[CONTRIBUTION FROM MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

Chloromethylmethylpolysiloxanes

BY JOHN L. SPEIER

The availability of chlorochloromethylmethylsilanes[1] has prompted the preparation of the linear polymers derived from these and their linear copolymers containing dimethyl or trimethylsiloxy units. The compounds prepared may be regarded as the chlorinated derivatives of the open chain dimethylsiloxanes with trimethylsiloxy end-groups described by Hunter[2] and others.[3,4,5] Data concerning these compounds are to be found in Table I.

TABLE I

CHLOROMETHYLMETHYLSILOXANE POLYMERS

x =	B. p. °C.	B. p. Mm.	$n^{25}D$	d^{25}_4	Mol. ref. Found	Mol. ref. Theory[6]	Cs. viscosity 0°C.	Cs. viscosity 99.4°C.	F. p., °C.	Chlorine, % Found	Chlorine, % Calcd.	
						Series I—$ClCH_2SiMe_2O(Me_2SiO)_xSiMe_2CH_2Cl$						
0[1]	110	40	1.4363	1.034	58.5	58.50	3.54	0.76	−90			
1	142	40	1.4283	1.020	77.1	77.24	4.55	1.00	−79	23.16	23.23	
2	168	40	1.4231	1.008	95.9	95.88	5.61	1.20	−94	18.74	18.69	
3	190	40	1.4200	1.002	114.8	114.52	6.80	1.41	−85	15.86	15.64	
4	223	40	1.4173	0.996	133.2	133.30	...	..	−77	13.41	13.44	
						Series II—$Me_3SiO(MeSiCH_2ClO)_xSiMe_3$						
0[2]	62	225	1.3748	0.757	48.9	48.92	0.87					
1	102	40	1.4058	0.918	72.5	72.48	2.46	0.70	−85	13.15	13.09	
2	162	40	1.4212	1.006	95.5	95.88	6.02	1.18	−77	18.72	18.70	
3	210	40	1.4311	1.063	118.9	119.36	9.83	1.67	−85	21.60	21.80	
4	251	40	1.4375	1.100	142.2	142.8	21.17	2.68	−77	23.24	23.78	
						Series III—$ClCH_2Me_2SiO(MeSiCH_2ClO)_xSiMe_2CH_2Cl$						
							55.8°		Si, % Found	Si, % Calcd.	Mol. wt. Found	Mol. wt. Calcd.
1	176	40	1.4465	1.112	81.8	82.07	2.75	1.44	24.8	24.75	341	340
2	167	5	1.4520	1.157	104.4	105.57	4.97	2.45	25.2	25.03	440	448
3	210	5	1.4553	1.182	128.2	129.01	8.00	3.61	25.2	25.18	560	557

Experimental Part and Discussion

The polymers of series I were prepared by refluxing for two hours in aqueous alcoholic solution, chlorochloromethyldimethylsilane (178 g., 1.24 moles) and hexamethylcyclotrisiloxane (46 g., 0.62 mole). The products of the reaction were washed with water, dried over calcium chloride and distilled.

The polymers of series II were prepared by refluxing for three and one-half hours an aqueous alcoholic solution of hexamethyldisiloxane (162 g., 1 mole), and dichlorochloromethylmethylsilane (163.5 g., 1 mole) followed by washing with water, drying over calcium chloride and distilling.

The polymers of series III were prepared by copolymerizing chlorochloromethyldimethylsilane (2 moles) and dichlorochloromethylmethylsilane (1 mole). The mixture of chlorosilanes was added to aqueous alcohol and shaken. The products were then given the same treatment afforded series I and II.

Despite the fact that three different methods were used to form the three series of polymers the molar distribution of products was the same in each case as nearly as can be determined by distillation analysis.

Also of interest is the fact that only in the case of series I was the slightest trace of cyclic polymers detected in the mixtures. This is surprising in view of the findings of Scott[7] and Wilcock[8] who found that cyclic compounds form when methylpolysiloxane systems were "equilibrated." Perhaps this difference is due to the differences in methods of "equilibrating" or it may be due to an influence of the chloromethyl group which hinders the formation of cyclic polymers. In series I, an indication of the presence of about 2 ml. of hexamethylcyclotrisiloxane, b. p. about 133°, was detected.

A curious fact is that each of the members of series I possesses very nearly the same specific refraction and energy of activation for viscous flow.

The chlorine contents of the compounds of series I and II were determined by heating the chloride with a known excess of potassium hy-

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(1) Krieble and Elliott, THIS JOURNAL, **67**, 1810 (1945).

(2) Hunter, Warrick, Hyde and Curry, *ibid.*, **68**, 2284 (1946).

(3) Patnode and Wilcock, *ibid.*, **68**, 358 (1946).

(4) Hurd, *ibid.*, **68**, 364 (1946).

(5) Wilcock, *ibid.*, **68**, 691 (1946).

(6) Warrick, *ibid.*, **68**, 2455 (1946).

(7) Scott, *ibid.*, **68**, 2294 (1946).

(8) Wilcock, paper presented at 110th meeting of the American Chemical Society, Chicago, Ill., Sept., 1946.

droxide in diethylene glycol in a closed bottle at about 150–175°, followed by titrations of the excess alkali with standard acid. Series III formed gels when treated in this way. Titration of the excess alkali in the gel was difficult and led to variable results. Therefore, the molecular weights of the members of series III were determined ebulliometrically. The values given are those obtained by extrapolation to zero concentration.

