ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 2, pp. 299–302. © Pleiades Publishing, Ltd., 2013.

Original Russian Text © A.S. Gordetsov, S.V. Zimina, V.F. Ur'yash, E.M. Moseeva, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 2, pp. 245–248.

Reaction of Vanadocene and Vanadocene Dichloride with *ortho*-Iodobenzoic Acid

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Received December 13, 2011

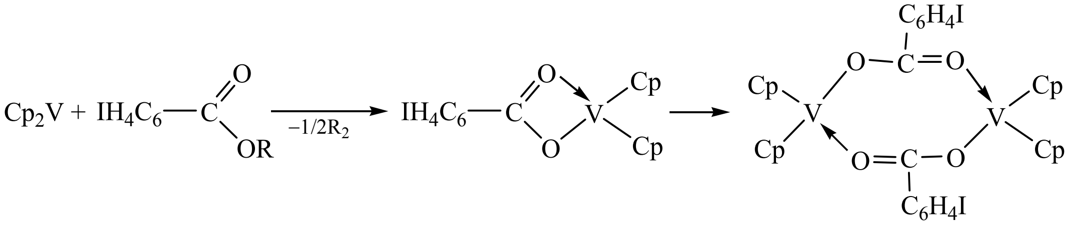
Abstract—At the interaction of bis (η^5-cyclopentadienyl)vanadium with iodobenzoic acid or trimethylsilyl *o*-iodobenzoate in toluene depending on the ratio of the initial reagents bis(η^5-cyclopentadienyl)vanadium(*o*-iodobenzoate) or η^5-cyclopentadienylvanadium-bis-*o*-iodobenzoate were obtained in high yields. The latter was also formed in the reaction of bis(η^5-cyclopentadiene)vanadium dihloride with trimethylsilyl *o*-iodobenzoate.

DOI: 10.1134/S1070363213020114

The reaction of vanadocene (Cp_2V) with carboxylic acids is known to afford depending on the ratio of initial reagents mono- or dicarboxylate derivatives of the type Cp_2VOCOR and $CpV(OCOR)_2$ [1–3]. It was also found that vanadocene was able to break covalent bonds between carbon and halogens [4]. It was therefore appropriate to examine the reaction of vanadocene with compounds containing both a carboxy group and an active carbon–halogen bond, especially because as a result new biologically active organovanadium complexes like the Cp_2VCl_2 could be obtained [5].

Thus, in the reaction of Cp_2V with *o*-iodobenzoic acid (evacuated sealed ampule, toluene, room temperature, 60–72 h) at a ratio of initial reagents 2:1 and 1:1 *o*-iodo-bis(η^5- cyclopentadienyl)vanadium-benzoate (**I**) was obtained in the form of fine black-violet crystals with the yield up to 70% (Scheme 1). In the study of compound **I** by IR spectroscopy and differential thermal analysis (DTA) we found that it dimerizes in the reaction process to afford compound **Id** (Scheme 1). As a by-product hydrogen is produced (proved by GLC).

Scheme 1.

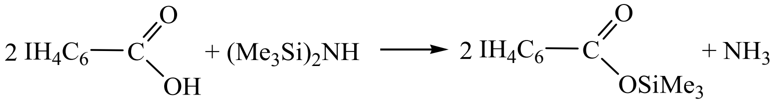


I **Ie**

R = H, Me_3Si.

In the reaction of vanadocene with a specially synthesized trimethylsilyl *o*-iodobenzoate (**II**) (Scheme 2) in the same ratio and conditions iodobenzoate **I** was also obtained, and in solution hexamethyldisilane was detected.

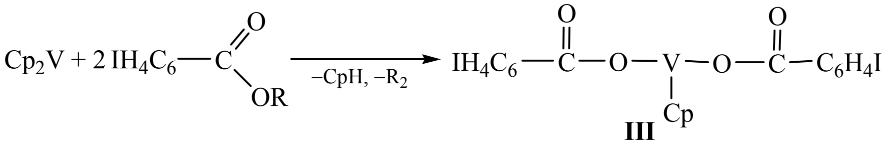
Scheme 2.



The iodobenzoate **II** has not been previously obtained as an individual substance but was only mentioned in one publication as an intermediate in the synthesis of aromatic polyamides [6].

