CIV.—*The Action of Inorganic Halides on Organometallic Compounds.*

By Frederick Challenger and Freda Pritchard.

The formation of compounds of the type R_3MX_2 is well known in connexion with the Michaelis and Reese reaction (compare *Annalen*, 1886, **233**, 45, 60), but very few instances have been recorded in the case of the Grignard reaction (Morgan and Micklethwait, P., 1912, **28**, 68). On attempting to prepare tri-*m*-tolylstibine (Michaelis and Genzken, *Annalen*, 1887, **242**, 184) by this method, we obtained the corresponding *hydroxychloride*, doubtless arising from the action of water on the dichloride $(C_6H_4Me)_3SbCl_2$. Similarly, in the preparation of triphenylphosphine from phosphorus trichloride and magnesium phenyl bromide, we have observed the production of the oxide, which was not detected by Sauvage (*Compt. rend.*, 1904, **139**, 675) or by Pfeiffer and Pietsch (*Ber.*, 1904, **37**, 4621), although according to Stilp (*Diss.*, Rostock, 1910, p. 15) it may form the principal product when sodium and bromobenzene react with phosphorus trichloride.

An attempt has been made to explain the interchange of radicals between inorganic halides and organo-metallic compounds observed previously (J., 1922, **121**, 104) and during this investigation (see table on p. 866). Transference of the phenyl group takes place most readily when this radical is attached to the comparatively electro-positive element bismuth, the sparingly soluble diphenylchlorobismuthine being produced. Thus reaction 1A occurs in ether at the ordinary temperature, while 2B and 3C require temperatures above 200° (see p. 867). This recalls the use of the organo-derivatives of zinc, magnesium, and mercury in numerous synthetic reactions and in the preparation of other organo-metallic compounds, and is in agreement with the work of Goddard and Goddard (J., 1922, **121**, 256) on the use of the tetraphenyl derivatives of tin and lead in the preparation of diphenylthallium halides. The phenyl group readily leaves lead and tin for mercury (Krause and Schmitz, *Ber.*, 1919, **52**, 2150; Goddard, Ashley, and Evans, J., 1922, **121**, 978). On the other hand, mercury diphenyl converts stannic chloride into a phenylchlorostannane (Aronheim, *Annalen*, 1878, **194**, 152). These reactions are largely determined by the insolubility of the phenyl halogen derivatives of lead, mercury, and thallium.

It will be seen from the table that the migration of phenyl from bismuth may be effected either to electronegative elements such as arsenic and phosphorus, or to relatively electropositive ones like tin and mercury, from which it may be inferred that polarity is not the sole factor in the reaction. Hilpert and Grüttner (*Ber.*, 1913, **46**, 1675), investigating the affinity of the phenyl group for metals,* showed that this group is transferred from a less positive to a more positive element. This is not in agreement with the present results, but the two sets of observations are not comparable owing to the use of halides in our experiments. Hilpert and Grüttner state that " the course of the reaction is entirely modified by the presence of halogen."

The present authors consider that many of the ready migrations of phenyl groups now described are partly conditioned by the insolubility of one of the possible products. Perhaps the reason why this is particularly noticeable in the case of phenyl derivatives of positive elements like lead, mercury, and bismuth is that some slight ionisation occurs in solutions of these compounds, but is absent or much weaker in the case of the stibines, arsines, and phosphines, which are derived from the negative phenyl group and

---

* Some of the work of Kraft and Neumann on this subject (*Ber.*, 1901, **34**, 565) has not been confirmed by Steinkopf and Buchheim (*ibid.*, 1921, **54**, 1030).

