ADDITIONS OF DICHLOROMETHYLVINYLSILANE AND OF UNSATURATED ORGANIC COMPOUNDS TO PENTAMETHYLDISILOXANE AND TO 3H-HEPTAMETHYLTRISILOXANE

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Of the addition reactions of unsaturated organic compounds with pentamethyldisiloxane the following have been described: the reactions of acetylene and 1-octene [1], of 3,4-epoxy-1-butene [2], of 1-(allyloxy)-2,3-epoxypropane [2, 3] and other unsaturated epoxy compounds [2], of tetramethyl-1,3-divinyldisiloxane [3], and of p-divinylbenzene, butenyne, and other alkenynes [4]; of addition reactions with 3H-heptamethyltrisiloxane those of acetylene and 1-octene have been described [1].

In the present work we studied the addition reactions of unsaturated organic compounds and of dichloromethylvinylsilane with pentamethyldisiloxane and with 3H-heptamethyltrisiloxane. Pentamethyldisiloxane and 3H-heptamethyltrisiloxane were synthesized by the cohydrolysis of chlorodimethylsilane with chlorotrimethylsilane and of dichloromethylsilane with chlorotrimethylsilane, respectively. Analogously, by the cohydrolysis of dichloromethylvinylsilane and of allyldichloromethylsilane with chlorodimethylsilane we synthesized 1,1,3,5,5-pentamethyl-3-vinyltrisiloxane and 3-allyl-1,1,3,5,5-pentamethyltrisiloxane. In a study of the reactions of pentamethyldisiloxane and of 3H-heptamethyltrisiloxane with 1-heptene, cyclohexene, styrene, indene, allyl bromide, acrylonitrile, maleonitrile, 2-vinylpyridine, 1-heptyne, 3-methyl-1-butyne, cyclopentadiene, and dichloromethylvinylsilane it was shown that the addition reactions go in different ways: in some cases addition goes readily, but in others – not at all.

Thus, we were unable to bring about the addition of acrylonitrile and of maleonitrile with the use of amines, their derivatives, and also Speier catalyst and Pd/C as catalysts. This may be due to the steric effects of surrounding groups. 2-Vinylpyridine does not add to pentamethyldisiloxane in absence of catalyst and with $(C_2H_5)_3N$ and $(C_4H_9)_3N$. When H_2PtCl_6 is used as catalyst, the reaction goes satisfactorily.

In the reaction between allyl bromide and pentamethyldisiloxane, as would be expected we obtained bromopentamethyldisiloxane as reaction product. The reaction can be recommended for the preparative synthesis of bromopentamethyldisiloxane.

In the reaction of cyclopentadiene with pentamethyldisiloxane and with 3H-heptamethyltrisiloxane, even at 30° the dimerization of the cyclopentadiene occurred, and the dimer then underwent the addition reaction. It is interesting that the addition reactions go more readily with pentamethyldisiloxane than with 3H-heptamethyltrisiloxane. The properties of the new compounds synthesized are given in Table 1.

The NMR spectra contained the following peaks (all the chemical shifts are relative to the CH_3–Si groups of the compounds themselves) (frequency 22.68 MHz): (X) – peaks characteristic for the protons of CH groups (quadruplet) and for the protons of CH_3 groups (doublet for the CH_3 on CH) with the following average chemical shifts $\delta CH = 2.30$ and $\delta CH_3 = 1.26$ p.p.m.; (V) – two symmetrical groups of peaks with average chemical shifts of $\delta(CH_2–Si) = 0.89$ and $\delta(CH_2C_6H_5) = 2.35$ p.p.m.; (XIX) – one unsplit peak characteristic for protons of CH_2–Si groups with a chemical shift of $\delta CH_2 = 0.68$ p.p.m., but peaks characteristic for protons of the CH and CH_3 (on CH) groups are absent; (XI) – a multiplet group of peaks with average chemical shift of $\delta(=CH–) = 1.47$ p.p.m.

