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SYNTHESIS AND RESOLUTION OF OPTICALLY ACTIVE CARBONFUNCTIONAL ORGANOSILICON COMPOUNDS

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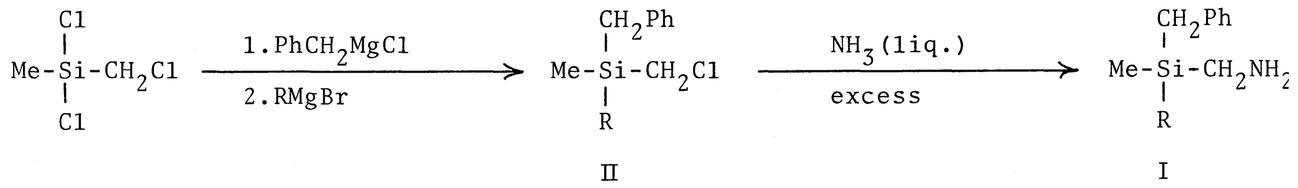
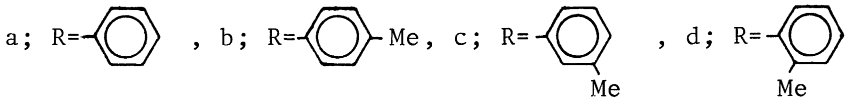
Triorganosilylmethylanimes, $Me(PhCH_2)RSiCH_2NH_2$ [$R=C_6H_5$(Ia), p-MeC_6H_4(Ib), m-MeC_6H_4(Ic), and o-MeC_6H_4(Id)] were resolved by fractional crystallization of the (+)-tartaric acid salts of the racemic triorganosilylmethylamines from methanol. The following optically active amines were obtained from the less soluble diastereoisomers; (+)-Ia($[\alpha]_D^{21}$ +9.9 (c=5, in Et_2O)), (-)-Ib ($[\alpha]_D^{21}$ -16.6 (c=5, in Et_2O)), (+)-Ic($[\alpha]_D^{22}$ +11.1 (c=5, in Et_2O)), and (+)-Id ($[\alpha]_D^{21}$ +7.0 (c=5, in Et_2O)).

Sommer *et al.* have reported on the synthesis and resolution of organosilicon compounds, such as 1-naphthylphenylmethylsilane and its derivatives$^{1)}$. Except for their works, a few successful methods for obtaining optically active organosilicon compounds have been reported$^{2)}$.

We now wish to report a successful preparation of new optically active compounds of the type, $MePhCH_2RSiCH_2NH_2$ by fractional crystallization of the (+)-tartaric acid salts of the amines from methanol.

The racemic amines Ia, Ib, Ic, and Id were prepared as follows.





The chloromethylorganosilanes IIa, IIb, IIc, and IId were synthesized by stepwise treatment of $MeCl_2SiCH_2Cl$ with the corresponding Grignard reagents in 57, 53, 80, and 66% yield, respectively. The prepared chloromethylsilanes were treated in an autoclave with about 40-fold excess of liquid ammonia at 100°C over a two-hour period. The primary amines were obtained in 50-60% yield from the reaction mixture$^{3)}$ [Table 1].

Table 1. The amination of the chloromethylsilanes.

R	II	NH_3(liq.)		I	
	g(mol)	g(mol)	bp(°C/mmHg)	yield g(%)	n_D(°C)
Ph	33.8(0.15)	70(4.1)	160-163/4	18.2(58.1)	1.5803(16)
p-tolyl	30.6(0.12)	74(4.3)	163-165/3	16.2(57.0)	1.5728(15)
m-tolyl	70.7(0.26)	240(14.1)	155-158/2	34.6(52.7)	1.5737(17)
o-tolyl	15.1(0.06)	36(2.2)	161-164/3	7.5(53.4)	1.5790(16)

The structural assignments of Ia, Ib, Ic, and Id were accomplished by the analysis of IR and NMR spectra.

