

is formed from iodine vapor and solid "V" amylose.

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for several valuable discussions and thank Mr. F. H. Schneider for assisting in the completion of some of the hydration experiments.

[CONTRIBUTION FROM MONSANTO CHEMICAL CO., RESEARCH DEPT., INORGANIC CHEMICALS DIV., ST. LOUIS, MO.]

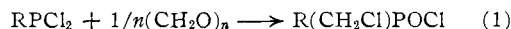
Synthesis and Properties of Phosphinic and Phosphonic Acid Anhydrides*

BY KURT MOEDRITZER

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A new method for the preparation of phosphinic acid anhydrides, $R_1R_2P(O)OP(O)R_2R_1$, in good yields is described. It involves the action of paraformaldehyde on phosphinic chlorides. Several new symmetrical ($R_1 = R_2$) and unsymmetrical ($R_1 \neq R_2$) phosphinic acid anhydrides were prepared and their physical constants and characteristic infrared frequencies are reported. Regularities in their P^{31} (nuclear magnetic resonance) n.m.r. chemical shifts are discussed. The P-O-P bond in the phosphinic acid anhydrides is cleaved by PCl_3 and by protolytic agents, such as HOH, HOR, HNR_2 . It is shown that this new method can be used to prepare phosphonic acid anhydrides and anhydrides of other acids.

In connection with some other work in this Laboratory, Kabachnik's¹ reaction to prepare alkyl-chloromethylphosphinic chlorides from paraformaldehyde and alkyl-dichlorophosphine has been repeated.



The above authors suggested that paraformaldehydes or aldehydes in general react with alkyl-dichlorophosphines by the way of formation of an α -chlorinated ester of triply connected phosphorus, which then undergoes intermolecular Arbuzov rearrangement to give the alkyl-chloromethylphosphinic chloride in yields varying from 36 to 50%.

In our Laboratory, Dr. L. C. D. Groenweghe independently observed that in the reaction of methyl-dichlorophosphine with paraformaldehyde a P^{31} n.m.r. peak was obtained which could not be accounted for by reaction 1. In repeating this reaction with several alkyl and aryl-dichlorophosphines the crude reaction products always exhibited three resonance peaks, indicating the presence of three different species of phosphorus compounds. One of the peaks could be assigned to unreacted alkyl-dichlorophosphine. The chemical shift of the second signal checked with that of a pure sample of alkyl-chloromethylphosphinic chloride, isolated from the reaction product by fractional distillation. The third peak represented a phosphorus compound, the chemical shift of which has not been reported in previous compilations of shift constants.² The latter resonance peak was observed again as the only signal given by a sample of residue of the alkyl-chloromethylphosphinic chloride distillation. This suggested that the residue consisted of a uni-form phosphorus compound. High vacuum distillation of this dark, viscous residue yielded almost quantitatively a colorless liquid which was identified as alkyl-chloromethylphosphinic acid anhydride.

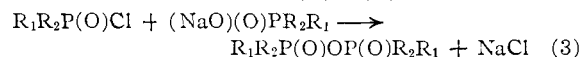
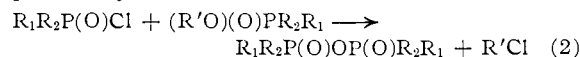
* Presented at the 140th Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961.

(1) M. I. Kabachnik and E. S. Shepeleva, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 862 (1953); *C. A.*, **49**, 843 (1955).

(2) H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953); H. S. Gutowsky and D. W. McCall, *ibid.*, **22**, 162 (1954); N. Muller, P. C. Lauterbur and J. Goldenson, *J. Am. Chem. Soc.*, **78**, 3557 (1956); J. R. Van Wazer, C. F. Callis, J. N. Shoolery and R. C. Jones, *ibid.*, **78**, 5715 (1956); H. Finegold, *Ann. New York Acad. Sci.*, **70**, 875 (1958).

This paper reports the utilization of the reaction to prepare phosphinic acid anhydrides in general. Such a method is of significance, since phosphinic acid anhydrides cannot be prepared by simple dehydration of the corresponding phosphinic acid.³ It will be shown that this new method can be applied also to the preparation of anhydrides of other acids.

