dodecyl)dichlorosilane in 100 ml. of anhydrous ethyl ether over a period of 2 hr. After the addition was completed the mixture was stirred for an additional hour and then refluxed overnight (*ca.* 20 hr.). The excess lithium particles were filtered off with suction and the filtrate was poured slowly over ice to decompose the excess alkyllithium. The solution was then neutralized with 3*N* hydrochloric acid and the ether layer phase separated. The water layer was extracted three times with 100 ml. of ethyl ether and the extracts, together with the ether layer, were dried over anhydrous calcium sulfate. After removal of the ether by distillation, fractionation of the liquid residue through a 30-cm. short-path Vigreux column gave 59.1 gm. (61.0%) of the product, b.p. 209° (0.04 mm.), n_D^{25} 1.4594, d_4^{25} 0.8212. See Table II for analysis.

Di(n-dodecyl)diphenylsilane. This aralkyl derivative, as well as the corresponding dimethyl and diethyl derivatives, was prepared by the reverse reaction of that used for the preparation of the di(*n*-dodecyl)dialkylsilanes. Thus, 127.0 g. (0.5 mol.) of diphenyldichlorosilane was added dropwise to an ether solution of 1.4 mol. of *n*-dodecyllithium (prepared by the same procedure used for the *n*-hexyllithium described above) over a period of 4 hr. The mixture was stirred for an additional hour and the unreacted lithium metal and salts were removed by suction filtration. The filtrate was treated in the same manner as described in the preparation of the di(*n*-dodecyl)di(*n*-hexyl)silane. The product was obtained, upon fractional distillation through a glass helices-packed column, as a colorless liquid, weighing 17.4 g. (79.1%), b.p. 216° (0.05 mm.), n_D^{25} 1.5053, d_4^{25} 0.9023.

Anal. Calcd. for $C_{36}H_{60}Si$: Si, 5.39; MR_D, 171.45. Found, Si, 5.68; MR_D, 171.30.

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WRIGHT-PATTERSON AIR FORCE BASE, OHIO

[CONTRIBUTION FROM MATERIALS LABORATORY, WRIGHT AIR DEVELOPMENT CENTER]

Organosilicon Compounds. II. 1,1-Disubstituted Silacyclohexanes

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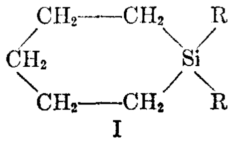
1,1-Disubstituted-silacyclohexanes were prepared by the reaction of 1,1-dichlorosilacyclohexane with an alkyl- or aryllithium compound. Attempts to effect cyclization of 1,5-dilithiopentane and a dialkyl(or diaryl)dichlorosilane were unsuccessful. Certain physical properties of the 1,1-dialkylsilacyclohexanes are presented.

In the first paper of this series,[1] the preparation and properties of two classes of long-chain tetraalkylsilanes were reported as part of a program on thermally stable fluids in which various properties of different types of organosilanes were correlated with molecular structure. The present paper describes the synthesis and properties of a series of cyclic organosilicon compounds, the 1,1-disubstituted-silacyclohexanes. In this class of compounds, represented by I, silicon is contained in a six-membered ring in which two alkyl or aryl groups are attached to the heterocyclic atom.


I

A review of previous attempts to prepare cyclic organosilicon compounds is contained in a paper by West.[2] The first 1,1-disubstituted-silacyclohexane to be prepared was reported by Bygden[3] more than forty years ago. He synthesized 1,1-dimethylsilacyclohexane by reacting methylmagnesium bromide with 1,1-dichlorosilacyclohexane, which was prepared from the Grignard reagent of 1,5-dibromopentane and silicon tetrachloride.

$$BrMg(CH_2)_5MgBr + SiCl_4 \longrightarrow (CH_2)_5SiCl_2 + 2MgBrCl$$

$$(CH_2)_5SiCl_2 + 2CH_3MgBr \longrightarrow (CH_2)_5Si(CH_3)_2 + 2MgBrCl$$

This compound was also prepared by West[2] in somewhat greater yield (72%) by the reaction of 1-chloro-1-methylsilacyclohexane with the Grignard reagent obtained from methyl iodide. The only other compound of this type described in the literature is the diethyl derivative of I, 1,1-diethylsilacyclohexane.[4] This was apparently prepared through a Wurtz type reaction in which a mixture of 1,5-dibromopentane and diethyldichlorosilane was treated with sodium metal. However, no details of the synthetic procedure used, yield

$$Br(CH_2)_5Br + (C_2H_5)_2SiCl_2 + 2Na \longrightarrow (CH_2)_5Si(C_2H_5)_2 + 2NaCl$$

obtained, or physical properties of the product were reported.

Bygden[3] also attempted the preparation of the diethyl derivative by the reaction of the Grignard reagent of 1,5-dibromopentane and diethyldichlorosilane but failed to obtain a pure product.

