UDC 547.245

SILALACTONES AND SILALACTAMS

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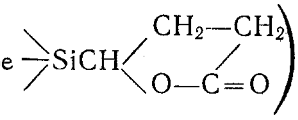
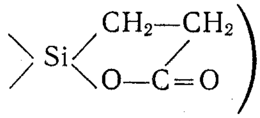
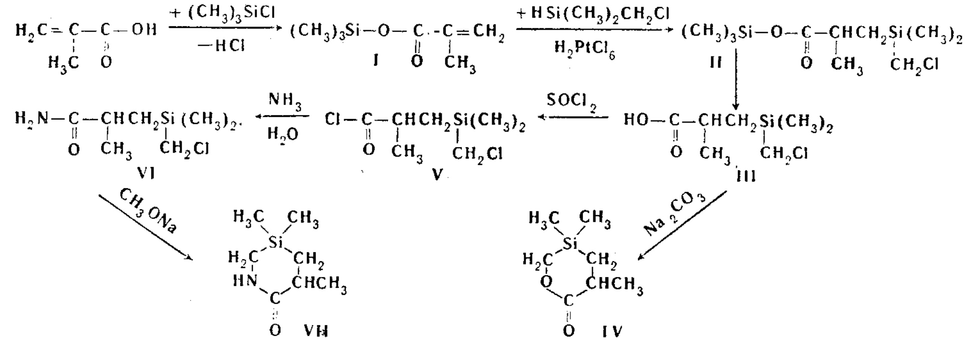
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 3, pp. 453-456, 1966

Silalactones and silalactams are prepared, these having in the ring a silicon atom linked to carbon only.

The literature describes organosilicon lactones with silicon atoms both outside [1] (type ) and inside [2] (sillilactones of the type ) the ring. However, the presence of the Si–O link in silalactones leads to instability in respect to hydrolysis both for the compounds themselves, and for polymers derived from them.

We have now synthesized lactones and lactams having in the ring a silicon atom linked only to carbon atoms, the starting point being methacrylic acid:



Similarly, starting from acrylic and vinylacetic acids, the corresponding silalactones and silalactams have been prepared, and detailed information about these will be given in a future communication.

The table gives the physical constants and yields of starting materials and end products.

Experimental

Trimethylsilyl methacrylate (I). 51 g (0.59 mole) methacrylic acid was added, with stirring, to a mixture of 70 g (0.64 mole) Me_3SiCl, 95 g (0.63 mole) diethylaniline, and 500 ml dry ether. The precipitate was then filtered off, and washed with ether. Distillation of the filtrate gave 83 g (89%) I. The literature [3] records a 58% yield. VIII and IX were prepared similarly.

Trimethylsilyl β-(chloromethyldimethylsilyl)isobutyrate (II). 62 g I was added, over 2 hr, to a refluxing mixture of 43 g $ClCH_2Me_2SiH$ and 1 ml 0.1 M H_2PtCl_6 in iso-PrOH, when the boiling point of the mixture rose to 160° C. Vacuum-distillation gave 82 g II. Found: C 45.19, 45.25; H 8.79, 8.80; Si 21.26, 21.14; Cl 13.22, 13.48%. Calculated for $C_{10}H_{23}Si_2O_2Cl$: C 44.98; H 8.68; Si 21.04; Cl 13.29%. X and XI were prepared similarly.

β-(Chloromethyldimethylsilyl) isobutyric acid (III). A mixture of 77 g II and 50 ml water was energetically stirred while held at 60° C for 2 hr. The organic layer was separated off, and vacuum-distilled, to give 55.5 g (98.5%). Found: C 43.21, 43.34; H 7.55, 7.70; Si 14.79, 14.54; Cl 18.41, 18.24%. Calculated for $C_7H_{15}SiO_2Cl$: C 43.16; H 7.76; Si 14.42; Cl 18.23%. Acids XII and XIII were prepared similarly.

Si-Dimethyl-1-methyl-3-silavalerolactone (IV). To 40 g III was added 20 g anhydrous finely-powdered Na_2CO_3, Physical Constants and Yields of Starting Materials and Final Products