Phosphinic Acid Anhydrides.—Evidently, the phosphinic anhydride formation described above has occurred *via* the primarily formed phosphonic chloride (reaction 1), which in a second step reacted with paraformaldehyde to give the phosphinic anhydride. This assumption was confirmed when a slurry of paraformaldehyde in a phosphinic chloride in the mole ratio 1:1 was heated to 100–150°. A clear solution was obtained, which on distillation gave the corresponding phosphinic anhydride in good yield. The latter was found to be identical with an authentic sample prepared by one of the previously known methods.^{4,5}



As compared to reactions 2 and 3, the new method described here offers the advantage of requiring phosphinic chloride only as starting material. Also, alkyl or aryl-chloromethylphosphinic anhydrides, $R_1 = \text{alkyl or aryl}$, $R_2 = \text{CH}_2\text{Cl}$, can be prepared directly from an alkyl or aryl-dichlorophosphine by reaction with an excess of paraformaldehyde.

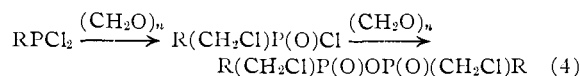


Table I lists the phosphinic acid anhydrides prepared by this new method and some of their physical data.

Mechanism of the Reaction.—Phosphorus halides are known to react with paraformaldehyde to give dihalomethyl ether, and if the reaction is pushed to its extreme limit, methylene halides are

(3) J. N. Collie, *J. Chem. Soc.*, **127**, 964 (1925).

(4) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **73**, 4101, 5466 (1953).

(5) N. Kreutzkamp and H. Schindler, *Arch. Pharm.*, **293**, 296 (1960).

TABLE I
 PHYSICAL CONSTANTS, YIELDS AND ANALYSES OF PHOSPHINIC ACID ANHYDRIDES, $R_1R_2P(O)OP(O)R_2R_1$

R_1	R_2	B.p., °C., mm.		M.p., °C.	Yield, %	Carbon		Hydrogen		Phosphorus		Chlorine	
		Found	Calcd.			Found	Calcd.	Found	Calcd.	Found	Calcd.		
CH_2Cl	CH_2Cl	205–2102		74	85.7	15.73	15.60	2.85	2.62	20.30	20.12	45.17	46.06
CH_3	CH_2Cl	180	1	63	83.5	18.93	20.12	4.51	4.22	24.90	25.92	30.04	29.67
CH_3	CH_3	135	0.2	120 ^a	93.5	27.82	28.24	7.45	7.11	37.88	36.42
C_6H_5	CH_3	200	2	94	90.4	57.12	57.13	5.72	5.48	20.94	21.05
C_6H_5	CH_2Cl	210	1	..	80.5	45.30	46.30	4.14	3.89	16.21	17.06	18.17	19.53
C_6H_5	C_6H_5	230	0.2	143 ^b	84.5	68.46	68.90	5.52	4.82	15.39	14.81

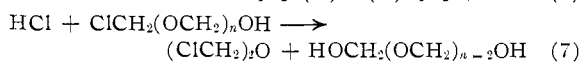
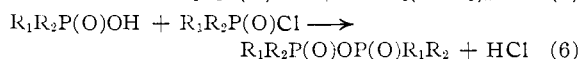
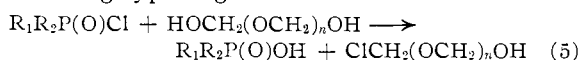
^a Lit. 119–121°. ^b Lit. 142–143°.

 TABLE II
 PHYSICAL DATA AND ANALYSES OF PHOSPHINIC CHLORIDES, $R_1R_2P(O)Cl$, AND PHOSPHINIC ACIDS, $R_1R_2P(O)(OH)$, OBTAINED FROM PHOSPHINIC ANHYDRIDES

