Hydrolysis of 2-Aminothiazolo(5,4-*b*)pyridines. These compounds were hydrolyzed as described by Takahashi and Yoshii (*14*) and later modified by Okafor (*10*).

Attempted Hydrolysis of 2-Amino-5-*n*-butoxythiazolo(5,4-*b*)pyridine, IX. The procedure adopted here is similar to that described for the hydrolysis of 2-amino-5-methoxythiazolo(5,4-*b*)pyridine. The following concentrations were tried:—10, 20, 30, 40, and 50% sodium hydroxide solution and saturated barium hydroxide. Even after the reflux time was increased to 24 hours, no hydrolysis took place and in all cases the starting material was recovered in yields better than 80%.

(3,5-Dinitro-2-thienyl)-3-amino-6-methoxy-2-pyridyl Sulfide, XI. 6-Methoxy-3-amino-2-mercaptopyridine (1.56 grams, 0.01 mole) was dissolved in 40 ml of boiling methanol and added to a methanolic solution of 2-bromo-3,5-dinitrothiophene (*15*) (3.04 grams, 0.012 mole). The mixture was stirred in an ice bath for 2 hours. The yellow precipitate formed was collected by filtration and recrystallized from acetone after treatment with decolorizing carbon. Yellow plates of (3,5-dinitro-2-thienyl)-3-amino-6-methoxy-2-pyridyl sulfide separated (3.15 grams; 96%) (mp 240–41° C).

Anal. Calcd. for $C_{10}H_8N_4O_5S_2$: C, 36.58; H, 2.46; N, 17.06; S, 19.54.

Found: C, 36.39; H, 2.50; N, 17.05; S, 19.59.

Compound XII was prepared in a similar manner (mp 141–42° C).

3,5-Dinitro-2-thienyl-2-aminopyridines. These compounds, XIII to XVI, were prepared from 2-aminopyridine, 6-amino-2-picoline, 6-amino-2-pyridinol (*16*), and 2-amino-5-chloropyridine, respectively, by procedures similar to that reported for (3,5-dinitro-2-thienyl)-3-amino-6-methoxy-2-pyridyl sulfide, except that the reaction time varied as indicated in Table II.

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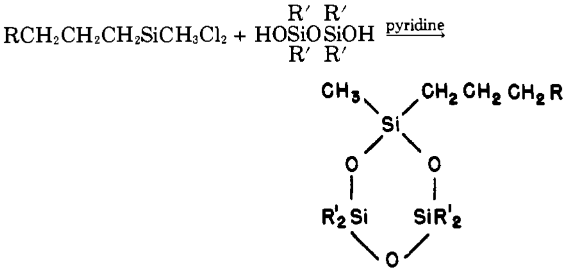
Organodichlorosilanes and Cyclotrisiloxanes Containing Polar Groups

TSE C. WU
Silicone Products Department, General Electric Co., Waterford, N. Y. 12188

The preparation and properties of 28 new organodichlorosilanes and cyclotrisiloxanes containing polar groups are described.

A convenient way to introduce an organofunctional group into a polysiloxane is to synthesize a cyclotrisiloxane and to rearrange it into a polymer in the presence of a basic catalyst. To study the effects of some polar groups on the polysiloxane properties, some organocyclotrisiloxanes were prepared by condensing a tetrasubstituted disiloxane diol with a dichlorosilane. The dichloromethyl-(γ-substituted-propyl)silanes were prepared by adding dichloromethylsilane to an olefinic compound in the presence of a platinum catalyst. The reactions involved are shown below.

$$CH_3SiHCl_2 + CH_2{=}CHCH_2R \xrightarrow{Pt} RCH_2CH_2CH_2SiCH_3Cl_2 \qquad (1)$$



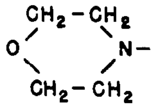
$$RCH_2CH_2CH_2SiCH_3Cl_2 + HO\underset{R'}{\overset{R'}{Si}}O\underset{R'}{\overset{R'}{Si}}OH \xrightarrow{pyridine}$$

(2)

The properties of 10 dichlorosilanes thus prepared are summarized in Tables I and II. The relatively low yields

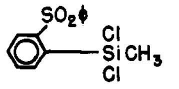
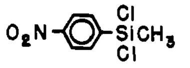
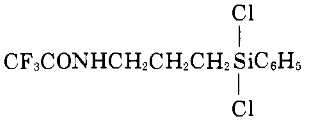
Table I. Organodichloromethylsilanes[a]

