Formation and Reactions of Some Mono- and Diquaternary Phosphonium Halides

NATHAN L. SMITH
Department of Chemistry, University of Florida, Gainesville, Fla.

Mono-and diquaternary phosphonium halides were prepared by the interaction of tertiary phosphines with alkyl halides and dihalides. The compounds prepared by this reaction are (*p*-2-chloroethylbenzyl)triphenylphosphonium chloride, (9, 10- anthrylenedimethylene)bis(triphenylphosphonium chloride), and 9, 10-anthrylenedimethylene)bis(tri-*n*-butylphosphonium chloride). Gold (II), iron (III), mercury (II), palladium (II), and platinum (IV) halide complexes are readily formed by the reaction of mono- and diquaternary phosphonium halides with the halides of these metals. The dehydrochlorination of benzyldiphenyl (*tert*-butylamino)phosphonium chloride with magnesium hydride or 1,1,3,3,-tetramethylguanidine gave benzyldiphenyl-*N*-(*tert*-butyl)phosphinimine.

SEVERAL communications concerning the synthesis of mono- and diquaternary phosphonium salts have recently emanated from this laboratory, (*4, 5, 6, 7*). These studies show that halomethyl compounds containing alkyl, alkene, aryl, ether, and siloxyl groups react with aminophosphines.

This report covers the synthesis of several new phosphonium chlorides: (*p*-2-chloroethylbenzyl)triphenylphosphonium chloride (VII), (2,3,4,6-tetramethylbenzyl)triphenylphosphonium chloride (IX), (9,10-anthrylenedimethylene)bis(triphenylphosphonium chloride) (XI), (9,10-anthrylenedimethylene)bis(tri-*n*-butylphosphonium chloride) (XV). Furthermore, iron (I, X, XIII, XIV, XVI), gold (II, VIII, XII), mercury (III, palladium (IV), and platinum (V) halide complexes are readily formed by the reaction of mono- and diquaternary phosphonium halides with the halides of these metals (*3*).

As a corollary to this and other recent investigations (*1, 4*), it was found that benzyl(*tert*-butylamino)diphenylphosphonium chloride is dehydrochlorinated by magnesium hydride and 1,1,3,3-tetramethylquanidine to give benzyldiphenyl-*N*-(*tert*-butyl)phosphinimine (VI) in 63% and 55% yield, respectively. The use of 1,1,3,3-tetramethylguanidine as a dehydrohalogenation agent has the advantage of requiring a relatively short reaction time, and the product is easily isolated. In contrast magnesium hydride maintains an anhydrous condition in the mixture, but the process is subject to the usual difficulties associated with a heterogeneous reaction. Confirmation of structure for VI was obtained via oxidation to benzyldiphenylphosphine oxide.

EXPERIMENTAL

The elementary analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tennessee. The melting and boiling points given are uncorrected.

Materials. Benzyl(*tert*-butylamino)diphenylphosphonium chloride, *p*-durylenedimethylene)bis[(*tert*-butylamino)diphenylphosphonium chloride)], and 9.10-bis(chloromethyl)-anthracene were prepared by methods previously described (*6, 7*). *p*-Xylyenebis(triphenylphosphonium chloride) was prepared in essentially quantitative yield by the method of Campbell and McDonald except that monochlorobenzene rather than dimethylformamide was used as solvent (*2*). 1,1,3,3-Tetramethylguanidine was supplied by American Cyanamid Co. and used as received. Magnesium hydride was obtained from Dow Chemical Co. and used as received. *p*-(2-Chloroethyl)benzyl chloride was kindly supplied as a research sample by Monsanto Chemical Co. Humble Oil and Refining Co. kindly supplied a sample of chloromethyldurene.

Reaction of Trisubstituted Phosphines with RCH_2X Compounds. The preparation of (9,10-anthrylenedimethylene)-bis(triphenylphosphonium chloride) is described as an example of the reaction of a trisubstituted phosphine with and organic halide.

A mixture of 5.2 grams (0.02 mole) of triphenylphosphine, 2.8 grams (0.01 mole) of 9,10-bis(chloromethyl)anthracene, and 50 ml. of monochlorobenzene were stirred at reflux for 1 hour. The reaction product was filtered, and the yellow solids washed thoroughly with ethyl ether. The air-dried product weighed 7.4 grams (93% yield) and melted with decomposition at 307° C.

