[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

Studies in Phosphinemethylene Chemistry. III. Triphenylphosphinechloromethylene[1]

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RECEIVED OCTOBER 10, 1960

Triphenylphosphinechloromethylene has been prepared by the reaction of triphenylphosphine and chlorocarbene and by the action of phenyllithium on chloromethyltriphenylphosphonium bromide. Examples of its use in the Wittig reaction are given; this represents a new general synthesis of vinylic chlorides of the type RCH=CHCl and R_2C=CHCl.

The electrophilic nature[2] of halocarbenes is believed to be due to their electronic structure where carbon is in the singlet ground state, in which an electron pair fills a carbon sp^2 orbital not used in bonding, leaving the p_z orbital vacant. If this description of carbenes is accepted, then triphenylphosphinemethylenes, $(C_6H_5)_3\overset{\oplus}{P}\text{—}\overset{\ominus}{C}X_2 \longleftrightarrow (C_6H_5)_3P{=}CX_2$, can be regarded as donor-acceptor complexes formed between the nucleophile triphenylphosphine and the electrophilic carbene. This suggested that the direct reaction between triphenylphosphine and carbenes might provide a new synthesis of the useful triphenylphosphinemethylene reagents. The heretofore unknown triphenylphosphinehalomethylenes would be of interest, since their study would allow an assessment of the inductive effect of electronegative substituents on the methylene carbon as a possible contributing factor to the stability of phosphinemethylenes. They would also be of synthetic importance in organic chemistry, especially if they would undergo the Wittig reaction,[3] since this would result in a new general synthesis of vinyl and vinylidene halides.

We report here the trapping of chlorocarbene with triphenylphosphine and the use of the resulting triphenylphosphinechloromethylene in the Wittig reaction.

When chlorocarbene was generated by adding ethereal butyllithium to methylene chloride in ether at −30°[4] in the presence of triphenylphosphine, the deep yellow-orange color characteristic of phosphinemethylene reagents developed. This mixture (a moderate amount of yellow-brown solid also was always present) reacted with ketones and aldehydes to produce the expected 1-chloroolefins in yields averaging *ca.* 30%. In this manner acetophenone was converted to 1-chloro-2-phenyl-1-propene, diethyl ketone to 1-chloro-2-ethyl-1-butene, 4-methyl-2-pentanone to 1-chloro-2,4-dimethyl-1-pentene, cyclohexanone to chloromethylenecyclohexane and benzaldehyde to β-chlorostyrene. In the acetophenone reaction the two geometric isomers of 1-chloro-2-phenyl-1-propene were formed in about equal amounts as detected by gas chromatography. In the reactions with benzaldehyde and 4-methyl-2-pentanone the two possible isomers of each chloroolefin may have been present, but they were not resolved in the gas chromatographic analysis of the reaction products.

$$(C_6H_5)_3P + :CHCl \longrightarrow (C_6H_5)_3P{=}CHCl \xrightarrow{R_2C=O} R_2C{=}CHCl + (C_6H_5)_3PO$$

In an attempt to determine the cause of the low over-all yields of chloroölefins, each of the two steps of this synthesis was investigated separately. The known reaction of triphenylphosphinemethylenes with hydrogen halides, which produces crystalline phosphonium salts in apparently quantitative yield, was used to determine the yield of triphenylphosphinechloromethylene formed in the trapping reaction. Hydrogen bromide was bubbled into the triphenylphosphinemethylene solutions formed under various reaction conditions to convert the phosphinemethylene into ether-insoluble chloromethyltriphenylphosphonium bromide. The unreacted triphenylphosphine present in the reaction mixture also reacted with hydrogen bromide to form ether-insoluble triphenylphosphonium bromide, $[(C_6H_5)_3PH]Br$. Separation of these two phosphonium salts was made possible by the instability of the latter in water. An independent experiment showed that when triphenylphosphonium bromide was placed in water, it decomposed to water-insoluble triphenylphosphine and hydrobromic acid. Thus, solution of the phosphonium salt mixture in water caused precipitation of triphenylphosphine and left an acidic solution containing the chloromethyltriphenylphosphonium ion. Filtration was followed by addition of aqueous sodium tetraphenylborate to the filtrate, which resulted in quantitative precipitation of chloromethyltriphenylphosphonium tetraphenylborate. The yield of this derivative allowed calculation of the triphenylphosphinechloromethylene yield. The accuracy of this method was shown by analyzing four mixtures of pure chloromethyltriphenylphosphonium bromide and pure triphenylphosphonium bromide of known composition. The chlorocarbene capture reaction was repeated many times, using different ratios of reactants, but the yield did not seem to change in any sensible manner, varying from 44 to 68%.

