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LETTERS TO THE EDITOR

Reaction of Vanadocene Dichloride with Organosilicon Derivatives of Cyanuric Acid and Pyrimidine

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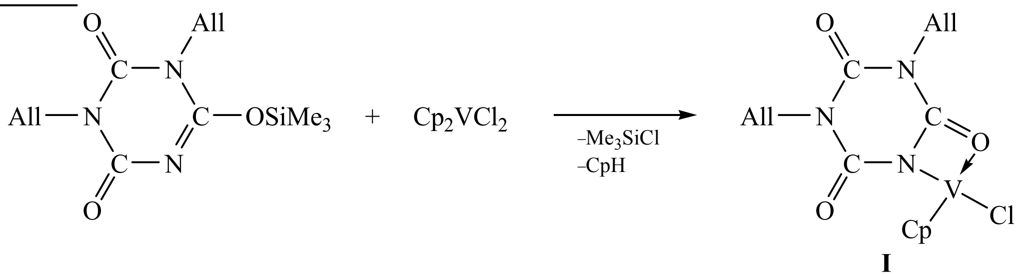
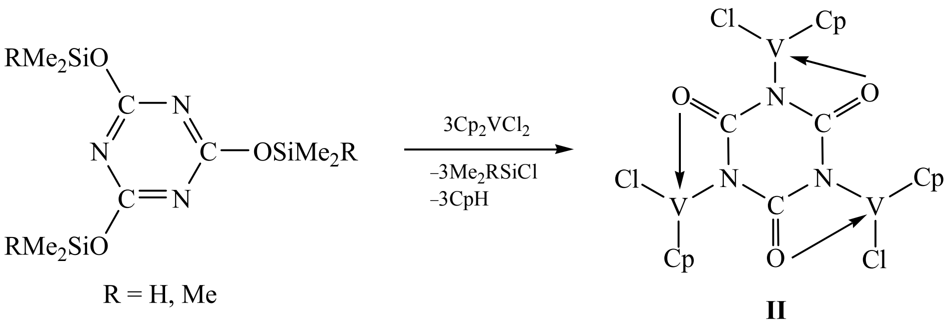
The reaction of vanadocene (Cp_2V) with organosilicon, organogermanium, and organotin derivatives of diallyl isocyanurate (DAIC) is known to give bis(η^5-cyclopentadienylvanadium) diallyl isocyanurate. It was shown by X-ray diffraction analysis that the vanadocene fragment is connected with the triazine ring through the nitrogen atom [1–3]. Vanadocene was also shown to be able to react with triacyl isocyanurates with the formation of tris(η^5-cyclopentadienylvanadium) isocyanurate but does not enter directly the reaction with the corresponding organosilicon, organo-germanium or organotin derivatives of isocyanuric acid [4]. At the same time tris(η^5-cyclopentadienylvanadium) isocyanurate was prepared by the reaction of tris(tributylstannyl) isocyanurate with Cp_2VCl, and bis(η^5-cyclopentadienylvanadium) diallyl isocyanurate was prepared by the reaction of Cp_2VCl and Cp_2V with silver, cesium, rubidium and other salts of DAIC [4, 5]. Therefore, it was of special interest to evaluate relative chemical activity of Cp_2VCl_2, Cp_2VCl, and Cp_2V with respect to the same organoelemental derivatives of *symm*-triazine.

Aiming at this goal we have studied the reaction of trimethylsilyl diallyl isocyanurate with Cp_2VCl_2 (evacuated sealed tube, toluene, 100°C, 60–72 h) with the ratio of reagents equal 2 : 1 and 1 : 1. In both cases, (η^5-cyclopentadienyl)vanadiumchloro diallyl isocyanurate (**I**) was obtained in the yield of more than 80% as a dark-green fine-crystalline powder. Note that the most pure product is formed at the ratio equal 2 : 1, since in this case the product contains practically no admixture of the starting dichloride, and the excess of organosilicon isocyanurate is easily washed out by organic solvents like toluene [Eq. (1)].



(1)

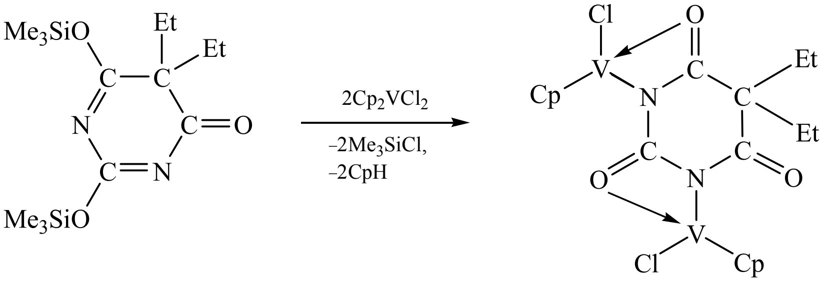
Similarly the reaction of tris(dimethylsilyl) or tris(trimethylsilyl) cyanurate [4] with Cp_2VCl_2 (toluene, 100–110°C, 72 h) with the ratio of the reagents of 1 : 3 affords tris[(η^5-cyclopentadienyl)vanadiumchloro] isocyanurate (**II**) in the yield up to 88% as a green fine-crystalline powder [Eq. (2)].



