Reactions of σ-derivatives of trivalent titanium and vanadium with ketones

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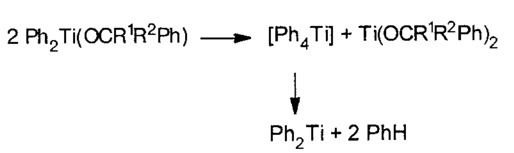
The interaction of Ph_3Ti with a number of ketones (acetone, 2-butanone, 3,3-dimethyl-2-butanone, benzophenone) was studied. The $PhTi(OCR^1R^2Ph)_2$ complexes, where $R^1=R^2=Me$ (**a**), $R^1=Me$, $R^2=Et$ (**b**), $R^1=Me$, $R^2=t\text{-}Bu$ (**c**), and $R^1=R^2=Ph$ (**d**) were isolated in satisfactory yields. These compounds were characterized by ESR and IR spectroscopy and elemental analysis. Their thermal stability was determined by the DTA method. The reaction of Bn_3V with acetone gives $V(OCMe_2Bn)_3$. In analogy with titanium compounds, Bn_4V reacts with acetone at the ratio 1 : 2 to give $Bn_2(OCMe_2Bn)_2$.

Key words: ketones; phenyltitanium dialkoxides; dibenzylvanadium dialkoxide, vanadium trialkoxide

Previously we have studied the interaction of Ph_4Ti and Ph_2Ti with ketones, and some particular features of these reactions were observed.[1,2] However, such reactions are unknown for the σ-derivatives of trivalent titanium and vanadium.

In a continuation of these investigations we have studied the reactions of Ph_3Ti (**1**), Bn_3V (**2**), and Bn_4V (**3**) with acetone (**4**), methylethylketone (**5**), benzophenone (**6**), pinacoline (**7**), dimesytylketone (**8**), and di-*t*-buthylketone (**9**).

It was found that at low temperatures **1** adds to the carbonyl group to give the corresponding diphenyltitanium (III) alkoxides $Ph_2Ti(OCR_2Ph)$ (**10**). The attempts to isolate compounds **10** proved unsuccessful because their disproportionation occurs at room temperature to give the derivatives of bi- and tetravalent titanium:



$$2\,Ph_2Ti(OCR^1R^2Ph) \longrightarrow [Ph_4Ti] + Ti(OCR^1R^2Ph)_2$$
$$[Ph_4Ti] \longrightarrow Ph_2Ti + 2\,PhH$$

Benzene (0.98 mol calculated for 1 mole of starting **1**) was found in the reaction mixture by GC. The bivalent titanium was detected according to a previously described procedure.[3]

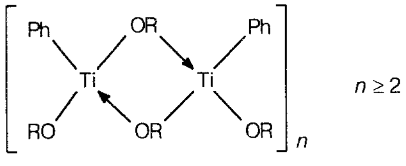
In the reaction of **1** with two equivalents of ketone the outcome of the reaction depends on the size of the radical. (A similar situation was observed earlier for Ph_4Ti.) In a contrast to Ph_4Ti, compound **1** does not react either with the second mole of ketone **8** or with ketone **9**.

The reaction of **1** with two molar equivalents of ketones **4**, **5**, and **6** gives the corresponding phenyl titaniumdialkoxides $PhTi(OCR_2Ph)_2$ (**11a—d**). The acidolysis of the latter gives almost quantitatively tertiary alcohols. Compounds similar to compounds **11** were isolated and characterized by us earlier.[1]

The parameters of the anisotropic ESR spectrum of the d^1-complex $PhTi(OCR_2Ph)_2$, **11a**, obtained for its glassified solution, were found to be $g_i = 1.987$; $g_{\|} = 1.940$.

Analysis of the IR spectra of **11** points to the existence of both terminal (1140, 1190 cm^{-1}) and bridging (910, 990, 1035 cm^{-1}) alkoxy groups.

We presume that complexes **11** are associates of the following composition:



The alkoxides of phenyltitanium (III) are thermally stable compounds. Their thermogramms are characterized by a single irreversible exothermic effect caused by the decomposition of the substance. The decomposition temperatures are given in Table 1. The main volatile product of the decomposition of mixed alkoxides of trivalent titanium **11** is benzene.

