PHENYL DERIVATIVES OF ORGANOTITANIUM COMPOUNDS

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There has been a considerable advance in the chemistry of the organometallic compounds of the transition metals during the last few years. Titanium compounds, which are used to a large extent in olefin polymerisation reactions, are of special interest both from the theoretical and practical points of view.

The titanium alkyl derivatives such as R_nTiX_{4-n} (where $R = CH_3, C_2H_5, C_4H_9$) produced by interaction of $TiCl_4$ with the alkyl derivatives of aluminium, tin, zinc and other metals have been very fully investigated. They are coloured and thermally unstable compounds whose strong reactivity depends upon the instability of the alkyl–titanium bond. Their isolation in the pure state requires special conditions[1–4].

Although the aryltitanium derivatives were the first to be prepared, they have still not been fully investigated. The first representative of this series, $C_6H_5Ti(OR)_3$, was produced as a colourless, easily hydrolysed compound, stable in air at room temperature[5].

Attempts to synthesise Ar_nTiX_{4-n} by the interaction of $TiCl_4$ with diphenylmercury, tetraphenyltin, or phenylsodium were unsuccessful. The reaction which takes place at about 200° can be summarised by the following equation[6]:

$$(C_6H_5)_2Hg + TiCl_4 \longrightarrow C_6H_5HgCl + TiCl_3 + \tfrac{1}{2}(C_6H_5)_2$$

These reactions resemble the Grignard-type reactions of the aryl halides with the salts of the transition metals in which formation of unstable organometallic compounds has been postulated.

It should be possible to isolate the initial interaction products, the phenyltitanium derivatives, by decreasing the temperature used in the previous experiments, and the interaction of titanium tetrachloride with diphenylmercury was therefore carried out at 90°. The formation of the characteristic precipitate of the main reaction product, phenylmercury chloride, could then be regarded as evidence of the reaction course. This precipitate was observed, in the absence of oxygen, only after heating the components at 90° for some hours. It should be noted that oxygen initiated the reaction. Under an atmosphere of dry air or oxygen the pearly sheets of phenylmercury chloride were immediately precipitated when titanium tetrachloride was added to a solution of diphenylmercury in benzene, chloroform or carbon tetrachloride at room temperature. In the presence of oxygen, phenol was also isolated together with phenylmercury chloride by hydrolysis of the reaction mixture.

It is known that phenol cannot be obtained from either the starting material, diphenylmercury, or the main product, phenylmercury chloride. Thus the presence of phenol in the reaction products can be explained only by oxidation of the phenyltitanium compound formed at the first step according to the exchange reaction:

$$(C_6H_5)_2Hg + TiCl_4 \longrightarrow C_6H_5HgCl + C_6H_5TiCl_3$$

Experiments carried out on the oxidation of the system $[(C_6H_5)_2Hg + TiCl_4]$ showed that considerable absorption of oxygen took place. Phenol, biphenyl and titanic acid were found in the reaction product after hydrolysis (Table 1). Oxygen was absorbed to a much less extent during the oxidation in the chloroform solution. Phenol, biphenyl and benzene were found in the reaction products; the formation of benzene can be explained by the dehydrogenation of the solvent.

TABLE I

REACTIONS OF DIPHENYLMERCURY WITH $TiCl_4$ AT ROOM TEMPERATURE

	Experiments							
	1	2[a]	3	4	5[b]	6[b]	7[c]	8[d]
Reagents (*mmoles*)								
$(C_6H_5)_2Hg$	8.9	11	22	36.4	18	18	18	18
$TiCl_4$	8.9	11	11	8.9	18	18	18	18
Solvent	C_6H_6	C_6H_6	C_6H_6	C_6H_6	CCl_4	CCl_4	$CHCl_3$	$CHCl_3$
Conditions								
Time (h)	10	9	7	9	12	7	12	7
O_2 absorbed	5.9	—	—	—	10	—	3.6	—
Products (mmoles)								
C_6H_5HgCl	8.6	10	20	31.6	17.5	14	16	14
Biphenyl	1.8	5.0	1.0	1.4	4.2	3.0	1.8	1.8
Phenol	1.9	—	0.6	1.6	2.9	3.3	1.5	—
TiO_2	8.7	9.0	10	8.7	17.8	17.0	15.3	16.0

[a] Expt. was conducted in atmosphere of dry N_2 at 80°.
[b] Chlorobenzene was not found.
[c] 8.2 mmole benzene was found.
[d] Expt. was conducted in atmosphere of dry N_2 at 60°; 7.3 mmole of benzene was found.