II

(2)

It turned out that Cp_2VCl_2 is capable of reacting not only with organosilicon derivatives of *symm*-triazine but also with trimethylsilyl-substituted pyrimidines. Thus, the reaction of bis(trimethylsilyl)barbital [6] with Cp_2VCl_2 (evacuated sealed tube, toluene, 100–110°C, 80 h) with the ratio of the reagents of 1 : 2 gives 1,3-bis[(η^5-cyclopentadienyl)vanadiumchloro]-5,5-diethyl-2,4,6-trioxopyrimidine (**III**) in the yield up to 85% as a light-green fine-crystalline powder [Eq. (3)].



III

(3)

As by products of reactions (1)–(3) trimethylchlorosilane and cyclopentadiene are formed (GC). Acid or alkaline hydrolysis of compounds **I–III** leads, as expected, to the formation of diallyl isocyanurate, cyanuric acid or barbital, respectively. This is indicative of the fact that all starting heterocyclic structures are retained in the course of all transformations.

In the IR spectra of all obtained vanadium-containing heterocycles the following proncipal absorption bands were observed (cm^{-1}):

Compound I: 3090, 980, 930 (vibrations of allyl groups), 1710, 1675, 1630 ($\nu_{C=O}$), 1410, 770 (vibrations of isocyanurate ring), 3020, 1010, 805 (cyclopentadienyl) [1];

Compound II: 1770, 1705, 1690 ($\nu_{C=O}$), 1410, 760 (vibrations of isocyanurate ring), 3010, 1020, 1000, 805 (cyclopentadienyl);

Compound III: 1760, 1710, 1680 ($\nu_{C=O}$), 800 ($\nu_{C–N}$ in the ring), 3010, 1005, 810 (cyclopentadienyl).

We failed to detect the presence of any paramagnetic vanadium compounds using the ESR method (except for residual starting Cp_2VCl_2).

Compound **I** was studied by the method of magnetic susceptibility. The effective magnetic moment at 300K was shown to be 2.83 μB, which is typical for vanadium(III), as in the structure we suggested [7].

IR spectra were obtained on spectrophotometers Specord IR-75 and Specord M-80 in thin layer or in mineral oil slurry on KBr or ZnSe windows. ESR spectra were recorded on a Bruker EMX spectrometer with diphenylpicrylhydrazyl as a standard for determination of the *g*-factor ($g_i = 2.0037$). GC analysis was performed on a Tsvet-69A chromatograph, stationary phaseReoplex-400 on Chromaton N-AW, columns 2 m, temperature of columns 70°C, temperature of catharometer 120°C, temperature of injector 150°C. All chemical operations with organovanadium compounds were carried out in a vacuum. Starting organosilicon derivatives of heterocycles were prepared as described in [2, 6].

Synthesis of (η^5-cyclopentadienyl)vanadiumchloro dially isocyanurate (I). A mixture of 0.75 g of trimethylsilyl diallyl isocyanurate, 0.67 g of Cp_2VCl_2 (ratio of reagents 1 : 1) and 25 mL of toluene was heated in an evacuated sealed tube for 72 h. The precipitate formed was washed with toluene, filtered off, and dried in a vacuum to obtain 0.77 g (80%) of compound **I** as a fine-crystalline green powder. Found, %: C 47.09; H 4,28; Cl 10.05; V 14.16. $C_{14}H_{15}N_3O_3ClV$. Calculated, %: C 46.75; H 4.20; Cl 9.86; V 14.16. In the filtrate, cyclopentadiene (80%) and Me_3SiCl were detected by GC analysis.

Synthesis of tris[(η^5-cyclopentadienyl)vanadium-chloro] isocyanurate (II). *a.* A mixture of 0.15 g of tris(trimethylsilyl) cyanurate and 0.32 g of Cp_2VCl_2 (ratio of reagents 1 : 3) in 30 mL of toluene was kept in a sealed evacuated tube for 70 h on a water bath at 100°C. The formed green precipitate was washed with toluene, filtered off, and dried in a vacuum to obtain 0.22 g (88%) of compound **II** as a light-green fine-crystalline powder. Found, %: C 37.84; H 3.00; Cl 18.78; V 25.99. $C_{18}H_{15}N_3O_3Cl_3V_3$. Calculated, %: C 37.24; H 2.60; Cl 18.32; V 26.32. In the filtrate, cyclopentadiene (80%) and Me_3SiCl were detected by GC analysis.

b. Similarly, from the mixture of 0.21 g of tris(dimethylsilyl) cyanurate and 0.52 g of Cp_2VCl_2 in 30 mL of toluene under the same conditions 0.36 g (90%) of isocyanurate **II** was obtained as a green fine-crystalline powder. Found, %: C 37.70; H 2.99; Cl 18.98; V 26.08. In the filtrate, cyclopentadiene and dimethylchlorosilane were detected by GC analysis.

Synthesis of 1,3-bis[(η^5-cyclopentadienyl)vanadium-chloro]-5,5-diethyl-2,4,6-trioxo-pyrimidine (III). A mixture of 1.15 g of bis(trimethylsilyl)barbital and 1.77 g of Cp_2VCl_2 (ratio of reagents 1 : 2) in 30 mL of toluene was kept for 100 h in a sealed evacuated tube at 100°C. The formed precipitate of bright-green color was washed with toluene, filtered off, and dried in vacuum to obtain 1.45 g (85%) of compound **III**. Found, %: C 44.97; H 4,58; Cl 14.44; V 20.45. $C_{18}H_{20}N_2O_3Cl_2V_2$. Calculated, %: C 44.56; H 4.16; Cl 14.61; V 21.00. In the filtrate, cyclopentadiene and Me_3SiCl were detected by GC analysis (up to 70%).

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