The reaction of **1** with three equivalents of ketones **4** and **5** gives rise to the corresponding compounds $Ti(OR)_3$. Crystalline polymeric $Ti(OR)_3$ (R = Me, Et, Ph) have already been described in the literature.[4] All attempts to

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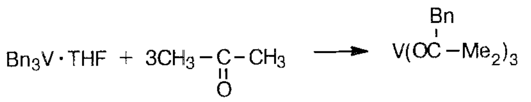
Table 1. Phenyltitanium alkoxides of Ti^{III}

Compound	Yield (%)	T.decomp./°C	Found / Calculated (%) C	H	Ti	Molecular formula
10a	95	110	72.47 72.91	6.70 6.83	12.12 12.15	$C_{24}H_{27}O_2Ti$
10b	93	125	73.47 73.75	7.06 7.32	11.05 11.34	$C_{26}H_{31}O_2Ti$
10c	91	130	74.78 75.15	7.60 8.14	9.45 8.99	$C_{30}H_{39}O_2Ti$
10d	90	165	81.90 82.11	5.19 5.44	7.21 7.45	$C_{44}H_{35}O_2Ti$

obtain other individual $Ti(OR)_3$ were unsuccessful. In our case titanium trialkoxides were not isolated either. This is caused by the predominantly dimeric structure of the alkoxides possessing secondary and tertiary substituents at the alkoxy groups, which leads to easy thermal decomposition. This is evidenced by the formation of $Ti(OR')_4$ (0.75 mol) on the decay of $Ti(OR')_3$ in a quasi-flowing system.

$$2Ti(OR')_3 \longrightarrow Ti(OR')_2 + Ti(OR')_4$$

The reactivity of R_nV (n = 3.4) towards ketones was studied in detail using acetone as an example. In contrast to titanium compounds, which can add ketone molecules one by one, tribenzylvanadium tetrahydrofuranate reacts with three molar equivalents of **4** even at low temperatures giving vanadium trialkoxide.



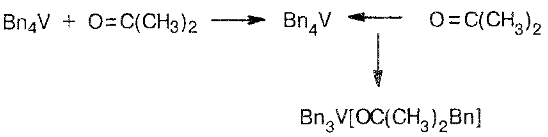
$$Bn_3V\cdot THF + 3CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow V(O\overset{\overset{Bn}{|}}{C}-Me_2)_3$$

For vanadium, more strict spatial restrictions are characteristic. Unlike the titanium compounds, the vanadium derivatives **2** and **3** do not react with ketones 7.

Taking a compound of tetravalent vanadium, **3**, as an example one can follow the step by step addition of the first and second molecule of acetone. After the reaction of **3** with **4** (in a 1:1 ratio), two ESR signals for two vanadium compounds were detected in the reaction solution. The first signal was most distinct in "glassy" diethyl ether and had g = 1.965; it corresponds to tetrabenzylvanadium. The second signal corresponds to vanadium alkoxides of the type $R_2V(OR')_2$, and had the following ESR parameters: g_i = 1.972, A_i^{51V} = 48.5 E.

When the reaction mixture is kept for 1 h at 20 °C, the signal of compound **3** disappears almost completely, and only the signal of the alkoxide remains in the ESR spectrum.

On the basis of these data we assume that at the onset of the reaction a transient complex of compound **3** with the molecule **4** is formed, in which the insertion of a carbonyl group into the vanadium-carbon bond takes place giving rise to compound $Bn_3V[OC(CH_3)_2Bn]$.



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Similarly to other compounds of the type R_3VX alkoxide **12** is unstable and undergoes symmetrization under the conditions of the experiment:

$$2\,R_3V(OCR'_2R) \longrightarrow R_4V + R_2V(OCR'_2R)_2$$

When **3** was reacted with acetone (**4**) in a ratio of 1:2 or 1:4 only the signal of $R_2V(OR')_2$ was detected. At the ratio of starting compounds 1:4, unreacted **4** was identified in the reaction solution (2 moles for 1 mole of starting **3**). After removal of the solvent *in vacuo* $(PhCH_2)_2V(OCMe_2CH_2Ph)_2$ was isolated as a green oily substance. The composition of this product was confirmed by acidolysis, which resulted in toluene (2 moles) and dimesitylcarbinol (2 moles) calculated per 1 mole of the starting compound.