EXPERIMENTAL

Synthesis of 1,1,3,5,5-Pentamethyl-3-vinyltrisiloxane and 3-Allyl-1,1,3,5,5-pentamethyltrisiloxane. A three-necked flask was charged with a mixture of 150 g of ice and 100 ml of ether and was cooled to between –10 and –15°; in the course of 1 h a mixture of 28.2 g of dichloro-

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TABLE 1. Physicochemical Properties of Compounds Synthesized

No.	Organosilane	B.p., °C (p, mm)	n_D^{20}	d_4^{20}	Found		Calculated		Found, %			Molecular formula	Calculated, %			Characteristic frequencies of IR spectrum,* cm^{-1}
					MR	mol. wt.	MR	mol. wt.	Si	C	H		Si	C	H	
I	Heptylpentamethyldisiloxane	39—41 (1)	1.4243	0.8202	76.63	239	76.70	246	22.47	58.21	12.09	$C_{12}H_{30}OSi_2$	22.36	58.54	12.20	1190, 1390, 1478, 2861, 2920
II	3-Heptylheptamethyltrisiloxane	68—69 (2)	1.4115	0.8355	95.24	328	95.34	320	26.07	52.06	11.07	$C_{14}H_{36}O_2Si_3$	26.25	52.50	11.25	1190, 1390, 1478, 2860, 2920
III	Cyclohexylpentamethyldisiloxane	74—75 (5)	1.4308	0.8504	69.99	234	69.94	230	24.25	56.70	11.26	$C_{11}H_{26}OSi_2$	24.35	57.39	11.30	1180, 1200, 1365, 1469, 2853, 2921
IV	3-Cyclohexylheptamethyltrisiloxane	79—81 (3)	1.4243	0.8761	88.64	296	88.58	304	27.95	50.52	10.46	$C_{13}H_{32}O_2Si_3$	27.63	51.31	10.53	1178, 1201, 1360, 1466, 2852, 2920
V	Pentamethylphenethyldisiloxane	80—81 (3)	1.4636	0.9015	77.05	246	76.79	252	21.39	61.95	9.61	$C_{13}H_{24}OSi_2$	22.22	61.90	9.52	1190, 1473, 1506, 1540, 1561, 1610, 2910, 3025, 3066, 3089
VI	Heptamethyl-3-phenethyldisiloxane	94—95 (2)	1.4517	0.9185	95.70	338	95.43	326	25.45	54.84	9.16	$C_{15}H_{30}O_2Si_3$	25.77	55.21	9.20	1190, 1471, 1505, 1540, 1561, 1610, 2910, 3028, 3066, 3088
VII	Indanylpentamethyldisiloxane	66—67 (1)	1.4862	0.9445	80.25	251	80.10	264	20.97	62.78	9.00	$C_{14}H_{24}OSi_2$	21.21	63.64	9.09	950, 1212, 1489, 1606, 1720, 2855, 2905, 3013, 3075
VIII	3-Indanylheptamethyltrisiloxane	84—86 (1)	1.4690	0.9515	98.93	349	98.74	338	24.38	56.09	8.73	$C_{16}H_{30}O_2Si_3$	24.85	56.80	8.88	950, 1212, 1488, 1605, 1723, 2850, 2908, 3012, 3070
IX	Bromopentamethyldisiloxane	136—138	1.4140	1.0773	52.65	210	51.75	227	24.88	—	Br 34.93	$C_5H_{15}BrOSi_2$	24.67	—	Br 35.24	672
X	Pentamethyl[1-(2-pyridyl)ethyl]disiloxane	63—65 (2)	1.4644	0.9145	76.38	248	76.19	253	21.92	—	N 5.60	$C_{12}H_{23}NOSi_2$	22.13	—	N 5.53	1165, 1176, 1213, 1336, 1389, 1445, 1489, 1598, 2900, 3008, 3071
XI	(1-Heptenyl)pentamethyldisiloxane	64—66 (3)	1.4230	0.8116	76.57	236	76.23	244	23.09	58.64	11.54	$C_{12}H_{28}OSi_2$	22.95	59.02	11.47	942, 982, 1010, 1320, 1390, 1478, 1628, 2860, 2928, 3045
XII	3-(1-Heptenyl)heptamethyltrisiloxane	56—57 (1)	1.4075	0.8237	95.18	325	94.87	318	26.55	52.35	10.75	$C_{14}H_{34}O_2Si_3$	26.42	52.83	10.69	942, 1011, 1190, 1330, 1391, 1472, 1625, 2860, 2928, 3051

Table 1 (continued)