Pure chloromethyltriphenylphosphonium bromide was obtained by recrystallization of the product of the hydrogen bromide–triphenylphosphinechloromethylene reaction. This salt, suspended in ether, reacted with phenyllithium to form an orange solution of triphenylphosphinechloromethylene; a moderate amount of yellow solid

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[1] This work was summarized in part in a preliminary communication: D. Seyferth, S. O. Grim and T. O. Read, *J. Am. Chem. Soc.*, **82**, 1510 (1960); for part II, see *ibid.*, **83** 1613 (1961).

[2] (a) W. von E. Doering and A. K. Hoffmann, *ibid.*, **76**, 6162 (1954); (b) J. Hine and A. M. Dowell, *ibid.*, **76**, 2688 (1954); (c) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); W. von E. Doering and W. A. Henderson, *ibid.*, **80**, 5274 (1958).

[3] G. Wittig and U. Schöllkopf, *Chem. Ber.*, **87**, 1318 (1954); see also U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959).

[4] G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **81**, 4996 (1959).

was present as well. The reaction of this mixture with acetophenone and benzaldehyde afforded 1-chloro-2-phenyl-1-propene (91%) and β-chlorostyrene (76%), respectively. Other conversions are described in the Experimental section.

Thus when triphenylphosphinechloromethylene was prepared by the dehydrohalogenation of chloromethyltriphenylphosphonium bromide, much better yields were obtained in the subsequent Wittig reactions than when the phosphinemethylene reagent was prepared by trapping chlorocarbene with triphenylphosphine. This probably is due to the formation of triphenylphosphinechloromethylene in much better yield in the former method and also to the absence of excess triphenylphosphine, which appears to make isolation of the chloroölefins more difficult when the phosphinemethylene reagent was prepared by the latter method. For preparation of 1-chloroölefins by the Wittig procedure, it is recommended that the chloromethyltriphenylphosphonium bromide–phenyllithium reaction be used to generate triphenylphosphinechloromethylene, and that the required chloromethylphosphonium salt be prepared by the procedure reported recently by Hoffmann.[5]

After a report of the present work had been submitted as a preliminary communication,[1] a paper by Speziale, Marco and Ratts[6] reported that dichlorocarbene could be captured with triphenylphosphine and that the resulting triphenylphosphinedichloromethylene could be used in the Wittig reaction. Wittig and Schlosser[7] reported the chlorocarbene–triphenylphosphine reaction and the use of triphenylphosphinechloromethylene in chloroölefin synthesis shortly after our initial report, and further work by Wittig and Franzen[8] showed that CH_2, generated in the decomposition of trimethylammonium methylide, could be trapped with triphenylphosphine.

The early work of Staudinger and Meyer[9] is of interest in this connection. Their synthesis of the first triphenylphosphinealkylidene, $(C_6H_5)_3P{=}C(C_6H_5)_2$, was effected by thermal decomposition of the phosphazine, $(C_6H_5)_3P{=}N{-}N{=}C(C_6H_5)_2$. It is possible (but not proved) that this reaction involves decomposition to triphenylphosphine, nitrogen and $(C_6H_5)_2C$, followed by combination of triphenylphosphine and diphenylmethylene. Evidence has been presented[10] that $(C_6H_5)_2C$ is a diradical species in which the methylene carbon atom is in a triplet state rather than in a singlet state. Reactions of triphenylphosphine with radical reagents have been reported,[11,12] and so the formation of a phosphinemethylene in a reaction of triphenylphosphine with a diradical does not seem impossible. This presents the interesting possibility that triphenylphosphinemethylenes could result from reactions of triphenylphosphine with divalent carbon species in the triplet or the singlet ground state.

