CHEMISTRY OF THE TRIFLUOROMETHYL GROUP

PART III. PHENYLBISTRIFLUOROMETHYLPHOSPHINE AND RELATED COMPOUNDS[1]

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ABSTRACT

The reaction of trifluoroiodomethane with tetraphenylcyclotetraphosphine leads to the formation of phenylbistrifluoromethylphosphine and phenyltrifluoromethyliodophosphine. The mechanism of the reaction is discussed and the physical and chemical properties of these compounds are reported. Bromine reacts with phenylbistrifluoromethylphosphine to form phenylbistrifluoromethyldibromophosphorane which is hydrolyzed to phenyltrifluoromethylphosphinic acid, $C_6H_5(CF_3)P(O)OH$.

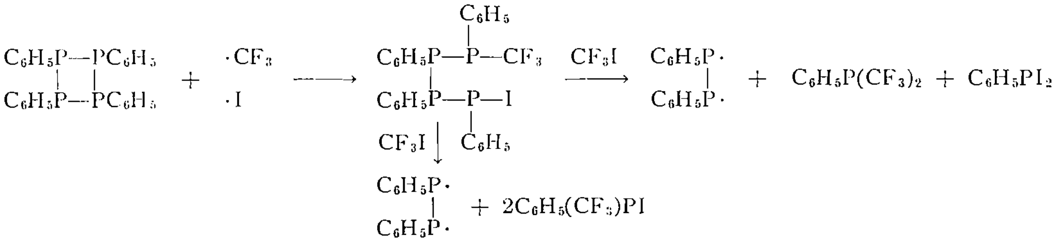
INTRODUCTION

In previous papers in this series, the donor properties of methyl-trifluoromethyl-phosphines were studied by the investigation of their ability to form complexes with boron trifluoride and platinum (II) chloride (1), and with a series of nickel (II) salts (2). Since much is known of the corresponding complexes of aryl phosphines, it seemed worthwhile to study the donor properties of aryl-trifluoromethyl-phosphines. Unlike the methyl-trifluoromethyl-phosphines which have been known for some time (3, 4, 5), the phenyl-trifluoromethyl-phosphines had not been previously reported, although their arsine analogues had been prepared (6). We now report the preparation of phenylbistrifluoromethylphosphine.

DISCUSSION AND RESULTS

Phenylbistrifluoromethylphosphine has been prepared by the reaction of trifluoroiodomethane with tetraphenylcyclotetraphosphine, the properties of which have been reported by other workers (7, 8, 9). The reaction was performed at 185°, above the melting point of the tetraphosphine, and the other reaction products, besides phenylbistrifluoromethylphosphine, are phenyltrifluoromethyliodophosphine, which is a very involatile reddish brown liquid, and small amounts of fluoroform and hexafluoroethane.

The mechanism of this reaction, involving the interaction of a perfluoroiodoalkane with a four-membered phosphorus ring is of some interest. A free-radical mechanism involving fission of phosphorus–phosphorus bonds by the attack of CF_3 radicals seems probable. This is supported by the fact that the reaction will occur thermally or on ultraviolet irradiation of the tetraphosphine with trifluoroiodomethane. Since the simultaneous breaking of four P—P bonds is unlikely, the following reaction scheme may be suggested.



$$2C_6H_5(CF_3)PI \rightleftharpoons C_6H_5P(CF_3)_2 + C_6H_5PI_2.$$

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This scheme is supported by the observation that the reaction products contain phenylbistrifluoromethylphosphine and phenyltrifluoromethyliodophosphine in an approximately 2:1 ratio, and also by the results of a separate experiment which indicated extensive disproportionation of the iodophosphine at 200° as indicated above.

Phenylbistrifluoromethylphosphine is a colorless liquid boiling at 148–150°; it is stable at 200° and prolonged heating to 300° causes only partial decomposition. It is not hydrolyzed by acids, but reacts very slowly with water at 100° and much more rapidly with aqueous sodium hydroxide at 80°. The hydrolysis products are fluoroform and either phenylphosphonous acid $C_6H_5PO_2H_{27}$, or its sodium salt.

Phenylbistrifluoromethylphosphine does not react with iodine at room temperature, but at 185° the trifluoromethyl groups are cleaved as trifluoroiodomethane. There is no evidence of the formation of the diiodophosphorane, $C_6H_5(CF_3)_2PI_2$. However, the phosphine reacted vigorously with bromine at room temperature to form phenylbistrifluoromethyldibromophosphorane. This is in agreement with the usual decrease in stability for dichloro-, dibromo-, and diiodo-phosphoranes. Phenylbistrifluoromethyldibromophosphorane is readily hydrolyzed by water losing only one of the two trifluoromethyl groups per molecule as fluoroform and producing phenyltrifluoromethylphosphinic acid, $C_6H_5(CF_3)P(O)OH$.

