BRIEF COMMUNICATIONS

SYNTHESIS OF SILALACTAMS

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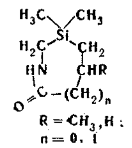
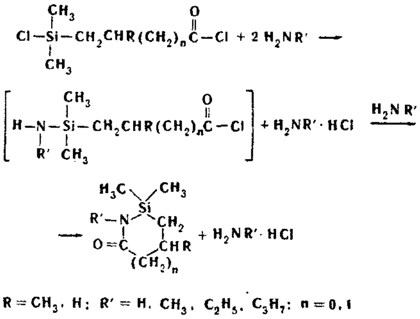
The action of ammonia or primary aliphatic amines on dialkylchlorosilyl-substituted carboxylic acid chlorides has given silalactams and N-alkylsilalactams, which are readily hydrolyzed by water with the formation of siloxanedicarboxamides.

We have recently reported the synthesis of organosilicon lactams in which the silicon atom is bound to two carbon atoms [1,2], i. e., silalactams of the type

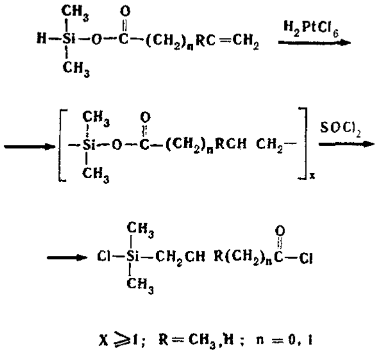


There is no information in the literature on the synthesis of silalactams in which the nitrogen atom is connected directly to the silicon atom.

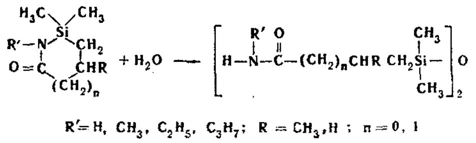
We have found that these new heterocyclic systems are readily formed by the reaction of ammonia or primary amines with chlorodialkylsilyl-substituted carboxylic acid chlorides.



The initial chlorodialkylsilyl-substituted carboxylic acids [3] were obtained by the action of thionyl chloride or phosphorus pentachloride on silyl esters of silyl carboxylic acids of cyclic or polymeric structures:



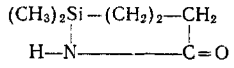
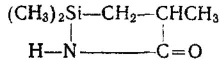
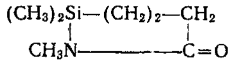
Silalactams synthesized are light yellow or colorless liquids with a peculiar odor. Si-Dimethyl-N-methylvalerolactam is a colorless crystalline substance. Silalactams react with water with unusual readiness with the evolution of heat, forming the corresponding siloxanedicarboxamides:



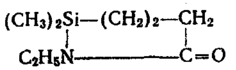
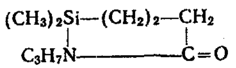
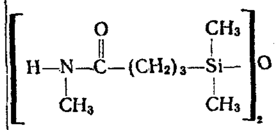
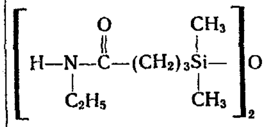
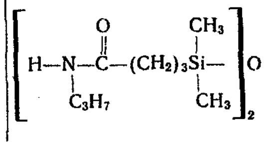
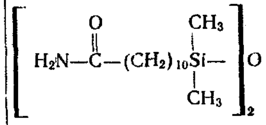
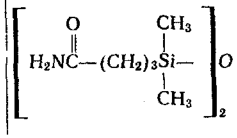
Because of the ease of hydrolysis of the silalactams, the ammonia and alkylamines used in the reaction with the silyl-substituted carboxylic acid chlorides must be carefully dried.

Determination of the molecular weights of the silalactams has shown that all the N-alkyl-substituted silalactams are monomeric while the silalactams with an N—H bond have enhanced molecular weights.

Silalactams

Compound	Formula	Mp, °C Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	Found, % C	Found, % H	Found, % Si	Found, % N	Calculated, % C	Calculated, % H	Calculated, % Si	Calculated, % N	Yield, %
I	 $(CH_3)_2Si-(CH_2)_2-CH_2$ $H-N$————$C=O$	166—169(3)	0.9655	1.4538	40.17	40.37	50.58	9.12	19.8	9.5 9.6	50.3	9.15	19.6	9.77	64
II	 $(CH_3)_2Si-CH_2-CHCH_3$ $H-N$————$C=O$	172—176(2.5)	0.9826	1.4625	40.23	40.37	50.6 50.65	9.08 9.30	19.2 19.3	9.82 9.63	50.3	9.15	19.6	9.77	58.5
III	 $(CH_3)_2Si-(CH_2)_2-CH_2$ CH_3N————$C=O$	76—77(2) 45—47	—	—	—	—	53.5 53.7	9.75 9.73	16.92 16.62	9.06 8.89	53.45	9.61	17.86	8.91	41

Silalactams
(cont'd)