Experimental[13]

(1) **Preparation of Triphenylphosphinechloromethylene from Triphenylphosphine and Chlorocarbene, and Its Reaction with Hydrogen Bromide.**—Triphenylphosphine (30 g., 0.115 mole) was placed in a 500-ml., three-necked round-bottom flask equipped with an addition funnel, a mechanical stirrer and an inlet tube which protruded halfway into the flask. This tube was connected to a three-way stopcock which led to the nitrogen atmosphere system and to a cylinder of anhydrous hydrogen bromide (Matheson Co.). Anhydrous ether (200 ml.) and 11 g. (0.13 mole) of methylene chloride, freshly distilled from phosphorus pentoxide, were added. The flask was immersed in a Dry Ice-acetone-bath maintained at −40° to −30°, and 40 ml. of 2.48 *M* (0.10 mole) *n*-butyllithium solution was added slowly with vigorous stirring. The solution became yellow at first and the color deepened to orange as the addition progressed. After the addition had been completed, the addition funnel was replaced by a connecting tube which was attached to a mercury overpressure valve. The cooling bath was removed. As hydrogen bromide was bubbled into the flask, the orange color was discharged immediately with formation of copious quantities of white precipitate. The resulting mixture was filtered through a sintered glass filter funnel; the solids were washed with benzene and petroleum ether and dried in vacuum at 60° for 12 hr. The dried product weighed 33.6 g. A sample of this solid (0.4983 g.) was placed in 40 ml. of water; the solid was broken up with a stirring rod and the mixture stirred for 10 min. in order to ensure solution of the chloromethyltriphenylphosphonium bromide and complete decomposition of triphenylphosphonium bromide. The mixture was filtered and the filtrate collected in a 400-ml. beaker. The beaker in which the solution had been prepared, filter paper and the solid were washed carefully with successive small portions of water, the washings being added to the filtrate. A solution of *ca.* 0.5 g. of sodium tetraphenylborate in 20 ml. of water then was added dropwise to the filtrate. The mixture was stirred during the addition to effect rapid coagulation of the resulting precipitate. The insoluble chloromethyltriphenylphosphonium tetraphenylborate was collected by filtration using a tared Gooch-type filter funnel with a sintered glass filter. The residue was washed with water and dried in vacuum over phosphorus pentoxide. The dry tetraphenylborate weighed 0.6163 g., which corresponded to a product composition of 76.7% chloromethyltriphenylphosphonium bromide and an over-all yield (based on butyllithium) of 65.7%.

The reaction was repeated several times with varying ratios of reagents. The results are listed in Table I.

TABLE I

TRIPHENYLPHOSPHINECHLOROMETHYLENE *via* THE REACTION OF TRIPHENYLPHOSPHINE WITH CHLOROCARBENE

$(C_6H_5)_3P$, mole	*n*-BuLi, mole	CH_2Cl_2, mole	Yield, %
0.115	0.10[d]	0.13	66[a]
.115	.20	.10[d]	53
.085[d]	.14	.14	56
.60	.60	.65	44[b]
.229	.076[c,d]	.10	54

[a] Recrystallized yield 46%. [b] Recrystallized yield 32%. [c] Phenyllithium used instead of butyllithium. [d] Limiting reagent; yields based on this figure.

Determination of the Composition of Mixtures of Chloromethyltriphenylphosphonium Bromide and Triphenylphosphonium Bromide.—Triphenylphosphonium bromide (0.0469 g.) and chloromethyltriphenylphosphonium bromide (0.1750 g.) were placed in 20 ml. of water, and operations

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[5] H. Hoffmann, *Angew. Chem.*, **72**, 77 (1960).

[6] A. J. Speziale, G. J. Marco and K. W. Ratts, *J. Am. Chem. Soc.*, **82**, 1260 (1960).

[7] G. Wittig and M. Schlosser, *Angew. Chem.*, **72**, 324 (1960).

[8] V. Franzen and G. Wittig, *ibid.*, **72**, 417 (1960).

[9] H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 619 (1919).

[10] R. M. Etter, H. S. Skovronek and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959).

[11] F. Ramirez and N. McKelvie, *ibid.*, **79**, 5829 (1957).

[12] L. Horner and H. Hoffmann, *Chem. Ber.*, **91**, 45, 50 (1958).