Phenyltrifluoromethyliodophosphine is a reactive liquid which is readily hydrolyzed. Whereas alkaline hydrolysis produced fluoroform and the sodium phenylphosphonate, treatment with water gives phenyltrifluoromethylphosphine and phenyltrifluoromethylphosphinic acid, $C_6H_5(CF_3)P(O)OH$.

The production of phenyltrifluoromethylphosphinic acid from the aqueous hydrolysis of phenylbistrifluoromethyldibromophosphorane provides an interesting link between the trifluoromethyl- and aryl-phosphorus compounds. Whereas hydrolysis of triaryldichlorophosphoranes yields phosphine oxides (10), hydrolysis of tristrifluoromethyldichlorophosphorane (11) gives bistrifluoromethylphosphinic acid and one equivalent of fluoroform.

$$(CF_3)_3PCl_2 \xrightarrow{H_2O} [(CF_3)_3P(OH)_2] \rightarrow (CF_3)_2P(O)OH + CF_3H$$

The hydrolysis of phenylbistrifluoromethyldibromophosphorane shows that the intermediate compound $C_6H_5(CF_3)_2P(OH)_2$ is unstable.

$$C_6H_5(CF_3)_2PBr_2 \xrightarrow{H_2O} [C_6H_5(CF_3)_2P(OH)_2] \rightarrow C_6H_5(CF_3)P(O)OH + CF_3H$$

The trifluoromethyl groups behave in the same way as in the hydrolysis of tristrifluoromethyldichlorophosphorane and the phenyl group shows its customary resistance to hydrolytic attack.

The formation of phenyltrifluoromethylphosphinic acid from the hydrolysis of phenyltrifluoromethyliodophosphine is consistent with the general reactions of halophosphines (12). The spontaneous oxidation–reduction of the apparently unstable hydrolysis product leads to the production of phenyltrifluoromethylphosphine and phenyltrifluoromethylphosphinic acid.

$$2C_6H_5(CF_3)PI \xrightarrow{H_2O} [2C_6H_5(CF_3)POH] \rightarrow C_6H_5(CF_3)PH + C_6H_5(CF_3)P(O)OH$$

The infrared spectra of these phenyl-trifluoromethylphosphorus compounds show the expected features. Absorption associated with the strong carbon–fluorine stretching vibrations occurred in the 1100–1200 cm^{-1} region. However, it is of interest to notice that the spectrum of silver phenyltrifluoromethylphosphinate, $C_6H_5(CF_3)P(O)OAg$, showed absorption at 1225 cm^{-1} corresponding to the P:O vibration. This absorption occurs in the same region for the aryl and alkyl phosphinic acids $R_2P(O)OH$, which are weak acids. For the strong acid, trifluoromethylphosphonic acid, this vibration is shifted to the higher frequency of 1300 cm^{-1} (13, 14). This might suggest that phenyltrifluoromethylphosphinic acid is a fairly weak acid.

EXPERIMENTAL

The preparations of the starting materials were carried out in a nitrogen atmosphere. Reactions with trifluoroiodomethane were carried out in sealed evacuated Pyrex tubes and the products and reactants were manipulated by standard vacuum techniques, out of contact with air and moisture.

Preparation of Tetraphenylcyclotetraphosphine

Phenyldichlorophosphine was obtained by the method of Buchner and Lockhart (15). The preparation of phenylphosphine by the Michaelis method (16, 17) is very cumbersome and gives a low yield. A much easier method (9, 18) is by reduction of phenyldichlorophosphine with lithium aluminum hydride. Phenyldichlorophosphine (18.8 g) dissolved in 100 ml diethyl ether was added cautiously to a well-stirred suspension of lithium aluminum hydride (3 g) in 100 ml ether. The reaction was vigorous and cooling was necessary. After the addition of phenyldichlorophosphine had been completed, the mixture was refluxed for 30 minutes and 5 ml of water were added dropwise. After being refluxed for an hour, the mixture was distilled and the resulting phenylphosphine, distilling at 160°, was dried over calcium chloride (yield 55%).

