Russian Journal of General Chemistry, Vol. 73, No. 10, 2003, pp. 1557–1560. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 10, 2003, pp. 1650–1653.

Reaction of Phenylurea and *N*-Trimethylsilyl-*N*'-phenylurea with Vanadocene and *N*-Bromosuccinimide

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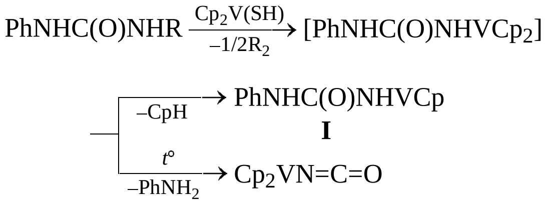
Received March 12, 2002

Abstract—Phenylurea and *N*-trimethylsilyl-*N*'-phenylurea react with vanadocene (Cp_2V) in toluene to give *N*-(η^5-cyclopentadienyl)vanadio-*N*'-phenylurea as a major product and $Cp_2VN{=}C{=}O$ and aniline as by-products. The reaction of *N*-trimethylsilyl-*N*'-phenylurea with *N*-bromosuccinimide in THF produces, instead of expected *N*-phenylureidosuccinimide and bromotrimethylsilane, succinimide and *N*-(*p*-bromophenyl)-*N*-trimethylsilylurea which hydrolyzes to form (*p*-bromophenyl)urea.

Proceeding with research into the synthesis and chemical properties of new biologically and catalytically active organoelement derivatives of phenylurea [1–4], we synthesized the first organovanadium derivative, *N*-(η^5-cyclopentadienyl)vanadio-*N*'-phenylurea (**I**). The reaction of Cp_2V with phenylurea (evacuated sealed ampule, toluene, 70–100°C, 48 h, reagent ratio 1 : 1) gave compound **I** as a major product (yield 70%) as greenish-brown fine crystals. By GLC we also detected in the reaction ampule hydrogen and cyclopentadiene.

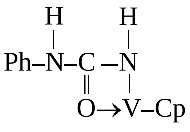
With a silicon-containing analog of phenylurea, *N*-trimethylsilyl-*N*'-phenylurea, the yield of compound **I** (the reaction was performed in THF) increased to 94%. Instead of hydrogen, hexamethyldisilane formed (GLC data).



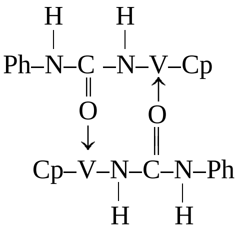
$$PhNHC(O)NHR \xrightarrow[-1/2R_2]{Cp_2V(SH)} [PhNHC(O)NHVCp_2] \begin{cases} \xrightarrow{-CpH} \underset{\mathbf{I}}{PhNHC(O)NHVCp} \\ \xrightarrow[-PhNH_2]{t^\circ} Cp_2VN{=}C{=}O \end{cases} \quad (1)$$

If R = H or Me_3Si and SH is a protic solvent, the IR spectrum of compound **I** contains the following principal absorption bands, cm^{-1}: 3310 (N–H), 1645 (C=O), 1590, 1530, 1500, 830, 740, 710, 590 (Ph), 1010, 1005, 810 (Cp).

The ESR spectra of urea **I** (toluene or THF) or reaction mixtures show no signals of paramagnetic vanadium complexes (including, the parent vanadocene). It thus can be suggested that compound **I** can exist as monomer **A** or dimer **B** with strong vanadium–oxygen coordination bonds, like organovanadium sulfo derivatives we obtained previously [5, 6].



A



B

The reaction in more rigid conditions (120°C, more than 70 h) provided, along with the major product, much bis-(η^5-cyclopentadienylvanadio) isocyanate. The amount of the latter increased with increasing reaction time. At the same time, the isocyanate concentration no longer increased when the reaction temperature was raised further (thermolysis began). Unambiguous evidence for isocyanate formation was provided by the observation in the IR spectra of the reaction mixture of the following characteristic absorption bands, cm^{-1}: 2210 (N=C=O), 3100, 1005, 800 (isocyanate Cp) [7]. From the filtrate we isolated aniline.