[13] Analyses were performed by Dr. S. M. Nagy (M.I.T.) and by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting points were determined using a Mel-Temp melting point apparatus. All reactions involving the preparation or use of organolithium reagents were carried out under an atmosphere of prepurified nitrogen. Starting materials either were purchased and, if necessary, subjected to further purification, or were prepared by methods described in the literature.

for the precipitation, filtration, drying and weighing of chloromethyltriphenylphosphonium tetraphenylborate were repeated as described above. This procedure was tested for several product compositions. The results are given in Table II.

TABLE II

ANALYSIS OF MIXTURES OF TRIPHENYLPHOSPHONIUM BROMIDE AND CHLOROMETHYLTRIPHENYLPHOSPHONIUM BROMIDE

$[(C_6H_5)_3PH]$ Br, g.	$[(C_6H_5)_3$-$PCH_2Cl]Br$, g.	$[(C_6H_5)_3$-$PCH_2Cl]$-Br, %	$[(C_6H_5)_3PCH_2Cl]$ $[B(C_6H_5)_4]$, g. Found	Calcd.
0.0469	0.1750	79	0.2825	0.2819
.1025	.1985	67	.3152	.3198
.0380	.2281	86	.3675	.3675
0	.2782	100	.4470	.4482

Recrystallization of Chloromethyltriphenylphosphonium Bromide and Preparation of Derivatives.—Pure chloromethyltriphenylphosphonium bromide from the triphenylphosphinemethylene–hydrogen bromide reaction was isolated as follows: 2.0 g. of the reaction product was dissolved in 8 ml. of isopropyl alcohol and filtered; to the filtrate was added 300 ml. of ether. The resulting precipitate was filtered, washed with ether and dried. The slightly yellow solid, m.p. 195–208°, weighed 0.92 g. Another recrystallization resulted in pure material, white solid of m.p. 209–211°.

Anal. Calcd. for $C_{19}H_{17}BrClP$: C, 58.26; H, 4.38; Cl, 9.05; Br, 20.40. Found: C, 58.47; H, 4.31; Cl, 8.56; Br, 20.31.

Picrate.—A sample of chloromethyltriphenylphosphonium bromide, 0.5 g., was dissolved in 30 ml. of water and added to an excess of picric acid dissolved in 20 ml. of 1:1 methanol–water mixture. The solution was heated and more methanol was added to dissolve the precipitate that had formed. The solution was filtered and, on cooling, the filtrate yielded yellow crystals. These were recrystallized from methanol; m.p. 192–194°.

Anal. Calcd. for $C_{25}H_{19}ClN_3O_7P$: C, 55.61; H, 3.55; Cl, 6.56. Found: C, 55.60; H, 3.76; Cl, 6.32.

Tetraphenylborate.—This derivative was prepared as described above and was recrystallized from methanol–ether to give pure material, m.p. 189–192°.

Anal. Calcd. for $C_{43}H_{37}ClPB$: C, 81.84; H, 5.91; Cl, 5.62. Found: C, 82.03; H, 6.17; Cl, 5.37.

(2) **Preparation of Triphenylphosphinechloromethylene from Triphenylphosphine and Chlorocarbene, and Its Reaction with Ketones.**—Triphenylphosphine (30 g., 0.115 mole) was placed in a 500-ml., three-necked flask equipped with an addition funnel, stirrer and condenser topped with a nitrogen inlet tube. Anhydrous ether (230 ml.) and methylene chloride (11 g., 0.13 mole) were added. The flask was cooled to −40° to −30°. The mixture was stirred rapidly while 77 ml. of 1.3 *M* (0.1 mole) *n*-butyllithium solution was added slowly over a period of 1 hr. After the addition had been completed, the solution was orange, and a considerable amount of yellow solid was present. When acetophenone (12 g., 0.1 mole), recently distilled and stored over Linde 5A Molecular Sieves, was added, the orange solution immediately turned light yellow and more solid was formed. This mixture was heated at reflux for 10 hr.; subsequently the ether was removed by distillation. The residue dissolved completely in 120 ml. of tetrahydrofuran, and this solution was heated at reflux for 6 hr. The tetrahydrofuran solution was shaken with 100 ml. of water, and the layers were separated. This operation was repeated. The aqueous extracts were washed with pentane and the washings added to the organic layer. After removal of the solvents by distillation, the head temperature rose rapidly. The distillate, 7.52 g., was collected from 84° (15 mm.) to 120° (15 mm.); it was analyzed using vapor phase chromatography[14] and was found to be composed of 1-chloro-2-phenyl-1-propene (both isomers) (56%), acetophenone (40%) and impurities (4%). These results established that the chloroölefin had been obtained in 28% yield (based on butyllithium).