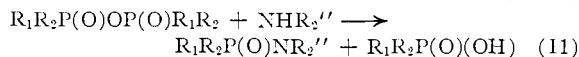
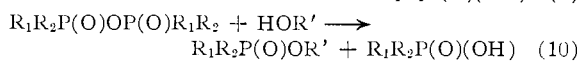
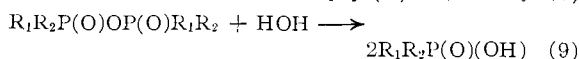
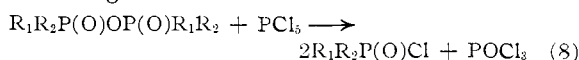
R_1	R_2	B.p., °C.		Yield, %	Chlorine ^a		M.p., °C.	$R_1R_2P(O)(OH)$	
		Found	Calcd.		Found	Eq. wt. ^b Calcd.			
CH_2Cl	CH_2Cl	98–1011		84.5	19.43	19.55	78	165	163
CH_3	CH_2Cl	70	0.8	77.0	24.25	24.13	..	130	128
CH_3	CH_3	82	10	87.3	31.40	31.52	91	92	94
C_6H_5	CH_3	152	10	90.3	20.11	20.31	133	159	156
C_6H_5	CH_2Cl	125	0.5	82.0	16.75	16.96	96	190	191
C_6H_5	C_6H_5	145	0.1	88.6	14.88	14.98	194	222	218

^a Hydrolyzable chlorine only. ^b Equivalent weight from acid-base titration.

obtained.⁶ Although no quantitative study of the other reaction products of the phosphinic anhydride formation has been made, the presence of the strong lachrymator dichloromethyl ether in the reaction products became apparent when the liquid air trap of the distillation apparatus was brought to room temperature. Other products collected in the trap were nonstoichiometrical amounts of hydrochloric acid and paraformaldehyde. In view of these observations, it is very likely that reactions of the following type might have occurred.



Reactions of Phosphinic Acid Anhydride.—The chemical reactivity of phosphinic acid anhydrides is determined by their P–O–P bond which may be cleaved easily by PCl_5 and protolytic agents, according to one of the reactions



Reaction 8 reconverts a phosphinic acid anhydride to the corresponding phosphinic chloride. This reaction has been found useful to increase the yield of the Kabachnik reaction (equation 1) to prepare alkyl or aryl-chloromethylphosphinic chlorides by simply treating the residue of the phosphinic chloride distillation with PCl_5 , thus obtaining an additional quantity of phosphinic chloride. Hydrolysis

of the described phosphinic acid anhydrides with base gave the phosphinic acids in Table II. It was found that the unsymmetrical, Cl-containing phosphinic acid anhydrides, $R_1 = CH_2Cl$, $R_2 = CH_3$ (I) and $R_1' = CH_2Cl$, $R_2' = C_6H_5$ (II), were difficult to hydrolyze. Several days of refluxing with concd. hydrochloric acid did not hydrolyze compounds I and II, whereas the other phosphinic anhydrides were cleaved by this treatment. Aqueous base hydrolyzed compounds I and II only partially under conditions where the other anhydrides were hydrolyzed completely. This remarkable stability apparently is due to steric hindrance. The reactions of the phosphinic acid anhydrides with alcohols and amines (equations 10 and 11) result in the protolytic cleavage of the P–O–P bond, forming phosphinic acid and phosphinic esters or amides, respectively.

Infrared and P^{31} n.m.r. Spectra of Phosphinic Acid Anhydrides.—Bands at 970–940 cm^{-1} in pyrophosphates have been assigned to the antisymmetrical stretching of the P–O–P linkage.⁷ In the phosphinic acid anhydrides, these bands have been found in the range 988–960 cm^{-1} which is slightly shifted to shorter wave lengths. An additional band near 715 cm^{-1} has been considered to be associated with the P–O–P link.⁸ The frequencies assigned to the P–O–P linkage as well as the P=O stretching frequency in phosphinic acid anhydrides have been compiled in Table III.

The P^{31} n.m.r. chemical shifts of the prepared phosphinic acid anhydrides as well as those of the corresponding phosphinic chlorides and acids are listed in Table IV. Certain general regularities may be observed.

(1) The P^{31} chemical shifts of the phosphinic acid anhydrides investigated range from –52.6 to –32.3 p.p.m. Electronegative groups such as CH_2Cl or C_6H_5 tend to increase the chemical shift. This be-

(7) E. D. Bergmann, U. Z. Littauer and S. Pinchas, *J. Chem. Soc.*, 847 (1952).

(8) B. Holmstedt and L. Larsson, *Acta Chem. Scand.*, **5**, 1179 (1951).