$RCH_2CH_2CH_2SiCH_3Cl_2$

R	Bp, °C/mm	Yield, %
CH_3CONH	158-160/8	18
CCl_3CONH	178-180/7	87
CF_3CONH	133-135/8	65
C_6H_5CONH	188-191/2	71
$CNCH_2CONH$	207/0.08	19
	135-138/9	40
CF_3COO	196-197/756	55

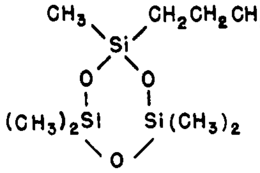
[a] Elemental analyses for Cl in agreement with theoretical values have been obtained and submitted for review.

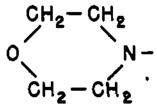
Table II. Other Diorganodichlorosilanes[a]

Compound	Bp, °C/mm	Yield, %
	200/0.07	19
	130-131/4	87
 $CF_3CONHCH_2CH_2CH_2\overset{Cl}{\underset{Cl}{Si}}C_6H_5$	158-160/3	79

[a] Elemental analyses for Cl in agreement with theoretical values have been obtained and submitted for review.

Table III. Organopentamethylcyclotrisiloxanes



Compound designation	R	Mp, °C or bp, °C/mm	Yield, %
I	CH_3CONH	94.5-95.5	50
II	CCl_3CONH	94-95	56
III	C_6H_5CONH	83.5-85	46
IV	$CNCH_2CONH$	103-104	37
V		38.5-40	36
VI	CF_3COO	91-92/9	14
VII	CH_3SO_2	68-69	42
VIII	$C_6H_5SO_2$	61-62	49

of the amide-containing chlorosilanes are probably due to side reactions such as the silylation of amides by the chlorosilanes. Also, 18 new cyclotrisiloxanes are summarized in Tables III and IV and their infrared data are given in Table V. In all cases, these compounds exhibit characteristic infrared absorptions consistent with the proposed structures. For example, all the organocyclotrisiloxanes have a strong band at about 9.8μ due to the asymmetric SiOSi stretching vibration in the 6-membered ring. The infrared spectra were recorded on a Perkin-Elmer Infracord equipped with an NaCl prism.

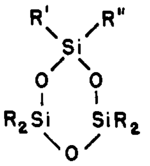
EXPERIMENTAL

Melting points and boiling points are uncorrected.

General Procedure for the Preparation of Diorganodichlorosilanes. The allyl compound was added slowly to an excess of dichloromethylsilane in the presence of $PtCl_4$. The addition was carried out at such a rate as to keep the reaction mixture refluxing gently by the heat of reaction throughout the addition. At the completion of addition, the reaction mixture was refluxed for a few hours and then it was distilled to give the dichlorosilane. The procedure is similar to that previously reported (*2*). The sulfone-containing dichlorosilane was prepared by treating 2-lithiodiphenyl sulfone with methyltrichlorosilane. The nitro-containing dichlorosilane was prepared by nitrating difluoromethylphenylsilane followed by treatment with silicon tetrachloride (*3*).

General Procedure for the Preparation of Organocyclotrisiloxanes. A toluene solution containing the disiloxanediol and an excess of pyridine was added, along with another toluene solution containing the dichlorosilane, to a small amount of toluene at room temperature with stirring. The addition of these two solutions was carried out simultaneously and

Table IV. Organocyclotrisiloxanes



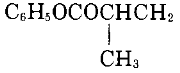
Compound designation	R	R′	R″	Mp, °C or bp, °C/mm	Yield, %
IX	CH_3	C_6H_5	$CF_3CONH(CH_2)_3$	79-80	59
X	C_6H_5	CH_3	$CF_3CONH(CH_2)_3$	104-105	64
XI	C_6H_5	CH_3	$CH_3SO_2(CH_2)_2$	127.5-129	41
XII	C_6H_5	CH_3	$ClCH_2$	86.5-88	53
XIII	CH_3	CH_3	$ClCH_2$	35-37	40
XIV	m-$CF_3C_6H_4$	CH_3	CH_3	162-6/0.01	42
XV	CH_3	CH_3	o-$C_6H_5SO_2C_6H_4$	110.5-112	18
XVI	CH_3	CH_3	p-$(CH_3)_2NC_6H_4$	55-56	30
XVII	CH_3	CH_3	p-$O_2NC_6H_4$	92-93/0.35	23
XVIII	CH_3	CH_3	 $C_6H_5OCO\underset{CH_3}{CH}CH_2$	53.5-55.5	15