No.	Organosilane	B.p., °C (p, mm)	n_D^{20}	d_4^{20}	Found		Calculated		Found, %			Molecular formula	Calculated, %			Characteristic frequencies of IR spectrum,* cm^{-1}
					MR	mol. wt.	MR	mol. wt.	Si	C	H		Si	C	H	
XIII	Pentamethyl(3-methyl-1-butenyl)disiloxane	170—172	1.4150	0.8076	66.99	227	67.08	216	25.14	55.78	11.23	$C_{10}H_{24}OSi_2$	25.91	55.55	11.11	930, 1010, 1170, 1324, 1350, 1387, 1465, 1620, 2920
XIV	2,5-Dimethyl-3-(pentamethyldisiloxanyl)-3-cyclohexene-2,5-diol	M.p. 64—65	—	—	—	278	—	290	18.79	54.44	10.29 OH 11.07	$C_{13}H_{10}O_3Si_2$	19.31	53.79	10.34 OH 11.71	915, 969, 983, 1001, 1149, 1082, 1230, 1601, 3180,
XV	Pentamethyl(2-methyl-3-butenyl)disiloxane	64—66 (10)	1.4218	0.8223	66.74	209	67.08	216	25.15	56.34	11.21	$C_{10}H_{24}OSi_2$	25.91	55.55	11.11	1160, 1318, 1351, 1383, 1452, 1578, 1650, 2908, 3012, 3072
XVI	[3-Chloro-1-(chloromethyl)propenyl]pentamethyldisiloxane	75—77 (2)	1.4585	1.0324	71.69	256	72.02	271	19.87	39.29	7.22 Cl 26.18	$C_9H_{20}Cl_2OSi_2$	20.66	39.85	7.38 Cl 26.20	560, 666, 961, 1190, 1212, 1351, 1455, 1470, 1620, 2908, 3030
XVII	(Δ^2-Hexahydro-4,7-methanoinden-8-yl)pentamethyldisiloxane	104—105 (5)	1.4717	0.9479	82.66	286	83.67	280	20.06	63.68	9.90	$C_{15}H_{28}OSi_2$	20.0	64.29	10.00	915, 960, 1190, 1208, 1338, 1368, 1461, 1614, 3045
XVIII	3-(Δ^2-Hexahydro-4,7-methanoinden-8-yl)heptamethyltrisiloxane	112—113 (3)	1.4544	0.9471	101.30	368	102.31	354	24.27	56.58	9.55	$C_{17}H_{34}O_2Si_3$	23.73	57.63	9.60	915, 960, 1190, 1208, 1335, 1370, 1461, 1615, 3048
XIX	[2-(Dichloromethylsilyl)ethyl]pentamethyldisiloxane	62—64 (3)	1.4338	0.9881	76.30	273	76.33	289	28.76	33.29	7.86 Cl 24.70	$C_8H_{22}Cl_2OSi_3$	29.07	33.22	7.61 Cl 24.57	1149, 2860, 2912
XX	3-[2-(Dichloromethylsilyl)ethyl]heptamethyltrisiloxane	87,89 (2)	1.4255	0.9745	95.53	350	94.97	363	31.25	—	Cl 19.15	$C_{10}H_{28}Cl_2O_2Si_4$	30.85	—	Cl 19.56	1155, 2854, 2926
XXI	1,1,3,5-Pentamethyl-3-vinyltrisiloxane	41—42 (15)	1.3959	0.8423	62.75	209	62.98	220	38.22	38.44	9.42	$C_7H_{20}O_2Si_3$	38.18	38.18	9.09	930, 981, 1605, 2129, 3018, 3060
XXII	3-Allyl-1,1,3,5,5-pentamethyltrisiloxane	48—49 (15)	1.4056	0.8516	67.43	218	67.79	234	36.03	41.51	9.42	$C_8H_{22}O_2Si_3$	35.90	41.03	9.40	929, 1185, 1440, 1640, 2145, 2855, 2921, 3039, 3068, 3088

*All the compounds have the following frequencies, which are not given in the table, in common (cm^{-1}): 760-780, 800-820, 850-870, 1250-1280, and 1410-1425 arise from the presence of Si–CH_3 bonds; 1080-1090 arise from the stretching vibrations of the Si–O bond; 2860-2980 and 2950-2970 are characteristic for the stretching vibrations of C–H bonds in CH_3 groups.