In order to investigate the mechanism of the initial decomposition of phenyltitanium trichloride, experiments were carried out on converting it to biphenyl and titanium trichloride at 90° in the absence of oxygen in different solvents such as benzene and carbon tetrachloride or in the excess of titanium tetrachloride. In chloroform solution, phenyltitanium trichloride decomposed with formation of a considerable amount of benzene, and biphenyl was also found. In tetrahydrofuran, the yield of benzene was greater than that of biphenyl.

The results of specially devised experiments have shown that the decomposition of phenyltitanium trichloride in benzene solution labelled with ^{14}C leads to the formation of biphenyl which does not carry the label from the solvent. It seems more probable that biphenyl is formed via the bimolecular disproportionation reaction:

$$2C_6H_5TiCl_3 \longrightarrow (C_6H_5)_2TiCl_2 + TiCl_4$$

$$(C_6H_5)_2TiCl_2 \longrightarrow (C_6H_5)_2 + TiCl_2$$

$$TiCl_2 + TiCl_4 \longrightarrow 2TiCl_3$$

Diphenyltitanium dichloride changes intermolecularly into biphenyl and titanium dichloride, the latter being oxidised by titanium tetrachloride to titanium trichloride. An analogous scheme for the decomposition of the phenylvanadium compounds has already been proposed[7].

By an analogous disproportionation reaction De Vries[8] explained the formation of ethane and methyl chloride in the case of the decomposition of methyltitanium trichloride. There have, however, been some contradictory data published for the mechanism of the decomposition of methyltitanium trichloride. In a recently published article[9], it was shown that methyl radicals of methyltitanium trichloride were fixed on the surface of the metallic mercury specially added to the reaction mixture. Hexachloroethane, methyl chloride and some other products of the homolytical reaction with carbon tetrachloride have also been isolated.

It is quite possible that the biphenyl was produced by the intermolecular decomposition of diphenyltitanium dichloride. Therefore it was of interest to synthesise compounds with two and more phenyl groups per atom of titanium, particularly as such compounds have not yet been described in the literature; only alkyl derivatives of this kind are known.

Using the proportions of the initial components, $(C_6H_5)_2Hg$:$TiCl_4$, of 2:1 or 4:1, about 95% of the theoretical yields of phenylmercury chloride were obtained, but only in tetrahydrofuran solution. The taking-up of all four atoms of chlorine by the phenyl groups did not occur in any other solvent[*].

It should be more convenient to obtain tetraphenyltitanium by the interaction of titanium tetrachloride with phenyllithium[10]. At —80° four moles of phenyllithium react with the etherate of titanium tetrachloride forming yellow-orange sheets of tetraphenyltitanium. That the phenyllithium reacted completely was checked by a special experiment in which solid carbon dioxide was added to the reaction mixture. No benzoic acid was formed.

The presence of the phenyl–titanium bond has been proved by the reaction with the mercuric chloride at —80°:

$$(C_6H_5)_4Ti + 4HgCl_2 \longrightarrow 4C_6H_5HgCl + TiCl_4$$

Phenylmercury chloride was isolated quantitatively.

The formation of tetraphenyltitanium has been confirmed by the reaction with cyclopentadiene. The introduction of the π-bond of the transition metal with the cyclopentadienyl group into the molecule of the organometallic compound strengthens the σ-bond metal–radical. An example of such a compound is dicyclopentadienyldiphenyltitanium having two π-bonded cyclopentadienyl groups forming the sandwich, and two σ-bonded phenyl groups, σ-$(C_6H_5)_2Ti$-π-$(C_5H_5)_2$.[11] This compound is stable under ordinary conditions.

