SYNTHESIS AND CONVERSION REACTIONS OF ALKENYL- AND HYDRIDE SILOXANES

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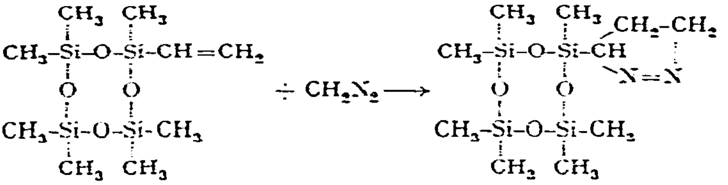
(Received May 12th, 1965)

The syntheses of methylvinylcyclosiloxanes[1,2], ethylvinylcyclosiloxanes[3], tetraphenyltetravinylcyclotetrasiloxane[4] prepared by hydrolysis, and vinyl-containing cyclosiloxanes prepared by co-hydrolysis of various monomers[5–7], have been described in the literature. Of the allyl derivatives of cyclosiloxanes, trimethyltriallylcyclotrisiloxane, tetramethyltetraallylcyclotetrasiloxane[8] and hexaallylcyclotrisiloxane[9] have been described, and of the organosiloxanes containing the alkenyl group and hydrogen attached to silicon, 1-allyl-3-*H*-tetramethyldisiloxane and 1-allyl-5-*H*-hexamethyltrisiloxane[10] are known. With regard to conversion reactions of alkenyl- and hydride siloxanes, only the addition reactions of non-saturated organic compounds to hydride siloxanes[10–14] have been fully discussed in the literature.

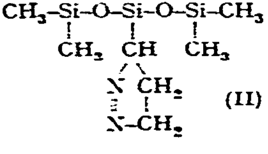
In the present work, the addition reactions of diazomethane and phenyl azide, and the Diels–Alder diene synthesis reaction for vinyl- and allyl-containing organosiloxanes (both linear and cyclic) have been studied.

The experimental work shows that vinylheptamethylcyclotetrasiloxane and 3-vinylheptamethyltrisiloxane react readily with diazomethane:



(I)

Under conventional conditions and at temperatures between —15° and +20° this reaction proceeds easily yielding up to 77.1 % of (I). Ultraviolet irradiation does not affect the course of the reaction: the same quantity of pyrazoline (I) is obtained. Under the conditions indicated 3-vinylheptamethyltrisiloxane reacts with diazomethane giving yields up to 72.6 % of (II):



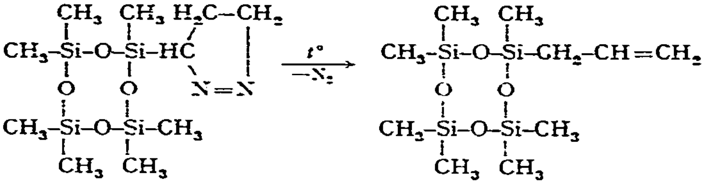
(II)

In the infrared spectra of compounds (I) and (II) a rather strong band is observed at 1545 cm^{-1} which is evidently associated with the $N{=}N$ bond vibrations of the pyrazoline ring.

In NMR spectra a proton peak of the CH groups and two symmetrical doublets for the protons of the CH_2 groups were observed at a fixed frequency of 40 Mc/sec and the following values of chemical shifts [relative to $(CH_3)_4Si$]: $\tau(CH) = 5.74$ ppm; $\tau'(CH_2) = 6.96$ ppm; $\tau'(CH_2) = 7.12$ ppm; $\tau''(CH_2) = 7.36$ ppm; $\tau''(CH_2) = 7.58$ ppm. The two doublets for the protons of the CH_2 groups of the pyrazoline ring indicated a 3-substituted 1-pyrazoline structure for compounds (I) and (II).

It is interesting to note that siloxanes containing a vinyl group in the β-position to silicone (allylheptamethylcyclotetrasiloxane) react only slowly with diazomethane and the corresponding pyrazoline derivatives cannot be isolated from the reaction products.

When compounds (I) and (II) are heated to 180–200° they decompose and liberate nitrogen to form allyl derivatives of organosiloxanes. The thermal decomposition of these compounds is likely to proceed according to a mechanism involving free radicals.

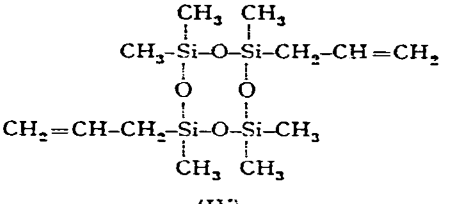


(I) (III)

3-Allylheptamethyltrisiloxane, $(CH_3)_3Si{-}O{-}Si(CH_3)(CH_2{-}CH{=}CH_2){-}O{-}Si(CH_3)_3$, was obtained in the thermal decomposition of compound (II).

