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Abstract

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REACTIONS OF BENZOYL PEROXIDE WITH TITANOCENE DERIVATIVES

In our previous work it was indicated that biscyclopentadienyltitanium, C_2Ti ($C = C_5H_5$), is formed during the thermal decomposition of biscyclopentadienyldiphenyltitanium in alcoholic and benzene solutions. C_2Ti is a highly reactive compound, readily reacting with metal halides and alkyl halides with formation of the stable dichloride of titanocene ([1]). It is especially necessary to note the extreme sensitivity of C_2Ti to atmospheric oxygen.

It therefore seemed of interest to us to trace the interaction of biscyclopentadienyltitanium with acyl peroxides, which readily cleave the O—O bond and are donors of acyloxy radicals.

The action of benzoyl peroxide on sandwich compounds has been described only in one example, the reaction with ferrocene. Under comparatively mild conditions (in benzene solution at 78°) complete destruction of the sandwich structure occurs, with formation of iron tribenzoate. The cyclopentadienyl groups evidently polymerize to a high-molecular compound ([2]).

In our case, in the interaction of benzoyl peroxide with C_2Ti in the cold in benzene or isopropyl alcohol solution, decomposition of the titanocene group did not occur. An instantaneous change in the color of the solution from dark green to bright yellow was observed; CO_2 was not evolved during the reaction. The yellow crystalline product obtained in an atmosphere of dry nitrogen was the expected biscyclopentadienyltitanium dibenzoate:

$$C_2Ti + (C_6H_5COO)_2 \rightarrow C_2Ti(OCOC_6H_5)_2.$$

For identification of the previously undescribed $C_2Ti(OCOC_6H_5)_2$, a counter synthesis was carried out from titanocene dichloride and silver benzoate:

$$C_2TiCl_2 + 2C_6H_5COOAg \rightarrow C_2Ti(OCOC_6H_5)_2 + 2AgCl.$$

The biscyclopentadienyltitanium dibenzoate thus obtained was characterized by elemental analysis, determination of molecular weight, melting point, and

content of benzoate groups (Table 1). $C_2Ti(OCOC_6H_5)_2$ hydrolyzes extremely readily with decomposition of the molecule of the titanocene salt and formation of cyclopentadiene, the salt of benzoic acid, and titanic acid:

$$C_2Ti(OCOC_6H_5)_2 + 2NaOH + H_2O \rightarrow 2CH + 2C_6H_5COONa + H_2TiO_3.$$

Upon alcoholysis in absolute isopropyl alcohol, cyclopentadiene, acetone, and benzoic acid were detected among the reaction products. In an atmosphere of moist air the molecule of titanocene dibenzoate loses two moles of cyclopentadiene and can be converted into dibenzoxytitanoxide ([3]):

$$C_2Ti(OCOC_6H_5)_2 \xrightarrow{H_2O} 2CH + O—Ti(OCOC_6H_5)_2.$$

The isolated solid infusible product was characterized by elemental analysis, as well as by the content of benzoate groups.

An analogous representative of compounds of the type $_2Ti(OCOR)_2$ was obtained in the example of the reaction of titanocene dichloride with silver acetate:

$$_2TiCl_2 + 2CH_3COOAg \rightarrow {}_2Ti(OCOCH_3)_2 + 2AgCl.$$

The yellow compound formed in this reaction, with m.p. 127-130°, corresponds by elemental analysis to biscyclopentadienyltitanium diacetate.

Alcoholysis of this compound in absolute isopropyl alcohol proceeded with cleavage of the acetate groups and partial formation of cyclopentadiene. A yellow amorphous substance, insoluble in organic solvents, whose structure has not been established, precipitated. Acetone was found in the isopropyl alcohol solution. Hydrolysis with dilute alkali proceeded completely, with formation of cyclopentadiene, acetic acid, and titanic acid.