The change in the ratio of *o*-iodobenzoic acid (or iodobenzoate **II**) and vanadocene to 2:1 and the application of more rigid conditions (toluene, 100°C, 48–60 h) led to the formation of η^5-cyclo-pentadienylvanadium bis(*o*-iodobenzoate) **III** as black-violet fine crystalline powder as the main reaction product (yield up to 59%). In the reaction mixtures were also found cyclopentadiene and hydrogen or hexamethyldisilane, respectively.

Scheme 3.



$$Cp_2V + 2\,IH_4C_6{-}C({=}O)OR \xrightarrow[-CpH,\,-R_2]{} IH_4C_6{-}C({=}O){-}O{-}V(Cp){-}O{-}C({=}O){-}C_6H_4I$$

III

R = H, Me_3Si.

Using vanadocene dichloride (Cp_2VCl_2) instead of the vanadocene in the reaction with organosilicon iodobenzoate **II** also resulted in the bisiodobenzoate **III** obtained in the form of greenish-black crystals (reagents ratio 2:1, toluene, 100°C, 48–60 h, yield of 41% .) The ESR method revealed a small admixture of the original Cp_2VCl_2. From the reaction solution cyclopentadiene and trimethylchlorosilane were isolated.

Thus, in contrast to the data [4], vanadocene did not react with the iodine–carbon bonds, obviously owing to the electronic influence of the benzene aromatic ring. This is confirmed by the failure at the attempted reaction of vanadocene with iodobenzene (toluene, 100°C, 48–60 h), which did not result in Cp_2VI_2 or Cp_2VI. Instead a dark green complex compound formed readily soluble in toluene that decomposed to the initial reagents at the attempt to isolate. It should also be noted that the iodine–carbon bond in the studied compounds is inert with respect to hexamethyldisilazane (e.g., see Scheme 2).

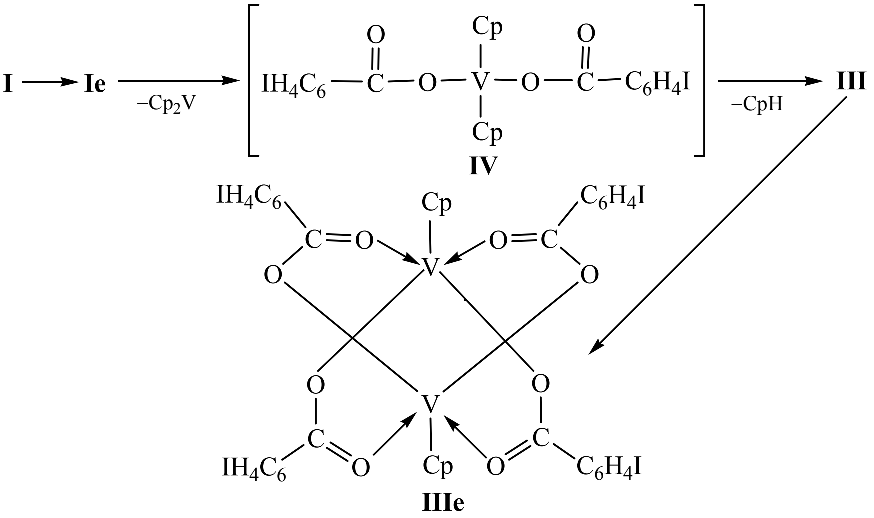
Hydrolysis of the reaction mixtures 1–3 leads to the formation of the initial *o*-iodobenzoic acid as the main product. We failed to detect the presence of any paramagnetic vanadium compounds (except for the residual original vanadocene complexes) by ESR, which indirectly confirms the proposed structure of the products **I**–**III**.

IR spectra of the newly acquired iodobenzoates contain the following main absorption bands, cm^{-1}: compound **Id**, 3060, 1550, 1070, 795, 710 (C_6H_5), 1510 (ν_{as} OCO), 1405 (ν_s OCO), 3020, 1010, 820 (cyclopentadienyl), 590 (iodine–carbon bond); compound **III**, 3050, 1590, 1080, 800, 705 (C_6H_5), 1630 (ν_{as} OCO), 1410 (ν_s OCO), 3005, 1005, 830 (cyclopentadienyl), 580 (iodine–carbon bond) [7]; compound **II**, 3050, 1580, 1450, 1090, 760, 730 (C_6H_5), 1700 (ν_{as} OCO), 1420 (ν_s OCO), 2940, 2890, 1250, 860 (Me_3Si), 605 (iodine–carbon).