The infrared spectra of compound (III) and 3-allylheptamethyltrisiloxane show bands at 1640–1635 cm^{-1}, and two bands for each compound at 3010 and 3085 cm^{-1} in the region of the stretching vibrations of the C–H bonds which should be referred to vibrations of $=C{-}H$ and $=CH_2$ in the $C{=}C$ bond region. The appearance of these three bands indicates that this structure should be assigned to the compounds obtained.

Compound (III) was also synthesized by the co-hydrolysis reaction of methylallyldichlorosilane with dimethyldichlorosilane (1:1 molar ratio) where 1,5-diallylhexamethylcyclotetrasiloxane* was formed together with compound (III):



(IV)

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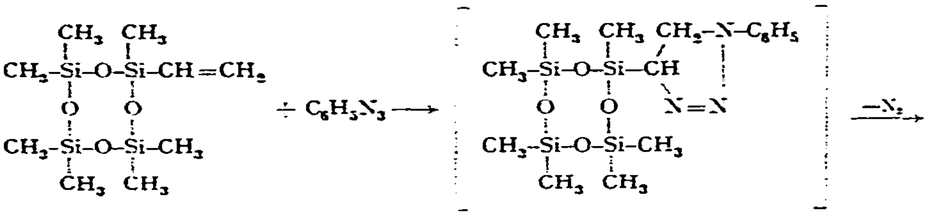
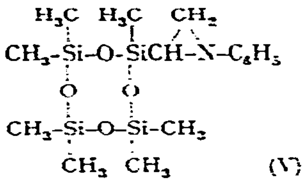
* For this compound the isomeric structure is possible.

The presence of the 8-membered ring in compounds (III) and (IV) was proved by the infrared band at 1085 cm^{-1}.

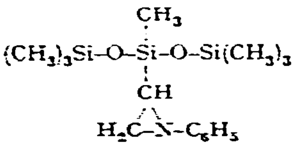
The addition reaction of phenyl azide to vinylheptamethylcyclotetrasiloxane and 3-vinylheptamethyltrisiloxane gives the corresponding N-phenylaziridinyl derivatives of organosiloxanes. The reaction probably proceeds through the formation of triazoline derivatives which are decomposed to the corresponding N-phenylaziridinyl derivatives while being recovered.





(V)

Compound (VI) was obtained from phenyl azide and 3-vinylheptamethyltrisiloxane in a similar manner:

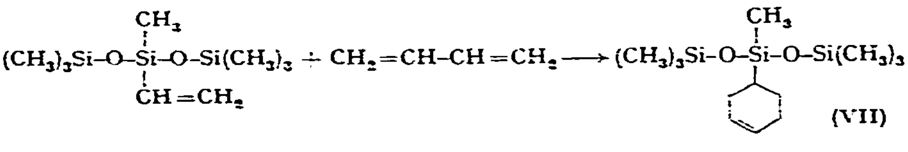


(VI)

In the infrared spectra of compounds (V) and (VI), a band characteristic of the C–N bonds was observed at 1352 cm^{-1}; the presence of the phenyl group in these compounds was proved by the bands in the region of 1505, 1605, and 3030 cm^{-1}.

Allylheptamethylcyclotetrasiloxane reacted only slowly with phenyl azide, *c.f.* the reaction with diazomethane, and we could not isolate the corresponding N-phenylaziridinyl derivative from the reaction products. These facts conform to the theory, that in regard to nucleophilic reagents in the addition reactions, the vinyl group in the α-position to silicon is much more reactive than that in the β-position.

The Diels–Alder diene synthesis reaction was exemplified by the reaction of 3-vinylheptamethyltrisiloxane with 1,3-butadiene. The reaction proceeds comparatively easily giving a satisfactory yield of the condensation product according to the following scheme:



(VII)

The infrared spectrum of this compound shows a band characteristic of the double bond of cyclohexene derivatives at 1655 cm^{-1} indicating the almost complete absence of mutual influence of the double-bond π-electrons and the free 3-*d*-orbitals of silicon.

In addition to the reactions already mentioned the addition reactions of unsaturated organic compounds and methylvinyldichlorosilane with pentamethyldisiloxane and 3-*H*-heptamethyltrisiloxane have also been investigated. Pentamethyldisiloxane and 3-*H*-heptamethyltrisiloxane were synthesized by the co-hydrolysis reaction of dimethylchlorosilane with trimethylchlorosilane and methyldichlorosilane with trimethylchlorosilane, respectively.

1,1,3,5,5-Pentamethyl-3-vinyltrisiloxane (VIII) and 1,1,3,5,5-pentamethyl-3-allyltrisiloxane (IX) were synthesized similarly by the co-hydrolysis of methylvinyldichlorosilane and methylallyldichlorosilane with dimethylchlorosilane. The presence of the Si–H bonds in the compounds indicated is shown by a very strong infrared band in the region 2130–2145 cm^{-1}. Moderately intense bands at 1605, 3018, and 3060 cm^{-1} [for compound (VIII)] and at 1640, 3039, 3068 cm^{-1} [for compound (IX)] confirm the presence of the $Si-CH=CH_2$ and $Si-CH_2-CH=CH_2$ bonds.