Compound	Formula	Mp, °C Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	MR_D		Found, %				Calculated, %				Yield, %
					found	calc.	C	H	Si	N	C	H	Si	N	
IV		95—98(10)	0.9715	1.4732	49.49	49.86	55.9 56.3	9.9 10.2	16.5 —	8.38 8.02	56.09	10.0	16.39	8.18	69
V		78—79(1.5)	0.9491	1.4687	54.35	54.50	58.22 58.22	10.36 10.37	15.12 —	7.62 7.43	58.32	10.33	15.15	7.56	66.4
VI	 $[\mathrm{H{-}N(CH_3){-}C({=}O){-}(CH_2)_3{-}Si(CH_3)_2{-}}]_2\mathrm{O}$	235—236(2)	0.9942	1.4696	93.30	93.22	50.55 50.27	9.74 9.77	16.77 16.51	8.92 9.22	50.56	9.70	16.89	8.43	51.2
VII	 $[\mathrm{H{-}N(C_2H_5){-}C({=}O){-}(CH_2)_3Si(CH_3)_2{-}}]_2\mathrm{O}$	230—231(2)	0.9776	1.4687	102.68	102.51	52.86 52.78 52.95	10.36 10.33 10.13	15.84 15.24	—	53.29	10.06	15.58	7.77	69
VIII	 $[\mathrm{H{-}N(C_3H_7){-}C({=}O){-}(CH_2)_3Si(CH_3)_2{-}}]_2\mathrm{O}$	254—258(3)	0.9672	1.4690	111.92	111.81	55.38 55.65	10.37 10.28	— 14.36	—	55.62	10.37	14.45	7.21	69.5
IX	 $[\mathrm{H_2N{-}C({=}O){-}(CH_2)_{10}Si(CH_3)_2{-}}]_2\mathrm{O}$	112—113	—	—	—	—	62.5 62.2	11.0 11.10	11.16 11.21	5.86 5.74	62.34	11.26	11.21	5.59	45.2
X	 $[\mathrm{H_2NC({=}O){-}(CH_2)_3Si(CH_3)_2{-}}]_2\mathrm{O}$	124—126	—	—	—	—	47.9 47.5	9.3 9.2	—	9.28 9.35	47.33	9.27	18.44	9.20	15

EXPERIMENTAL

Si-Dimethyl-4-silavalerolactam (I). A 1-liter three-necked flask, fitted with a reflux condenser, stirrer with seal, and bubbler, was charged with a solution of 39.5 g (0.2 mole) of 4-(chlorodimethylsilyl)butyryl chloride in 400 ml of absolute ether. Dry ammonia was passed through the ethereal solution for 3 hr. The precipitate of ammonium chloride was filtered off rapidly and washed with ether. The ether was distilled off from the mother ethereal solution and the residue was distilled in vacuum to give 18.3 g (64%) of I in the form of a colorless viscous oil. Compounds II–V, the properties of which are given in the table, were obtained similarly.

1,1,3,3-Tetramethyl-1,3-bis(4'-N-methylbutyramide)disiloxane (VI). The addition of 0.5 g of water to 3.15 g (0.02 mole) of III caused a marked evolution of heat. The aqueous layer was separated from the organic layer; the latter was dried over $MgSO_4$ and distilled in vacuum to give 1.7 g of VI in the form of a colorless viscous oil. Compounds VII and VIII were obtained similarly. Compounds IX and X were obtained by the passage of undried ammonia through ethereal solutions of the corresponding acid chlorides. The properties of the siloxane dicarboxylic amides synthesized are given in the table.

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1. V. F. Mironov and N. S. Fedotov, KhGS [Chemistry of Heterocyclic Compounds], 2, 453, 1966.
2. V. F. Mironov, N. S. Fedotov, and V. L. Kozlikov KhGS [Chemistry of Heterocyclic Compounds], 4, 354, 1968.
3. N. S. Fedotov, I. G. Rybalka, and V. F. Mironov, ZhOKh, 38, 896, 1968.

28 August 1967

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SYNTHESIS OF ARYLETHYLENE DERIVATIVES OF 2,5-DIPHENYL-1,3,4-OXADIAZOLE

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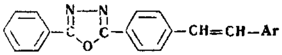
The synthesis of arylethylene derivatives of 2,5-diphenyl-1,3,4-oxadiazole by the Wittig reaction from 2-(p-bromomethylphenyl)-5-phenyl-1,3,4-oxadiazole and aromatic aldehydes is described. The compounds obtained fluoresce strongly on irradiation with UV light.

We have obtained arylethylene derivatives of 2,5-diphenyloxazoles which fluoresce strongly on irradiation with UV light [1]. In the present paper, compounds of similar structure containing, instead of the oxazole ring, the 1,3,4-oxadiazole nucleus (I) are described.



I

The starting material for the synthesis of these compounds was the p-bromomethyl derivative of 2,5-diphenyl-1,3,4-oxadiazole, from which compounds I were obtained by the Wittig reaction, using the method that we have described in the production of the vinyl derivatives of 2,4-diaryl-1,3,4-oxadiazoles [2] with the only difference that, instead of paraformaldehyde, the corresponding aldehyde was added. The arylethylene derivatives I fluoresce on irradiation with UV light.

EXPERIMENTAL

A mixture of equimolecular amounts (0.01 mole) of 2-(4'-bromomethylphenyl)-5-phenyl-1,3,4-oxadiazole and triphenylphosphine was boiled in 15 ml of dimethylformamide for 2 hr. The precipitate that deposited was filtered off, washed with petroleum ether, and dried in the air. Then it was dissolved in 100 ml of methanol and treated with a small excess of the appropriate aldehyde (0.011 mole) and 50 ml of a 0.2 N solution of lithium methoxide in methanol. The mixture was left at room temperature for 5–6 hr. The precipitate that had deposited was filtered off, washed with a small amount of methanol, dried, and isomerized for complete conversion into the trans isomer by being boiled in xylene with a small crystal of iodine for 4–5 hr. Then it was purified on a chromatographic column of alumina in benzene or xylene with subsequent recrystallization from toluene or chlorobenzene.

The analyses, melting points, and yields of the substances obtained are given in the table on p. 126.

REFERENCES

1. V. I. Grigor'eva and B. M. Krasovitskii, KhGS [Chemistry of Heterocyclic Compounds], 3, 761, 1967.
2. V. I. Grigor'eva and R. S. Mil'ner, KhGS [Chemistry of Heterocyclic Compounds], 4, 23, 1968.

13 July 1967

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