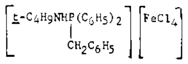
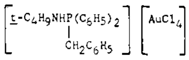
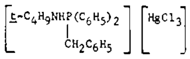
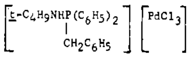
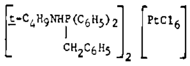
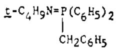
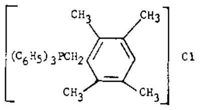
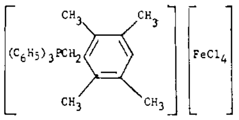
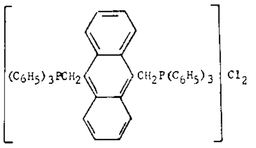
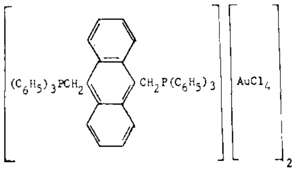
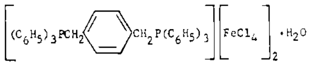
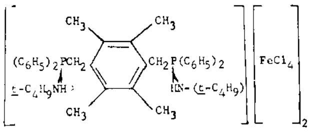
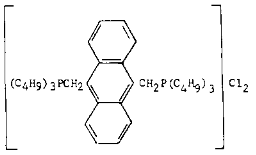
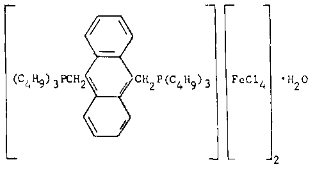
The physical properties, analytical data, and yields for the various phosphonium salts and their reaction products synthesized in this investigation are listed in Table I. A characteristic of all the spectra of these phosphonium halides is an intense band at 1120 cm.$^{-1}$ and two moderately strong bands between 940 and 820 cm.$^{-1}$. Bands also appeared at 1440 and 1000 cm.$^{-1}$ in the spectra of the P-phenyl compounds (*6*). The spectra of the metal halide complexes did not differ appreciably from those of the phosphonium halides in the region 4000–650 cm.$^{-1}$.

Preparation of Metal Halide Complexes. The metal halide complexes were prepared in good yields by the interaction of equimolar quantities of the mono- and diquaternary phosphonium halides and the appropriate metal halides in ethanol (*3*).

Dehydrochloroination of Benzyl(*tert*-butylamino)diphenylphosphonium Chloride. With 1,1,3,3-Tetramethylguanidine. A mixture of 3.8 grams (1 m mole) of benzyl(*tert*-butylamino)diphenylphosphonium chloride, 1.1 grams (1 m mole) of 1,1,3,3-tetramethylquanidine and 75 ml. of benzene were stirred at reflux for 5 minutes. The resultant product was filtered, and the solids were washed with benzene and ethyl ether. The solvents from the combined filtrate and washings were evaporated at reduced pressure. The residue weighed 1.9 grams (55% yield) and melted at 82–85° C. The product, purified by sublimation, melted sharply at 92.5–93.0° C.

With Magnesium Hydride. An intimate mixture of 1.9 grams (5 m mole) of benzyl(*tert*-butylamino)diphenylphosphonium chloride and 1.0 gram of MgH_2 was heated at the decomposition temperature (ca. 200° C.). When decomposition ceased, the product was subjected to sublimation at 1.0 mm. The sublimate weighed 1.1 grams (63% yield)