A sample of distillate, 7.9 g., from another reaction similar to the one described above was dissolved in 10 ml. of pentane and chromatographed using 120 g. of Merck reagent aluminum oxide in a water-jacketed column. The first 500 ml. eluted with pentane was freed of solvent by distillation. The residue, 4.9 g., contained some ketone (positive 2,4-dinitrophenylhydrazine test), and for this reason was chromatographed again. Distillation of the pentane from the first five 100-ml. portions of eluate left as residue 0.37, 1.97 0.41, 0.11 and 0.0 g. of liquid, respectively. Vapor phase chromatographs of these fractions showed that the geometric isomers expected for 1-chloro-2-phenyl-1-propene were present, with the lower boiling isomer decreasing and higher boiling isomer increasing in relative amounts in the successive fractions. No ketone or other impurities were detected by vapor phase chromatography. A sample of the third fraction was subjected to a short path distillation; the distillate, n^{25}_D 1.5539, was a nearly 1:1 mixture of the isomers; infrared spectrum (pure liquid): 3080(m), 2980(m), 1602(m), 1610(m), 1572(w), 1495(s), 1436(s), 1370(m), 1322(m), 1240(w), 1204(w), 1071(m), 1029(s), 1010(s), 985(m), 911(m), 831(s), 790(s), 748(s), 690(s) cm.$^{-1}$.

Anal. Calcd. for C_9H_9Cl: C, 70.82; H, 5.94. Found: C, 70.81; H, 5.95.

A number of runs were carried out in which reagent ratios were varied. The best yield (46%) resulted when the reaction was effected with 0.11 mole of triphenylphosphine, 0.1 mole of methylene chloride, 0.2 mole of butyllithium and 0.2 mole of acetophenone. It is likely that careful study of conditions may result in better yields, but this aspect of the problem will not be investigated further.

Similar reactions were carried out in which triphenylphosphinechloromethylene prepared from the triphenylphosphine–chlorocarbene reaction was treated with other ketones. The following chloroölefins were prepared.

1-Chloro-2,4-dimethyl-1-pentene (from 4-methyl-2-pentanone), 27% isolated yield, n^{25}_D 1.4339. *Anal.* Calcd. for $C_7H_{13}Cl$: C, 63.39; H, 9.88. Found: C, 63.44; H, 9.89.

1-Chloro-2-ethyl-1-butene (from diethyl ketone), 20% yield, n^{25}_D 1.4369. *Anal.* Calcd. for $C_6H_{11}Cl$: C, 60.74; H, 9.30. Found: C, 60.78; H, 9.40.

Chloromethylenecyclohexane (from cyclohexanone), 30% yield, n^{25}_D 1.4829. *Anal.* Calcd. for $C_7H_{11}Cl$: C, 64.36; H, 8.49. Found: C, 64.24; H, 8.48.

(3) **Preparation of Triphenylphosphinechloromethylene from Chloromethyltriphenylphosphonium Bromide and Phenyllithium, and Its Reaction with Ketones.**—A sample of chloromethyltriphenylphosphonium bromide (6.23 g., 0.0159 mole) was placed in a 300-ml., three-necked flask equipped in the manner described in the previous experiment. After the air in the system had been displaced with nitrogen, 80 ml. of anhydrous ether was added and 17 ml. of 0.93 *M* phenyllithium solution (0.0158 mole) was added rapidly. The mixture (some solid was always present) was orange after it had been stirred for 30 min. at room temperature. Acetophenone (4.5 g., 0.038 mole) was added, and the mixture was heated for 23 hr. without stirring. During the last 10 hr. the ether solvent was distilled off slowly, and the residue was heated at higher temperature. The mixture was distilled without filtering. The distillate, 3.54 g., was collected from 80–125° (15 mm.). The yield of the two isomers of 1-chloro-2-phenyl-1-propene, present in 56:44 molar ratio, was 91% (vapor phase chromatography).

