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SYNTHESIS OF Si-CONTAINING CYCLIC UREAS

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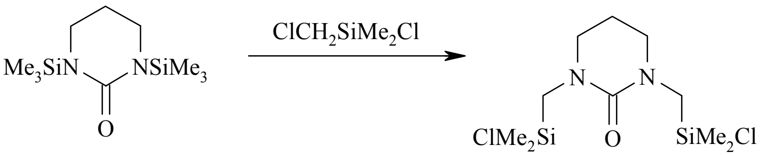
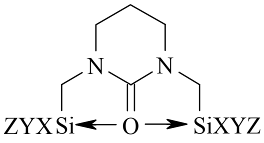
1,3-Bis[(triethoxysilyl)methyl]tetrahydropyrimidin-2-one and 1,3-bis[(dimethoxysilyl)methyl]tetrahydropyrimidin-2-one have been synthesized on interacting urea with N,N'-bis(silylmethyl)propylenamines $(EtO)_{3-n}Me_nSiCH_2NH(CH_2)_3NHCH_2SiMe_n(OEt)_{3-n}$ *(n = 0, 2). Their interaction with boron trichloride has been studied. The structures of all the compounds synthesized have been demonstrated by multinuclear NMR spectroscopy.*

Keywords: pentacoordinated silicon atom, Si-containing cyclic ureas.

The chemistry of compounds of pentacoordinated silicon has developed vigorously in the past three decades [1-8]. However some of its apects remain sparsely studied. In particular this concerns the methods of construction and the structure of compounds with competing and bridging interaction of two acceptor silicon atoms with a single donor center (Si←D→Si). Up to the present time there are only certain examples of bridging silicon complexes [9-12]. We have recently proposed a method of obtaining N,N'-bis(dimethylchlorosilylmethyl)propyleneureas [13-15].



Based on this lies a method of transsilylating the N-TMS derivative of chloromethyl(or chloro)dimethylsilane already becoming classical in the synthesis of pentacoordinated compounds of silicon with a coordination unit C_3SiOCl [6,7]. We propose that in this compound it is possible to effect an intramolcular bridging coordination Si←O→Si (**A**) bond.



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Dedicated to the 50th Anniversary of the Latvian Institute of Organic Synthesis

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Regretably we did not obtain convincing proof of this. It was shown later by methods of quantum chemistry (B3LYP, MP2) [16] that the stability of intramolcular bridging complexes of the Si←O→Si type depends both on the dimensions of the equatorial substituents and the electronegativity of the axial substituent at silicon, and also on the change of donor properties of the carbonyl group. Evidently to bring about bridging intramolcular interactions of the Si←O→Si type it is necessary to change the valence environment of the silicon atom. Synthesis of cyclic ureas containing a selection of different substituents at the silicon atom, according to the scheme given above, is a difficult problem. The aim of the present work was the search for alternative methods of synthesizing such ureas, and results are given in this paper on the transamination reaction of ureas with Si-containing 1,3-propylenediamines. Transamination is one of the well known reactions for synthesizing alkylated ureas [17], including certain organosilicon ureas [18-20].

We obtained N,N'-bis(silylmethyl)propylenediamines **1**, **2** by the interaction of $ClCH_2SiMe_n(OEt)_{3-n}$ with 1,3-diaminopropane.

$$ClCH_2SiMe_n(OEt)_{3-n} + H_2N(CH_2)_3NH_2 \xrightarrow[-Et_3N \cdot HCl]{Et_3N}$$

$$\longrightarrow (EtO)_{3-n}Me_nSiCH_2NH(CH_2)_3NHCH_2SiMe_n(OEt)_{3-n}$$

1, **2**

1 $n = 0$, **2** $n = 2$

The yields of compounds **1**, **2** did not exceed 50% (Table 1). In addition to compounds **1**, **2**, products of monosilylation, intramolcular cyclization, quaternization, and unidentified polymeric products were formed. The compounds obtained, high boiling colorless liquids with strong specific amine odors, were extremely sensitive to moisture from the air. The structures of compounds **1**, **2** were confirmed by data of ^1H and ^{13}C NMR (Table 2).