As show the IR spectral data of compound **Id**, the band ν_{as} of free carbonyl group is absent, which may be explained by the formation of the dimeric structure with the C=O groups well coordinated with vanadium (Scheme 4). However, the difference between asymmetric and symmetric vibrations of the ester group OCO of compound (**III**) is 215 cm^{-1}, which confirms the presence of the dimeric bridge structure **IIId** by analogy with the organovanadium salicylate and carboxytriazine derivatives [3, 8, 9].

Phase transitions of the synthesized compounds **Id** and **III** were studied by the differential thermal analysis (DTA) in the temperature range from –50 to 350°C. In all thermograms 1–3 in the range 0–50°C there are glass-like transition of G-type [10, 11]. For samples obtained at a ratio of 2:1 of the starting materials (thermograms 2 and 3) about 120°C a significant heat evolution begins with a maximum at 168–174°C, which apparently corresponds to the transition of the intermediate structure **IV** in the structure **III** in the crystalline state (Scheme 4). The transition ends at about 190°C. Almost immediately begins the second exothermic transition with a maximum at 254–255°C, corresponding to the transition of structure **III** to **IIId**. The thermograms of both samples are similar, indicating identity of the crystal structures of the products of synthesis at the specified ratio of the starting materials.

Scheme 4.

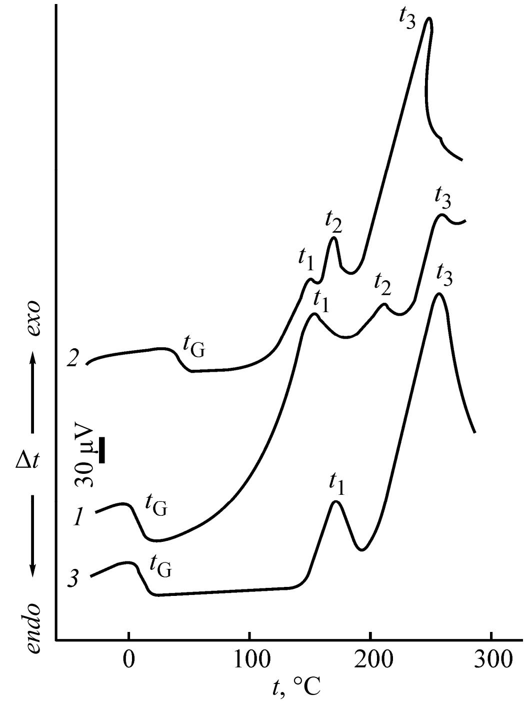


The thermogram (see the figure) shows the results of DTA for the sample obtained at 1:1 ratio of precursors (compound **I**). There is an exothermic transition with a maximum at 155°C, which can be attributed to the conversion of **Id** to **IV**, accompanied by the release of a significant amount of Cp_2V (mp 168°C). In connection with this, the exothermic transition of structure **IV** in the structure **III** is shifted to higher temperatures with a maximum at 206°C. The transition of structure **III** to **IIId** occurs at 261°C, which corresponds to a similar transition in the thermograms 2 and 3. Slight exothermic transition (with maximum at 151°C) in the thermogram 2, apparently, is also associated with the presence in the compound **III** of a small admixture of the compound **Id**, which is absolutely excluded in the synthesis of compound **III** from Cp_2VCl_2 (thermogram 3).

Thus, the DTA data also confirm the proposed scheme of interconversions.