Table I. Description of Mono- and Diquaternary Phosphonium Salts

		Yield, %	M.P., °C.	C % Calcd. Found	H % Calcd. Found	N % Calcd. Found	P % Calcd. Found	Cl % Calcd. Found
I	 $[t\text{-}C_4H_9NHP(C_6H_5)_2CH_2C_6H_5][FeCl_4]$	84	134–136	50.58 50.20	4.98 5.10	2.57 2.61	5.67 5.77	25.97 25.87
II	 $[t\text{-}C_4H_9NHP(C_6H_5)_2CH_2C_6H_5][AuCl_4]$	[a]	143 (dec)	40.18 40.24	3.96 4.01	2.04 2.03	4.50 4.62	20.63 20.49
III	 $[t\text{-}C_4H_9NHP(C_6H_5)_2CH_2C_6H_5][HgCl_3]$	[a]	166–167	42.14 41.87	4.15 3.96	2.14 2.15	4.73 4.93	16.23 15.94
IV	 $[t\text{-}C_4H_9NHP(C_6H_5)_2CH_2C_6H_5][PdCl_3]$	[a]	214 (dec)	49.19 48.90	4.85 4.73			18.94 18.67
V	 $[t\text{-}C_4H_9NHP(C_6H_5)_2CH_2C_6H_5]_2[PtCl_6]$	[a]	191 (dec)	50.00 49.78	4.93 4.82	2.54 2.54		
VI	 $t\text{-}C_4H_9N{=}P(C_6H_5)_2CH_2C_6H_5$	63(55)	89–91	79.51 79.62	7.54 7.32	4.05 4.15	8.92 9.07	
II	$[(C_6H_5)_3PCH_2C_6H_4CH_2CH_2Cl]Cl$	73	228.0 228.5	71.52 71.38	6.00 5.89		6.83 7.05	15.64 15.39
VIII	$[(C_6H_5)_3PCH_2C_6H_4CH_2CH_2Cl][AuCl_4]$	[a]	143 (dec)	42.95 43.21	3.34 3.21		4.10 4.25	23.48 23.20
IX		90	255–258	78.27 78.30	6.80 6.90		6.96 7.07	7.97 8.14
X		[a]	182–183	57.36 57.54	4.98 5.03		5.10 5.23	23.36 23.31
XI		93	307 (dec)	77.90 77.56	5.53 5.55		7.73 7.38	8.84 9.09
XII			283 (dec)	44.33 43.87	3.15 3.34		4.40 4.21	
XIII		50	228 (dec)	50.71 50.52	3.87 3.99		5.94 5.93	27.22 27.40
XIV		[a]	206 (dec)	49.28 49.04	5.26 5.33	2.61 2.69	5.78 5.66	26.46 26.19
XV			328	70.67 70.47	9.79 9.53		9.11 9.31	10.43 10.29
XVI			225–227	46.99 46.91	6.70 6.87			27.75 28.09

[a] Yield essentially quantitative.

and melted at 82-85°. Resublimation raised the melting point to 89-91°.

The infrared spectrum of benzyldiphenyl-*N*-(*t*-butyl) phosphinimine supports the presence of the $N=P$ linkage which occurs at 1300 cm.$^{-1}$. A solution of the phosphinimine in practical cyclohexane on standing overnight in a humid atmosphere yielded white needles (m.p. 186-189°). This product, which crystallized from aqueous ethanol as fine needles (m.p. 191-192°), was identified as benzyldiphenylphosphine oxide by its infrared spectrum and by mixed melting points (191-193°) with a known sample of the compound.

LITERATURE CITED

(1) Appel, R., Hauss, A., *Chem. Ber.* **93**, 405 (1960).
(2) Campbell, T.W., McDonald, R.N., *J. Org. Chem.* **24**, 1247 (1959).
(3) Gill, N.S., *J. Chem. Soc.* **1961**, 3512.
(4) Sisler, H.H., Ahuja, H.S., Smith, N.L., *J. Org. Chem.* **26**, 1819 (1961).
(5) Sisler, H.H., Sarkis, A., Ahuja, H.S., Drago, R.J., Smith, N.L., *J. Am. Chem. Soc.* **81**, 2982 (1959).
(6) Sisler, H.H., Smith, N.L., *J. Org. Chem.* **26**, 4733 (1961).
(7) Smith, N.L., Sisler, H.H., *Ibid.*, **28**, 273 (1963).

RECEIVED for review November 1, 1962. Accepted February 1, 1963.

Reaction of Titanium Tetrachloride with Some Aromatic Hydroxy Compounds

DONALD SCHWARTZ and WILLIAM CROSS
College of Chemical Technology, North Dakota State University, Fargo, N. Dak.

Titanium tetrachloride reacts in a 1:2 ratio with phenol, *o*-bromophenol, *p*-bromophenol, *p*-chlorophenol, *p*-nitrophenol, *p*-cresol, and β-naphthol to form the dichlorodisubstituted titanates.

A RECENT literature survey by Shiihara (*9*) indicates that there has been numerous studies made on the reaction of titanium tetrachloride with various classes of organic compounds. A lesser amount of work has been done on the reaction of hydroxy aromatic compounds with titanium tetrachloride.