It should be noted that aniline and organoelement isocyanates ($Bu_3SnN{=}C{=}O$, $Me_3SiN{=}C{=}O$) were earlier found among reaction products of phenylurea with the corresponding tin- and silicon-containing reagents [4].

On contact with air the absorption bands of $Cp_2VN{=}C{=}O$ quickly disappear, whereas the characteristic absorption bands of compound **I** practically do not change their intensity. However, on prolonged

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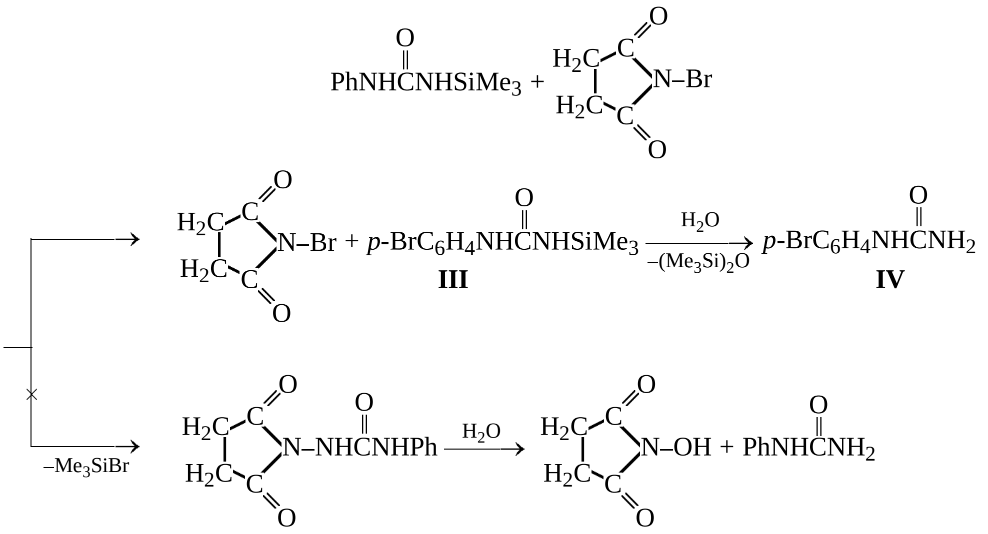
exposure to air (about 2 months) compound **I** is oxidized to phenylureidovanadium oxide (**II**), whereas when boiled in water it undergoes hydrolysis into the parent phenylurea.

$$\mathbf{I} \xrightarrow[-\mathrm{CpH}]{O_2(H_2O)} \underset{\mathbf{II}}{\mathrm{PhNHC(O)NHV{=}O}}$$
$$\xrightarrow{H_2O\ (100°C)} \mathrm{PhNHC(O)NH_2}. \qquad (2)$$

The IR spectra of compound **II** show no Cp absorption bands but acquire a vanadium–oxygen absorption band at 1035 cm^{-1} [6].

Unlike reaction (1), the reaction of *N*-trimethylsilyl-*N'*-phenylurea with *N*-bromosuccinimide gave unexpected results. It was found that the reaction begins already as the reagents are mixed in THF without heating and is accompanied by strong heat release. To complete the reaction, the mixture was refluxed (66°C) for 24 h. The solvent was then removed to leave a thick sticky reddish substance containing, according to the elemental analysis, primarily *N*-(*p*-bromophenyl)-*N'*-trimethylsilylurea (**III**) whose hydrolysis in air in ether resulted in isolation of up to 50% of (*p*-bromophenyl)urea (**IV**) and succinimide (yield 74%).



(3)

The IR spectra of compound **III** contain the following principal absorption bands, cm^{-1}: 3390, 3280, 3180, 1600, 1580 (NH), 1650 (C=O), 3090, 1540, 1060, 1000, 805, 750, 705, 490 (Ph), 1480, 1460 (C–N), 1240, 850 (M_3Si). The lack in the IR spectra of compound **IV** of M_3Si absorption bands provides further evidence for its purity.

The ^1H NMR spectrum of compound **IV** (200 MHz; acetone-d_6), δ, ppm: 5.56 br.s [2H, $H_2NC(O)$], 7.34–7.49 m (*AA'BB'*, 4H, C_6H_4), 8.25 br.s [1H, C(O)NHPh].