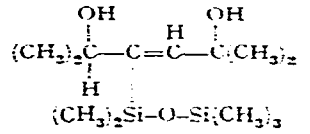
A study of the reaction of pentamethyldisiloxane and 3-*H*-heptamethyltrisiloxane with styrene, indene, 1-heptyne, 2,5-dimethyl-3-hexyne-2,5-diol, 2-vinylpyridine, cyclopentadiene, 1,4-dichloro-2-butyne, methylvinyldichlorosilane, acrylonitrile and *sym*-dicyanoethylene showed that the addition reaction proceeds differently: in some cases the addition takes place easily; in others not at all. Thus, we have not been successful in carrying out the addition reaction of acrylonitrile and *sym*-dicyanoethylene using as catalysts, amines and their derivatives, the Speiers catalyst and palladium on charcoal. This is probably caused by the steric factor of the groups in the vicinity of the Si–H bond in the original organosiloxanes. 2-Vinylpyridine does not combine so easily with pentamethyldisiloxane in the absence of a catalyst as when using $(C_2H_5)_3N$ and $(C_4H_9)_3N$ as catalysts. With $H_2PtCl_6 \cdot 6H_2O$ as a catalyst the reaction proceeds well.

Styrene reacts with pentamethyldisiloxane yielding the compound $C_6H_5CH_2CH_2Si(CH_3)_2OSi(CH_3)_3$, (X); in the same manner, 3-*H*-heptamethyltrisiloxane and styrene produce the compound $C_6H_5CH_2CH_2Si(CH_3)[OSi(CH_3)_3]_2$, (XI). NMR spectra of compound (X) contain two absolutely symmetrical groups of peaks at a fixed frequency of 22.68 Mc/sec with the following mean values of chemical shifts (here and later the chemical shifts are given relative to the CH_3–(Si) groups of the compounds themselves): $\delta[CH_2(-Si)] = 0.89$ ppm and $\delta[CH_2(-C_6H_5)] = 2.35$ ppm. Infrared spectra of this compound show the presence of the phenyl group by bands in the following regions: 1505, 1610, 3028, 3066, 3088 cm^{-1}. The presence of the band characteristic of the C–H bond stretching vibrations in the CH_2 groups in the region of 2910 cm^{-1} together with the bands characteristic of the C–H bond stretching vibrations in the CH_3 groups (2880 cm^{-1} and 2965 cm^{-1}) again proves the structure of compound (X). The infrared spectrum of compound (XI) is identical to that of compound (X).

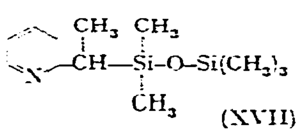
Indene gives an addition product, (2-indanyl)$Si(CH_3)_2OSi(CH_3)_3$, (XII), with pentamethyldisiloxane. Similarly, compound (2-indanyl)$Si(CH_3)[OSi(CH_3)_3]_2$, (XIII), was obtained from indene and 3-*H*-heptamethyltrisiloxane. NMR spectra of compound (XII) at a fixed frequency of 40 Mc/sec contains one unsplit peak shifted considerably to the region of the phenyl group protons at a value of chemical shift $\delta(CH_2) = 3.36$ ppm and two peaks from the phenyl group protons with values of chemical shifts $\delta' = 4.22$ ppm and $\delta'' = 4.33$ ppm. The structure indicated for compound (XII) is also proved by the presence of frequencies 1489, 1606, 2855, 2905, 3013, and 3075 cm^{-1} in the infrared spectra of the compound. The infrared spectrum of compound (XIII) agrees with that of compound (XII).

1-Heptyne gives the addition product, $CH_3(CH_2)_4CH{=}CHSi(CH_3)_2OSi(CH_3)_3$, (XIV), with pentamethyldisiloxane. Similarly, compound $CH_3(CH_2)_4CH{=}CH{-}Si(CH_3)[OSi(CH_3)_3]_2$, (XV), was obtained from 1-heptyne and 3-*H*-heptamethyltrisiloxane. NMR spectra of compound (XIV) at a fixed frequency of 40 Mc/sec contains a multiplet group of peaks characteristic of the double-bond protons with the mean value of chemical shifts $\delta = CH- = 1.47$ ppm. The structure indicated for compound (XIV) is proved by the presence of frequencies 1010, 1628, 2860, 2928, and 3045 cm^{-1} in the infrared spectrum of the compound. The infrared spectrum of compound (XV) coincides with that of compound (XIV).

2,5-Dimethyl-3-hexyne-2,5-diol combined with pentamethyldisiloxane at the triple bond leaving the hydroxyl groups unchanged, forming compound (XVI). The structure indicated for this compound is proved by a quantitative determination of the hydroxyl groups and by the presence of frequencies 1001, 1601 cm^{-1} in the infrared spectrum.