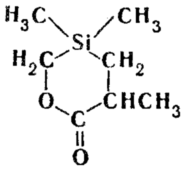
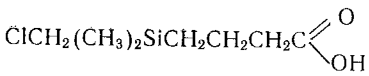
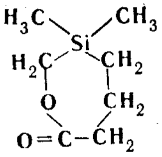
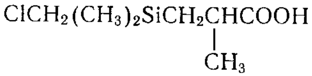
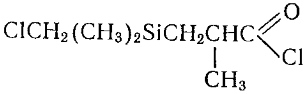
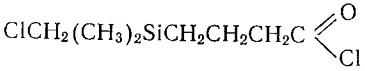
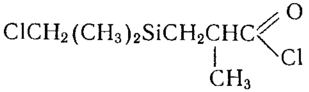
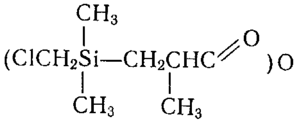
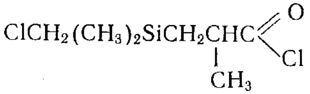
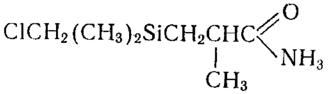
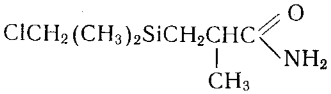
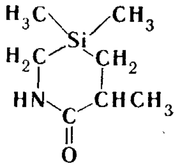
Starting materials		Compound prepared	Bp (pressure mm)	n_D^{20}	d_4^{20}	MR_D		Yield, %
						Found	Calc.	
$H_2C{=}(CH_3)COOH$	$(CH_3)_3SiCl$	$(CH_3)_3Si{-}O{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{CH_3}{|}}{C}{=}CH_2$ **(I)**	43—45 (23)	1.4147	0.8854	44.73	44.45	89
$H_2C{=}CHCOOH$	" "	$(CH_3)_3SiO{-}\underset{\underset{O}{\|}}{C}{-}CH{=}CH_2$ **(VIII)**	52—54 (57)	1.4109				81
$H_2C{=}CHCH_2COOH$	" "	$(CH_3)_3Si{-}O{-}\underset{\underset{O}{\|}}{C}{-}CH_2CH{=}CH_2$ **(IX)**	41—42 (11)	1.4121	0.8893	44.29	44.44	83
$(CH_3)_3Si{-}O{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{CH_3}{|}}{C}{=}CH_2$	$(CH_3)_2HSiCH_2Cl$	$(CH_3)_3Si{-}O{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{CH_3}{|}}{C}HCH_2Si(CH_3)_2CH_2Cl$ **(II)**	78—80 (1.5)	1.4431	0.9654	73.32	73.24	79
$(CH_3)_3SiO\underset{\underset{O}{\|}}{C}CH_2CH{=}CH_2$	" "	$(CH_3)_3SiO\underset{\underset{O}{\|}}{C}CH_2CH_2CH_2\underset{\underset{CH_2Cl}{|}}{Si}(CH_3)_2$ **(X)**	81—82 (1)	1.4451	0.9777	72.81	73.24	81
$(CH_3)_3SiO{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{CH_3}{|}}{C}{=}CH_2$	$(CH_3)_2C_2H_5SiH$	$(CH_3)_3SiO\underset{\underset{O}{\|}}{C}{-}\underset{\underset{CH_3}{|}}{C}HCH_2Si(CH_3)_2C_2H_5$ **(XI)**	87—88 (4)	1.4333	0.8714	77.70	77.70	51.6
$(CH_3)_3SiO\underset{\underset{O}{\|}}{C}{-}\underset{\underset{CH_3}{|}}{C}HCH_2\underset{\underset{CH_2Cl}{|}}{Si}(CH_3)_2$	H_2O	$(CH_3)_2\underset{\underset{CH_2Cl}{|}}{Si}CH_2\underset{\underset{CH_3}{|}}{C}HCOOH$ **(III)**	107—109(1.5)	1.4630	1.0595	50.63	50.60	98.5
$(CH_3)_3SiO\underset{\underset{O}{\|}}{C}\underset{\underset{CH_3}{|}}{C}HCH_2\underset{\underset{C_2H_5}{|}}{Si}(CH_3)_2$	" "	$C_2H_5(CH_3)_2SiCH_2\underset{\underset{CH_3}{|}}{C}HCOOH$ **(XII)**	121—122 (3)	1.4480	0.9164	55.02	55.06	68.7
$(CH_3)_3SiO\underset{\underset{O}{\|}}{C}CH_2CH_2CH_2\underset{\underset{CH_2Cl}{|}}{Si}(CH_3)_2$	" "	$(CH_3)_2\underset{\underset{CH_2Cl}{|}}{Si}CH_2CH_2CH_2COOH$ **(XIII)**	116—117 (1)	1.4629	1.0646	50.63	50.38	95.6
$ClCH_2(CH_3)_2SiCH_2\underset{\underset{CH_3}{|}}{C}HC{\overset{\displaystyle O}{\underset{\displaystyle OH}{\lessgtr}}}$	Na_2CO_3	 **(IV)**	93—94 (3)	1.4665	1.0032	43.73	43.83	64

table continued on next page.