Experimental

IR spectra were recorded on a Specord 75-IR instrument. Analysis of thermal decomposition was carried out using a specially constructed device with vacuumated cells. The rate of sample heating was 5 grad/min. All reactions were carried out in ahydrous, chemically inert solvents under an atmosphere of dry argon. The GC analysis was performed on a Tsvet-104 chromatograph. Yields, decomposition temperatures, and elemental analysis data are given in Table 1. The syntheses of tri- and tetravalent vanadium derivatives were performed according to an earlier procedure.[5]

Synthesis of triphenyltitanium. A solution of diphenylmagnesium (9 mmol) in ether was added to a solution of $TiCl_3\cdot 3THF$ (2.22 g, 6 mmol) in 50 mL of an ether—THF mixture at −70 °C. The mixture wass stirred at this temperature for 4 h, then the temperature was raised to 40 °C and the reaction mass was stirred for an additional 4 h. Then the solution was filtered at 40 °C to remove the precipitate. The content of the Ti^{III} species in the solution thus obtained was 5.5 mmol as determined by a previously described procedure.[3]

Reaction of triphenyltitanium with acetone in a 1:3 ratio. Acetone (0.35 g, 6.0 mmol) was added to compound **1** (2.0 mmol) in ether-THF at −40 °C. At this temperature the mixture was stirred for 4—5 h. Then the temperature was raised to ~20 °C and the mixture was stirred for several additional hours. The solvent was removed *in vacuo*, and a viscousus yellow liquid was distilled from the resinous residue at 105 °C (1 Torr). Yield 0.53 g (45 %). Found (%): C, 73.05; H, 7.14; Ti, 8.02. $C_{36}H_{44}O_4Ti$. Calculated (%): C, 73.46; H, 7.48; Ti, 8.14.

Phenyltitanium-bis(2-phenylbutyl-2-oxide). 2-Butanone 0.29 g (4 mmol) was added to a solution of compound **1** (2 mmol) in ether-THF at −40 °C. The mixture was stirred at this temperature for 4 h, then the temperature was raised to ~20 °C and the reaction mass was stirred for several additional hours. 4.0 molar equivalents of benzene was determined in the resulting solution by GC. The solvents were removed *in vacuo*, and 50 mL of toluene was added. The resulting solution was filtered through a Shott filter No 4. Then the solvent was removed and the residue was dried to give 0.80 g (95 %) of phenyltitanium-bis(2-phenylbutyl-2-oxide) as a dark brown crystalline substance which decomposed at 125 °C.

Reaction of tetrabenzylvanadium with acetone. Acetone 2.32 g (40.0 mmol) was added to a solution of **3** (4.15 g 10.0 mmol) in diethyl ether (100 mL) at −20 °C. The temperature was raised to ~20 °C, and the solvent was removed under reduced pressure. The residue was extracted several times with pentane. Then the pentane was removed *in vacuo* to give 1.91 g (50 %) of dibenzylvanadium-bis-phenylpropyl-2-oxide as a green tar.

Acidolysis of dibenzylvanadium-bis-(2-phenylpropyl-2-oxide). 20 mL of 10 % aqueous sulfuric acid was added to a solution of dibenzylvanadium-bis-(2-phenylpropyl-2-oxide) 1.91 g (3.6 mmol) in 30 mL of hexane at −10 °C. Toluene (0.64 g 7.0 mmol) and dimethylbenzylcarbinol 1.05 g (7.0 mmol) were quantitatively assayed in the organic layer by GC.

Reaction of tribenzylvanadium tetrahydrofuranate with acetone. 7.5 mmol of **4** was added to a THF solution of of **2** (2.5 mmol) at −40 °C. The mixture was stirred for 3 h at this temperature, then the temperature was raised to ~ 20 °C and the mixture was stirred for an additional 2 h. The solvent was removed in a vacuum. The residue was dissolved in hexane and treated with 10 mL of 10 % H_2SO_4. 1.05 g (7.0 mmol) of dimethylbenzylcarbinol was determined in the organic layer by GC.

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