(XVI)

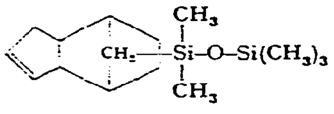


(XVII)

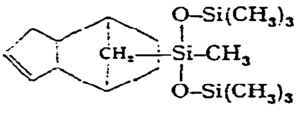
The reaction of 2-vinylpyridine with pentamethyldisiloxane gives the product (XVII). In the NMR spectrum of this compound at a fixed frequency of 22.68 Mc/sec, some peaks chracteristic of the CH group protons (quadruplet) and peaks characteristic of the CH_3 group protons at C–H (doublet) with the following values of chemical shifts, $\delta(CH) = 2.30$ ppm and $\delta(CH_3) = 1.26$ ppm, were observed. The structure indicated for compound (XVII) is also proved by the presence of frequencies 1389, 1489, 1598, 2900, 3008, and 3071 cm^{-1} in the infrared spectrum of the compound.

In the reaction of cyclopentadiene with pentamethyldisiloxane and 3-*H*-heptamethyltrisiloxane, dimerization of cyclopentadiene has already taken place at 30° and then the dimer formed react with pentamethyldisiloxane giving (XVIII), and with 3-*H*-heptamethyltrisiloxane giving (XIX). The structure indicated for compounds (XVIII) and (XIX) is proved by the presence of frequencies 1614 and 3045 cm^{-1} in their infrared spectra.

The organic silicon compounds containing halogen in the β-position to silicon are known to be unstable (especially when heated). But in the reaction of 1,4-dichloro-2-butyne with pentamethyldisiloxane a rather stable compound, $ClCH_2CH{=}C(CH_2Cl){-}Si(CH_3)_2OSi(CH_3)_3$, (XX), is obtained. This phenomenon is probably due to the stabilizing influence of the double bond in the α-position to silicon. The structure of the product is proved by the elementary analysis and the following frequencies in the infrared spectra of compound (XX): 1620, 2908, and 3030 cm^{-1}.



(XVIII)



(XIX)

Methylvinyldichlorosilane and pentamethyldisiloxane yielded the addition product $Cl_2(CH_3)SiCH_2CH_2Si(CH_3)_2OSi(CH_3)_3$, (XXI). Similarly, the compound $Cl_2(CH_3)SiCH_2CH_2Si(CH_3)[OSi(CH_3)_3]_2$, (XXII), was obtained from methylvinyldichlorosilane and 3-*H*-heptamethyltrisiloxane. In the NMR spectra of compound (XXI) at a fixed frequency of 40 Mc(sec) one unsplit peak characteristic of the CH_2–Si group protons with the value of chemical shift $\delta(CH_2) = 0.68$ ppm was detected; peaks characteristic of the CH and CH_3 group protons (at CH) were absent. The structure indicated for the compound (XXI) is also proved by the presence of frequencies 2860 and 2912 cm^{-1} in the infrared spectrum of the compound. The infrared spectrum of compound (XXII) is identical to that of compound (XXI).

In conclusion it should be noted that addition reactions with pentamethyldisiloxane proceed easier than those with 3-*H*-heptamethyltrisiloxane.

The properties of the newly synthesized compounds are given in Table 1.

TABLE 1

PROPERTIES OF THE SYNTHESIZED COMPOUNDS

Organosiloxanes		*B.p.,* (*°C/mm Hg*)	n_D^{20}	d_4^{20}
(I)	(1-Pyrazolin-3-yl)heptamethylcyclotetrasiloxane	82–83/2	1.4305	1.0177
(II)	3-(1-Pyrazolin-3-yl)heptamethyltrisiloxane	84–86/4	1.4285	0.9115
(III)	Allylheptamethylcyclotetrasiloxane	41/3	1.4119	0.9616
(IV)	1,5-Diallylhexamethylcyclotetrasiloxane	57–58/3	1.4243	0.9684
(V)	(N-Phenylaziridinyl)heptamethylcyclotetrasiloxane	109–111/1	1.4678	1.0500
(VI)	3-(N-Phenylaziridinyl)heptamethyltrisiloxane	105–107/2	1.4673	0.9571
(VII)	3-(3-Cyclohexenyl)heptamethyltrisiloxane	62–64/1	1.4309	0.8834
(VIII)	1,1,3,5,5-Pentamethyl-3-vinyltrisiloxane	41–42/15	1.3959	0.8423
(IX)	1,1,3,5,5-Pentamethyl-3-allyltrisiloxane	48–49/15	1.4056	0.8516
(X)	(2-Phenylethyl)pentamethyldisiloxane	80–81/3	1.4636	0.9015
(XI)	3-(2-phenylethyl)heptamethyltrisiloxane	94–95/2	1.4517	0.9185
(XII)	(2-Indanyl)pentamethyldisiloxane	66–67/1	1.4862	0.9445
(XIII)	3-(2-Indanyl)heptamethyltrisiloxane	84–86/1	1.4690	0.9515
(XIV)	(1-Heptenyl)pentamethyldisiloxane	64–66/3	1.4230	0.8116
(XV)	3-(1-heptenyl)heptamethyltrisiloxane	56–57/1	1.4075	0.8237
(XVI)	(2,5-dimethyl-2,5-dihydroxy-3-hexen-3-yl)pentamethyldisiloxane	m.p.	64–65°	
(XVII)	[1-(2-pyridyl)ethyl]pentamethyldisiloxane	63–65/2	1.4644	0.9145
(XVIII)	Tricyclo[5.2.1.0^{2,6}]dec-3-enylpentamethyldisiloxane	104–105/5	1.4717	0.9479
(XIX)	3-(tricyclo[5.2.1.0^{2,6}]dec-3-enyl)heptamethyltrisiloxane	112–113/3	1.4544	0.9471
(XX)	[1-(chloromethyl)-3-chloro-1-propenyl]pentamethyldisiloxane	75–77/2	1.4585	1.0324
(XXI)	[2-(methyldichlorosilyl)ethyl]pentamethyldisiloxane	62–64/3	1.4338	0.9881
(XXII)	3-[2-(methyldichlorosilyl)ethyl]heptamethyltrisiloxane	87–89/2	1.4255	0.9745

