Properties of Several Arylated Silicon Compounds

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MANY arylated silicon compounds exhibit unusually good thermolytic stability. Examples of these are tetraphenylsilane, tetraphenoxysilane and phenyl triphenoxysilane (*2, 3*).

During an extensive search for other such compounds for potential use as heat transfer fluids, which in addition to thermolytic stability may possess such additional desirable properties as wide liquid range, good oxidative stability, and high flash and fire points, many new compounds were prepared which did not entirely meet these criteria. Nevertheless, they are of interest for kindred uses such as hydraulic fluids, lubricants, and additives. These novel compositions are reported here for the first time in Table I.

Table I. Physical Properties of a

No.	Empirical Formula	Compound	Formula
1	$SiC_{18}H_{16}O$	Triphenoxysilane	$HSi(OC_6H_5)_3$
2	$SiC_{18}H_{16}O_2$	Phenyl diphenoxysilane	$C_6H_5SiH(OC_6H_5)_2$
3	$Si_3C_{57}H_{50}O_3$	1,2,3-Tris(triphenylsiloxy)propane	$C_3H_5[OSi(C_6H_5)_3]_3$
4	$SiC_{24}H_{18}O_2$	Diphenyl cyclo-2,2′-biphenyldioxysilane	$(C_6H_5)_2SiOC_6H_4C_6H_4O$
5	$SiC_{48}H_{60}O_4$	Tetra-*o*-cyclohexylphenoxysilane	$(C_6H_{11}C_6H_4O)_4Si$
6	$SiC_{48}H_{36}O_4$	Tetra-*p*-biphenyloxysilane	$(C_6H_5C_6H_4O)_4Si$
7	$SiC_{40}H_{44}O_4$	Tetra-ar.-5,6,7,8-β-tetralyloxysilane	$[(C_2H_4)_2=C_6H_3O]_4Si$
8	$SiC_{36}H_{44}O_4$	Tetra-*o,p,i*-propylphenoxysilane	$(C_3H_7C_6H_4)_4Si$
9	$SiC_{30}H_{24}O_3$	*m,p*-Biphenylyl triphenoxysilane	$C_6H_5C_6H_4Si(OC_6H_5)_3$
10	$SiC_{36}H_{28}O_3$	*o*-Terphenylyl triphenoxysilane	$C_6H_5C_6H_4C_6H_4Si(OC_6H_5)_3$
11	$SiC_{36}H_{28}O_3$	*m*-Terphenylyl triphenoxysilane	$C_6H_5C_6H_4C_6H_4Si(OC_6H_5)_3$
12	$SiC_{36}H_{28}O_3$	*p*-Terphenylyl triphenoxysilane	$C_6H_5C_6H_4C_6H_4Si(OC_6H_5)_3$
13	$SiC_{30}H_{24}O_4$	*p*-Phenoxyphenyl triphenoxysilane	$C_6H_5OC_6H_4Si(OC_6H_5)_3$
14	$SiC_{24}H_{24}O_3$	Cyclohexenyl triphenoxysilane	$C_6H_9Si(OC_6H_5)_3$
15	$SiC_{36}H_{38}O_3$	Phenyl tri-ar.-5,6,7,8-β-tetralyloxysilane	$C_6H_5Si[OC_6H_3=(C_2H_4)_2]_3$
16	$SiC_{42}H_{42}O_3$	*m,p*-Biphenylyl tri-ar.-5,6,7,8-β-tetralyloxysilane	$C_6H_5C_6H_4Si[OC_6H_3=(C_2H_4)_2]_3$
17	$SiC_{48}H_{36}O_3$	*m,p*-Biphenylyl tri-*m*-biphenyloxysilane	$C_6H_5C_6H_4Si(OC_6H_4C_6H_5)_3$
18	$SiC_{48}H_{36}O_3$	*m,p*-Biphenylyl tri-*p*-biphenyloxysilane	$C_6H_5C_6H_4Si(OC_6H_4C_6H_5)_3$
19	$Si_2C_{42}H_{34}O_8$	Hexaphenoxy-*m*-disiloxybenzene	$(C_6H_5O)_3SiOC_6H_4OSi(OC_6H_5)_3$
20	$Si_2C_{42}H_{34}O_6$	Hexaphenoxy-*m*-disilylbenzene	$(C_6H_5O)_3SiC_6H_4Si(OC_6H_5)_3$
21	$Si_2C_{42}H_{34}O_6$	Hexaphenoxy-*p*-disilylbenzene	$(C_6H_5O)_3SiC_6H_4Si(OC_6H_5)_3$
22	$Si_2C_{48}H_{46}O_6$	Hexa-*o*-tolyloxy-*m,p*-disilylbenzene	$(CH_3C_6H_4O)_3SiC_6H_4Si(OC_6H_4CH_3)_3$