Ia: NMR;(CCl_4) δ 0.32(s., 3H, Si-CH_3), 1,20(s., 2H, NH_2), 2.33(s., 4H, Si-CH_2-Ph, CH_2-N), 6.70-7.50(m., 10H, Si-C_6H_5, C-C_6H_5) : IR; 3400, 3300(w, NH_2), 1250(s, Si-Me), 770, 700(s, mono-substituted benzene)cm^{-1}: Found: N, 5.74% ; Calcd for $C_{15}H_{19}NSi$: N, 5.80%.

Ib: NMR;(CCl_4) δ 0.14(s., 3H, Si-CH_3), 1.30(s., 2H, NH_2), 2.15-2.30(7H, CH_3-C_6H_4, Si-CH_2-Ph, CH_2-N), 6.70-7.40(m., 9H, Si-C_6H_4, C-C_6H_5): IR; 3300, 3200(w, NH_2), 1250(m, Si-Me), 810(s, p-substituted benzene), 770, 690(s, mono-substituted benzene)cm^{-1}: Found: N, 5.34%, Calcd for $C_{16}H_{21}NSi$: N, 5.48%.

Ic: NMR;(CCl_4) δ 0.20(s., 3H, Si-CH_3), 0.57(s., 2H, NH_2), 2.10-2.25(7H, CH_3-C_6H_4, Si-CH_2-Ph, CH_2-N), 6.40-6.90(m., 9H, C-C_6H_5, Si-C_6H_4-C): IR; 3350, 3250(w, NH_2), 1250(m, Si-Me), 770, 690(s, mono-substituted benzene), 810(m, m-substituted benzene)cm^{-1}: Found: N, 5.54%, Calcd for $C_{16}H_{21}NSi$: N, 5.48%.

Id: NMR;(CCl_4) δ 0.26(s., 3H, Si-CH_3), 0.77(s., 2H, NH_2), 2.30-2.40(7H, CH_3-C_6H_4, Si-CH_2-Ph, CH_2-N), 6.66-7.43(m., 9H, Si-C_6H_4-, C-C_6H_5): IR; 3300, 3200(w, NH_2), 1250(m, Si-Me), 770, 690(s, mono-substituted benzene), 740(s, o-substituted benzene)cm^{-1}: Found: N, 5.38%, Calcd for $C_{16}H_{21}NSi$: N, 5.48%.

Optical resolutions of Ia, Ib, Ic, and Id were carried out by using (+)-tartaric acid as a resolving reagent [Table 2].

In a typical experiment, a solution of amine Ia (5.37g) and (+)-tartaric acid (3.34g) in methanol (245ml) was allowed to stand overnight at room temperature. Precipitated white crystalline salt (3.72g, 42.8% yield, Found: N, 3.54%; Calcd for $C_{19}H_{25}NO_6Si$: N, 3.58%) was separated from the solution by filtration. Further recrystallization of the less soluble salt was not undertaken, since the salt was observed to be unstable in solution above the temperature of 40°C. The less soluble diastereoisomer was treated with caustic alkali solution and the liberated amine was extracted with ether. Removal of ether and distillation of the residue gave (+)-Ia(1.98g, 36.9% yield). Similar treatment of the more soluble salt (4.90g) which was obtained from the mother liquor gave the impure (-)-Ia(1.52g, 28.4% yield).

Table 2. Resolution of triorganosilylmethylamines.