EXPERIMENTAL

All the products synthesized were isolated by repeated vacuum distillation using a flask equipped with a dephlegmator, except for compounds (III) and (IV) which were isolated by vacuum column distillation, and compound (XVI) which was recrystallized. The infrared spectra were recorded by a UR-10 Zeiss spectrometer; the samples were investigated by the method of "thin layer"; the NMR spectra were recorded by a CLA spectrometer (Moscow).

(1-Pyrazolin-3-yl)heptamethylcyclotetrasiloxane (I)

An ether solution of diazomethane prepared from 7.5 g of nitrosomethylurea and 8.1 g of potassium hydroxide, was added to 9.24 g (0.03 mole) of vinylheptamethylcyclotetrasiloxane. The mixture was kept at 0° for 10 h and then left at room temperature until excess diazomethane had completely evaporated; 9.1 g (77.1 %) of (I), b.p. 82–83° (2 mm), were isolated by distillation. (Found: C, 34.50; H, 7.41; N, 8.76; Si, 31.94; mol. wt., 341; MR_D, 88.76. $C_{10}H_{26}N_2O_4Si_4$ calcd.: C, 34.29; H, 7.43; N, 8.00; Si, 32.00 %; mol. wt., 350; MR_D, 89.39.)

3-(1-Pyrazolin-3-yl)heptamethyltrisiloxane (II)

By means of the above technique, 7.4 g (72.6 %) of (II) were prepared from 8.7 g (0.035 mole) of 3-vinylheptamethyltrisiloxane, b.p. 84–86° (4 mm). (Found: C, 41.68; H, 9.08; N, 10.01; Si, 29.37; mol. wt., 315; MR_D, 81.81. $C_{10}H_{26}N_2O_2Si_3$ calcd.: C, 41.38; H, 9.08; N, 9.65; Si, 28.97 %; mol. wt., 290; MR_D, 82.39.)

Decomposition of (I) and (II)

Allylheptamethylcyclotetrasiloxane (III) (1.23 g, 26.1 %), b.p. 42–43 (3 mm), n_D^{20} 1.4318, was prepared by decomposing 5.1 g (0.0146 mole) of (I) at 170–200° for 3.5 h in a flask equipped with a reflux-condenser.

Similarly, 2.63 g (69.4 %) of 3-allylheptamethyltrisiloxane, [b.p. 57.5–59° (10 mm), n_D^{20} 1.4049 from the literature[15]] b.p. 103–103.5° (59 mm), n_D^{20} 1.4013, were prepared by decomposing 4.2 g (0.0145 mole) of (II) for 30 min.

Synthesis of (III) and 1,5-diallylhexamethylcyclotetrasiloxane (IV)

A mixture of 120.5 ml (1.0 mole) of dimethyldichlorosilane and 132 ml (1.0 mole) of methylallyldichlorosilane was added to a mixture of 500 ml of water and 200 ml of ether at a temperature below 30° over 2 h with stirring. As soon as the reaction was completed, the ether layer was separated, washed with water until the washings were neutral and dried over calcium chloride. The ether was removed by distillation yielding 159 g of the reaction product from which 98 g of volatile compounds [b.p. 40–95° (3 mm)] were isolated. Distillation of this mixture resulted in 21.14 g (19.7 %) of (III), b.p. 41° (3 mm), and 17.09 g (10.9 %) of (IV), b.p. 57–58 °(3 mm). (Found: C, 38.15; H, 8.38; Si, 33.93; rhodan number, 50.6; mol. wt., 298; MR_D, 83.31. $C_{10}H_{26}O_4Si_4$ calcd.: C, 37.26; H, 7.45; Si, 34.78 %; rhodan number, 49.6; mol. wt., 322; MR_D, 83.61. Found: C, 41.35; H, 8.46; Si, 31.86; rhodan number, 87.0; mol. wt., 325; MR_D, 91.78. $C_{12}H_{28}O_4Si_4$ calcd.: C, 41.37; H, 8.07; Si, 32.18 %, rhodan number, 92.0; mol. wt., 348; MR_D, 92.10.)