In the present work, a series of alkyl derivatives of I was prepared in good yield by the reaction of 1,1-dichlorosilacyclohexane with an alkyllithium in a 1 to 2 molar ratio:

$$(CH_2)_5Si(Cl)_2 + 2RLi \longrightarrow I + 2LiCl$$

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[1] H. Rosenberg, J. D. Groves, and C. Tamborski, *J. Org. Chem.*, **25**, 243 (1960).

[2] R. West, *J. Am. Chem. Soc.*, **76**, 6012 (1954).

[3] A. Bygden, *Ber.*, **48**, 1236 (1915).

[4] G. Gruttner and M. Wiernik, *ibid.*, **48**, 1474 (1915).

TABLE I

1,1-DISUBSTITUTED-SILACYCLOHEXANES, $(CH_2)_5SiR_2$

							Analyses[a]							
		Yield,					MR_D		Carbon, %		Hydrogen, %		Silicon, %	
R	Formula	%	B.P.	Mm.	n_D^{25}	d_4^{25}	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
CH_3	$C_7H_{16}Si$	74.2	131–133	760	1.4390	0.7994	42.04	42.29	65.53	65.89	12.57	12.40	21.89	21.62
C_2H_5	$C_9H_{20}Si$	77.1	184	760	1.4565	0.8346	51.30	50.96	69.13	69.25	12.89	12.68	17.97	17.69
n-C_3H_7	$C_{11}H_{24}Si$	80.1	78	3.5	1.4590	0.8338	60.56	60.46	71.64	71.63	13.12	13.14	15.23	14.94
n-C_4H_9	$C_{13}H_{28}Si$	85.8	52	0.10	1.4614	0.8365	69.82	69.74	73.49	73.33	13.28	13.41	13.22	12.96
n-C_5H_{11}	$C_{15}H_{32}Si$	81.3	79	0.12	1.4623	0.8370	79.08	78.87	74.91	75.16	13.41	13.38	11.68	11.27
n-C_6H_{13}	$C_{17}H_{36}Si$	74.9	101	0.13	1.4631	0.8376	88.34	88.31	76.02	76.01	13.51	13.40	10.46	10.47
n-C_7H_{15}	$C_{19}H_{40}Si$	80.1	120	0.12	1.4638	0.8386	97.60	97.56	76.93	77.20	13.59	13.67	9.47	9.33
n-C_8H_{17}	$C_{21}H_{44}Si$	92.4	147	0.20	1.4645	0.8387	106.9	106.9	77.68	77.84	13.66	13.47	8.65	9.10
n-C_9H_{19}	$C_{23}H_{48}Si$	79.2	158	0.18	1.4650	0.8397	116.1	116.1	78.32	78.85	13.72	13.22	7.96	7.96
n-$C_{10}H_{21}$	$C_{25}H_{52}Si$	83.1	202	0.80	1.4656	0.8402	125.4	125.4	78.85	79.05	13.77	13.70	7.38	7.29
n-$C_{11}H_{23}$	$C_{27}H_{56}Si$	86.3	196	0.20	1.4661	0.8410	134.6	134.6	79.32	79.62	13.81	13.77	6.88	6.70
n-$C_{12}H_{25}$	$C_{29}H_{60}Si$	93.1	198	0.10	1.4667	0.8416	143.9	144.0	79.72	79.78	13.84	13.62	6.43	7.05
n-$C_{14}H_{29}$	$C_{31}H_{64}Si$	87.5	215	0.02	1.4679	0.8425	162.4	162.6	80.39	80.51	13.90	13.14	5.70	5.74
n-$C_{16}H_{33}$	$C_{33}H_{68}Si$	91.4	257	0.07	1.4685	0.8431	180.9	181.2	80.93	81.12	13.95	13.53	5.12	5.09
n-$C_{18}H_{37}$	$C_{35}H_{72}Si$	89.7	282	0.07	1.4689	0.8435	199.5	199.8	81.36	81.44	13.99	13.92	4.62	4.72
i-C_5H_{11}	$C_{15}H_{32}Si$	79.0	61	0.05	1.4600	0.8335	79.08	79.02	74.91	75.06	13.41	13.52	11.68	11.23
$(C_2H_5)_2CHCH_2$	$C_{17}H_{36}Si$	80.0	96	0.10	1.4621	0.8503	88.34	86.84	76.02	76.16	13.51	13.53	10.46	10.31
C_6H_5	$C_{17}H_{20}Si$	83.2	122	0.12	1.5820	1.0319	81.46	81.64	80.89	80.75	7.99	8.19	11.13	11.06

[a] Analyses by Schwarzkopf Microanalytical Laboratories, Woodside, New Jersey.

In the above equation R represents *n*-alkyl groups of from one to eighteen carbon atoms (with the exception of C_{13}, C_{15}, and C_{17}). In addition, two branched-chain derivatives, 1,1′-diisoamylsilacyclohexane and 1,1-di(2-ethylbutyl)silacyclohexane, were prepared from isoamyllithium and 2-ethylbutyllithium, respectively. An aryl derivative, 1,1-diphenylsilacyclohexane was obtained from the corresponding reaction with phenyllithium. The synthesis of all these compounds was carried out by the addition of the 1,1-dichlorosilacyclohexane to an ethereal solution of the alkyllithium derivative, followed by hydrolysis of unreacted organolithium and fractionation of the product. The alkyllithium compounds were prepared by standard procedures[5] from the alkyl bromides (with the exception of methyllithium[6] which was obtained from the iodide).