		A.	B.	C.	D.	E.	F.	G.
		$BiCl_3$.	$SbCl_5$.	$AsCl_3$.	PCl_3.*	$SiCl_4$.	$TiCl_4$.	$TlCl_3$.
1	Ph_3Bi	Ph_2BiCl	Ph_2BiCl Ph_3SbCl_2	Ph_2BiCl Ph_2AsCl $PhAsCl_2$	Ph_2BiCl $PhPCl_2$	Ph_2BiCl in cold ether	Ph_2BiCl	Ph_2BiCl Ph_2TlCl
2	Ph_3Sb	Ph_3SbCl_2 and inorganic Bi compound	Ph_2SbCl $PhSbCl_2$ 240°	Ph_3SbCl_2 As and trace of PhHalAs	Ph_3SbCl_2 and trace of $PhPCl_2$	In boiling C_6H_6 Ph_3SbCl_2 probably a PhHalSb	Ph_3SbCl_2	Ph_3SbCl_2 $TlCl$
3	Ph_3As	Additive compound and trace of PhHalAs	Additive product $PhAsCl_2$ 100°	Ph_2AsCl $PhAsCl_2$ 240°	No action at 80° Ph_2AsCl at 160°	No action	Additive product	Ph_3AsCl_2 $TlCl$ Ph_2TlCl
4	Ph_3P	Additive product $\downarrow$ 200° Ph_3PCl_2 and Bi	Additive product $\downarrow$ 200° trace of Sb	Additive product $\downarrow$ 110° Ph_3PCl_2 and As	Ph_3PCl_2 and P_2Cl_4 (?)			$TlCl$ Ph_3PCl_2 (?)
5	Ph_4Pb	With $BiBr_3$ Ph_2BiBr Ph_2PbBr_2 66°	Ph_2SbCl Ph_2PbCl_2 110°	Ph_2AsCl Ph_2PbCl_2 110°	No action at 134°			Ph_2TlCl Ph_2PbCl_2

The results with lead tetraphenyl and with thallic chloride were obtained by Goddard and his co-workers.

a negative element. Such ionisation, however, was not detected by von Hevesy and Zechmeister (*Ber.*, 1920, **53**, 411).

With triphenylstibine, migration occurs very rarely (see table). It has been observed with silicon tetrachloride, mercuric chloride (on heating), and possibly to a slight extent with phosphorus trichloride. It may again be noted that mercury and phosphorus are very dissimilar, but that phenyl mercury chloride is very insoluble.

With triphenylarsine and triphenylphosphine, additive products are almost always produced with inorganic halides, except in reactions 3C, 3D, and 4D (compare Burrows and Turner, J., 1921, **119**, 1448). This is in agreement with the tendency of arsines and phosphines to form quaternary salts, which is absent in the bismuthines and the purely aromatic stibines.*

With triphenylarsine, migration of a phenyl group occurs at the ordinary temperature only with the chlorides of bismuth (3A) and thallium (3G). In the first case, the phenylchloroarsine was identified by its odour; only traces could have been present (J., 1922, **121**, 116). The production of diphenyl thallium chloride, Ph_2TlCl, from thallic chloride and the arsine (Goddard and Goddard, *loc. cit.*, p. 486) is probably due to the insolubility of this compound (*loc. cit.*, p. 256) disturbing an equilibrium and so favouring the progress of a reaction of the " migration " type which is usually kept in the background.

In 3B and 3D no reaction occurs in cold ether, but at 80° an additive compound is formed from the arsine and antimony trichloride, and also some phenyldichloroarsine, whilst with phosphorus trichloride diphenylchloroarsine is produced at 160°.

The high temperature (about 250°) required for reactions 2B and 3C (Morgan and Micklethwait, J., 1911, **99**, 2295; Morgan and Vining, J., 1920, **117**, 780) is further evidence of the stability of the union between phenyl and electronegative elements.

The additive compounds obtained from triphenylphosphine give rise, when heated, to the free element and (after addition of water) to triphenylphosphine oxide :

$$3Ph_3P + 2MCl_3 = 3Ph_3PCl_2 + 2M.$$
$$Ph_3PCl_2 + H_2O = Ph_3PO + 2HCl.$$

The metal was isolated in the case of arsenic, antimony (traces only), and bismuth, but no phenylhalogenarsines or bismuthines were detected. With phosphorus trichloride, the phosphine oxide was produced as usual, and also a yellow decomposition product of

---

* Mixed aromatic stibines containing one or two alkyl groups can form quaternary stibonium iodides (Grüttner, *Ber.*, 1915, **48**, 1759).

phosphorus subchloride, P_2Cl_4 (Besson and Fournier, *Compt. rend.*, 1910, **150**, 102). No phosphenyl chloride was formed. The tendency for migration of the phenyl group is therefore almost entirely absent in triphenylphosphine, even at about 200°. The stability of the mercuric chloride additive compounds of triphenylphosphine and triphenylarsine may be compared with the instability of the corresponding stibine and bismuthine derivatives (*Annalen*, 1886, **233**, 49; J., 1922, **121**, 106).