The preparation of biscyclopentadienyltitanium dibenzoate in the interaction of $_2Ti$ with benzoyl peroxide shows that, in contrast to ferrocene, the structure of titanocene remains unchanged under the reaction conditions. Therefore it seemed of interest to trace the action of acyl peroxides on organometallic compounds of tetravalent titanium.

For this purpose, the reaction of diphenylbiscyclopentadienyltitanium with benzoyl peroxide was carried out. In this case also, under mild conditions (in isopropyl alcohol solution at room temperature), an interesting displacement of phenyl radicals by the acyloxy groups of the peroxide occurs:

$$_2Ti(C_6H_5)_2 + (C_6H_5COO)_2 + CH_3CH(OH)CH_3 \rightarrow$$

$$\rightarrow {}_2Ti(OCOC_6H_5)_2 + 2C_6H_6 + CH_3COCH_3,$$

with formation of biscyclopentadienyltitanium dibenzoate. The phenyl radicals are converted into benzene by dehydrogenation of the alcohol to acetone.

On comparing the IR spectra of biscyclopentadienyltitanium acetate and benzoate with the initial ${}_2TiCl_2$ and ${}_2Ti(C_6H_5)_2$, the following absorption bands were found (in reciprocal centimeters): ${}_2Ti(C_6H_5)_2$ 448; 459; 606; 690; 720; 770; 822; 886; 930; 990; 1024; 1076; 1286; ${}_2TiCl_2$ 769; 814; 828; 872; 880; 930; 960; 1018; ${}_2Ti(OCOCH_3)_2$ 404; 520; 600; 624; 822; 865; 1024; ${}_2Ti(OCOC_6H_5)_2$ 720; 830; 865; 1024; 1068; 1132. The absorption bands 822–830 and 1018–1024 cm^{-1}, characteristic of all the compounds, should be assigned to vibrations of the cyclopentadienyl ring. The absorption band 865 cm^{-1}, absent from the spectra of ${}_2Ti(C_6H_5)_2$ and ${}_2TiCl_2$, may be assigned to vibrations of the Ti–O bond.

Experimental Part

All operations for isolation of compounds ${}_2Ti(OCOR)_2$, where R = CH_3, C_6H_5, were carried out in an atmosphere of dry nitrogen.

Reaction of ${}_2Ti$ with benzoyl peroxide. To a strongly cooled benzene or alcohol solution of ${}_2Ti$, obtained beforehand from 1.66 g (0.005 mole) of ${}_2Ti(C_6H_5)_2$ in 10 ml of solvent, a solution of 1.2 g (0.005 mole) of $(C_6H_5COO)_2$ was added dropwise. A sharp change in color from dark green to bright yellow was observed. From the solution, 0.8 g (0.002 mole) of ${}_2Ti(OCOC_6H_5)_2$ with m.p. 185° was isolated. A mixed sample with the substance prepared by independent synthesis melted at 186°.

On hydrolysis of 0.21 g (0.0005 mole) of ${}_2Ti(OCOC_6H_5)_2$ with 0.1 N alkali, 0.12 g (0.001 mole) of benzoic acid with m.p. 120° was isolated.

Reaction of ${}_2Ti(C_6H_5)_2$ with benzoyl peroxide in isopropyl alcohol. 2.5 g (0.0075 mole) of ${}_2Ti(C_6H_5)_2$ and 1.82 g (0.0075 mole) of $(C_6H_5COO)_2$ in 25 ml of isopropyl alcohol were shaken

at room temperature for 50 h. The yellow precipitate of $C_2Ti(OCOC_6H_5)_2$ that formed was filtered off: its weight was 1.5 g, m.p. 188°.

On hydrolysis of 0.2 g (0.0005 mole) of the substance, 0.12 g (0.001 mole) of benzoic acid, m.p. 121°, was isolated.

Benzene was isolated from the solution in the form of *m*-dinitrobenzene (0.3 g), m.p. 90°, and acetone in the form of 2,4-dinitrophenylhydrazone (0.2 g), m.p. 126°.