It is possible in this case to replace the phenyl–titanium bond by the more stable cyclopentadienyl–titanium bond. For this purpose the tetraphenyltitanium reaction in ether solution with freshly-distilled cyclopentadiene was carried out at —80°. The ethereal solution became yellow after hydrolysis of the reaction mixture. On removing the solvent, a yellow crystalline substance was separated. It was con-

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[*] Phenylmercury chloride can be isolated quantitatively from diphenylmercury and titanium tetrachloride in the ratio 4:1, in benzene solution in the presence of oxygen.

verted into the stable dicyclopentadienyltitanium dichloride by the action of concentrated hydrochloric acid[12]. After proceeding through the various reaction stages, a 35–40 % yield of $(C_5H_5)_2TiCl_2$, based on the concentration of the initial $TiCl_4$, was obtained:

$$(C_6H_5)_4Ti + 2C_5H_6 \longrightarrow (C_6H_5)_2Ti(C_5H_5)_2 + 2C_6H_6$$

$$(C_6H_5)_2Ti(C_5H_5)_2 + 2HCl \longrightarrow (C_5H_5)_2TiCl_2 + 2C_6H_6$$

Tetraphenyltitanium is thermally unstable. On heating to —10° it decomposes to biphenyl and biphenyltitanium:

$$(C_6H_5)_4Ti \xrightarrow{-10^\circ} (C_6H_5)_2Ti + 2(C_6H_5)_2$$

The latter is more stable thermally but extremely sensitive to oxygen. Oxidation of samples of diphenyltitanium in benzene solution gives 20–30 % yield of biphenyl and 25–27 % of phenol because of the presence of the two phenyl groups. The results of specially conducted experiments on the oxidation of diphenyltitanium in benzene, labelled with ^{14}C, indicated that the biphenyl and phenol produced do not carry the label from the solvent.

It should be possible to obtain more stable diphenyltitanium complexes, and with this aim in view, diphenyltitanium was treated with ammonia. A benzene solution of diphenyltitanium in an ampoule was vacuumed and then saturated with gaseous ammonia. The ampoule was kept under an atmosphere of ammonia for 20 h at room temperature. The black colour of the solution was almost unchanged. The solvent and excess of ammonia were removed *in vacuo* and the dark grey precipitate of the ammoniate dried *in vacuo* at room temperature. In the sealed ampoule it can be kept for a few days without decomposition. On contact with oxygen it is vigorously oxidised with production of heat and changes its colour to yellow. In this case a yield of about 66 % of biphenyl is obtained. Diphenyltitanium ammoniate hydrolyses with liberation of gaseous ammonia; 0.975 mole of ammonia is isolated per g-atom of titanium, which corresponds to the ratio $Ti:NH_3 = 1.025:1$.

$$(C_6H_5)_2Ti + NH_3 \longrightarrow (C_6H_5)_2Ti \cdot NH_3$$

As has already been mentioned above, the formation of benzene was observed when $C_6H_5TiCl_3$ was decomposed in chloroform or tetrahydrofuran. This can be explained by an attack of the phenyl radical on the solvent. A similar reaction took place when diphenyltitanium reacted with chloroform. The reaction proceeded for 4 h at room temperature, the black colour of the solution gradually changing to yellow. 50 mole-% of benzene, 15 mole-% of biphenyl and titanium tetrachloride were found in the reaction products, but no Ti^{2+} or Ti^{3+} derivatives. In this case the phenyl groups, probably in the form of phenyl radicals, dehydrogenate the solvent and titanium abstracts chlorine atoms from the chloroform to form titanium tetrachloride. A small portion of the phenyl radicals is dimerised to biphenyl. Such reactions have often been observed before during the homolytical decomposition of phenyl-organo compounds of other metals.

Our efforts to determine quantitatively the phenyl groups bonded with titanium have occasionally led to other interesting examples of the diphenyltitanium homolytical reaction.