On heating an equimolar mixture of thoroughly dried urea and compound **1** or **2** the formation was observed of the corresponding silylmethylated cyclic ureas, *viz*. 1,3-bis[(triethoxysilyl)methyl]-tetrahydropyrimidin-2-one (**3**) and 1,3-bis[(dimethyloxysilyl)methyl]tetrahydropyrimidin-2-one (**4**).

TABLE 1. Physicochemical Characteristics of the Synthesized Compounds

Com-pound	Empirical formula	Found, % / Calculated, % C	H	N	Bp, °C (mm Hg)	n_D^{20}	Yield, %
1	$C_{17}H_{42}N_2O_6Si_2$	47.99 47.85	9.65 9.92	6.73 6.57	212-215 (2)	1.4432	38
2	$C_{13}H_{34}N_2O_2Si_2$	50.68 50.93	10.93 11.18	8.91 9.14	158-160 (2)	1.4361	49
3	$C_{18}H_{40}N_2O_7Si_2$	47.49 47.76	8.63 8.91	6.25 6.19	240-245 (1)	1.4497	67
4	$C_{14}H_{32}N_2O_3Si_2$	50.39 50.56	9.51 9.70	8.52 8.42	183-186 (1.5)	1.4439	81
5	$C_6H_{10}Cl_6N_2OSi_2$	18.72 18.24	2.84 2.55	7.36 7.09	—	—	100*
6	$C_{10}H_{22}Cl_2N_2OSi_2$	38.57 38.33	7.28 7.08	9.11 8.94	194-196 (1)	1.4712	49

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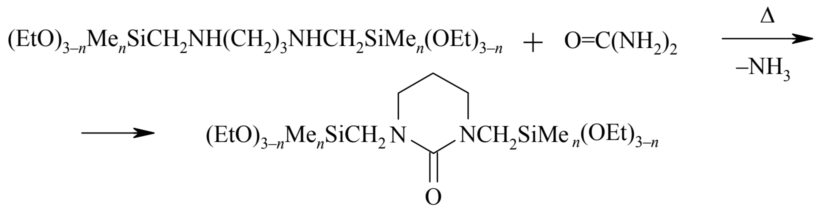
*Without additional purification.

TABLE 2. ^{1}H, ^{13}C, and ^{29}Si NMR Spectra (CDCl$_3$)

Compound	^{1}H NMR, δ, ppm (J, Hz)				^{13}C NMR, δ, ppm.					^{29}Si NMR, δ, ppm
	CH_3–Si, s	C_2H_5O	$SiCH_2N$, s	$(CH_2)_3$	CH_3–Si	C_2H_5O	$SiCH_2N$	$(CH_2)_3$	C=O	
1		1.15 (t, $^3J = 7.0$); 3.74 (q, $^3J = 7.0$)	2.09	1.63 (m); 3.08 (t, $^3J = 6.9$)		18.37; 57.65	29.86	23.58; 52.49		—
2	0.21	1.15 (t, $^3J = 7.0$); 3.69 (q, $^3J = 7.0$)	1.85	1.61 (m); 2.98 (t, $^3J = 6.9$)	-2.67	18.53; 57.96	36.57	21.58; 52.17		—
3		1.19 (t, $^3J = 7.0$); 3.78 (q, $^3J = 7.0$)	2.88	1.95 (m); 3.30 (t, $^3J = 5.9$)		17.41; 58.15	29.73	21.07; 47.95	156.55	-56.82 (25 °C)
4	0.31	1.18 (t, $^3J = 7.0$); 3.76 (q, $^3J = 7.0$)	2.92	2.10 (m); 3.21 (t, ^3J=5.8)	-2.25	17.98; 57.12	35.37	21.23; 48.15	159.63	5.83 (25 °C)
5		—	3.16	1.99 (m); 3.51 (t, $^3J = 6.0$)			45.98	21.09; 45.11	149.87	-13.12 (25 °C) -12.95 (-85 °C)
6	0.55	—	2.87	2.03 (m); 3.36 (t, ^3J=5.8)	4.94		43.24	21.07; 47.02	157.96	-6.65 (25 °C) -6.46 (-90 °C)