The viscosities were obtained in a carefully calibrated Fenske pipet.

Summary

Three series of open chain chloromethylmethylpolysiloxanes were prepared and characterized. The boiling points, index of refraction, density, viscosity and freezing point of the polymers were determined.

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Some Aminodibenzothiophenes

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In connection with studies concerned with antimalarial and antituberculous compounds, some substituted dibenzothiophenes[1] were prepared.

2-Acetyldibenzothiophene[2] is an important starting material for the preparation of 2-amino- and 2-acetaminodibenzothiophenes. 2-Aminodibenzothiophene can be prepared in excellent yields by a Beckmann rearrangement of the oxime of 2-acetyldibenzothiophene followed by hydrolysis of the resulting acetamino compound. This amine can also be prepared by the nitration and reduction of the parent heterocycle, but the over-all yields are lower, although catalytic reduction of the 2-nitro compound gives high yields of the amine.

2,8-Diacetyldibenzothiophene[3] was prepared and was found to be a suitable intermediate in the preparation of 2,8-diaminodibenzothiophene. Formation of the dioxime of the diacetyl compound, treatment of the dioxime with phosphorus pentachloride, and hydrolysis of the resulting diacetamino compound (m. p. 304–305°) gave a good yield of the 2,8-diamino compound (m. p. 199.5–200°). These same melting points were recently reported.[4] The older literature reported the melting point of the diamino compound to be 178°[5] and 194°,[3] and the melting point of the diacetamino derivative as 237°[5] and 254°.[3]

In order to confirm the structure of the 2,8-diaminodibenzothiophene, an authentic specimen was prepared by nitration of 2-nitrodibenzothiophene followed by catalytic reduction of the resulting 2,8-dinitrodibenzothiophene. Acetylation of this diamino compound gave 2,8-diacetaminodibenzothiophene. The melting points of the latter two compounds were in agreement with the melting points of the compounds obtained from 2,8-diacetyldibenzothiophene, and mixed melting points were not depressed.

The oxidation of 2,8-diacetaminodibenzothiophene to the 5-dioxide was accomplished with either hydrogen peroxide or hypochlorous acid where it had been previously reported[4] that hydrogen peroxide oxidation was not possible.

The authors are grateful to Parke, Davis and Company for arranging for pharmacological tests, the results of which will be reported elsewhere.

Experimental

2-Nitrodibenzothiophene.—Since the previous directions[6] could not be duplicated to give the reported 40% yield, the following procedure was developed. To 10 g. (0.054 mole) of dibenzothiophene dissolved in 80 cc. of glacial acetic acid at 30° was added 10 cc. of fuming nitric acid (d., 1.51) over a period of thirty minutes. When the addition was complete the reaction mixture was stirred at room temperature for one hour and filtered. The yellow solid was refluxed for several hours with 100 cc. of 95% ethanol and the insoluble 2-nitrodibenzothiophene removed by filtration. The yield of product was 3.5 g. (28%) melting at 186–187°.

2,8-Dinitrodibenzothiophene.—The following procedure was worked out from the brief directions reported previously.[5] To 18 cc. of fuming nitric acid (d., 1.51) in 25 cc. of glacial acetic acid was added 7.2 g. (0.031 mole) of 2-nitrodibenzothiophene in small portions. When the addition was complete an additional 10 cc. of fuming nitric acid was added dropwise. The reaction mixture was stirred for one hour and poured into water; the resulting yellow product was recrystallized from glacial acetic acid to give 4 g. (47%) of product melting at 320–330°. Recrystallization from dioxane gave 3.2 g. (38%) of the dinitro compound melting at 339–340° (previously reported, 324–325°[5]).

One attempt to prepare this compound by direct nitration of dibenzothiophene gave only 12% of the 2-nitrodibenzothiophene.

2-Aminodibenzothiophene-5-dioxide.—2-Nitrodibenzothiophene-5-dioxide was prepared in 88% yield by refluxing the 2-nitro compound with an excess of hydrogen peroxide.[6] The crude product was recrystallized from dioxane and from acetone to give pure material melting at 255–256°. A mixture of 9 g. (0.034 mole) of this nitro compound, 23 g. of granular tin metal, 115 cc. of hydrochloric acid, and 100 cc. of ethanol was refluxed for one hour, cooled, and the amine hydrochloride removed by filtration. An 87% yield of the amine (m. p. 274–276°) was obtained by treatment of the salt with ammonium

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(1) Gilman and Avakian, THIS JOURNAL, **68**, 1514 (1946); Gilman and Nobis, *ibid.*, **67**, 1479 (1945).

(2) (a) Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1938); (b) Burger and Bryant, *ibid.*, **4**, 119 (1939).

(3) Burger, Wartman and Lutz, THIS JOURNAL, **60**, 2628 (1938).

(4) Neumoyer and Amstutz, *ibid.*, **69**, 1920 (1947).

(5) Courtot and Pomonis, *Compt. rend.*, **182**, 893 (1926).

(6) Cullinane, Davies and Davies, *J. Chem. Soc.*, 1435 (1936).