(N-Phenylaziridinyl)heptamethylcyclotetrasiloxane (V)

Vinylheptamethylcyclotetrasiloxane (5.16 g, 0.0167 mole) and 1.99 g (0.0167 mole) of phenyl azide were poured into a well-stoppered flask and allowed to stand for 40 days. Attempts to isolate a crystalline product were unsuccessful, and the reaction product was isolated by distillation. In all, 0.71 g (9.9 %) of (V), b.p. 109–111° (1 mm), were obtained. (Found: C, 45.10; H, 7.30; N, 3.41; Si, 27.45; mol. wt., 387; MR_D, 105.37. $C_{15}H_{29}NO_4Si_4$ calcd.: C, 45.11; H, 7.27; N, 3.51; Si, 28.07 %; mol. wt., 399; MR_D, 105.79.)

3-(N-Phenylaziridinyl)heptamethyltrisiloxane (VI)

By means of the above technique, 0.78 g (10.6 %) of (VI), b.p. 105–107° (2 mm), were obtained from 4.96 g (0.02 mole) of 3-vinylheptamethyltrisiloxane and 2.38 g (0.02 mole) of phenyl azide. (Found: C, 52.01; H, 8.05; N, 3.85; Si, 25.29; mol. wt., 357; MR_D, 98.15. $C_{15}H_{29}NO_2Si_3$ calcd.: C, 53.09; H, 8.55; N, 4.13; Si, 24.78 %; mol. wt., 339; MR_D, 98.79.)

3-(3-Cyclohexenyl)heptamethyltrisiloxane (VII)

3-Vinylheptamethyltrisiloxane (7.44 g, 0.03 mole) and 1.62 g (0.03 mole) of 1,3-butadiene were sealed in an ampoule. The temperature of the mixture was raised from 20° to 160° over 10 h and then maintained at 160–180° for 20 h; 4.7 g (52 %) of (VII), b.p. 62–64° (1 mm), were isolated by distillation. (Found: C, 51.11; H, 9.75; Si, 27.56; mol. wt., 326; MR_D, 88.32. $C_{13}H_{30}O_2Si_3$ calcd.: C, 51.65; H, 9.93; Si, 27.81 %; mol. wt., 302; MR_D, 87.96.)

1,1,3,5,5-Pentamethyl-3-vinyltrisiloxane (VIII)

A mixture of 28.2 g (0.2 mole) of methylvinyldichlorosilane and 37.8 g (0.4 mole) of dimethylchlorosilane was added to a stirred mixture of 150 g of ice and 100 ml of ether at a temperature of —10 to —15° for 1 h. After treatment of the reaction mass using a technique similar to that in the synthesis of compounds (III) and (IV), 31.4 g (71.4 %) of (VIII), b.p. 41–42° (2 mm), were isolated. (Found: C, 38.44; H, 9.42; Si, 38.22; mol. wt., 209; MR_D, 62.75. $C_7H_{20}O_2Si_3$ calcd.: C, 38.18; H, 9.09; Si, 38.18 %; mol. wt., 220; MR_D, 62.98.)

1,1,3,5,5-Pentamethyl-3-allyltrisiloxane (IX)

By means of the above technique, 20.4 g (67 %) of (IX), b.p. 48–49° (15 mm), were obtained from 25 g (0.26 mole) of dimethylchlorosilane and 18.3 g (0.13 mole) of methylallyldichlorosilane. (Found: C, 41.51; H, 9.42; Si, 36.03; mol. wt., 218; MR_D, 67.43. $C_8H_{22}O_2Si_3$ calcd.: C, 41.03; H, 9.40; Si, 35.90 %; mol. wt., 234; MR_D, 67.79.)

(2-phenylethyl)pentamethyldisiloxane (X)

Styrene (7.28 g, 0.07 mole) and 10.36 g (0.07 mole) of pentamethyldisiloxane were placed in a one-neck flask. Then 5 drops of the catalyst (0.1 N solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol) were added and the temperature of the mixture raised from 80° to 150° over 4 h; 14.2 g (80.5 %) of (X), b.p. 80–81° (3 mm), were isolated by distillation. (Found: C, 61.95; H, 9.61; Si, 21.39; mol. wt., 246; MR_D, 77.05. $C_{13}H_{24}OSi_2$ calcd.: C, 61.90; H, 9.52; Si, 22.22 %; mol. wt., 252; MR_D, 76.79.)

3-(2-phenylethyl)heptamethyltrisiloxane (XI)

By means of the above technique, 4.7 g (72 %) of (XI), b.p. 94–95° (2 mm), were obtained from 2.08 g (0.02 mole) of styrene and 4.44 g (0.02 mole) of 3-*H*-heptamethyltrisiloxane, when the temperature was raised from 100° to 170° over 5 h. (Found: C, 54.84; H, 9.16; Si, 25.44; mol. wt., 338; MR_D, 95.70. $C_{15}H_{30}O_2Si_3$ calcd.: C, 55.21; H, 9.20; Si, 25.77 %; mol. wt., 326; MR_D, 95.43.)