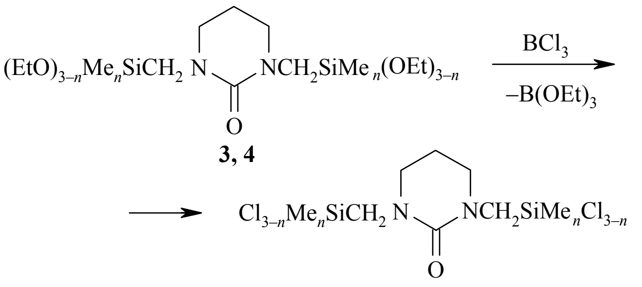


3, **4**

3 $n = 0$, **4** $n = 2$

The end of the reaction is indicated by cessation of ammonia evolution. As a result of the reaction a viscous glassy mass is formed, which contains secondary polymeric products. The desired products are extracted with boiling chloroform, distillation of which and vacuum fractionation gives pure compounds **3** and **4**, the structures of which were demonstrated by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy.

Treatment of compounds **3** and **4** with boron trichloride leads to the formation of the corresponding 1,3-bis[(trichlorosilyl)methyl]tetrahydropyrimidin-2-one (**5**) and 1,3-bis[(dimethylchlorosilyl)methyl]tetrahydropyrimidin-2-one (**6**).

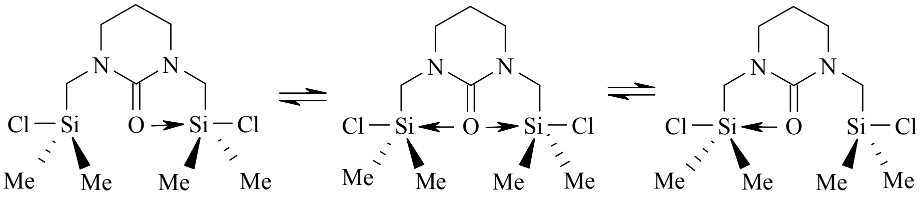


5, **6**

5 $n = 0$, **6** $n = 2$

Compound **5** is hydrolytically extremely unstable, it is decomposed on heating, and on extended storage. We were unsuccessful in finding satisfactory methods of purifying it. Nonetheless if the reaction is carried out in thoroughly dried solvent, in an atmosphere of dry argon, then after distillation of the solvent and $B(OEt)_3$ in vacuum, this compound is obtained practically pure. Its spectral characteristics were unchanged for several days on storage of a sealed evacuated sample at -78°C. Compound **6** is readily purified by vacuum distillation and is stored in sealed evacuated ampuls for an extended time without change.

Compounds **5** and **6** were studied by multinuclear NMR spectroscopy. The ^{29}Si NMR spectra demonstrate the equivalence of the two silicon atoms (for compound **5** δ $^{29}Si = -13.12$ and for compound **6** δ $^{29}Si = -6.65$ ppm). However the chemical shifts are at a significantly lower field compared with the chemical shifts of (O-Si)-chelated monosilylmethylated ureas having identical surroundings for the silicon atom. The δ ^{29}Si for 1-trimethylsilyl-3-[(dimethylchlorosilyl)methyl]-tetrahydropyrimidin-2-one is -41.42, and for N,N-diethyl-N'-phenyl-N'-trichlorosilylurea δ $^{29}Si = -87.9$ ppm [21]. The ^{29}Si chemical shifts of compounds **5**, **6** are practically unchanged on reducing the temperature (Table 2). The nature of the substituents R and R^1 in the amide group $RC(O)NR^1$ in a series of (O-Si)-chelated amides of carboxylic acids has an appreciable effect on the degree of intramolcular coordination C=O→Si bonding [22-24]. Introduction of a second N-acetyl group into N-chloro(dimethyl)silylmethyl-N-acetylacetamide (δ $^{29}Si = -24.2$ [22]) leads to a significant weakening of the intramolcular coordination C=O→Si interaction in comparison with that of N-chloro(dimethyl)silylmethyl-N-methylacetamide (δ $^{29}Si = -37.6$ ppm [23, 24]). This is probably caused by the competing interaction of one silyl group with two donor C=O groups. Probably in the **5** and **6** molcules a competing interaction of two silyl groups with one donor C=O center exists, well known as a "flip-flop" rearrangement [25,26].