In triphenylamine, the phenyl groups are very firmly fixed to the negative nitrogen (J., 1921, **121**, 116) and Mr. R. J. Salmon has recently shown that no methyldiphenylamine is formed when triphenylamine is boiled with dimethylaniline. The additive compounds obtained from phenyldimethylarsine, and many of those now described, are sparingly soluble and therefore the tendency to their formation due to the unsaturated nature of tervalent arsenic and phosphorus is augmented by solubility considerations. On the other hand, the aryl halogen stibines, arsines, and phosphines, R_2MX and RMX_2, are liquids or readily soluble solids. The probability of their production, which is already depressed by the formation of the additive compound, is thus still further diminished, with the result that they are but rarely formed (see table and below).

In experiments 1E and 2E no organic derivative of silicon was isolated, but considering the quantity of silicon tetrachloride employed this is not surprising. A minute quantity of a solid was obtained in 1E which evolved an inflammable gas on addition of sodium hydroxide (compare Martin and Kipping, J., 1909, **95**, 314; Martin, J., 1915, **107**, 1043).

Goddard's statement (J., 1923, **123**, 1163) that, in the case of (organo-) compounds of the elements in group 5, phosphorus and antimony yield no organo-thallium derivatives, whereas arsenic and bismuth are capable of yielding compounds of the type R_2TlX can be expanded into a generalisation applicable to most of the reactions discussed in the preceding pages : The phenyl derivatives of phosphorus and antimony do not as a rule readily yield their aryl group in exchange for the halogen atom of an inorganic halide; those of bismuth and arsenic can undergo this reaction, which, however, occurs much more readily in the case of the bismuthines.

EXPERIMENTAL.

Tri-α-naphthylstibine and its Dichloride and Dibromide.—Antimony trichloride (20 grams; 1 mol.) in benzene (200 c.c.) was slowly added to an ethereal solution of magnesium α-naphthyl bromide (3 mols.). The solvents were then removed and the residue was treated with water, filtered, and extracted with benzene. This yielded a solid which on recrystallisation from benzene and then from acetone melted at 218° [Found: Sb estimated volumetrically (Schmidt, *Annalen*, 1920, **421**, 244) = 24·43, 24·10. $C_{30}H_{21}Sb$ requires Sb = 23·95 per cent.]. *Tri-α-naphthylstibine* is sparingly soluble in most organic solvents.

The *dichloride* was prepared as a white solid by adding 2 grams of the stibine to a solution of 0·3 gram of chlorine in carbon tetrachloride and diluting with light petroleum. The product, being insoluble in most organic solvents, was repeatedly extracted with hot chloroform, when it melted at 260° [Found: Cl by Robertson's method (J., 1915, **107**, 902), = 11·98. $C_{30}H_{21}Cl_2Sb$ requires Cl = 12·40 per cent.]. The *dibromide*, similarly prepared and purified, is a pale yellow solid, m. p. 229° (decomp.) (Found: by Robertson's method, Br = 24·04. $C_{30}H_{21}Br_2Sb$ requires Br = 24·18 per cent.).

*Tri-*m*-tolylbismuthine Dibromide.*—The bismuthine (1·5 grams) in dry chloroform was treated with 0·5 gram of bromine in dry ether. On addition of light petroleum yellow crystals were deposited which after four crystallisations from chloroform–light petroleum were colourless and on rapid heating melted at 92° (Found: Br = 25·30, 25·25. $C_{21}H_{21}Br_2Bi$ requires Br = 24·92 per cent.).

*Tri-*m*-tolylarsine.*—Arsenic trichloride (7·2 grams) in 72 c.c. of dry benzene was gradually added to the Grignard reagent (3 mols.) prepared from 23·9 grams of *m*-bromotoluene and 3·36 grams of magnesium, and the mixture was heated under reflux for about 2 hours. The solvent was then removed, by-products were distilled with steam, and the arsine was recrystallised from alcohol. Yield 55 per cent. It melted at 95° and was identical with the product obtained from sodium, *m*-bromotoluene, and arsenic trichloride (Michaelis, *Annalen*, 1902, **321**, 216).