Table V. Infrared Spectra of Cyclotrisiloxanes

(Band positions in microns)[a]

I	Mull. 3.0(m) (NH), 3.2(w), 6.0(m) and 6.4(w) (CONH), 7.7(w), 7.9(s) ($SiCH_3$), 8.4(w), 8.5(w), 9.9(s) (SiOSi), 11.4(w), 12.3(s), 13.1(w), 13.3(w)
II	Mull. 3.0(m) (NH), 5.9(s) and 6.5(m) (CONH), 7.9(s) ($SiCH_3$), 8.4(w), 8.5(w), 9.9(s) (SiOSi), 11.5(sh), 12.3(s), 12.6(sh), 13.4(w)
III	Solid film.[b] 3.0(m) (NH), 3.3(w), 3.4(m), 6.1(s) and 6.5(m) (CONH), 6.2(w), 6.3(w), 6.7(w), 7.0(w), 7.3(w), 7.6(w), 7.7(m), 7.9(s) ($SiCH_3$), 8.4(m), 8.5(w), 9.3(sh), 9.8(s) (SiOSi), 11.5(w), 12.3(s), 13.4(w), 14.2(m), 14.4(m) (C_6H_5)
IV	Mull. 3.0(m) (NH), 3.2(w), 4.4(vw) ($C{\equiv}N$), 6.0(s) and 6.4(m) (CONH), 7.4(w), 7.7(w) 7.9(s) ($SiCH_3$), 8.4(w), 8.5(w), 9.8(s) (SiOSi), 11.4(w), 12.3(s), 12.4(m), 13.4(w), 14.8(w)
V	Solid film.[b] 3.4(m), 3.6(w), 6.9(w), 7.1(w), 7.4(w), 7.7(w), 7.9(s) ($SiCH_3$), 8.3(w), 8.5(w), 8.8(w), 8.9(m) (COC), 9.3(w), 9.8(s) (SiOSi), 10.9(w), 11.5(m), 12.3(s), 13.3(m)
VI	Liquid. 3.4(m), 5.6(s) (CF_3COOCH_2), 6.8(w), 7.2(m), 7.4(m), 7.5(m), 7.9(s) ($SiCH_3$), 8.2(m), 8.7(s), 9.9(s) (SiOSi), 10.4(sh), 10.6(sh), 11.6(sh), 12.3(s), 12.8(m), 13.3(w), 13.7(m)
VII	Solid film.[b] 3.4(m), 6.9(w), 7.1(w), 7.6(m), 7.8(s) and 8.8(s) (SO_2), 7.9(s) ($SiCH_3$), 8.5(m), 9.9(s) (SiOSi), 10.4(sh), 10.6(sh), 11.4(w), 12.3(s), 13.0(m), 13.3(w), 14.2(w), 14.8(m)
VIII	Mull. 7.6(w), 7.7(m) and 8.7(s) (SO_2), 7.9(s) ($SiCH_3$), 8.4(m), 9.2(m), 9.8(s) (SiOSi), 10.5(w), 11.4(sh), 12.0(sh), 12.2(s), 12.6(sh), 13.1(w), 13.2(m), 14.1(w), 14.5(m) (C_6H_5)
IX	Mull. 3.1(m) (NH), 3.2(w), 5.9(s) and 6.4(m) (CONH), 7.0(w) (SiC_6H_5), 7.6(w), 7.9(m) ($SiCH_3$), 8.2(m), 8.4(s), 8.5(sh), 8.9(m) (SiC_6H_5), 9.7(sh), 9.8(s) (SiOSi), 10.0(w) (SiC_6H_5), 11.3(w), 11.6(w), 12.3(s), 13.0(w), 13.8(m), 14.3(m) (C_6H_5), 14.7(w)
X	Mull. 3.0(m) (NH), 5.9(s) and 6.4(m) (CONH), 6.3(w), 7.0(m) (SiC_6H_5), 7.5(w), 7.9(m) (SiC_6H_5), 8.3(m), 8.4(s), 8.5(w), 8.8(m) and 8.9(m) [$Si(C_6H_5)_2$], 9.6(s) and 10.0(s) (SiC_6H_5), 9.8(s) (SiOSi), 10.5(w), 12.8(m), 13.1(w), 13.3(m), 13.5(m), 13.8(m), 13.9(sh), 14.3(m) (C_6H_5)
XI	Solid film.[b] 3.3(w), 3.4(sh), 6.3(m), 7.0(m) (SiC_6H_5), 7.1(sh), 7.6(m) and 8.8(sh) (SO_2), 7.9(m) ($SiCH_3$), 8.5(m), 8.9(m) and 9.0(m) [$Si(C_6H_5)_2$], 9.7(s) (SiC_6H_5), 9.9(s) (SiOSi), 10.1(s) (SiC_6H_5), 10.4(sh), 11.3(w), 12.0(sh), 12.4(m), 12.7(sh), 12.8(m), 13.0(sh), 13.1(sh), 13.4(w), 13.8(m), 14.3(m) (C_6H_5)