Other conversions carried out in a similar manner were: cyclohexanone to chloromethylenecyclohexane (80%), 4-methylcyclohexanone to chloromethylene-4-methylcyclohexane[17] (51%), diethyl ketone to 1-chloro-2-ethyl-1-pro-

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[14] Gas chromatography columns[15] were 8 mm. Pyrex tubes of 190 cm. length containing 30% by weight of Dow Corning Silicone Oil No. 550 on 48–80 mesh firebrick support. The columns were operated at the temperatures of 120–190°, depending on the b.p. of the compounds chromatographed. Helium at 15 p.s.i. was the carrier gas, and thermistors were employed for detecting sample peaks. Collection of samples was made in a cooled small trap fitted with "no-air" stoppers and a Drierite drying tube. At the moment the sample peak was detected by the automatic recorder, the trap was placed on the hypodermic needle attached to the column exit. Percentage composition analyses were approximated by assuming that the area under the curve is proportional to the mole per cent. of the constituents.[16]

[15] A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1647 (1959).

[16] A. I. M. Keulemans, "Gas Chromatography," Reinhold Publ. Corp., New York, N. Y., 1957, pp. 31–32.

[17] Not completely pure; n^{22}_D 1.4800. *Anal.* Calcd. for $C_8H_{13}Cl$: C, 66.43; H, 9.06. Found: C, 65.42; H, 8.92.

pene (66%), 4-methyl-2-pentanone to 1-chloro-2,4-dimethyl-1-pentene (60%), benzaldehyde to β-chlorostyrene[18] (76%).

(4) **Reaction of Triphenylphosphine with Hydrogen Bromide.**—Triphenylphosphine (3.06 g., 0.0116 mole) was dissolved in 60 ml. of ether, and hydrogen bromide was bubbled into the solution. The white solid which resulted was filtered, washed with ether and dried. A 96% yield (3.85 g.) was obtained. The product was very soluble in methylene chloride and was recrystallized from methylene chloride by adding ether. The resulting triphenylphosphonium bromide decomposed between 170–198°.

Anal. Calcd. for $C_{18}H_{16}BrP$: C, 62.99; H, 4.70. Found: C, 63.20; H, 4.69.

In addition, 0.2228 g. of the solid was placed in 30 ml. of water and stirred for a short time. The triphenylphosphine was filtered off and washed. The filtrate and washings required 5.54 ml. of 0.1164 *N* NaOH for titration of the HBr formed in the decomposition of triphenylphosphonium bromide. Calcd. for $C_{18}H_{16}BrP$: HBr, 23.58. Found: HBr, 23.42.

The tetraphenylborate, $[(C_6H_5)_3PH][B(C_6H_5)_4]$, could be prepared by mixing concentrated solutions of triphenylphosphonium bromide and sodium tetraphenylborate in methanol. The resulting white crystals decomposed beginning *ca.* 170° to a brown melt at 200°.

Anal. Calcd. for $C_{42}H_{36}PB$: C, 86.59; H, 6.23. Found: C, 86.89; H, 6.69.

Acknowledgments.—The authors are indebted to the U. S. Army Quartermaster Research and Engineering Command (Chemicals and Plastics Division, Chemical Products Branch) for partial support of this work under Contract No. DA19-129-QM-1277, and to the National Science Foundation for the award of a Predoctoral Fellowship to S.O.G.

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(18) n^{25}_D 1.5728. *Anal.* Calcd. for C_8H_7Cl: C, 69.33; H, 5.09. Found: C, 69.50; H, 5.25.

[Contribution from the Chemical Engineering Division, Argonne National Laboratory,[1a] Argonne, Illinois]

Reactions of Sulfur Tetrafluoride with Oxides, Oxyfluorides, and Fluorides of Uranium and Plutonium[1b]

By Carl E. Johnson, Jack Fischer and Martin J. Steindler

Received October 27, 1960

Some quantitative and qualitative observations concerning the reaction of sulfur tetrafluoride with various fluorides, oxyfluorides and oxides of uranium and plutonium are presented. The reaction of sulfur tetrafluoride with plutonium hexafluoride in which plutonium hexafluoride is reduced to plutonium tetrafluoride is reported.