This arsine and tri-*p*-tolylarsine did not react with benzaldehyde or ethyl oxalate in presence of pyridine or sodium ethoxide as catalyst (experiments by Mr. A. L. Smith).

*Attempted Preparation of Tri-*m*-tolylstibine.*—In a similar experiment [reacting quantities: antimony trichloride 18 grams in 180 c.c. of benzene, *m*-bromotoluene 41·6 grams (3 mols.), and magnesium 5·84 grams], after treatment with steam, the oily non-volatile portion, on extraction with light petroleum, left *tri-*m*-tolylstibine hydroxychloride* as a white powder which, recrystallised from benzene, melted at 209° (Found: by Robertson's method, Cl = 7·21, 7·25. $C_{21}H_{22}OClSb$ requires Cl = 7·97 per cent.). No stibine was isolated. With hot alcoholic hydrogen chloride, the hydroxychloride gave tri-*m*-tolylstibine dichloride, m. p. 137° (Michaelis and Genzken, *Annalen*, 1887, **242**, 184).

Action of Phosphorus Trichloride on Triphenylstibine, Triphenylarsine, and Triphenylphosphine.—The stibine (10 grams) was treated with 4 grams (1 mol.) of phosphorus trichloride in light petroleum. Triphenylstibine dichloride gradually separated and was identified by its m. p. and conversion into the hydroxychloride, m. p. 215—216°. The mother-liquor, which had an unpleasant odour,* was decanted, heated under reflux, and treated with water. The filtered aqueous extract (A) on concentration deposited traces of antimony oxychloride, whilst a pungent odour resembling that of the phenyl halogen derivatives of tervalent arsenic or antimony was evolved. Only traces of these compounds could have been present, however, the solution consisting largely of phosphorous acid. The amount of phenylphosphinous acid, $C_6H_5{\cdot}P(OH)_2$, present (compare J., 1922, **121**, 114) was not sufficient to give more than a slight turbidity with ferric chloride (the ferric salt is insoluble, *Annalen*, 1876, **181**, 309).

Triphenylarsine did not react with phosphorus trichloride (1 mol.) either in cold ether or in absence of a solvent at 78°. With 4 mols. of the trichloride in a sealed tube at 160°, some diphenylchloroarsine was produced. It was distilled in steam, leaving unchanged arsine, and characterised by conversion into diphenylarsenious oxide with sodium hydroxide (McKenzie, J., 1920, **117**, 412).

Triphenylphosphine (2·5 grams) was dissolved in 7·5 c.c. (2 mols.) of cold phosphorus trichloride, when a yellow flocculent solid (A) was deposited. After boiling for 6 hours, cooling and filtering, the excess of trichloride was removed under diminished pressure; from the residual oil, on treatment with 50 c.c. of warm 10 per cent. sodium carbonate solution, triphenylphosphine oxide was obtained as a white solid (2·4 grams).

The yellow solid (A) contained chlorine and phosphorus and appeared to be a decomposition product of phosphorus subchloride † (compare Besson and Fournier, *Compt. rend.*, 1910, **150**, 102). The sodium carbonate solution was concentrated, but gave no acid on acidification and extraction with ether.

Arsenic Trichloride and Triphenylstibine.—The stibine (2·8 grams) was unchanged when treated with arsenic trichloride (1·4 grams; 1 mol.) in dry ether. After 3½ hours at 80°, extraction with light petroleum left triphenylstibine dichloride, m. p. 142°. The solution yielded traces of an oil with an irritating odour resembling that of a

---

* This odour may have been due to the formation and decomposition of some P_2Cl_4. Traces of a yellow solid were observed in the reaction mixture (see above).

† Traces of a similar product were noticed during the interaction of triphenylstibine and phosphorus trichloride.

phenylchloroarsine or a phenylchlorostibine and a small amount of inorganic residue containing arsenious oxide and black metallic arsenic.

On repeating this experiment with four times the above quantities, 0·9 gram of arsenic was obtained, some of which was gradually deposited from the mother-liquors (see pp. 872, 874). The quantity of phenylhalogenarsines was too small to be detected by oxidation with chlorine water to phenylarsinic acids (J., 1922, **121**, 115).