Starting materials		Compound prepared	Bp (pressure mm)	n_D^{20}	d_4^{20}	MR_D Found	MR_D Calc.	Yield %
 $ClCH_2(CH_3)_2SiCH_2CH_2CH_2C(=O)OH$	Na_2CO_3	 (XIV)	82—84 (2)	1.4728	1.0238	43.30	43.83	21.2
 $ClCH_2(CH_3)_2SiCH_2CH(CH_3)COOH$	SO_2Cl	 $ClCH_2(CH_3)_2SiCH_2CH(CH_3)C(=O)Cl$ (V)	77—78 (2,5)	1.4706	1.0935	53.77	54.40	97
$ClCH_2(CH_3)_2SiCH_2CH_2CH_2COOH$	”	 $ClCH_2(CH_3)_2SiCH_2CH_2CH_2C(=O)Cl$ (XV)	99—100 (4)	1.4700	1.0971	53.77	54.28	94
 $ClCH_2(CH_3)_2SiCH_2CH(CH_3)C(=O)Cl$	H_2O	 $(ClCH_2Si(CH_3)_2-CH_2CH(CH_3)C(=O))_2O$ (XI)	172—174 (2)	1.4750	1.0773	97.60	97.07	57
 $ClCH_2(CH_3)_2SiCH_2CH(CH_3)C(=O)Cl$	NH_3, H_2O	 $ClCH_2(CH_3)_2SiCH_2CH(CH_3)C(=O)NH_3$ (VI)	37—38*					73
 $ClCH_2(CH_3)_2SiCH_2CH(CH_3)C(=O)NH_2$	CH_3ONa	 (VII)	55—56*					81.5

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*Melting temperature

and the mixture heated at 100°–120° C for about an hour, after which the reaction products were cooled and extracted with ether. The ether extract gave 20 g (64%) IV. Found: C 53.39, 53.56; H 8.95, 8.96; Si 17.30, 17.52%. Calculated for $C_7H_{14}SiO_2$: C 53.13; H 8.92; Si 17.70%. Silalactone XIV was prepared similarly.

Si-Dimethyl-1-methyl-3-silavalerolactam (VII). 8.2 g NaOMe in 50 ml dry MeOH was added to 10 g VI, and the mixture refluxed for 1 hr. The precipitate of NaCl was filtered off, and the MeOH distilled off from the filtrate, to give, on vacuum-distilling the residue, 6.6 g (81.5%) VII. Found: C 53.20, 53.42; H 9.57, 9.74; Si 17.22, 17.41; N 9.3, 9.1%. Calculated for $C_7H_{15}SiNO$: C 53.45; H 9.61; Si 17.85; N 8.9%.

REFERENCES

1. R. A. Benkeser, E. W. Bennet, and R. A. Hickner, J. Am. Chem. Soc., 79, 6253, 1957.
2. L. H. Sommer, U.S. Patent no. 2 589 446, 1952; C. A., 47, 145, 1953; U. S. Patent no. 2 963 500, 1960; C.A., 55, 10386, 1961.
3. D. N. Andreev and E. V. Kukharskaya, ZhOKh, 30, 2782, 1960.

13 September 1965

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RESEARCHES ON TETRAZOLE AND s-TRIAZOLE FORMAZANS

II. Synthesis and Colors of 1-(1'-Phenyltetrazolyl)-5-arylformazans Containing Nitro and Dimethylamino Groups*

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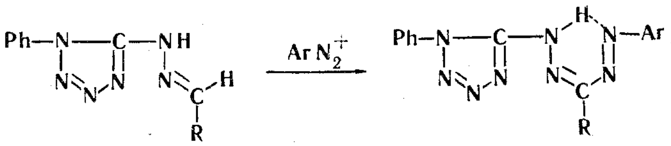
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 3, pp. 456–459, 1966

New 1-(1'-phenyltetrazolyl)-5-arylformazans are synthesized, and their IR and visible region spectra are investigated. The effects of electron-donating and -accepting groups on the colors of the formazans and on the stability of intramolecular hydrogen bonding of the formazyl ring are elucidated.

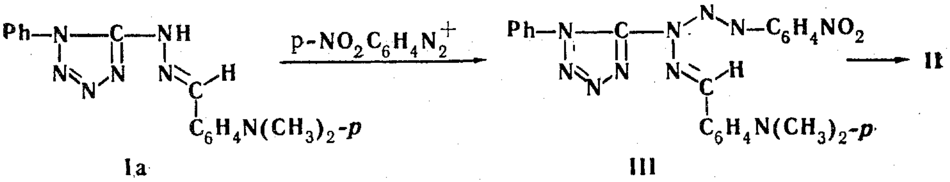
In further investigating the relationship between structure and color of formazans having a heteroaromatic group at N_1, it was of interest to study the effects of para electron-donating and -accepting groups in aryl groups at C_3 and N_5. In this connection, 1-(1'-phenyltetrazolyl)-5-arylformazans (II) with R and Ar containing p-nitro and p-dimethylamino groups have now been synthesized.

The formazans were prepared by coupling arylidiazonium salts with 1-phenyltetrazolyl-5-hydrazones (I, with R = Me, Ph, $PhNO_2$, $PhNMe_2$) in ethanolic alkali, pyridine, or mixed pyridine-ethanol in the presence of alkali:



I II

The low yield of formazan XI (table) is striking. Apparently, this is due to the electron-donor group Me_2N, present in the phenyl group of the hydrazone Ia, giving rise to a high electron density at the imino nitrogen, thus facilitating electrophilic substitution with formation of an intermediate product, the tetrazene III, but simultaneously the aldehyde hydrogen acquires low mobility, and rearrangement of the tetrazene to formazan is hindered (cf. [2]).



Ia III

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* For Part I see [1].