[a] Viscosity at 210° F. = 2.80 cs. [b] Viscosity at −13° F. = 169 cs.; at −37° F. = 1947 cs. [c] Viscosity at 210° F. = 18.2 cs. [d] Pour-point.

EXPERIMENTAL

With the exception of 1,2,3-tris(triphenylsiloxy) propane, all compounds were prepared (*1, 4*) in the following manner: To a 1000 ml. round-bottomed, three-necked flask fitted with a dropping funnel, thermometer, motor-driven glass stirrer and a water-cooled condenser (affixed below a dry-ice cooled condenser) was placed the appropriate phenol in 20% mole weight excess of that stoichimetrically required for 0.75 mole of the designated chlorsilane.

The chlorosilane was added slowly from the dropping funnel so as to maintain a moderate evolution of hydrogen chloride. Where the chlorosilane is a solid at ambient, an infrared lamp was shone upon the dropping funnel (as in the case of biphenylyl trichlorosilane) in order to keep the reactant fluid. After addition was completed, the reactants were brought slowly to reflux and there maintained for 18 hours in all instances. Upon cooling, the excess of phenol was removed by vacuum distillation, and the reaction products likewise distilled, using an 8-inch insulated Vigreaux column.

For example, 0.75 mole (102 grams) of trichlorosilane was added slowly to 2.7 moles (254 grams) of phenol with stirring at 45° C., or just above the melting point of the phenol. The rate of addition was such as to maintain a slow reflux of the low-boiling chlorosilane without permitting its loss with the escaping hydrogen chloride gas. Upon complete addition, the reactants were slowly heated to reflux at 198° C.

1,2,3-Tris(triphenylsiloxy) propane was prepared in a similar manner except that 2.7 moles (213 grams) of pyridine and 150 ml. of benzene were added to 2.7 moles (248 grams) of glycerol prior to the addition of 0.75 moles (221 grams) of triphenyl chlorosilane. Solid pyridine hydrochloride precipitated and was filtered off. Benzene was distilled from the reaction mixture under vacuum along with other low boiling reactants up to a head temperature of 280° C./3 mm. The residue on cooling solidified and was crystallized from hot toluene to a gray microcrystalline solid.

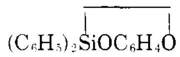
THERMOLYTIC STABILITY

Test Method. The thermolytic stability test was conducted in an inert atmosphere of nitrogen as follows: a borosilicate glass test tube of 500 ml.-capacity with a long riser tube fitted to a mercury column equipped with a blow-by rubber seal, set to release at 10 p.s.i.g., was charged with 300 to 400 ml. of organosilane and three mild carbon steel strips. The test tube was placed in a molten salt bath set at 750° F. At intervals of several weeks aliquot samples of 50 ml. each were removed for examination of unstripped and stripped viscosities and per cent of low boiler and polymer formations. An inordinate increase in viscosity and/or polymer with time indicated relatively poor thermal stability. An ability to withstand degradation to polymer with its resultant increase in viscosity over a period of time constituted evidence of excellent thermolytic stability.

This qualitative evaluation was indicated when the stripped viscosity was no more than double after 100 days of test. The time (in days) required to produce this viscosity increase was the criterion of relative thermal stability. While some of the new compounds described herein did not show a twofold viscosity increase after 100 days at 750° F., they were unsatisfactory because of other factors such as high melting or pour points, or high initial viscosity which made them unsuitable for use as heat transfer fluids. Test results are reported in Table II.