*Antimony Trichloride and Triphenylarsine.**—No reaction occurred when the arsine (3 grams) and antimony trichloride (2·2 grams; 1 mol.) were mixed with dry ether. After 2 hours at 80° in absence of a solvent, a viscous, red solid was obtained, from which light petroleum extracted large, white crystals, m. p. 78°, after recrystallisation (Found: Cl = 10·39, 10·35 per cent.). These appeared to be an additive product, since on warming with water, antimony oxychloride and triphenylarsine were obtained. The portion insoluble in light petroleum yielded a pale yellow oil, containing phenyldichloroarsine, since on oxidation with moist chlorine and recrystallisation from alcohol, a solid of constant m. p. 158° was obtained, containing arsenic but no antimony. Phenylarsenic acid melts at 156° (Schmidt, *Annalen*, 1920, **421**, 737).

Antimony Trichloride and Triphenylphosphine.—The white precipitate (3 grams) obtained by mixing dry ethereal solutions of the phosphine (4 grams) and antimony trichloride (3·5 grams; 1 mol.) melted between 50 and 70°, and at 96° after recrystallisation from benzene. A further quantity was obtained from the ethereal solution (Found: by Robertson's method, Cl = 29·02, 28·85. $C_{18}H_{15}Cl_6PSb_2$ requires Cl = 29·8 per cent.†). The compound on treatment with water gave triphenylphosphine and antimony oxychloride. On heating at 240°, only traces of antimony, and no triphenylphosphine oxide, were detected. If the trichloride solution be added rapidly to the phosphine, a viscid oil is deposited; the ethereal mother-liquor then gives colourless crystals which distil unchanged, melt at 124°, and with dilute hydrochloric acid give the phosphine and antimony trichloride. This additive compound has not been further examined.

Arsenic Trichloride and Triphenylphosphine.—The phosphine (3 grams) was treated with 2·1 grams (1 mol.) of arsenic trichloride—both in dry ether—when a viscous, pale yellow oil was precipitated.

---

* After boiling with lead dichloride (2 mols.) in dry ether for 3 hours, the arsine was all recovered unchanged.

† $C_{18}H_{15}Cl_3PSb$ requires Cl = 21·79; $C_{36}H_{30}Cl_3P_2Sb$ requires Cl = 14·18 per cent. The low result indicates the presence of some antimony oxychloride.

The mother-liquor deposited hard, white rosettes, and a dark red powder which became black on heating and was conclusively shown to be arsenic.*

The white crystals consist of an additive product, since with cold water or moist air triphenylphosphine and arsenious and hydrochloric acids are formed. The compound melted and decomposed at about 100°, the red powder being again produced. The temperature was raised to 145°, and the residue extracted twice with hot water which, on cooling, deposited long needles of triphenylphosphine oxide. At no time during the experiment was there any odour of a phenylchloroarsine.

The same products were obtained when the phosphine and arsenic chloride in molecular proportions were mixed in boiling pseudocumene (160°) and afterwards treated with water.

Bismuth Chloride and Triphenylphosphine.—The yellow precipitate (8 grams) obtained on mixing dry ethereal solutions of bismuth chloride (4·8 grams) and the phosphine (4 grams) became white on standing and melted at 100—105°. On warming with water or with aqueous ammonia, it yielded triphenylphosphine (m. p. and mixed m. p. 79°) and bismuth oxychloride. Analyses were carried out by decomposing the compound with dilute nitric acid, separating the triphenylphosphine and estimating the chlorine by Volhard's method (Found : Cl = 19·10, 19·86. $C_{18}H_{15}Cl_3PBi$ requires Cl = 18·44 per cent.).†

The additive product was gradually heated at 270° during 30 minutes. At 150—160°, the substance fused and became very black. On cooling and extracting with hot water, triphenylphosphine oxide, m. p. and mixed m. p. 155°, was obtained. The residue contained some unchanged additive product, bismuth oxychloride, and an easily recognised bead of metallic bismuth.‡ In boiling pseudocumene very little reduction occurred.