(6) J. F. Walker, "Formaldehyde," 2nd Ed., Reinhold Publishing Corporation, New York, N. Y., 1953.

TABLE III

 INFRARED ABSORPTION FREQUENCIES IN CM.⁻¹ OF THE P=O AND P-O-P LINKAGE IN PHOSPHINIC ACID ANHYDRIDES, R₁R₂P(O)OP(O)R₂R₁

R ₁	R ₂	P=O	P-O-P	
CH ₂ Cl	CH ₂ Cl	1239	971	685
CH ₃	CH ₂ Cl	1233	980	694
CH ₃	CH ₃	1272	988	706
C ₆ H ₅	CH ₃	1260	975	711
C ₆ H ₅	CH ₂ Cl	1233	975	691
C ₆ H ₅	C ₆ H ₅	1236	962	694

TABLE IV

 P³¹ CHEMICAL SHIFTS OF PHOSPHINIC AND PHOSPHONIC ACID ANHYDRIDES AND CORRESPONDING CHLORIDES AND ACIDS, IN P.P.M., RELATIVE TO 85% H₃PO₄

Phosphinic Compounds				
R ₁	R ₂	R ₁ R ₂ P(O)OP(O)R ₂ R ₁	R ₁ R ₂ P(O)Cl	R ₁ R ₂ P(O)OH
CH ₂ Cl	CH ₂ Cl	-39.0	-50.6	-32.0
CH ₃	CH ₂ Cl	-45.9	-57.0	-50.7
CH ₃	CH ₃	-52.6	-64.3	-48.6
C ₆ H ₅	CH ₃	-43.7	-51.2	-40.1
C ₆ H ₅	CH ₂ Cl	-32.3	-44.6	-36.3
C ₆ H ₅	C ₆ H ₅	-33.1	-42.7	-25.5

Phosphonic Compounds			
R	(RPO ₂) _n	RPOCl ₂	RPO(OH) ₂
CH ₂ Cl	-2.2 ^a	-38.0	-17.8
CH ₃	-13.8 ^b	-43.5	-29.8
C ₆ H ₅	0.0 ^c	-34.0	-18.5

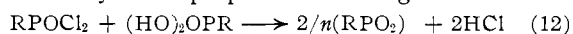
^a Minor peaks at -12.7 and -22.2 p.p.m. ^b Minor peaks at -18.3 and -42.3 p.p.m. ^c Minor peaks at -10.9, -19.6, -30.8 p.p.m.

comes apparent on successive substitution of the methyl groups in dimethylphosphinic anhydride by CH₂Cl groups. An increase of the chemical shift by 6.8 ± 0.1 p.p.m. per two symmetrically introduced CH₂Cl groups is observed. A similar constant increase of the chemical shift has been observed when methyl groups in dimethylphosphinic anhydride are substituted by phenyl groups. The chemical shift becomes more positive by 9.8 ± 0.9 p.p.m. per two symmetrically introduced phenyl groups.

(2) The chemical shifts of phosphinic acid anhydrides differ from their corresponding phosphinic chlorides by *ca.* -10.6 p.p.m.

(3) Because of the constant difference in chemical shift between corresponding phosphinic anhydrides and chlorides, a similar relationship as discussed in (1) above for the phosphinic anhydrides must exist for the phosphinic chlorides. Replacement of a methyl group in dimethylphosphinic chloride by chloromethyl groups increases the chemical shift by 6.9 ± 0.5 p.p.m. per replaced chloromethyl group. Substitution of the methyl groups by phenyl groups increases the chemical shift by 10.8 ± 2.8 p.p.m. per replaced phenyl group.

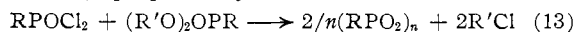
Phosphonic Acid Anhydrides.—Some phosphonic acid anhydrides prepared according to



have been reported earlier.⁹ The reaction of paraformaldehyde with alkyl and aryl phosphonic dichlorides produced dark, highly viscous liquids or glassy solids, the P³¹ n.m.r. spectrum of which

(9) A. Michaelis and F. Rothe, *Ber.*, **25**, 1747 (1892).

showed one strong and several weaker signals. The major peak agrees in its chemical shift with authentic samples of phosphonic acid anhydrides (RPO₂)_n prepared by the method



Apparently, the minor peaks result from "end" groups of the type Cl-PR(O)-O- or HO-PR(O)-O-. Compared with reaction 13, which according to its n.m.r. spectrum forms a uniform product of either ring or chain structure with *n* > 20 (one single peak, concentration of "end" groups < 5%), the paraformaldehyde reaction apparently forms polymers of shorter chain lengths indicated by the appearance of peaks for "end" groups. The yields of this reaction are not as good as in the case of the phosphinic acid anhydrides, and the substances obtained are not very similar in appearance to those obtained by equation 13.