DISCUSSION

Compound 4 is an interesting example of a seven-membered ring:



$(C_6H_5)_2SiOC_6H_4O$

Compounds 10 and 12 are mixtures of isomers produced from the designated isomeric terphenyl; its initial reaction

Series of Silicon Compounds

Mol. W.	Reaction Temp., ° C.	M.P., ° C.	B.P., ° C.	mm. Hg	R. 25_DI.	Viscosity, Cs., 77° F.	Silicon, % Calcd.	Silicon, % Found	Yield, %
308.43	198	42	210	1	. . .	[a]	9.11	8.94	60
292.43	202	. . .	195–7	2	. . .	9.75[b]	9.61	9.48	76
857.34	80	152	280–300	3	. . .	. . .	9.83	9.89	38
366.51	247	108	220	0.5	. . .	. . .	7.66	7.60	82
729.17	275	115	290–300	1	. . .	. . .	3.85	4.01	80
704.93	230	205	315–20	1	. . .	. . .	3.98	4.10	88
616.93	225	. . .	210	2	1.5810	200	4.55	4.50	85
768.89	208	. . .	200	0.5	1.5451	163	3.65	3.60	92
460.63	240	. . .	190	0.2	1.6010	350	6.10	6.07	94
536.73	250	. . .	182–5	0.5	1.6130	6900[c]	5.23	5.55	42
536.73	270	(70)[d]	200	0.5	. . .	[e]	5.23	5.32	60
536.73	310	135–7	220	0.5	. . .	. . .	5.23	5.28	82
476.63	235	. . .	180	0.2	. . .	58.3	5.89	6.10	73
388.57	200	. . .	210	1	. . .	40.3	7.23	7.10	80
546.83	225	. . .	220–5	0.5	1.6014	2000	5.14	5.10	85
622.93	235	(55)[d]	222–6	0.5	. . .	. . .	4.51	4.44	80
688.93	305	. . .	350	1	. . .	[f]	4.08	4.12	82
688.93	340	(75)[d]	>270	0.5	1.5908	[g]	4.08	4.15	78
722.94	235	. . .	210	1	1.5795	430	3.89	4.15	80
692.94	230	. . .	210	1	. . .	309	4.05	4.11	95
692.94	245	. . .	220	0.5	1.5917	250	4.05	4.15	90
775.12	235	. . .	200–10	0.2	1.5858	1300	3.62	3.55	82

[e] Viscosity at 210° F. = 13.4 cs. [f] Viscosity at 210° F. = 40.0 cs. [g] Viscosity at 300° F. = 19.3 cs.

Table II. Thermolytic Stabilities at 750° F. (400° C.)

Compound	Days Viscosity, Cs. 0	15	30	50	75	100	Visc. Increase, %
Tetraphenoxy silane	6.88[b]	6.92[b]	7.50[b]	. . .	11.5[b]	14.0[b]	104
Phenyl triphenoxysilane	11.6[b]	11.6[b]	. . .	13.2[b]	16.4[b]	18.5[b]	60
Triphenoxy silane	2.80[c]	Too volatile-Boiled Off					
Phenyl diphenoxysilane	9.75	Too volatile-Boiled Off					
Tetra-ar.-5,6,7,8-β-tetralyoxysilane	200	580	1085	1400	. . .	. . .	1100[d]
Tetra-*o,p,i*-propylphenoxy silane	163	720	2200	. . .	. . .	. . .	5000[d]
m,p-Biphenylyl triphenoxy silane	350	318	270	265	360	420	20
o-Terphenylyl triphenoxy silane	18.2[c]	162[c]	705[c]	1200[c]	. . .	. . .	3000[d]
m-Terphenylyl triphenoxy silane	13.4	17.2	28.0	99.2	115	130	123
p-Phenoxyphenyl triphenoxy silane	58.3	70.0	. . .	48.0	69.3	85.0	534
Cyclohexenyl triphenoxy silane	40.3	52.5	65.8	78.0	92.5	103	308
Phenyl tri-ar.-5,6,7,8-β-tetralyloxysilane	2000	. . .	7800	. . .	. . .	. . .	1100[d]
m,p-Biphenylyl tri-*m*-biphenyloxysilane	40.0	51.2	. . .	. . .	94.1	105	163
Hexaphenoxy-*m*-disiloxybenzene	430	640	760	. . .	1010	1220	184
Hexaphenoxy-*m*-disilylbenzene	309	382	455	560	628	700	127