(2-Indanyl)pentamethyldisiloxane (XII)

By means of the above technique, 4.9 g (62 %) of (XII), b.p. 66–67° (1 mm), were obtained from 3.48 g (0.03 mole) of indene and 4.44 g (0.03 mole) of pentamethyldisiloxane, when the temperature was raised from 100° to 150° over 30 h. (Found: C, 62.78; H, 9.00; Si, 20.97; mol. wt., 251; MR_D, 80.25. $C_{14}H_{24}OSi_2$ calcd.: C, 63.64; H, 9.09; Si, 21.21 %; mol. wt., 264; MR_D, 80.10.)

3-(2-Indanyl)heptamethyltrisiloxane (XIII)

By means of the above technique, 3.6 g (53 %) of (XIII), b.p. 84–86° (1 mm), were obtained from 2.32 g (0.02 mole) of indene and 4.44 g (0.02 mole) of 3-*H*-heptamethyltrisiloxane, when the temperature was raised from 100° to 160° over 30 h. (Found: C, 56.09; H, 8.73; Si, 24.38; mol. wt., 349; MR_D, 98.93. $C_{16}H_{30}O_2Si_3$ calcd.: C, 56.80; H, 8.88; Si, 24.85 %; mol. wt., 338; MR_D, 98.74.)

(1-Heptenyl)pentamethyldisiloxane (XIV)

By means of the above technique, 2.4 g (53 %) of (XIV), b.p. 64–66° (3 mm), were obtained from 1.78 g (0.0186 mole) of 1-heptyne and 2.75 g (0.0186 mole) of pentamethyldisiloxane, when the temperature was raised from 90° to 120° over 29 h. (Found: C, 58.64; H, 11.54; Si, 23.09; mol. wt., 236; MR_D, 76.57. $C_{12}H_{28}OSi_2$ calcd.: C, 59.02; H, 11.47; Si, 22.95 %; mol. wt., 244; MR_D, 76.23.)

3-(1-Heptenyl)heptamethyltrisiloxane (XV)

By means of the above technique, 2.1 g (44 %) of (XV), b.p. 56–57° (1 mm), were obtained from 1.44 g (0.015 mole) of 1-heptyne and 3.33 g (0.015 mole) of 3-*H*-heptamethyltrisiloxane when the temperature was raised from 100° to 140° over 54 h. (Found: C, 52.35; H, 10.75; Si, 26.55; mol. wt., 325; MR_D, 95.18. $C_{14}H_{34}O_2Si_3$ calcd.: C, 52.83; H, 10.69; Si, 26.42 %; mol. wt., 318; MR_D, 94.87.)

(2,5-Dimethyl-2,5-dihydroxy-3-hexen-3-yl)pentamethyldisiloxane (XVI)

2,5-Dimethyl-3-hexyne-2,5-diol (7.1 g, 0.05 mole) and 7.4 g (0.05 mole) of pentamethyldisiloxane were dissolved in 100 ml of benzene in the presence of 0.1 g of palladium on charcoal and then boiled for 30 h. After the removal of benzene, 8.2 g (56.5 %) of (XVI), m.p. 64–65° (from petroleum ether), were isolated. (Found: C, 54.44; H, 10.29; Si, 18.79; OH, 11.07; mol. wt., 278. $C_{13}H_{30}O_3Si_2$ calcd.: C, 53.79; H, 10.34; Si, 19.31; OH, 11.71 %; mol. wt., 290.)

[1-(2-Pyridyl)ethyl]pentamethyldisiloxane (XVII)

Using the method employed for the synthesis of (X), 7.2 g (57 %) of (XVII), b.p. 63–65° (2 mm), were obtained from 5.25 g (0.05 mole) of 2-vinylpyridine and 7.4 g (0.05 mole) of pentamethyldisiloxane, when the temperature was raised from 90° to

140° over 15 h. (Found: N, 5.60; Si, 21.92; mol. wt., 248; *MR*$_D$, 76.38. $C_{12}H_{23}NOSi_2$ calcd.: N, 5.53; Si, 22.13 %; mol. wt., 253; *MR*$_D$, 76.19.)

Tricyclo[5.2.1.0^{2,6}]-dec-3-enylpentamethyldisiloxane (XVIII)

Using the above technique, 5.8 g (68.5 %) of (XVIII), b.p. 104–105° (5 mm), were obtained from 4.0 g (0.06 mole) of cyclopentadiene and 8.9 g (0.06 mole) of pentamethyldisiloxane, when the temperature was raised from 30° to 140° over 33 h. (Found: C, 63.68; H, 9.90; Si, 20.06; mol. wt., 286; *MR*$_D$, 82.66. $C_{15}H_{28}OSi_2$ calcd.: C, 64.29; H, 10.00; Si, 20.00 %; mol. wt., 280; *MR*$_D$, 83.67.)