In an attempt to prepare 1,1-disubstituted-silacyclohexanes by an alternate procedure, 1,5-dilithiopentane was treated with dimethyldichlorosilane and di-*n*-dodecyldichlorosilane, as well as with diphenyldichlorosilane. In each of these cases, although there was some spectral evidence for ring closure and for the formation of a small amount of the desired cyclic silane derivative, the main products were extremely high-boiling liquids or tacky solids. These are apparently linear polymeric materials resulting from the reaction of a dialkyl (or diaryl)-dichlorosilane with an ω-lithioamyldialkyl (or aryl) chlorosilane, formed by the equimolar reaction of dialkyl (or diaryl) dichlorosilane with 1,5-dilithiopentane. Further work aimed at studying this polymer formation, as well as preparing the cyclic dialkylsilanes by modification of the ring closure method, is in progress in this Laboratory.

The yields, physical characteristics, and analytical data for the 1,1-disubstituted-silacyclohexanes prepared in the present study are shown in Table I. The yields of 75–93% were somewhat greater than that obtained by West[2] for the preparation of 1,1-dimethylsilacyclohexane and are definitely superior to the yield obtained by Bygden[3] for the latter compound using the Grignard method.

EXPERIMENTAL

1,1-Disubstituted-silacyclohexanes. The method for the preparation of this series is illustrated by the synthesis of 1,1-di(*n*-octyl)silacyclohexane. To a solution of 0.89 mole of *n*-octyllithium (prepared by the general procedure of Gilman and co-workers,[5] the yield determined by the double titration method of Gilman and Haubein[7]) in 550 ml. of anhydrous ethyl ether and maintained under a nitrogen atmosphere, 50.7 g. (0.3 mol.) of 1,1-dichlorosilacyclohexane (prepared by interaction of the Grignard reagent of 1,5-dibromopentane and silicon tetrachloride)[2] dissolved in 50 ml. of anhydrous ether was added dropwise with stirring. A temperature of 0–10° was maintained throughout the addition which was complete in 80 min. The reaction mixture was allowed to warm up to room temperature and then refluxed for 18 hr. The contents of the flask were filtered to remove unreacted lithium metal and the filtrate poured over cracked ice. A 3% hydrochloric acid solution was added to the mixture until the water layer was just slightly acidic. The water layer was extracted with three 100-ml. portions of ethyl ether and the combined ether layer and washings dried over anhydrous calcium sulfate. Following removal of the solvents by distillation, fractionation of the yellow liquid residue through a 30-cm. short-path Vigreaux column gave 86.4 g. (87.5%) of the 1,1-dialkylsilacyclohexane, b.p. 147° (0.20 mm.), n_D^{25} 1.4645, d_4^{25} 0.8391. See Table I for the analysis.

Attempted preparation of cyclopentamethylenedimethylsilane. As a typical example of experiments conducted in an effort to synthesize 1,1-disubstituted-silacyclohexanes by ring closure of 1,5-dilithiopentane and dialkyldichlorosilanes, the attempted preparation of 1,1-dimethylsilacyclohexane by this method is described. To 20.7 g. (3.0 g. atoms) of lithium ribbon and 200 ml. of anhydrous ethyl ether, under a dry nitrogen atmosphere, was added 150.9 g. (0.656 mol.) of 1,5-dibromopentane while the temperature was maintained between −10° to −20°. After all of the dihalide had been added, the reaction mixture was allowed to come to room temperature. Titration of an aliquot sample of the mixture indicated a yield of 64% of the dilithium compound.[7] To the 0.42 mole of 1,5-dilithiopentane in the flask was then added dropwise with stirring 51.6 g. (0.4 mole) of dimethyldichlorosilane (Anderson Laboratories, Inc.) dissolved in 100 ml. of anhydrous ether. The reaction was exothermic and precipitation of lithium chloride was observed almost immediately. The mixture was refluxed for 20 hr when the excess lithium metal was removed by filtration. The filtrate was poured over cracked ice and neutralized with 3 *N* hydrochloric acid. The ether layer was separated and the water layer extracted three times with 100-ml. portions of ether. The ether layer and washings were combined and dried over anhydrous calcium sulfate. After the ether was removed by distillation, the liquid residue was fractionated through a 30-cm. column packed with glass helices. Four fractions were obtained, none of which boiled at a constant temperature. The refractive index of fraction 2, n_D^{25} 1.4371, is in approximate agreement with that obtained by West[2] for cyclopentamethylenedimethylsilane. However, only a minute quantity of this fraction was obtained and the bulk of the reaction product was an extremely high-boiling (non-distillable) polymeric material which could not be readily characterized.

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