples were run at ambient temperature in CCl_4 solution with a Varian A-60 instrument. [b] S = singlet, C = complex, T = triplet.

Table I. Characterization of 3-Isocyanatopropylsilanes
$RR'Si(CH_3)CH_2CH_2CH_2NCO$

Compound	R	R′	Bp,°C/mm	n_D^{25}	d_4^{25}
I. Chlorodimethyl(3-isocyanatopropyl)silane	Cl	CH_3	66/1.0	1.4484	1.037
II. Dichloro(3-isocyanatopropyl)-methylsilane	Cl	Cl	77/2.8	1.4600	1.192
III. 2-Butanone *O,O′*-[(3-isocyanatopropyl)methylsilylidene]dioxime	$C_2H_5(CH_3)C{=}N{-}O$—	$C_2H_5(CH_3)C{=}N{-}O$—	127/0.8	1.4568	0.996
IV. Acetoxydimethyl(3-isocyanatopropyl)silane	CH_3COO—	CH_3	127/29	1.4363	1.019
V. Diacetoxy(3-isocyanatopropyl)methylsilane	CH_3COO—	CH_3COO—	127/7	1.4376	1.129

Table III. Infrared Spectra
(Band Positions in cm^{-1})^{a}

	—N=C=O	Si—H	$\mathrm{Si{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_3}$	Si—CH$_3$	Si—CH$_2$CH$_2$CH$_2$—	Si—O—Si	Si—O—N=C=	Si—Cl
I^{b}	2270 (vs)			1252 (s) 818 (s)	1182 (m)			478 (m)
III^{c}	2270 (vs)			1255 (s) 806 (s)	1185 (m)		920 (vs)	
IV^{d}	2270 (vs)		1730 (s) 1374 (m) 1255 (s) 1018 (m) 936 (m)	1255 (s) 830 (s)	1183 (w)			
V^{b}	2270 (vs)		1730 (s) 1369 (m) 1232 (s) 1015 (m) 938 (m)	1255 (sh) 805 (m)	1185 (w)			
VI^{b}		2180 (s)		1250 (s) 744 (m)			905 (vs)	
VII^{c}	2270 (vs)			1256 (s) 844 (s) 810 (s)	1186 (m)	1060 (s)		

^{a} s, strong; m, medium; w, weak; sh, shoulder; v, very. ^{b} Perkin-Elmer Model 521. ^{c} Perkin-Elmer Model 137. ^{d} Perkin-Elmer Model 21.

mole of the hydride was added cautiously. If no reaction was apparent, the mixture was heated at reflux 12–14 hr. The crude reaction mixtures were fractionally distilled at reduced pressure to isolate the products.

Preparation of 2-butanone O,O′-(methylsilylidene)dioxime, [(CH$_3$)C$_2$H$_5$CNO]$_2$Si(CH$_3$)H, Compound VI. A solution of 127 grams (1.46 moles) of 2-butanone oxime (Eastman Kodak Co.) and 115 grams (1.46 moles) of dry pyridine was prepared in 500 ml of hexane. Then 84 grams (0.73 mole) of dichloromethylsilane was added at 30–40°C with external cooling. All operations were conducted under a blanket of dry nitrogen. The mixture was stirred for 1 hr and filtered to remove pyridine hydrochloride. Distillation afforded a 90-gram fraction (66% yield) of product, bp 82–85°C at 7 mm, n_D^{25} 1.4412, d_4^{25} 0.935.

Preparation of dimethylsilanol acetate, (CH$_3$)$_2$Si(OCOCH$_3$)H. A slurry of 164 grams (2.0 moles) of oven-dried sodium acetate in 536 grams of acetic anhydride was prepared under a dry nitrogen atmosphere. Then 189 grams (2.0 moles) of chlorodimethylsilane was added with rapid agitation and external cooling to keep the temperature below 40°C. The mixture was stirred overnight and then filtered under dry nitrogen. The filtrate was distilled at atmospheric pressure to give a product fraction, bp 90–92°C, amounting to 146 grams (1.24 moles, 62% yield), n_D^{25} 1.3842, d_4^{25} 0.890.

1,3-Bis(3′-isocyanatopropyl) - 1,1,3,3-tetramethyldisiloxane, O[Si(CH$_3$)$_2$CH$_2$CH$_2$CH$_2$NCO]$_2$, Compound VII. To a solution of 50 grams of sodium carbonate in 300 ml of water at 60°C was rapidly added 100 grams of chlorodimethyl(3-isocyanatopropyl)silane. The reaction mixture was extracted with ether after stirring for 1 hr. The ether extract, dried over magnesium sulfate, was distilled to give 20 grams of product, bp 135–140°C at 0.8 mm, n_D^{25} 1.4483, d_4^{25} 0.9929.

1,3-Bis(3′-aminopropyl)-1,1,3,3 - tetramethyldisiloxane, O[Si(CH$_3$)$_2$CH$_2$CH$_2$CH$_2$NH$_2$]$_2$. To a solution of 118 grams of KOH in 382 ml of water at 55°C was added 88 grams of chlorodimethyl(3-isocyanatopropyl)silane. The mixture was refluxed overnight and then extracted with ether. Distillation gave 18 grams of product, bp 95–112°C at 0.6 mm, most at 104–106°C at 0.6 mm. *Anal.* Calcd for $C_{10}H_{28}N_2OSi_2$: NH$_2$, 12.88. Found: NH$_2$, 12.82. n_D^{25} 1.4482; ref. (5), n_D^{20} 1.4510.

Elemental analyses for the new compounds reported here (Compounds I–VII) in agreement with theoretical values have been obtained and submitted for review.

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Literature Cited

(1) Ashby, B. A. (to General Electric Co.), U.S. Patent 3,159,601 (December 1, 1964).
(2) Berger, A. (to General Electric Co.), U.S. Patent 3,494,951 (February 10, 1970).
(3) Mindlin, Y. I., Leznov, N. S., Andrianov, K. A., Zasypkina, P. S., Davydova, P. V., Kozyreva, T. I., Russian Patent 119,530 (May 10, 1959); *CA*, **54**, P4010d (1960).
(4) Schluyten, H. A., Weaver, J. W., Reid, J. D., *J. Amer. Chem. Soc.*, **69**, 2110–12 (1947).
(5) Sladkova, T. A., Freidlin, L. K., *Izv. Akad. Nauk SSSR, Ser. Khim*, **1965** (6) 1061-5; *CA*, **63**, 8395 (1965).
(6) Speier, J. L. (to Dow Corning Corp.), U.S. Patent 3,170,891 (February 23, 1965).
(7) Speier, J. L., Webster, J. A., Barnes, G. H., *J. Amer. Chem. Soc.*, **79**, 974 (1957).

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