Stannic Chloride and Triphenylbismuthine.—Stannic chloride (3·6 grams; 1 mol.) was gradually added to the bismuthine (6 grams)

---

* Erdmann and von Unruh (*Z. anorg. Chem.*, 1902, **32**, 449) describe the conversion of yellow arsenic into a red modification in carbon disulphide solution.

† The weight of the original precipitate also supports this formula. The high value for chlorine is due to the presence of bismuth chloride.

‡ No diphenylchlorobismuthine was produced, since on repeating the experiment and treating the reaction mixture with ammonia, no triphenylbismuthine could be detected in the resulting phosphine oxide or recovered phosphine either by m. p. or by evaporation with hydrochloric acid and treatment with hydrogen sulphide. With ammonia, diphenylchlorobismuthine yields triphenylbismuthine, which in 50 per cent. admixture with the phosphine melts at 60°.

both in dry benzene. A white, crystalline solid (4·6 grams) containing tin, bismuth, and halogen was at once deposited. This sintered above 140°, but had no definite m. p., and was rapidly decomposed in air and by alcohol, acetone, or chloroform.

With warm water, bismuth oxychloride and a white solid were obtained. This melted at 184° on recrystallisation from alcohol, contained tin and halogen, and was diphenylhydroxychlorostannane, $Ph_2Sn(OH)Cl$ (m. p. 187°). The original benzene solution on concentration and cooling in ice gave a solid which after three crystallisations from light petroleum melted at 42° with slight sintering from 38°. Diphenyldichlorostannane melts at 42° (Aronheim, *Annalen*, 1878, **194**, 152).

The Action of Silicon Tetrachloride on Triphenylbismuthine, Triphenylstibine, and Triphenylarsine.—The bismuthine (10·3 grams) in dry ether was treated with silicon tetrachloride (4 grams; 1 mol.) in the same solvent, when diphenylchlorobismuthine (m. p. 184—185°; 5 grams) was deposited. A further quantity (1·3 grams) separated on standing over-night. The ether was evaporated and organic bismuth compounds were decomposed by hydrochloric acid. The insoluble residue was very small in amount and with warm sodium hydroxide evolved an inflammable gas.*

Triphenylstibine (2 grams) did not react with silicon tetrachloride (1 gram; 1 mol.) in boiling ether but, after 5 hours in boiling benzene and removal of the solvent, the residue consisted of triphenylstibine dichloride and yielded the hydroxychloride with boiling water. The alcoholic mother-liquors deposited some antimony oxychloride and finally a viscid oil which, on warming, had a very irritating action on the mucous membrane and was probably a phenylchlorostibine.

Triphenylarsine (5 grams) did not react with silicon tetrachloride (2·83 grams; 1 mol.) either in ether or in boiling light petroleum, but was recovered unchanged. No odour of a phenylhalogenarsine was observed.

The Action of Titanium Tetrachloride on Triphenylbismuthine and Triphenylstibine.—Titanium tetrachloride (2·2 grams) and 20 c.c. of dry ether were cooled in ice and salt and slowly treated with 5 grams (1 mol.) of the bismuthine in dry ether. The mixture immediately became dark red. After 15 hours, the ether was decanted, the precipitate washed with ether and repeatedly extracted with benzene, whereby diphenylchlorobismuthine was obtained. The residue insoluble in benzene was free from organic matter:

---

* There was no interaction when tetraphenylsilicane (2·25 grams) and bismuth chloride (2·1 grams; 1 mol.) were boiled with 100 c.c. of dry benzene for 4 hours.

The ethereal washings deposited a few light yellow crystals containing bismuth, titanium, halogen, and organic matter. These were very hygroscopic and appeared to be an additive product; water yielded bismuth oxychloride and titanic hydroxide.

The main ethereal solution was evaporated under reduced pressure, yielding a red, viscid mass, which with water or solvents yielded only bismuth oxychloride, diphenylchlorobismuthine, and titanic hydroxide. The ethereal extract smelled strongly of diphenyl,* but only traces were isolated. By repeating the experiment in an atmosphere of nitrogen similar results were obtained; a portion of the ethereal solution appeared unaffected by a stream of dry air.

With triphenylstibine and titanium chloride in ethereal solution, a transient, red colour was produced. The only product isolated was triphenylstibine dichloride, m. p. 143°.