		(+)-tartaric			diastereoisomer*			optically active amine*	
R	A	acid	MeOH ml		yield	mp	$[\alpha]_D$	yield	$[\alpha]_D$
	g	g	(ml/g amine)		g(%)	°C	(C=5, in DMF)	g(%)	(C=5, in Et_2O)
Ph	5.36	3.34	250	B	3.72(42.8)	164	+21.0	1.98(36.9)	+ 9.2
			(46)	C	4.90(56.3)	150-5	———	1.52(28.4)	- 4.4
Ph	2.03	1.26	150	B	0.85(25.8)	164	———	0.30(14.8)	+ 9.3
			(75)	C	—— ——	——	———	0.34(16.7)	- 2.8
p-tolyl	2.00	1.18	100	B	0.85(26.6)	162	-26.9	0.27(13.5)	-12.9
			(50)	C	2.25(70.7)	134	+12.7	1.04(52.0)	+ 4.4
p-tolyl	5.10	3.00	255	B	2.34(28.8)	159	-23.8	0.92(18.0)	-11.4
			(45)	C	5.76(71.1)	140	+13.4	2.41(47.1)	+ 5.3
m-tolyl	5.06	2.98	400	B	2.18(27.1)	160	+34.1	1.29(25.5)	+10.7
			(80)	C	5.20(64.7)	150-7	———	2.52(49.4)	- 2.5
m-tolyl	4.93	2.90	350	B	2.32(29.6)	158	+31.9	1.32(26.7)	+10.3
			(70)	C	5.43(69.3)	148-50	———	2.40(48.6)	- 4.1
o-tylyl	3.02	1.77	150	B	1.77(36.9)	169	+15.1	0.90(29.8)	+ 4.9
			(50)	C	2.70(56.4)	140-2	- 8.2	0.81(26.8)	- 2.1
o-tolyl	5.14	3.02	128	B	4.58(56.1)	163-4	+12.0	2.31(44.9)	+ 3.9
			(25)	C	3.48(42.8)	149-50	-9.5	1.40(27.2)	- 2.2

A ; $Me(PhCH_2)RSiCH_2NH_2$

B ; less soluble diastereoisomer

C ; more soluble diastereoisomer

* Specific rotations of the diastereoisomers and amines were measured at 20°C.

As the recrystallization of the less soluble diastereoisomer could not be carried out, the partly resolved amines Ia, Ib, Ic, and Id were dealt with equimolar amount of (+)-tartaric acid in methanol several times in an analogous way until specific rotation of the less soluble salts became constant [Fig. 1] [Table 3].

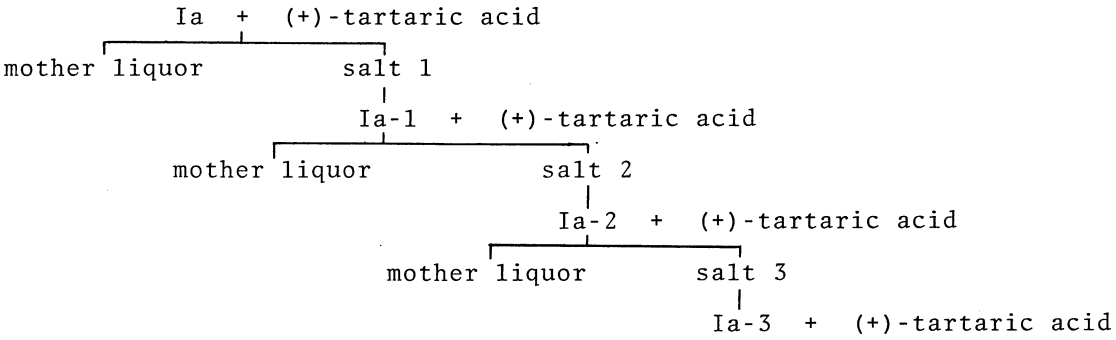


Fig. 1. Fractional recrystallization of the salt of Ia and (+)-tartaric acid.

Table 3. Specific rotation of the salts* and amines*.

Amine	salt 1	amine 1	salt 2	amine 2	salt 3	amine 3	salt 4
Ph	+21.6	+ 9.3	+29.0	+ 9.9	+29.5	——	——
p-tolyl	-30.4	-14.5	-40.0	-16.6	-39.9	——	——
m-tolyl	+34.1	+10.7	+35.4	+11.1	+35.6	——	——
o-tolyl	+12.4	+ 3.9	+17.6	+ 6.0	+22.1	+ 7.0	+22.5

* Specific rotations of the salts and amines were measured in DMF and in Et_2O at 20°C respectively.

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