The previously known synthesis of sulfur tetrafluoride from sulfur and cobalt trifluoride[2] or elemental fluorine[3] gave mixtures from which sulfur tetrafluoride could be isolated only with difficulty. It has now been found[4] that sulfur tetrafluoride can be prepared readily by the reaction of sodium fluoride with sulfur dichloride in refluxing acetonitrile or by fluorination of sulfur, with chlorine and sodium fluoride at elevated temperatures and pressures.

Recently sulfur tetrafluoride has been reported to be a unique fluorinating agent in that it provides a direct and simple method for the synthesis of inorganic fluorides[5] and the preparation of uranium hexafluoride from uranium trioxide.[6]

Experimental

Materials.—Uranium trioxide used in these experiments was obtained by thermal decomposition of $UO_4 \cdot 2H_2O$. It is necessary to dehydrate the $UO_4 \cdot 2H_2O$ above 300° to insure complete conversion to uranium trioxide. It was necessary to store the uranium trioxide in a desiccator to prevent its hydration. Chemical analyses were obtained on the uranium trioxide; found 82.7% U, 16.7% oxygen; calculated 83.2% U, 16.8% oxygen.

The uranyl fluoride used was purchased from General Chemical Company. X-Ray diffraction analyses indicated anhydrous uranyl fluoride[7] to be the predominant species present. Chemical analyses of the material gave the results: 76.8% U, 12.4% F and 10.8% oxygen. Calculated, 77.3% U, 12.3% F and 10.4% oxygen. The U_3O_8 used was "primary standard" material purchased from National Bureau of Standards and was used as received. The uranium dioxide used was material produced by the Argonne Chemical Engineering pilot plant group. Chemical analyses indicated it contained 87.2% U and 11.5% oxygen which compared favorably with the calculated content of 88.2% U and 11.8% oxygen. The uranium tetrafluoride was Mallinckrodt Chemical Works production grade material which was analyzed as containing 74.8% U and 25.2% F. The uranium hexafluoride used in the experiments was purchased from Oak Ridge National Laboratory. Prior to use the uranium hexafluoride was purified by distillation and fractionation to remove any hydrogen fluoride. The vapor pressure at zero degrees was determined and found to be 17.4 mm. The literature value[8] is given as 17.6 mm.

The plutonium dioxide used was obtained from Los Alamos. The material was ignited at high temperature with no noticeable weight loss. By analysis the plutonium content was 87.5% Pu compared to a calculated content of 88.2% Pu. The plutonium tetrafluoride was obtained from Rocky Flats. Chemical analysis indicated 75.8% Pu and 24.2% F. The calculated content is 75.9% Pu and 24.1% F. The plutonium hexafluoride used was prepared by the reaction of plutonium tetrafluoride with fluorine. The gaseous plutonium hexafluoride formed was trapped at −80° and residual fluorine was removed. The vapor pressure of plutonium hexafluoride was determined to be 17.8 mm. at zero degrees. The literature value[8] is 17.9 mm.

Prior to use commercial high purity fluorine, obtained from the Pennsylvania Salt Manufacturing Co., was passed

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(1) (a) Work performed under the auspices of the U. S. Atomic Energy Commission at the Argonne National Laboratory, operated by the University of Chicago under Contract No. W-31-109-eng-38. (b) Presented at ACS Meeting, New York City, N. Y., September, 1960, paper #71.

(2) J. Fischer and W. Jaenekner, *Z. angew. Chem.*, **42**, 810 (1929).

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(4) C. W. Tullock, F. S. Fawcett, W. C. Smith and D. D. Coffman, *J. Am. Chem. Soc.*, **82**, 539 (1960).

(5) W. C. Smith, C. W. Tullock, E. L. Muetterties, W. R. Hasek, F. S. Fawcett, V. A. Englehardt and D. D. Coffman, *ibid.*, **81**, 3165 (1959).

(6) A. L. Oppegard, W. C. Smith, E. L. Muetterties and V. A. Englehardt, *ibid.*, **82**, 3835 (1960).

(7) W. H. Zachariasen, *Acta Cryst.*, **1**, 277 (1948).

(8) B. Weinstock, E. E. Weaver and J. G. Malm, *J. Inorg. Nuclear Chem.*, **11**, 104 (1959).