For these experiments we used the reaction with the mercuric chloride which we had used so successfully with the tetraphenyltitanium and phenyltitanium trichloride derivatives. Diphenyltitanium also reacted with mercuric chloride in tetrahydrofuran or ether solution with formation of phenylmercury chloride. After 0.0378 mole of mercuric chloride had been mixed with diphenyltitanium (prepared from 0.0126 mole of titanium tetrachloride and 0.0252 mole of phenyllithium in ether solution) for 2 h at room temperature, 0.0106 mole of phenylmercury chloride was isolated from the reaction products. Metallic mercury and calomel were also found. The amount of phenylmercury chloride, however, was only 42 % of the theoretical quantity based on the quantity of diphenyltitanium used. Attempts to increase the yield of phenylmercury chloride in this reaction by more prolonged heating were unsuccessful. On the contrary this led to a sharp decrease in the amount of the phenylmercury chloride precipitate and after heating the components at about 30° for 10 h, phenylmercury chloride had disappeared entirely from the reaction mixture.

As a result of these findings, the interaction of diphenyltitanium with phenylmercury chloride was investigated. The reaction was carried out in ether solution using the reagents in the ratio $C_6H_5HgCl:(C_6H_5)_2Ti = 2:1$ in the gently boiling solvent for 10–12 h. It was noted that phenylmercury chloride reacted completely under these conditions. A point of special interest was the appearance of a considerable amount of ethylmercury chloride (in 20 % yield based on the concentration of titanium tetrachloride) in the reaction products. Ethylmercury derivatives could only be formed if the diethyl ether took part in the reaction. The mechanism of this process is rather complicated and at present any ideas on this subject can only be hypothetical.

In the interaction of diphenyltitanium with phenylmercury chloride the transition of the phenyl radicals to titanium and oxidation of Ti^{2+} to the higher valency state is assumed to be an initial step of the reaction. In addition, Hg^{2+} can be reduced to calomel or metallic mercury. The unstable organotitanium compounds are apparently decomposed with liberation of the phenyl radical which then dehydrogenates the solvent:

$$C_6H_5^{\bullet} + CH_3CH_2OCH_2CH_3 \longrightarrow C_6H_6 + CH_3{}^{\bullet}CHOCH_2CH_3$$

$$CH_3{}^{\bullet}CHOCH_2CH_3 \longrightarrow CH_3CH_2^{\bullet} + CH_3CHO$$

Kharasch[13] has noted the formation and decomposition of secondary radicals as a result of the dehydrogenation of ethyl ether when organomagnesium compounds were reacted with cobalt chloride.

The ethyl radicals are fixed by the metallic mercury or HgCl (*in statu nascendi*) by formation of ethylmercury chloride. The mechanism of this reaction is still under investigation.

EXPERIMENTAL

Reactions of diphenylmercury with titanium tetrachloride

The reactions of diphenylmercury with titanium tetrachloride were carried out using the components in the ratios 1:1, 2:1 and 4:1 under an atmosphere of nitrogen, air or oxygen in carefully evacuated, sealed ampoules.

Reactions in the absence of oxygen. A mixture of 3.18 g (0.0090 mole) of diphenylmercury and 30 ml of the solvent was placed in each of three ampoules; the reagents were cooled to the temperature of liquid nitrogen and 0.25, 0.50 and 1.00 ml (0.0023, 0.0045, 0.0090 mole) of $TiCl_4$ was added to each ampoule, respectively. The reaction mixture (after the ampoule had been carefully evacuated) was heated at 90° for 6–12 h. Pearly sheets of phenylmercury chloride were precipitated from the solution and violet titanium trichloride was formed. The ampoule was opened, the precipitate filtered off, the solution evaporated and an additional amount of phenylmercury chloride isolated. The filtrate was steam-distilled to isolate biphenyl. Benzene was determined by ultra-violet spectrophotometry.

Reactions in the presence of oxygen. These reactions were carried out in a three-necked flask equipped with a mechanical stirrer, a reflux condenser, a dropping funnel and a gas burette filled with dry oxygen.

To 6.4 g (0.018 mole) of diphenylmercury in 50–150 ml of the solvent was added 2.0 ml (0.018 mole) of titanium tetrachloride with stirring for 1 h at 20°. The abundant precipitate of phenylmercury chloride was collected and the reaction mixture stirred again for a period of 4 h. The absorbed oxygen was measured. The phenylmercury chloride precipitate was filtered off in a stream of dry gas. The amounts of phenylmercury chloride isolated varied from 80–98 % of the theoretical value (Table 1). After the filtration, the solvent was distilled and biphenyl was isolated from the residue by steam distillation. The benzene content was determined by infra-red spectrophotometry and the titanium was determined as titanium dioxide.