Also, these anhydrides, regardless of their preparation, may be subjected to similar cleavage reactions with PCl₅ and H₂O to give phosphonic dichlorides and phosphonic acids, respectively. Table IV also lists the P³¹ n.m.r. chemical shifts of the phosphonic acid anhydrides prepared by the paraformaldehyde and ester/chloride method and of the corresponding phosphonic dichlorides and acids.

The Preparation of Other Anhydrides.—In order to demonstrate the general applicability of this new method to form anhydridic compounds, the reactions of acid chlorides other than those of phosphorus were tried with paraformaldehyde. Acetyl chloride in a sealed tube reaction gave with paraformaldehyde acetic acid anhydride in 42% yield, trimethylchlorosilane gave hexamethyldisiloxane in 78% yield.

Experimental

Reagents.—Commercial paraformaldehyde, HO(CH₂O)_nH, has been used throughout this investigation. From melting point measurements, *n* is estimated to be in the range 6-100.⁶ Phosphinic chlorides not individually described have been prepared according to standard procedures in the literature.

Measurements.—The infrared spectra were recorded with a Beckmann IR-4 Double Beam spectrometer. The measurements of the P³¹ n.m.r. chemical shifts were made with a Varian Model V-4300B n.m.r. high resolution spectrometer, utilizing a Varian Magnet, Model V-4012-HR, and were reproducible to ± 0.5 p.p.m. The P³¹ spectra were obtained with a 16.2 mc. radio frequency oscillator using a field of about 9395 gauss.

Preparation of Bis-chloromethylphosphinic Chloride.—Chloromethylphosphonic dichloride was converted to the corresponding thionodichloride¹⁰ and the latter desulfurized with triphenyl phosphite¹¹ at 175° and 105 mm. to give chloromethyldichlorophosphine in 83% yield, b.p. 80° (105 mm.). Modifying the procedure given by Kabachnik and Shepeleva¹ by operating at atmospheric pressure 85 g. (2.48 mole "CH₂O") of paraformaldehyde was added to 245 g. (1.62 mole) of ClCH₂PCl₂ in small quantities through a nitrogen flushed feeding device. The reaction proceeded with heat evolution, and cooling of the reaction flask with water became necessary. Vacuum distillation of the reaction product gave 34 g. (0.22 mole) of unreacted ClCH₂PCl₂, b.p. 80-100° (105 mm.); 157 g. 2(0.865 mole) of (ClCH₂)₂POCl, b.p. 98-101° (1 mm.), equivalent to 53.5% yield based on ClCH₂PCl₂, and 87 g. (0.28 mole) of (ClCH₂)₂P(O)OP(O)(CH₂Cl)₂, b.p. 205-210° (2 mm.).

(10) M. I. Kabachnik and N. N. Godovikov, *Doklady Akad. Nauk S.S.S.R.*, **110**, 217 (1956); *C. A.*, **51**, 4982 (1957).

(11) L. C. D. Groenweghe, L. Maier and H. E. Ulmer, Abstract of Papers, 139th ACS Meeting, St. Louis, 1961, p. 17-M.

Preparation of Phosphinic Acid Anhydrides.—Dry paraformaldehyde was added in a 1:1 mole ratio (based on CH_2O) to the phosphinic chloride, and the resulting slurry was heated to 100–150° with stirring. After 0.5 hr. at this temperature, clear solutions usually were obtained which on distillation *in vacuo* yielded the phosphinic acid anhydride as viscous liquid. The latter crystallized on standing or, in the case of $\text{R}_1 = \text{R}_2 = \text{C}_6\text{H}_5$, after addition of a few ml. of diglyme. Physical data and analyses are listed in Table I.