The preparation of tetraphenylcyclotetraphosphine by the Michaelis' method (19) is not convenient and the compound was prepared by adding phenylphosphine (11 g) in 50 ml ether to a well-stirred solution of phenyldichlorophosphine (18 g) in 50 ml ether. The solution gradually turned yellow but solid was not immediately deposited. After the addition was complete, the solution was refluxed for 3 hours during which time a white solid was deposited. The ether solution was decanted and the remaining solid was washed and dried. The yield of tetraphenylcyclotetraphosphine (m.p. 149–50°) was 90%.

Reaction of Tetraphenylcyclotetraphosphine with Trifluoroiodomethane

Tetraphenylcyclotetraphosphine (1.0 g) was sealed with trifluoroiodomethane (2.025 g) and left at room temperature for 24 hours. The solid phosphine was insoluble in trifluoroiodomethane. No reaction occurred at 70° C over 24 hours, nor at 150° C for 12 hours, but on heating at 185° C for 12 hours a dark-red involatile liquid was obtained and 0.558 g of unreacted trifluoroiodomethane was recovered. The dark-red liquid was shaken with mercury and the remaining liquid extracted with ether. After removal of the ether, a liquid (0.45 g) of low volatility was obtained and identified as phenylbistrifluoromethylphosphine (Found: C, 39.35%; H, 2.10%; F, 45.40%; P, 12.30%. Calculated for $C_8H_5F_6P$: C, 39.03%; H, 2.03%; F, 46.36%; P, 12.60%).

Phenylbistrifluoromethylphosphine is a colorless oily liquid whose odor is not as obnoxious as those of other phosphines. It boils at 148–150° and its vapor pressure is given by the equation $\log p_{\text{mm}} = 7.5606 - (1985/T)$, whence the latent heat of vaporization is 9054 cal $mole^{-1}$ and the Trouton's constant is 21.37. It is stable in air and does not react with water up to 100° C. It does not react with silver iodide, a solution of silver iodide in potassium iodide, or with carbon disulphide.

Two separate experiments were performed to investigate the mechanism of the above reaction and to characterize the other reaction products.

(1) Tetraphenylcyclotetraphosphine (2 g) was sealed with trifluoroiodomethane (5 g) in a Pyrex tube and was irradiated with ultraviolet radiation from a 200-watt U.V. lamp. The reaction was slow (possibly because of the heterogeneous phases), but after 15 days phenylbistrifluoromethylphosphine (0.899 g) and unreacted trifluoroiodomethane (2.192 g) were obtained. The rest of the product was a thick reddish syrup which showed strong absorption in the I.R. between 8–9 μ, characteristic of C—F stretching frequencies. This was not identified.

(2) Tetraphenylcyclotetraphosphine (7.5 g) was sealed with 18 g trifluoroiodomethane and heated at 185° C for 12 hours. A volatile mixture of hexafluoroethane and fluoroform (0.022 g), and 5.5 g of unreacted trifluoroiodomethane were recovered. The remaining liquid was subjected to fractional distillation under 20 mm pressure. Two fractions were obtained, one boiling at 62–65° (4.9 g) and the other boiling at 112–116° (3.8 g). A thick liquid which solidified on standing remained in the distillation flask. This showed strong absorption in the I.R., corresponding to the C—F stretching frequencies. Another experiment to identify this completely involatile liquid showed that it contained some iodides, including phosphorus triiodide. When treated with a large excess of trifluoroiodomethane and mercury, some pure phenylbistrifluoromethyl phosphine was obtained, but the main product was a very viscous pale-yellow liquid, presumably polymeric.

The liquid distilling at 62–65° was identified as phenylbistrifluoromethylphosphine and the fraction distilling at 112–114° was identified as phenyltrifluoromethyliodophosphine. (Found: I, 41.2%. Calculated for $C_7H_5F_3PI$: I, 41.78%.)

Reactions of Phenylbistrifluoromethylphosphine

(a) Hydrolysis

Phenylbistrifluoromethylphosphine (0.277 g) was sealed with water (1.28 g). There was no reaction at room temperature and the reactants formed two separate layers. After heating at 80° for 24 hours, only a trace of fluoroform was obtained, while after 36 hours at 110°, 0.038 g fluoroform was evolved. Traces of benzene were also identified spectroscopically. There remained a white crystalline solid which melted at 69° and was identified as phenylphosphonous acid.