One of the first reactions of a phenol compound with titanium tetrachloride was reported by Luchinskii (*6*). He reported the reaction of titanium tetrachloride with phenol to form $TiCl_3(OC_6H_5)$, which could be used for the colormetric determination of either compound. Luchinskii (*5*) also reported the reaction of titanium tetrachloride with *o*-chlorophenol, *p*-chlorophenol, and *p*-nitrophenol to form the dichlorodisubstituted titanates which were all easily hydrolyzed, dark red compounds.

This paper reports the preparation and some of the properties, including infrared spectra, of the dichlorodissubstituted titanates obtained from the reaction of a 1:2 ratio of titanium tetrachloride and phenol (m.p. 41°), *o*-bromophenol (m.p. 4-5°), *p*-bromophenol (m.p. 63.5°), *p*-chlorophenol (m.p. 39-40°), *p*-nitrophenol (m.p. 114°), *p*-cresol (m.p. 32-34°), and β-naphthol (m.p. 122°).

The compounds formed are dark red powdery solids with the exception of *p*-nitrophenol, which is bright orange, and β-naphthol, which is black-red. They are insoluble in most common organic solvents, although they dissolve in absolute ethyl alcohol readily. They are very hygroscopic and decompose in basic solution to form the corresponding phenol, titanium dioxide, and hydrogen chloride.

It has not been possible to prepare the dark red $TiCl_2(p\text{-}OC_6H_4NO_2)_2$ reported by Luchinskii (*5*) or the ruby-red crystals from the reaction of titanium tetrachloride with the corresponding phenol as reported by Reeves (*7*). The dichlorobis-(β-naphthoxy) titanate reported by Funk and Rogler (*12*) has been isolated in our laboratories.

The reactions were run in either carbon tetrachloride or chloroform solutions. Changing the solvent to benzene did not produce any solvent addition products as reported by Funk and his co-workers (*3*) in the preparation of $Ti(p\text{-}OC_6H_4Cl)_4 \cdot p\text{-}HOC_6H_4Cl \cdot C_6H_{12}$ and $TiCl_2(p\text{-}OC_6H_4\text{-}CH_3)_2 \cdot 2\ p\text{-}HOC_6H_4CH_3$. Solvent addition is possible and aromatic complexes have been observed in our laboratories (*8*).

There was evolution of hydrogen chloride during the reactions, but not noticeable heat was generated. Upon hydrolysis in a dilute nitric acid-ethyl ether solution, the phenol was quantitatively regenerated (*2*).

$$TiCl_2(OC_6H_5)_2 \xrightarrow[\text{dilute } HNO_3]{\text{ethyl ether}} \frac{Ti(OH)_4 + Cl^-}{\text{water} \quad \text{layer}} + \frac{C_6H_5OH}{\text{ether layer}}$$

Empirical formulas of the compounds are listed in Table I. They were determined from the titanium, phenol, and

Table I. Some Properties of the Solid Products Formed from Titanium Tetrachloride and Some Aromatic Hydroxy Compounds

Empirical Formula	M.P., °C.	%, Titanium Calcd.	%, Titanium Found	%, Chloride Calcd.	%, Chloride Found	%, Phenol Calcd.	%, Phenol Found
$TiCl_2(OC_6H_5)_2$	130-135	15.8	14.1	23.2	20.2	61.0	59.7
$TiCl_2(o\text{-}OC_6H_4Br)_2$	70-75	10.4	11.1	15.3	16.3	74.3	78.0
$TiCl_2(p\text{-}OC_6H_4Br)_2$	95-98	10.4	10.3	15.3	15.8	74.3	73.5
$TiCl_2(p\text{-}OC_6H_4Cl)_2$	108-116	12.8	11.7	19.0	18.1	68.2	67.0
$TiCl_2(p\text{-}OC_6H_4NO_2)_2$	102-107	12.2	12.5	18.0	17.5	69.8	71.6
$TiCl_2(p\text{-}OC_6H_4CH_3)_2$	80-87	14.4	15.0	21.3	20.8	64.3	64.1
$TiCl_2(\beta\text{-}OC_{10}H_7)_2$	145-150	11.9	11.9	17.5	17.1	70.6	68.6