We are confidant that the development of alternative methods of synthesizing Si-containing cyclic ureas will in the future enable the synthesis of compounds in which bridging intramolcular coordination Si←O→Si interactions will be achieved.

EXPERIMENTAL

The ^1H, ^{13}C, and ^{29}Si NMR spectra of 20% solutions of compounds **1-6** were recorded on a JEOL FX 90Q spectrometer (90, 22.5, and 17.8 MHz respectively), internal standard was TMS. Solvents were purified according to the procedures of [27]. All syntheses were carried out in an atmosphere of dry argon. The physicochemical characteristics of compounds **1-6** are given in Table 1, and the spectral in Table 2.

N,N'-Bis(silylmethyl)propylenediamines 1 and 2 were synthesized by heating a mixture of 1,3-diaminopropane and the appropriate alkoxy(chloromethyl)silane in a 1 : 3 ratio in toluene in the presence of 5 equiv. triethylamine for 8 h. The precipitated triethylamine hydrochloride was filtered off, washed with pentane, and the pentane solution combined with the filtrate. Pentane, toluene, and the excess of triethylamine were distilled off at atmospheric pressure, and the residue was fractionated in vacuum.

Synthesis of 1,3-Bis[(triethoxysilyl)methyl]tetrahydropyrimidin-2-one (3) and 1,3-Bis-[(dimethylethoxysilyl)methyl]tetrahydropyrimidin-2-one (4). An equimolar mixture of thoroughly dried urea (0.05 mol) and silicon-containing amine **1** or **2** (0.05 mol) was stirred and slowly heated to 80-90°C on an oil bath. The mixture became homogeneous, the bath temperature was raised to 160-180°C, and maintained at this temperature until the end of ammonia evolution (litmus paper). The reaction mixture was cooled, extracted with boiling chloroform (100 ml), and decanted. The chloroform was distilled off at atmospheric pressure, and the residue fractionated in vacuum.

Synthesis of 1,3-Bis[(trichlorosilyl)methyl]tetrahydropyrimidin-2-one (5) and 1,3-Bis[(chlorodimethylsilyl)methyl]tetrahydropyrimidin-2-one (6). An equimolar amount of BCl_3 was added slowly to a solution of compound **3** or **4** in methylene chloride cooled to -50°C. The mixture was maintained at this temperature for 2 h, then the temperature was raised to 0°C and maintained at this temperature for one day. The temperature of the reaction mixture was then increased to room, and left for 3 h. The solvent and $B(OEt)_3$ were removed in vacuum, and the residue was evacuated for several hours. Compound **5**. a viscous yellow oil, was extremely sensitive to air moisture. On heating above 30°C, or on extended standing, it decomposed with the formation of polymeric products. Compound **6**, a viscous liquid, was redistilled in vacuum without decomposition.

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REFERENCES

1. S. N. Tandura, M. G. Voronkov, and N. V. Alekseev, *Top. Curr. Chem.*, **131**, 99 (1986).
2. R. R. Holmes, *Chem. Rev.*, **90,** 17 (1990).
3. R. R. Holmes, *Chem. Rev.*, **96,** 927 (1996).