Preparation of $C_2Ti(OCOC_6H_5)_2$. 3.0 g (0.012 mole) of C_2TiCl_2 and 5.53 g (0.024 mole) of C_6H_5COOAg in 60 ml of benzene were stirred at room temperature for 10–15 min. During this time the color of the solution changed from red to orange-yellow. On dilution of the solution with petroleum ether,

2.0 g (0.0047 mole) of $C_2Ti(OCOC_6H_5)_2$, m.p. 188–192° (with decomposition), precipitated. The substance is readily soluble in benzene, methylene chloride, and chloroform; sparingly soluble in alcohols and petroleum ether. The data of elemental analysis, molecular weight, and hydrolysis for the content of benzoate groups are given in Table 1.

Alcoholysis of $C_2Ti(OCOC_6H_5)_2$. On partial hydrolysis of $C_2Ti(OCOC_6H_5)_2$, a yellow infusible substance was isolated.

Found, %: C 54.70; H 3.59; Ti 16.36

$C_{12}H_{10}TiO_5$. Calculated, %: C 54.90; H 3.26; Ti 15.70

1.0 g of $C_2Ti(OCOC_6H_5)_2$ (0.0024 mole), m.p. 188°, in 53 ml of isopropyl alcohol, under a stream of dry oxygen, was kept for 3 h at 0°. The reaction mixture was distilled. Acetone was identified in the distillate (by formation of the 2,4-dinitrophenylhydrazone) and cyclopentadiene by formation of C_5H_5Tl with thallous reagent. 0.35 g (0.0013 mole) of C_5H_5Tl was isolated.

Preparation of $C_2Ti(OCOCH_3)_2$. 2.5 g (0.010 mole) of C_2TiCl_2 and 5.0 g (0.030 mole) of CH_3COOAg in 60 ml of benzene were stirred for 15–20 min at room temperature. Dilution with petroleum ether gave 0.7 g (0.0024 mole) of $C_2Ti(OCOCH_3)_2$, m.p. 127–130° (with decomposition). The substance is readily soluble in benzene, methylene chloride, chloroform, and isopropyl alcohol, and sparingly soluble in petroleum ether. In air it decomposes with liberation of acetic acid. The elemental-analysis data are given in Table 1.

Table 1

Substance	Elemental analysis*, %	Elemental analysis*, %	Elemental analysis*, %	Mol. wt. (cryoscopy)	M.p., °C	Content of acyloxy groups, moles per 1 mole of substance
	C	H	Ti			
$C_2Ti(OCOC_6H_5)_2$	Found 67.7	5.0	11.2	440	188–192with decomp.	2.0
Calculated	68.5	4.8	11.4	420		

Substance	Elemental analysis*, %	Elemental analysis*, %	Elemental analysis*, %	Mol. wt. (cryoscopy)	M.p., °C	Content of acyloxy groups, moles per 1 mole of substance
$C_2Ti(OCOCH_3)_2$	Found 57.3	5.6	16.2		127–130 with decomp.	1.8
Calculated	56.8	5.4	16.2			

* Average values of concordant analytical results are given.

Alcoholysis of $C_2Ti(OCOCH_3)_2$. 0.88 g (0.003 mole) of $C_2Ti(OCOCH_3)_2$ in 20 ml of isopropyl alcohol, at room temperature under a stream of dry nitrogen, was kept for several hours. During this time a yellow infusible precipitate (0.32 g) separated from the solution. Found, %: C 43.47; H 6.36; Ti 27.87.

The substance is insoluble in organic solvents and is destroyed by the action of alkali.

In the solution, 0.005 mole of acetic acid was determined. In addition, 0.12 g of acetone 2,4-dinitrophenylhydrazone, m.p. 126°, and 0.2 g of C_5H_5Tl were isolated.

On hydrolysis of 0.46 g (0.0015 mole) of $L_2Ti(OCOCH_3)_2$ with 0.1 *N* KOH, 0.0027 mole of acetic acid, 0.15 g of H_2TiO_3, and cyclopentadiene were determined.

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Note: Figure translations are in progress. See original paper for figures.