EXPERIMENTAL

IR spectra were registered on spectrophotometers Specord IR-75 and Specord M-80 from a thin layer of a substance in mineral oil or without it between KBr or ZnSe plates. The ESR spectra were recorded on a Bruker EMX instrument with diphenylpicrylhydrazyl (DPPH, g_i = 2.0037) as a reference substance for determining *g*-factor. Chromatographic studies were performed on a Tsvet-69A gas chromatograph with katharometer. The conditions: stationary phase Chromaton N-AW, mobile phase Reoplex-400, column length 2 m. The temperature of the oven 70°C, of katharometer 120°C, of evaporator 150°C. All chemical operations with organovanadium compounds were carried out in a vacuum. DTA was performed in the range 50–350°C on an installation whose construction and method of work were described in [12]. The thermal chamber was filled with helium, quartz was used as a reference. A sample and the reference of ~0.35 g weight were placed in sealed



Thermograms of the compounds: (*1*) **Id**, (*2*) **III**, synthesized from *o*-iodobenzoic acid and Cp_2V, (*3*) **III**, synthesized from the compound **II** and Cp_2VCl_2.

evacuated glass crucibles. The sample temperature and the temperature difference between the sample and the reference was measured with a chromel-copel thermocouple, error 0.5°C. The sample in the thermal chamber was cooled with liquid nitrogen to –190°C, and then heated at a rate of 5°C min^{-1}. The deviation from linearity did not exceed 1%. To test the DTA installation, melting temperature of the reference *n*-heptane and the glass transition temperature of the purified glycerol were determined. The results obtained agree with the literature data for *n*-heptane [13] and glycerol [14] with an accuracy of 0.2°C and 1°C, respectively.

Synthesis of trimethylsilyl *o*-iodobenzoate (II). A mixture of 12.0 g of *o*-iodobenzoic acid and 8.0 g of hexamethyldisilazane (ratio of reagents 2:1) was refluxed in the presence of a catalyst $(NH_4)_2SO_4$ for 11 h till the ammonia release ceased. From the reaction mixture 12.6 g of benzoate **II** was isolated by vacuum distillation (yield 81.4%) as a colorless oil, bp 115–117°C (2 mm Hg), d_4^{20} 1.4629, n_D^{20} 1.5416 [6], MR_D found 68.84, calculated 68.04.

Synthesis of bis(η^5-cyclopentadienyl)vanadim *o*-iodobenzoate (I). *a*. A mixture of 0.8 g of Cp_2V and 1.0 g of *o*-iodobenzoic acid (reagent ratio 1:1) in 30 ml of toluene was kept for 60 h in a sealed evacuated ampule at room temperature. The formed precipitate of black-violet color was washed with solvent, filtered off, and dried in a vacuum. We obtained 1.16 g (70%) of bis(η^5-cyclopentadienyl)vanadium *o*-iodobenzoate **I**. Found, %: C 47.98, H 3.50; I 29.14; V 12.30. $C_{17}H_{14}IO_2V$. Calculated, %: C 47.69, H 3.30; I 29.64; V 11.90. In the filtrate by GLC was determined cyclopentadiene (yield 80%).

b. Similarly, from a mixture of 1.8 g of Cp_2V and 0.95 g of iodobenzoate **II** (2:1 ratio) was isolated 0.77 g (69%) of bis(η^5-cyclopentadienyl)vanadium *o*-iodobenzoate **I**. In the filtrate hexamethyldisilane was determined by GLC.

Synthesis of η^5-cyclopentadienylvanadium bis-*o*-iodobenzoate (III). *a*. A mixture of 0.67 g of Cp_2V and 1.84 g of iodobenzoate **II** (the ratio of reagents 1:2) in 30 ml of toluene was kept for 100 h in an evacuated sealed ampule at room temperature. The precipitate of black-violet color was washed with solvent, filtered off, and dried in a vacuum. We obtained 1.32 g (59%) of η^5-cyclopentadienylvanadium bis-*o*-iodobenzoate **III**. Found, %: C 37.93, H 2.61; V 8.10. $C_{19}H_{13}I_2O_4V$. Calculated, %: C 37.41, H 2.15; V 8.35. In the filtrate hexamethyldisilane and CpH were identified by GLC (yields up to 70%).

b. Similarly, from 0.70 g of Cp_2VCl_2 and 1.80 g of *o*-iodobenzoate **II** (1:2 ratio) under the same conditions were isolated 0.70 g (41%) of η^5-cyclopentadienylvanadium bis-*o*-iodobenzoate **III** as black-green fine crystalline powder. Found, %: C 37.84, H 2.50; V 8.60. $C_{19}H_{13}I_2O_4V$. Calculated, %: C 37.41, H 2.15; V 8.35. In the filtrate Me_3SiCl and CpH were identified by GLC.

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