Reaction of titanium tetrachloride with phenyllithium

2.0 ml (0.018 mole) of titanium tetrachloride was added dropwise to 15–20 ml of absolute diethyl ether at 0° in a four-necked flask. 0.072 mole of phenyllithium in diethyl ether was added dropwise at −70° over a period of 2 h. Lithium chloride precipitated and orange sheets of tetraphenyltitanium were formed. The reaction mixture was stirred again at the same temperature for 1 h. At this stage of the reaction the mixture was tested for the presence of unreacted phenyllithium by adding solid carbon dioxide to the reaction mixture. No benzoic acid was found.

After the whole amount of phenyllithium had been added, the orange reaction mixture was heated slowly and left at room temperature for 10 h. The colour of the solution and precipitate gradually changed from orange to red, then to dark green and finally to black.

The solvent was distilled *in vacuo* at room temperature and the black precipitate of diphenyltitanium washed several times with petroleum ether to remove biphenyl formed by thermal decomposition of tetraphenyltitanium. The diphenyltitanium was then dissolved in benzene and filtered into ampoule A (Fig. 1). The lithium chloride residue was determined by titration and was found to be equal to 95–98 % of the theoretical value. A 85–90 % yield of biphenyl per mole of tetraphenyltitanium was obtained.

The solvent in the filtered solution in ampoule A was slowly evaporated and the diphenyltitanium precipitate was dried. The ampoule was kept at room temperature. The precipitate in the ampoule was sealed and the small ampoules a and b were filled with it. In this way 1.2–1.3 g of diphenyltitanium (33–35 % of the theoretical) was isolated.

Attempts to carry out an elementary analysis of diphenyltitanium samples were unsuccessful because of the extreme sensitivity of the compound to oxygen. However, in the partially oxidised samples the ratio Ti:C:H corresponded with the formula of diphenyltitanium and was 1:12:10 respectively. A method based upon the thermal decomposition of the substance was used for the analysis. When the diphenyltitanium samples in the sealed ampoule were heated to 200–250° for 6 h, the substance was observed to decompose with formation of biphenyl and metallic titanium as the main products. A yield of about 80 % of biphenyl was isolated. The titanium precipitate was freed from organic products by washing with ether and then titanium was precipitated as the hydroxide, ignited to the oxide and determined by weighing.

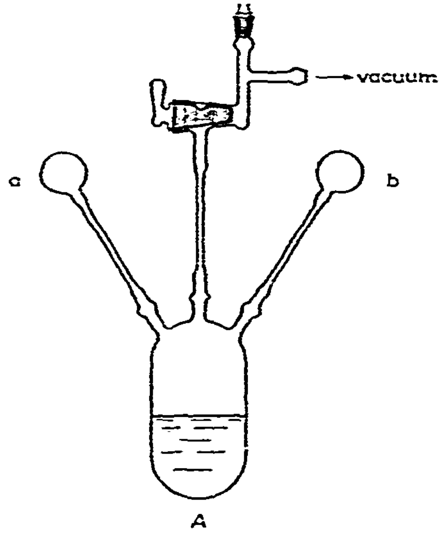

Fig. 1. The ampoule for the separation of diphenyltitanium.

This determination made it possible to calculate the quantity of titanium in the sample of diphenyltitanium taken. 0.0860 g of titanium was found in a sample of 0.3711 g of diphenyltitanium, which is equivalent to 23.2 % of titanium (for $C_{12}H_{10}Ti$, calc. Ti, 23.7 %).

Reaction of tetraphenyltitanium with mercuric chloride

To the orange-coloured ethereal solution of tetraphenyltitanium obtained from 1.5 ml (0.0135 mole) of titanium tetrachloride and 0.054 mole of phenyllithium in 70 ml of ether at —70° was added 14.6 g (0.054 mole) of mercuric chloride in 40 ml of tetrahydrofuran at the same temperature. The colour of the reaction mixture changed from orange to white and an abundant precipitate was formed. The reaction mixture was stirred for 4 h at —70°, then the temperature was gradually increased to room temperature. No further change of colour was observed. The precipitate was filtered off and the filtrate was steam-distilled. Traces of biphenyl were detected. The residue remaining after the steam distillation was filtered and both precipitates were combined together. The weight of the total precipitate was 20.1 g and 16.7 g (0.053 mole) of phenylmercury chloride (m.p. 251°) was extracted from it with hot acetone. A mixed melting point with a pure sample gave no depression.