XII	Solid film.[b] 3.3(w), 6.3(w), 6.7(w), 7.0(m) (SiC_6H_5), 7.2(w), 7.7(w), 7.9(m) ($SiCH_3$), 8.4(w), 8.9(m) and 9.0(m) [$Si(C_6H_5)_2$], 9.7(s) (SiC_6H_5), 9.9(s) (SiOSi), 10.1(s) (SiC_6H_5), 11.9(m), 12.4(m), 12.8(w), 13.1(w), 13.5(m), 13.8(m), 14.3(s) (C_6H_5), 14.6(w)
XIII	Mull. 7.9(s) ($SiCH_3$), 8.5(w) ($SiCH_2Cl$), 9.1(sh) 9.8(s) (SiOSi), 10.6(sh), 11.5(m), 12.2(s), 12.4(sh), 12.6(sh)
XIV	Liquid. 6.2(m), 7.1(m), 7.5(s), 7.9(m) ($SiCH_3$), 8.4(sh), 8.5(m), 8.9(s), 9.2(sh), 9.3(m), 9.8(s) (SiOSi), 10.1(m), 10.7(w), 11.0(w), 11.8(m), 12.1(w), 12.5(m), 13.3(w), 13.8(m), 14.3(m), 14.6(w)
XV	Solid film.[b] 3.3(w), 3.4(m), 6.3(w), 6.8(w), 6.9(m), 7.1(w), 7.2(w), 7.7(m) and 8.7(s) (SO_2), 7.8(w), 7.9(s) ($SiCH_3$), 8.9(sh), 9.0(m), 9.2(m). 9.7(s), 9.9(s) (SiOSi), 11.4(sh), 11.6(m), 12.3(s), 12.8(w), 12.9(w), 13.1(m), 13.2(sh), 13.4(s) (o-C_6H_4), 13.8(m), 14.2(m), 14.6(m) (C_6H_5)
XVI	Solid film.[c] 3.2(sh), 3.4(m), 3.5(sh), 3.6(sh), 5.3(w), 6.2(m) (aromatic ring), 6.5(w), 6.6(m), 6.9(m), 7.1(w), 7.3(m), 7.6(w), 7.8(w), 7.9(s) ($SiCH_3$), 8.1(m), 8.3(sh), 8.9(m), 9.4(sh), 9.6(s) and 9.9(s) (SiOSi), 10.4(sh), 10.6(w), 11.6(m), 12.2(sh), 12.4(s), 12.6(sh), 13.1(m), 13.4(m), 14.2(m), 14.5(w)
XVII	Liquid. 3.4(w), 6.2(w) (aromatic ring), 6.6(s) and 7.4(s) (NO_2), 7.1(w), 8.5(sh), 8.8(m), 9.9(s) (SiOSi), 10.0(sh), 11.4(m), 11.7(m), 12.4(s), 12.6(sh), 13.2(w), 13.6(sh), 13.7(m), 14.2(w), 14.7(m)
XVIII	Mull. 5.6(m) (COO-Aryl), 7.2(m), 7.3(m), 7.8(w), 7.9(s) ($SiCH_3$), 8.3(m), 8.9(w), 9.4(s), 9.9(s) (SiOSi), 10.8(m), 11.6(m), 12.0(sh), 12.2(s), 12.5(sh), 12.7(sh), 12.9(sh), 13.2(m), 13.4(w), 13.8(m)

[a] s, strong; m, medium; w, weak; sh, shoulder; v, very. [b] Deposited from trichloroethylene solution. [c] Deposited from toluene solution.

at about the same rate. After stirring for a few hours, the reaction mixture was filtered to remove the pyridine hydrochloride. The filtrate was distilled to remove the solvent. The residue was further purified by vacuum distillation and recrystallizations. A similar procedure has been reported (*1*).

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