3-(Tricyclo[5.2.1.0^{2,6}]dec-3-enyl)heptamethyltrisiloxane (XIX)

Using the above technique, 3.9 g (48 %) of (XIX), b.p. 112–113° (3 mm), were obtained from 3.0 g (0.045 mole) of cyclopentadiene and 10 g (0.045 mole) of 3-*H*-heptamethyltrisiloxane when the temperature was raised from 30 to 150° over 43 h. (Found: C, 56.58; H, 9.55; Si, 24.27; mol. wt., 368; *MR*$_D$, 101.30. $C_{17}H_{34}O_2Si_3$ calcd.: C, 57.63; H, 9.60; Si, 23.73 %; mol. wt., 354; *MR*$_D$, 102.31.)

[1-Chloromethyl)-3-chloro-1-propenyl]pentamethyldisiloxane (XX)

Using the above technique, 7.2 g (57.5 %) of (XX), b.p. 75–77° (2 mm), were obtained from 5.15 g (0.05 mole) of 1,4-dichloro-2-butyne and 7.4 g (0.05 mole) of pentamethyldisiloxane when the temperature was carefully raised (first violent reaction!) from 20° to 80° over 10 h. (Found: C, 39.29; H, 7.22; Cl, 26.18; Si, 19.87; mol. wt., 256; *MR*$_D$, 71.69. $C_9H_{20}Cl_2OSi_2$ calcd.: C, 39.85; H, 7.38; Cl, 26.20; Si, 20.66 %; mol. wt., 271; *MR*$_D$, 72.02.)

[2-(Methyldichlorosilyl)ethyl]pentamethyldisiloxane (XXI)

Pentamethyldisiloxane (8.88 g, 0.06 mole) was added to 8.46 g (0.06 mole) of methylvinyldichlorosilane containing $H_2PtCl_6 \cdot 6H_2O$ in a three-necked flask, with stirring. The temperature was gradually raised from 45 to 90° over 2.5 h. The mixture was then kept at 160–170° for 2.5 h 12.3 g (71 %) of (XXI), b.p. 62–64° (3 mm), were isolated by distillation. (Found: C, 33.29; H, 7.86; Cl, 24.70; Si, 28.76; mol. wt., 273; *MR*$_D$, 76.30. $C_8H_{22}Cl_2OSi_3$ calcd.: C, 33.22; H, 7.61; Cl, 24.57 Si, 29.07 % mol. wt., 289 *MR*$_D$, 76.33.)

3-[2-(Methyldichlorosilyl)ethyl]heptamethyltrisiloxane (XXII)

Using the above technique, 9.7 g (67 %) of (XXII), b.p. 87–89° (2 mm), were obtained from 5.65 g (0.04 mole) of methylvinyldichlorosilane and 8.90 g (0.04 mole) of 3-*H*-heptamethyltrisiloxane. (Found: Cl, 19.15; Si, 31.25; mol. wt., 350; *MR*$_D$, 95.53. $C_{10}H_{28}Cl_2O_2Si_4$ calcd.: Cl, 19.56; Si, 30.85 %; mol. wt., 363; *MR*$_D$, 94.97.)

SUMMARY

The reactions of organosiloxanes containing the vinyl group in the α- and β-positions, with diazomethane and phenyl azide have been studied. It is concluded that siloxanes containing the vinyl group in the α-position react with diazomethane and phenyl azide but not siloxanes with the vinyl group in the β-position. The 1-pyrazolin-

3-yl derivatives of organosiloxanes formed decompose when heated yielding the corresponding allyl derivatives.

The diene synthesis reaction of 3-vinylheptamethyltrisiloxane with 1,3-butadiene leads to the formation of the corresponding cyclohexenyl derivative.

The co-hydrolysis reaction of methylallyldichlorosilane with dimethyldichlorosilane (molar ratio, 1:1) gives allylheptamethylcyclotetrasiloxane and 1,5-diallylhexamethylcyclotetrasiloxane; the co-hydrolysis reaction of methylvinyldichlorosilane with dimethylchlorosilane produces 1,1,3,5,5-pentamethyl-3-vinyltrisiloxane; the co-hydrolysis reaction of methylallyldichlorosilane with dimethylchlorosilane gives 1,1,3,5,5-pentamethyl-3-allyltrisiloxane. The addition reactions of acrylonitrile, dicyanoethylene, styrene, indene, 1-heptyne, 2,5-dimethyl-3-hexyne-2,5-diol, 2-vinylpyridine, cyclopentadiene; 1,4-dichloro-2-butyne and methylvinyldichlorosilane with pentamethyldisiloxane and 3-*H*-heptamethyltrisiloxane have been studied. It is concluded that the addition reactions of the above-mentioned compounds give satisfactory yields with the exception of acrylonitrile and dicyanoethylene which do not enter into the addition reaction.

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