With triphenylarsine and titanium tetrachloride (1 mol.), much heat was evolved and a red additive product precipitated. On treatment with alcohol this regenerated the arsine. No trace of a phenylchloroarsine was formed.

Titanium Tetrachloride and the Grignard Reagent.

(With James Richard Ashworth Jinks.)

The Grignard reagent (5 mols.) prepared from 165 grams of bromobenzene and 25·6 grams of magnesium was slowly added to a mixture of 400 c.c. of dry ether and 40 grams of titanium tetrachloride at —20°, when a vigorous reaction occurred. After remaining for some days at the ordinary temperature, the ether (A) and a dark oil (B) were decanted, while a black, viscid mass (C) remained. No trace of a phenyl compound of titanium could be isolated from these products. Removal of ether from (A) and distillation in steam yielded 25 grams of diphenyl and some phenol. The non-volatile residue contained titanic hydroxide and on extraction with alcohol yielded about 2 grams of a product which after repeated crystallisation from alcohol and then from benzene was free from halogen, magnesium, and titanium, melted at 205°, and gave a blue fluorescence in benzene. It formed no picrate. These are the properties of *p*-diphenylbenzene (m. p. 205°), which was shown by Porter and Steele (*J. Amer. Chem. Soc.*, 1920, **42**, 2650) to be a product of the prolonged oxidation of magnesium phenyl bromide.

The dark oil (B) contained magnesium compounds, diphenyl, and a lower halide of titanium, since with water a bluish-black

---

* The addition of sodium hydroxide to an ethereal solution of triphenylbismuthine and titanium tetrachloride did not give the characteristic blue precipitate of titanous hydroxide, so that reduction does not appear to occur under these conditions (see p. 875).

precipitate was obtained which quickly oxidised in air to white titanic hydroxide. The solid (C) fumed in air due to unchanged etherate of titanium tetrachloride ($TiCl_4,C_4H_{10}O$). After extraction with benzene, the insoluble residue evolved hydrogen chloride and ethyl chloride on heating, leaving a solid containing titanium and magnesium.

An attempt to prepare titanium tetraphenyl from the tetrachloride, chlorobenzene, and sodium (8 atoms) in ether and in boiling benzene was unsuccessful, titanic hydroxide and diphenyl being produced.

With magnesium α-naphthyl bromide (3·5 mols.) considerable reduction of the titanium tetrachloride occurred, and was recognised as before by the colour change of the hydroxide. The ether on distillation with steam yielded traces of a non-volatile, halogen-free solid, m. p. 184°, on crystallisation from acetone. ββ′-Dinaphthyl melts at 183·5°.

These results are similar to those obtained by Kipping and one of us in 1909. When benzyl chloride (4 mols.) was added to magnesium (4 atoms), titanium tetrachloride, and ether, a black solid was deposited. Water gave a green solution which on boiling deposited a blue precipitate which gradually became grey.

In another experiment, the ether was evaporated, the residue heated at 140°, treated with water, filtered, and extracted with ether. Titanic hydroxide remained, its weight corresponding very nearly to that of the tetrachloride used. The ethereal extract on distillation in a vacuum yielded dibenzyl and a high-boiling, fluorescent oil free from titanium.

These results are in agreement with the preliminary experiments of earlier workers. Thus with mercury diphenyl and titanic chloride Levy (*Ann. Chim. Phys.*, 1892, [vi], **25**, 433) obtained diphenyl, phenyl mercury chloride, and titanous chloride.

Similar observations are recorded by Wöhler (*Ber.*, 1880, **13**, 1626), Schumann (*ibid.*, 1888, **21**, 1079), Paternò and Peratoner (*ibid.*, 1889, **22**, 467), and Stilp (*Diss.*, Rostock, 1910, 50).

Experiments on the preparation of organo-titanium compounds are being continued.

The authors are indebted to Mr. T. H. Bott, B.Sc., for valuable assistance in some of the experimental work, and to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this investigation. One of us (J. R. A. J.) gratefully acknowledges the assistance due to a grant from the Board of Industrial and Scientific Research.

THE UNIVERSITY, MANCHESTER. [*Received, December 20th,* 1923.]