TABLE 2. Conditions and Results of Experiments on the Addition of Unsaturated Organic Compounds and $CH_3(CH_2{=}CH)SiCl_2$ to Pentamethyldisiloxane and 3H-Heptamethyltrisiloxane

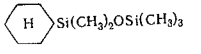
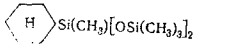
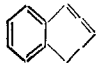
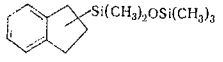
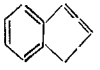
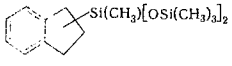
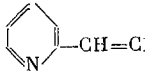
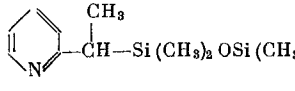
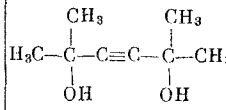
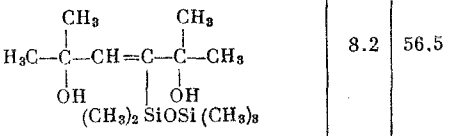
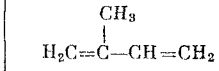
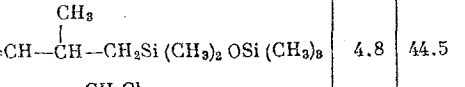
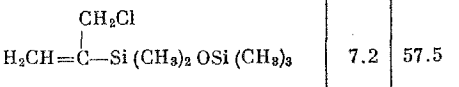
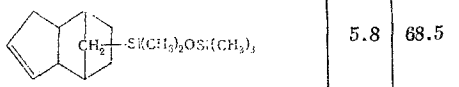
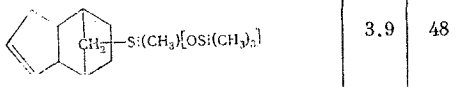
No.	Unsaturated component		Methylsiloxane		Reaction temp., °C	Time, h	Product	Yield	
	formula	amt., g	formula	amt., g				g	%
I	$CH_3(CH_2)_4CH{=}CH_2$	2.94	$(CH_3)_3SiOSi(CH_3)_2H$	4.44	80—140	30	$C_7H_{15}(CH_3)_2SiOSi(CH_3)_3$	4.2	57
II	$CH_3(CH_2)_4CH{=}CH_2$	1.96	$[(CH_3)_3SiO]_2Si(CH_3)H$	4.44	80—150	30	$C_7H_{15}(CH_3)Si[OSi(CH_3)_3]_2$	3.1	48.5
III		2.05	$(CH_3)_3SiOSi(CH_3)_2H$	3.7	90—150	40		3.1	54
IV		2.5	$[(CH_3)_3SiO]_2Si(CH_3)H$	6.7	90—150	18		4.05	44
V	$C_6H_5CH{=}CH_2$	7.28	$(CH_3)_3SiOSi(CH_3)_2H$	10.36	80—150	4	$C_6H_5(CH_2)_2Si(CH_3)_2OSi(CH_3)_3$	14.2	80.5
VI	$C_6H_5CH{=}CH_2$	2.08	$[(CH_3)_3SiO]_2Si(CH_3)H$	4.44	100—170	5	$C_6H_5(CH_2)_2Si(CH_3)[OSi(CH_3)_3]_2$	4.7	72
VII		3.48	$(CH_3)_3SiOSi(CH_3)_2H$	4.44	100—150	30		4.9	62
VIII		2.32	$[(CH_3)_3SiO]_2Si(CH_3)H$	4.44	100—160	30		3.6	53
IX	$CH_2{=}CH{-}CH_2Br$	3.63	$(CH_3)_3SiOSi(CH_3)_2H$	3.7	90—170	35	$Br(CH_3)_2SiOSi(CH_3)_3$	2.65	47
X		5.25	$(CH_3)_3SiOSi(CH_3)_2H$	7.4	90—140	15		7.2	57
XI	$CH_3(CH_2)_4C{\equiv}CH$	1.78	$(CH_3)_3SiOSi(CH_3)_2H$	2.75	90—120	29	$CH_3(CH_2)_4CH{=}CHSi(CH_3)_2OSi(CH_3)_3$	2.4	53
XII	$CH_3(CH_2)_4C{\equiv}CH$	1.44	$[(CH_3)_3SiO]_2Si(CH_3)H$	3.33	100—140	54	$CH_3(CH_2)_4CH{=}CHSi(CH_3)[OSi(CH_3)_3]_2$	2.1	44
XIII	$HC{\equiv}C{-}\underset{\displaystyle CH_3}{\underset{\vert}{C}}H{-}CH_3$	3.4	$(CH_3)_3SiOSi(CH_3)_2H$	7.4	20—160 160—170	8 17	$H_3C{-}\underset{\displaystyle CH_3}{\underset{\vert}{C}}H{-}CH{=}CHSi(CH_3)_2OSi(CH_3)_3$	4	37