The Reaction of Phosphinic Acid Anhydrides with PCl_5 .—A molar quantity of PCl_5 was added to a solution of the phosphinic acid anhydride in carbon tetrachloride. After refluxing for 1 hr., the solvent was removed and the formed phosphinic chloride distilled *in vacuo*. Table II is a listing of the yields, boiling points and analyses of the phosphinic chlorides obtained.

Hydrolysis of Phosphinic Acid Anhydrides.—Weighed samples of phosphinic acid anhydrides were dissolved in an excess of standardized aqueous sodium hydroxide solution and let stand overnight. Back titration of the unused sodium hydroxide gave the equivalent weights of the formed phosphinic acids as listed in Table II.

Alcoholysis of Phosphinic Acid Anhydrides.—A sample of 10 g. (0.033 mole) of $(\text{ClCH}_2)_2\text{P}(\text{O})\text{OP}(\text{O})(\text{CH}_2\text{Cl})_2$ in 100 ml. of dry ether was treated with an excess of dry ethanol and let stand overnight at room temperature. After separation of the formed phosphinic acid as trimethylammonium salt, 5.75 g. (0.030 mole) of ethyl bis-chloromethylphosphinate was obtained, b.p. 115–116° (1.5 mm.); P^{st} chemical shift was -39.9 p.p.m.

Anal. Calcd. for $\text{C}_4\text{H}_9\text{O}_2\text{Cl}_2\text{P}$: C, 25.16; H, 4.75; Cl, 37.13; P, 16.22. Found: C, 25.42; H, 4.59; Cl, 34.46; P, 16.37.

Aminolysis of Phosphinic Acid Anhydrides.—A quantity of 20 g. (0.055 mole) of $\text{ClCH}_2(\text{C}_6\text{H}_5)\text{P}(\text{O})\text{OP}(\text{O})(\text{C}_6\text{H}_5)\text{CH}_2\text{Cl}$ was dissolved in 250 ml. of dry ether, and excess of diethylamine was added slowly to the solution. After standing overnight, 14.2 g. (0.054 mole) of diethylammonium chloromethylphenylphosphinate was obtained as white precipitate. The filtrate of the precipitate gave on distillation 12.5 g. (0.051 mole) of chloromethylphenylphosphinic

diethylamide, $\text{ClCH}_2(\text{C}_6\text{H}_5)\text{PO}[\text{N}(\text{C}_2\text{H}_5)_2]$, b.p. 158° (5 mm.); P^{st} chemical shift was -30.5 p.p.m.

Anal. Calcd. for $\text{C}_{11}\text{H}_{17}\text{OCINP}$: C, 53.77; H, 6.97. Found: C, 53.77; H, 6.39.

Preparation of Phosphonic Acid Anhydrides.—Slurries of paraformaldehyde in the phosphonic dichloride in the mole ratio 1:2 were heated to 100–150° for 2 hr. Viscous liquids were obtained which on distillation gave about 50–60% unreacted phosphonic dichloride and a dark, very viscous residue. Samples of the latter were dissolved in tetrahydrofuran, and a n.m.r. spectrum was recorded.

Authentic samples of phosphonic acid anhydrides were prepared by heating molar quantities of phosphonic dihalides and dialkyl phosphonates at 100–150° until the expected amount of alkyl chloride had collected in the cold trap.

The Reaction of Acetyl Chloride with Paraformaldehyde.—A quantity of 20.5 g. (0.261 mole) of acetyl chloride and 7 g. (0.233 mole) of $(\text{CH}_2\text{O})_n$ was heated in a sealed tube for 19 hr. at 150°. The resulting dark liquid was distilled, yielding 8.5 g. (0.142 mole) of acetic acid and 5.8 g. (0.057 mole) of acetic acid anhydride, b.p. 140°.

The Reaction of Trimethylchlorosilane with Paraformaldehyde.—A quantity of 11 g. (0.102 mole) of trimethylchlorosilane and 3 g. (0.1 mole " CH_2O ") of paraformaldehyde was heated in a sealed tube for 2 hr. at 150°. The resulting light brown liquid yielded on distillation 6.1 g. (0.04 mole) of hexamethyldisiloxane, b.p. 98°.

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