[a] All viscosities given were taken at 77° F. except where noted. [b] Viscosities at 130° F. [c] Viscosities at 210° F. [d] Extrapolated.

with trichlorosilane to produce isomeric intermediates which in turn were used to produce isomeric end products. These end products contain small quantities of bis- bodies, which because of their extremely high boiling points, could not be separated from the parent material. In general, materials containing the following bonds showed a decreasing order of thermal stability: $C_6H_5C_6H_4Si > C_6H_5Si > C_6H_5OSi > C_6H_5OC_6H_4Si > C_6H_5C_6H_4OSi > C_6H_{11}C_6H_4Si > C_6H_5C_6H_4C_6H_4Si > C_nH_{2n+1}C_6H_4Si$.

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Organo-Silicon Nitrogen Compounds

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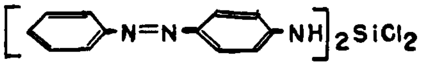
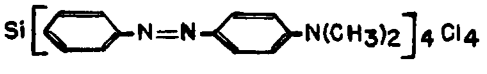
FORMATION of tetraanilinosilane by the reaction of aniline in benzene with tetrachlorosilane was reported by Reynolds (*7*). This reaction had been investigated earlier by Harden (*4*), who reported the production of one equivalent of dianilinodichlorosilane and two of aniline hydrochloride. Two silicon nitrogen-bonded compounds, dichlorodi(*p*-aminoazobenzene)silane,



and tetra(N,N-dimethylaminoazobenzene)silane tetrachloride,



have now been prepared by this method from *p*-aminoazobenzene and N,N-dimethylaminoazobenzene, respectively, in 74.4 to 78.5% yields (Table I). Both were formed as dark red crystals.

The infrared spectra of these compounds were determined between 3 and 15 microns (Figures 1 and 2).

In preparation of dichlorodi(*p*-aminoazobenzene)silane, *p*-aminoazobenzene hydrochloride was another product, identified by its infrared spectrum (Figure 3) which was determined between 3 and 15 microns.

The fact that tetrachlorosilane did not react with azobenzene indicated that only the amino group was affected in the reactions of the aminoazobenzenes with tetrachlorosilane.

Waterman (*8*) prepared a series of silicon-nitrogen compounds, namely, trichlorodiethylaminosilane, dichlorobis(diethylamino)silane, chlorotri(diethylamino)silane, and tetra(diethylamino)silane, and obtained their infrared spectra. A comparison of all these spectra with the spectrum of diethylamine indicates that the new bands occur between 7.45 and 7.48, 9.38 and 9.41, 9.69 and 9.78, 10.66 and 10.8, and 12.6 and 12.68 microns, and may be due to Si—N bonding. Strong new bands were obtained at 9.2, 9.7, and 12.4 microns for dichlorodi(*p*-aminoazobenzene)silane and at 9.35 microns for tetra(N,N-dimethylaminoazobenzene)-silane tetrachloride. Weak peaks occur in the latter compound at 9.7 and 12.4 microns.

Since new absorption bands occur in all these spectra at 9.2 to 9.4, 9.69 to 9.71, and 12.4 microns it seems likely that they are due to Si—N bonding.

Table I. Analysis of Si—N Bonded Compounds

Compound	Yield, %	Silicon, %		Nitrogen, %		Chlorine, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
$[C_6H_5—N=N—C_6H_4—NH]_2SiCl$	74.4	5.68	5.56	17.06	17.01	14.62	14.02
$Si[C_6H_5—N=N—C_6H_4—N(CH_3)_2]Cl_4$	78.5	2.61	2.56	15.6	15.1	13.3	13.07