4. R. J. P. Corriu, *J. Organomet. Chem.*, **400**, 81 (1990).
5. C. Chuit, R. J. P. Corriu, C. Reye, and J. C. Young, *Chem. Rev.*, **93**, 1371 (1993).
6. D. Kost and I. Kalikhman, in: Y. Apeloig and Z. Rappoport (editors), *The Chemistry of Organic Silicon Compounds*, Vol. 2, Wiley, Chichester, UK (1998), p. 1339.
7. M. G. Voronkov, V. A. Pestunovich, and Yu. I. Baukov, *Metalloorg. Khim.*, **4**, 1210 (1991)
8. E. Lukevics and O. Pudova, *Khim. Geterotsikl. Soedin.*, 1605 (1996). [*Chem. Heterocycl. Comp.*, **32**, 1381 (1996)].
9. K. Tamao, T. Hayashi, Y. Ito, and M. Shiro, *Organometallics*, **11**, 2099 (1992).
10. K. Tamao, T. Hayashi, Y. Ito, and M. Shiro, *J. Am. Chem. Soc.*, **112**, 2422 (1990).
11. T. Hoshi, M. Takahashi, and M. Kira, *Chem. Lett.*, 683 (1996).
12. K. Ebata, T. Inada, C. Kabuto, and H. Sakurai, *J. Am. Chem. Soc.*, **116**, 3595 (1994).
13. L. I. Belousova, O. B. Kozyreva, A. E. Pestunovich, V. A. Pestunovich, and M. G. Voronkov, *XVI International Conference on Organometall. Chemistry (10-15 July), Sussex, U. K., Abstracts* (1994), p. 331.
14. N. F. Lasareva, L. I. Belousova, O. B. Kosyreva, Yu. Ovchinnikov, and V. A. Pestunovich, *XI International Symposium of Organosilicon Chemistry, September 1-6, Montpellier II, France (1996), Abstracts*, PB80.
15. A. I. Albanov, A. Bassindale, E. F. Belogolova, N. N. Chipanina, G. A. Gavrilova, N. F. Lazareva, V. A. Pestunovich, V. F. Sidorkin, P. Taylor, anf V. K. Turchaninov, *12th International Symposium on Organosilicon Chemistry, May 23-28 (1999), Program, Abstracts, and List of Participants*, Sendai International Center, Sendai, Japan, p. 171.
16. V. F. Sidorkin, E. F. Belogolova, and V. A. Pestunovich, *Chem. Eur. J.*, **12**, 2021 (2006).
17. K. Weygand and G. Hilgetag, *Experimental Methods in Organic Chemistry* [Russian translation], Khimiya, Moscow (1968).
18. J. W. Gilkey and R. H. Kranke, US Patent 3208971 (1965), *Ref. Zh. Khim.*, 22S341 (1966).
19. D. Seyferth, A. W. Dow, H. Menzel, and T. C. Flood, *J. Am. Chem. Soc.*, **90**, 1080 (1968).
20. D. Seyferth, H. Menzel, A. W. Dow, and T. C. Flood, *J. Organomet. Chem.*, **44**, 279 (1972).
21. A. R. Bassindale, M. Borbaruah, S. J. Glynn, D. J. Parker, and P. G. Taylor, *J. Organomet. Chem.*, **606**, 125 (2000).
22. I. D. Kalikhman, O. B. Bannikova, L. I. Belousova, B. A. Gostevskii, E. Liepinsh, O. A. Vyazankina, N. S. Vyazankin, and V. A. Pestunovich, *Metalloorg. Khim.*, **1**, 683 (1988).
23. R. W. Hillard, C. M. Ryan, and C. H. Yoder, *J. Organomet. Chem.*, **153**, 369 (1978).
24. C. H. Yoder, C. M. Ryan, G. F. Martin, and P. S. Ho, *J. Organomet. Chem.*, **190**, 1 (1980).
25. N. Auner, R. Probst, F. Hahn, and E. Herdtweck, *J. Organomet. Chem.*, **459**, 25 (1993).
26. U. H. Berlekamp, P. Jutzi, A. Mix, B. Neumann, H.-G. Stammler, and W. W. Schoeller, *Angew. Chem.*, **111**, 2071 (1999).
27. A. J. Gordon and R. A. Ford, *Chemist's Companion, Handbook of Practical Data, Techniques, and References*, Wiley–Interscience, New York (1972), 560 pp.