Phenylbistrifluoromethylphosphine (0.273 g) was sealed with 5 ml of 20% aqueous sodium hydroxide solution. The reaction was slow at room temperature with the evolution of fluoroform. The tube was heated to 80° for 24 hours. The production of 0.149 g fluoroform (mol. wt. obtained 70.0, calculated 70.0) showed that the hydrolysis was 96.4% complete (CF_3 obtained as CF_3H: 54.8%; calculated for $C_6H_5P(CF_3)$: 56.1%). The solid obtained on evaporation of the solution was identified spectroscopically as the sodium salt of phenylphosphonous acid.

Phenylbistrifluoromethylphosphine (0.372 g) and 36 *N* hydrochloric acid (2 g) were sealed. There was no reaction at room temperature and the reactants formed separate layers. There was no reaction at 80° for 24 hours and at 110° for 48 hours. The tube was finally heated to 185° for 120 hours. At the end of this period the amount of fluoroform evolved was only 0.0022 g and the phosphine was recovered almost quantitatively.

(b) Reaction with Halogens

(1) Iodine.—Phenylbistrifluoromethylphosphine (0.389 g) and iodine (1.163 g) did not react at room temperature, nor after heating at 150° for 24 hours. The mixture was finally heated to 185° for 48 hours. The products obtained, were fluoroform (0.032 g),

trifluoroiodomethane (0.481 g), (mol. wt. 194, calculated 196), benzene (0.055 g), and traces of unreacted phosphine. The conversion into fluoroform and trifluoroiodomethane accounted for 91.5% of the trifluoromethyl group. The formation of fluoroform and benzene may be due to the presence of small traces of moisture on the iodine which is not removed even on extensive drying. The solid left in the tube, after pumping off the volatiles, contained phosphorus triiodide and no phenyltrifluoromethyliodophosphine.

(2) Bromine.—Phenylbistrifluoromethylphosphine (0.6965 g) and bromine (0.450 g) were combined. The ensuing vigorous reaction was controlled by performing the experiment in carbon tetrachloride solution and pumping off the volatiles after the reaction was complete. This was marked by the persistence of the bromine color. The reaction gave an orange-yellow solid which was very reactive towards moisture and was identified as phenylbistrifluoromethyldibromophosphorane (Found: Br, 38.93%. Calculated for $C_8H_5F_6PBr_2$: Br, 39.41%). On reacting the dibromophosphorane with water, one equivalent of CF_3 was lost and a white solid was left. The dibromophosphorane (0.324 g) was sealed with water (1.0 g) and left at room temperature overnight. Fluoroform (0.060 g) was evolved corresponding to a loss of one equivalent of CF_3 per mole (Found: CF_3, 18.4%. Calculated for $C_8H_5F_6PBr_2$:CF_3, 34.5%). A white solid was obtained by pumping off the liquids, recrystallizing the residue from water, and finally drying over phosphorus pentoxide. The solid was identified spectroscopically as phenyltrifluoromethylphosphinic acid, $C_6H_5(CF_3)P(O)OH$. The acid melted at 84–86°. The silver salt of the acid was obtained as needle-shaped crystals by treating the aqueous solution of the acid with silver oxide. The same salt could also be obtained from the reaction mixture of phenylbistrifluoromethyldibromophosphorane and water which had stood overnight and had lost one equivalent of CF_3. The silver salt $C_6H_5(CF_3)P(O)OAg$ (Found: Ag, 33.81%. Calculated for $C_7H_5F_3PO_2Ag$: Ag, 34.06%) melted at 294–96° and was very sensitive to light.

(c) Pyrolysis of the Phosphine

Phenylbistrifluoromethylphosphine (1.058 g) was heated to 210° for 48 hours; 1.004 g of the phosphine and traces of fluoroform and silicon tetrafluoride (identified spectroscopically) were obtained. Phosphine (0.639 g) was heated to 300° for 48 hours. The tube walls were etched but the phosphine was not all pyrolyzed: 0.48 g was recovered unchanged. The other volatile materials were fluoroform, silicon tetrafluoride, and some benzene trifluoride.

Reactions of Phenyltrifluoromethyliodophosphine

Phenyltrifluoromethyliodophosphine is a reddish-brown liquid which boils at 112–114° at 20 mm. It fumes in air and reacts slowly with water. The solution obtained by absorption of water is highly acidic. It disproportionates on heating.

(a) Hydrolysis

Phenyltrifluoromethyliodophosphine (0.334 g) was treated with 5 ml of 20% sodium hydroxide. There was immediate reaction at room temperature. The tube was heated to 100° for 15 hours. Fluoroform (0.0694 g) (mol. wt. found 69.8, calculated 70.0) was evolved (CF_3 found, 20.75%; calculated for $C_7H_5F_3PI$, 23.03%). The hydrolysis was only 90% complete. The residue contained a hygroscopic sodium salt whose I.R. spectrum corresponded with that of sodium phenylphosphonate.