Reaction of diphenyltitanium with mercuric chloride and phenylmercury chloride

To the black ethereal solution of diphenyltitanium [obtained by the interaction of 1.4 ml (0.0126 mole) of $TiCl_4$ with 0.0252 mole of phenyllithium in 100 ml of ether] at room temperature was added 10.2 g (0.0378 mole) of mercuric chloride dissolved in 30 ml of tetrahydrofuran. The reaction mixture was stirred for 2 h at 20° and then treated in the same manner as in the preceding experiment. 1.22 g (0.008 mole) of biphenyl (m.p. 70°) was isolated by steam distillation; 3.33 g (0.0106 mole) of phenylmercury chloride (m.p. 252°) was extracted with acetone from the residue after distillation; this is equivalent to a yield of 42% based on the two phenyl groups of diphenyltitanium. Both calomel and metallic mercury were found among the reaction products; their amount was considerably increased by more prolonged heating of the reaction mixture.

The interaction of diphenyltitanium (0.018 mole) with phenylmercury chloride (0.036 mole) was carried out by heating the components in ether solution in a ratio 1:2. After boiling the ether solution for 6 h, the phenylmercury chloride had completely reacted. The reaction mixture had the strong odour peculiar to alkyl derivatives of mercury. Calomel and metallic mercury were detected in the reaction products. The ether solution contained benzene which was identified by IR spectra. The ethylmercury derivatives were converted into ethylmercury iodide, m.p. 180°, by the addition of potassium iodide. A mixture with a specially prepared pure sample melted at 182°. 0.004 mole of ethylmercury iodide was thus identified. In addition 1.55 g of a resin-like substance was isolated by steam-distillation, but this was not investigated further.

Reaction of diphenyltitanium with ammonia

The diphenyltitanium solution in benzene in the ampoule A (Fig. 1) was evacuated and then saturated with dry ammonia. When absorption had ceased the solution was allowed to stand for 10 h under an atmosphere of ammonia. The black colour of the solution was almost unchanged. The solvent and excess of ammonia were removed *in vacuo*. The residue consisted of black diphenyltitanium ammoniate. It can be kept for a few days without decomposition in a sealed ampoule in the absence of oxygen. The ammine oxidation proceeds exothermally. During the oxidation the black colour gradually turns to yellow-brown and biphenyl crystals appear on the walls of the vessel. 0.88 g (66%, 0.0057 mole) of biphenyl, m.p. 70°, was obtained from 0.0086 mole of ammine. On the addition of hydrochloric acid (1:1) to the oxidised ammine neither hydrogen nor the colour peculiar to Ti^{3+} could be observed. Ammonia gas was evolved on hydrolysis; 0.0084 mole of hydrochloric acid was used for the neutralisation of the ammonia evolved from 1.90 g of diphenyltitanium ammine. The precipitate, after the separation of a water layer, was washed with ethyl alcohol and ether to remove biphenyl. The insoluble precipitate (0.91 g) was analysed for titanium content and 0.6880 g of titanium dioxide or 0.0086 g-atom of titanium was found. The ratio $Ti:NH_3 = 1.025:1.0$ was established.