Table 2 (continued)

No.	Unsaturated component		Methylsiloxane		Reaction temp., °C	Time, h	Product	Yield	
	formula	amt., g	formula	amt., g				g	%
XIV		7.1	$(CH_3)_3SiOSi(CH_3)_2H$	7.4	90—100	30		8.2	56.5
XV		3.4	$(CH_3)_3SiOSi(CH_3)_2H$	7.4	20—160 160—170	8 17		4.8	44.5
XVI	$ClCH_2C{\equiv}CCH_2Cl$	5.15	$(CH_3)_3SiOSi(CH_3)_2H$	7.4	20—80	10		7.2	57.5
XVII		4.0	$(CH_3)_3SiOSi(CH_3)_2H$	8.9	30—140	33		5.8	68.5
XVIII		3.0	$[(CH_3)_3SiO]_2Si(CH_3)H$	10.0	30—150	43		3.9	48
XIX	$CH_2{=}CH(CH_3)SiCl_2$	8.46	$(CH_3)_3SiOSi(CH_3)_2H$	8.88	45—90 160—170	2.5 2.5	$Cl_2Si(CH_3)(CH_2)_2Si(CH_3)_2OSi(CH_3)_3$	12.3	71
XX	$CH_2{=}CH(CH_3)SiCl_2$	5.65	$[(CH_3)_3SiO]_2Si(CH_3)H$	8.90	45—90 160—170	2.5 2.5	$Cl_2Si(CH_3)(CH_2)_2Si(CH_3)[OSi(CH_3)_3]_2$	9.7	67

methylvinylsilane and 37.8 g of chlorodimethylsilane added. When reaction was complete, the ether layer was separated, washed with water until neutral, and dried with $CaCl_2$. The product was isolated by fractionation. We obtained 31.4 g (71.4%) of 1,1,3,5,5-pentamethyl-3-vinyltrisiloxane.

Analogously, from 25 g of chlorodimethylsilane and 18.3 g of allyldichloromethylsilane we obtained 20.4 g (67%) of 3-allyl-1,1,3,5,5-pentamethyltrisiloxane.

General Procedure in the Addition Reactions. All the unsaturated organic compounds were distilled immediately before the reactions. The necessary amounts of reactants were weighed into a one-necked flask, and 3-6 drops of catalyst – a 0.1 N solution of H_2PtCl_6 in isopropyl alcohol – were added. The mixture was refluxed in a flask heated with an oil bath. The products were isolated by fractionation.

The addition of acrylonitrile, 3-methyl-1-butyne, and isoprene to pentamethyldisiloxane was conducted in sealed glass tubes. The addition of 2,5-dimethyl-3-hexyne-2,5-diol to pentamethyldisiloxane was conducted in benzene in presence of a Pd/C catalyst. At the end of the reaction solvent was driven off, and the product was vacuum-distilled off and then recrystallized (from petroleum ether).

The reactions of dichloromethylvinylsilane with pentamethyldisiloxane and 3H-heptamethyltrisiloxane were conducted by a procedure similar to that described earlier [5].

Experimental data on the procedure in the addition reactions are presented in Table 2.

CONCLUSIONS

1. A study was made of the addition reactions of various unsaturated organic compounds and dichloromethylvinylsilane with pentamethyldisiloxane and 3H-heptamethyltrisiloxane.

2. The cohydrolysis reactions of dichloromethylvinylsilane with chlorodimethylsilane and of allyldichloromethylsilane with chlorodimethylsilane and of allyldichloromethylsilane with chlorodimethylsilane were studied.

LITERATURE CITED

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