Phenyltrifluoromethyliodophosphine (0.334 g) was treated with 0.125 g water and left in a sealed tube overnight. When water and other liquids were removed, a white solid was left. The melting point was 84–86° and in all respects the compound was similar to that obtained from the hydrolysis of phenylbistrifluoromethyldibromophosphorane. The silver salt was also prepared by reacting more of the iodophosphine with water and precipitating the iodide as silver iodide. The solution was concentrated *in vacuo* and the solid dried over P_2O_5. The silver salt was identified analytically (Found: Ag, 33.80%. Calculated: Ag, 34.06%) by its melting point of 294–96°, and also spectroscopically.

The above treatment of the iodophosphine also gave a small amount of a liquid whose I.R. spectrum showed the presence of P—H, P—C_6H_5, and P—CF_3 bonds. The hydrolysis with water therefore appears to give some phenyltrifluoromethylphosphine.

(b) Reaction with Trifluoroiodomethane

The iodophosphine (2.347 g) was heated with trifluoroiodomethane (2.299 g) at 200° for 12 hours. Trifluoroiodomethane (2.210 g, 96.1%) was recovered and the main products of reaction, presumably from the disproportionation of the iodophosphine, were phenylbistrifluoromethylphosphine (0.617 g), phosphorus triiodide, and benzene. Some of the unreacted iodophosphine was also identified among the products.

(c) Reactions with Trifluoroiodomethane and Mercury

The iodophosphine (2.8 g) and trifluoroiodomethane (10 g), with 54 g mercury, were sealed in a tube and shaken for 24 hours. Trifluoroiodomethane (8.9 g) was recovered and phenylbistrifluoromethylphosphine (1.5 g) was obtained. The loss of 1.1 g of trifluoroiodomethane indicated that the reaction $C_6H_5PCF_3I+CF_3I \xrightarrow{Hg} C_6H_5(CF_3)_2P$ had occurred. Besides the phosphine, some polymers were also obtained as mentioned earlier.

Pyrolysis of phenyltrifluoromethylphosphine iodide: The iodophosphine (2.003 g) was heated in a sealed tube to 220° for 12 hours. Fluoroform (0.02 g) and trifluoroiodomethane (0.06 g) were obtained as the volatile products and there remained phenylbistrifluoromethylphosphine, benzene, phosphorus triiodide, and some unreacted phenyltrifluoromethyl iodophosphine.

The I.R. spectra were taken on a Perkin–Elmer model 21 double-beam instrument with rock salt optics. Liquid films were used for liquids and KBr pellets for solids. The following absorption bands were noted for the compounds mentioned.

		Phenylbistrifluoromethylphosphine			
3080 (w)	2920 (w)	2320 (w)	1980 (w)		
1870 (w)	1835 (w)	1810 (w)	1770 (w)	1745 (w)	
1730 (w)	1670 (w)	1645 (w)	1590 (w)	1490 (w)	
1445 (m)	1330 (w)	1265 (w)	1190 (s)	1140 (s)	
1100 (s)	1070 (m)	1030 (w)	1000 (m)	875 (w)	
805 (w)	750 (m)	745 (m)	690 (m)		
		Phenyltrifluoromethyliodophosphine			
3060 (w)	2900 (w)	2340 (w)	1880 (w)	1800 (w)	
1725 (w)	1710 (w)	1690 (w)	1675 (w)	1660 (w)	
1585 (w)	1490 (w)	1440 (m)	1385 (w)	1335 (w)	
1310 (w)	1270 (w)	1210 (m)	1150 (s)	1115 (s)	
1070 (m)	1025 (m)	1000 (m)	830 (w)	745 (s)	
715 (w)	690 (m)				
		Silver phenyltrifluoromethyl phosphinate			
3080 (w)	2900 (w)	2300 (w)	1860 (w)		
1815 (w)	1725 (w)	1710 (w)	1690 (w)	1756 (w)	
1640 (w)	1630 (w)	1590 (w)	1555 (w)	1485 (w)	
1440 (m)	1335 (w)	1225 (s)	1200 (m)		
1140 (s)	1110 (s)	1045 (m)	1015 (m)	995 (m)	
970 (m)	870 (w)	760 (w)	740 (m)	715 (m)	695 (m)

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