Reaction of tetraphenyltitanium with cyclopentadiene

To 2.0 ml (0.018 mole) of titanium tetrachloride in 20 ml of ether at −70° was added 0.072 mole of phenyllithium in 80 ml of ether, dropwise with vigorous stirring. 7.5 g (0.114 mole) of freshly-distilled cyclopentadiene (b.p. 40–42°) in 15 ml of ether was added over a period of 2 h. The reaction mixture was stirred at —70° for 3 h and then allowed to stand at this temperature for 24 h. The mixture was then slowly allowed to attain room temperature and the solvent was removed *in vacuo*. 50 ml of water was added to the black precipitate and the black colour gradually changed to yellow. A small portion of the precipitate was dissolved in ether and 0.2 g of a yellow crystalline substance (m.p. 138°) was isolated from the ether solution by evaporation of the solvent at room temperature. A mixed melting point with a specially prepared dicyclopentadienyldiphenyltitanium gave 140–142°. To the yellow precipitate obtained after hydrolysis was added 50 ml of concentrated hydrochloric acid and the mixture was left to stand for 2 h at room temperature. The precipitate and solution became distinctly red. The reaction mixture was extracted three times with chloroform and the solvent was distilled away. Bright dark-red dicyclopentadienyltitanium dichloride precipitated. It weighed 1.75 g (0.007 mole) and melted at 285° (from toluene). A mixed sample with a specially prepared pure compound gave no depression of the melting point. The ruby mother-liquor, after the removal of the precipitate, $(C_5H_5)_2TiCl_2$, was steam-distilled and 0.5 g (0.0032 mole) of biphenyl, m.p. 69°, was isolated. Titanium dioxide (0.4 g, 0.005 mole) was found in the reaction mixture remaining after the steam distillation.

SUMMARY

Thermally unstable tetraphenyltitanium has been obtained by the interaction of 4 moles of phenyllithium with titanium tetrachloride in benzene solution at —70°. It reacts with mercuric chloride at the same temperature with quantitative formation of phenylmercury chloride. In ether-cyclopentadiene solution, because of the replacement of two phenyl groups, dicyclopentadienyldiphenyltitanium is formed. At —10° tetraphenyltitanium decomposes, 1 mole of biphenyl is formed, and black pyrophoric diphenyltitanium, stable at room temperature and in an inert atmosphere, has been isolated.

The oxidation of diphenyltitanium in benzene labelled with ^{14}C shows that both products of the oxidation, phenol and biphenyl, do not contain the label. A chloroform solution of diphenyltitanium decomposes at room temperature with the formation of benzene, titanium tetrachloride and biphenyl. A black crystalline precipitate of diphenyltitanium ammine has been obtained by the action of ammonia on a solution of diphenyltitanium in benzene. It is easily oxidised in air.

Only about 40% of the theoretical yield of phenylmercury chloride is obtained by the action of mercuric chloride on a solution of diphenyltitanium in ether. Phenylmercury chloride reacts with the organotitanium compound with formation of benzene, metallic mercury, calomel and ethylmercury derivatives. The formation of ethylmercury chloride was the result of a homolytical procedure with the solvent, diethyl ether.

REFERENCES

1 C. Clauss and C. Beerman, *Angew. Chem.*, 71 (1959) 627.
2 C. Beerman and H. Bestian, *Angew. Chem.*, 71 (1959) 618.
3 H. J. Berthold and G. Groh, *Z. Anorg. Allgem. Chem.*, 319 (1963) 230.
4 H. J. Berthold and G. Groh, *Angew. Chem.*, 75 (1963) 576.
5 D. F. Herman and W. K. Nelson, *J. Am. Chem. Soc.*, 74 (1952) 2693; 75 (1953) 3877, 3882.
6 G. A. Razuvaev and I. F. Bogdanov, *J. Gen. Chem. USSR*, 3 (1933) 367.

7 W. L. CARRICK, W. T. REICHLE, F. PENNELLA AND J. J. SMITH, *J. Am. Chem. Soc.*, 82 (1960) 5319.
8 H. DE VRIES, *Rec. Trav. Chim.*, 80 (1961) 866.
9 G. A. RAZUVAEV AND L. M. BOBINOVA, *Dokl. Akad. Nauk SSSR*, 150 (1963) 325.
10 G. A. RAZUVAEV, V. N. LATJAEVA, A. V. MALISHEVA AND G. A. KILJAKOVA, *Dokl. Akad. Nauk SSSR*, 150 (1963) 563.
11 L. SUMMERS, R. H. ULOTH AND A. HOLMES, *J. Am. Chem. Soc.*, 77 (1955) 3604.
12 G. A. RAZUVAEV, V. N. LATJAEVA AND L. I. VISHINSKJA, *J. Gen. Chem. USSR*, 31 (1961) 2667.
13 W. A. WATERS, *The Chemistry of Free Radicals*, Oxford, 1946, p. 211.