In the NMR and IR spectra of the reaction mixtures we found signals assignable to the second product of reaction (3), succinimide [δ, ppm: 2.68 s (4H, CH_2), 9.98 br.s (1H, NH)]. The starting materials were not found.

In the UV spectra of the starting compounds and reaction products we found maxima at 200, 238 and 200, 245 nm, respectively. The band near 200 nm is formed by the σ–σ^* transition in the hydrocarbon skeleton and in not characteristic. The broad band near 240 nm is a superposition of bands formed by n–π^* (C=O) and π–π^* (benzene ring) electronic transitions. Whereas the carbonyl absorption band is only slightly affected by substituents, the benzene band is shifted bathochromically on introduction of substituents into the ring. For the reaction products, the absorption band not only shifts from 238 to 245 nm, but also it gets broader and acquires a shoulder at 255 nm, implying that the reaction products contain bromine in the ring.

According to our findings supported by UV, ^1H NMR, and IR spectral data, as well as DTA, the reaction does not take way characteristic of similar chemical systems and involving formation of trimethylhalosilane and corresponding ureide [3]. This is proved, for example, by the lack of Me_3SiBr among the reaction products (is not detected even with an indicator), of signals of phenylurea and *N*-hydroxysuccinimide in the ^{1}H NMR spectra {reference $PhNHC(O)NH_2$, δ, ppm: 4.68 br.s [2H, $H_2NC(O)$], 6.47 br.s [1H, C(O)NH], 7.1–7.4 m (5H, C_6H_5); reference *N*-hydroxysuccinimide, δ, ppm: 2.56 s (4H, CH_2), 4.65 (1H, NOH)}.

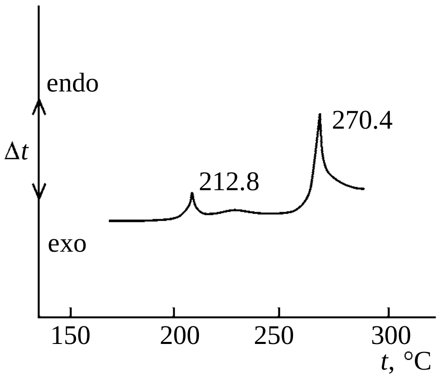
Compound **IV** was also subjected by DTA analysis. The themoanalytical curve (see figure) reveals two endothermic transitions: weak low-temperature at 212.8°C and principal high-temperature at 270.4°C. The first maximum corresponds to the melting point of compound **IV** and the second, to the melting point of *N*,*N*'-bis(*p*-bromophenyl)urea. The DTA data give evidence for the opinion of Kurzer [8] that monoaryl-substituted ureas undergo an extremely fast thermal transformation into diaryl-substituted, which is responsible for ill-defined melting points of these compounds prepared also other methods. Thus, as noted in [8, 9], the reported melting points of compound **IV** vary from 220 to 278°C, which corresponds to mixtures of mono- and *sym*-disubstituted ureas. According to DTA, compound **IV**, as well as its diaryl-substituted analog are present among products of the reaction of *N*-bromosuccinimide with phenylurea.

In conclusion it may be noted that *N*-trimethylsilyl-*N*'-phenylurea fails to react with Ph_3BiCl_2, Ph_4SbCl, tris(β-bromomethyl) isocyanurate, and tris(β,γ-dibromopropyl)isocyanurate under conditions similar to those of the reactions studied or even more rigid conditions (for instance, prolonged heating in an evacuated reactor).

EXPERIMENTAL

All chemical manipulations with organovanadium compounds were performed in evacuated devices or in sealed evacuated two-section ampules with a glass filter. The IR spectra were obtained on Specord IR-75 and Specord M-80 instruments for suspensions in mineral oil between KBr or ZnSe plates. The ESR spectra were recorded on a Bruker-ER-200D-SRC spectrometer at 9.4 GHz. The ^{1}H NMR spectra were measured on a Bruker DPX-200 spectrometer (200 MHz, acetone-d_6). The UV spectra were obtained on a Perkin–Elmer Coleman-575 spectrometer. Chromatography of CpH was performed by the procedure in [5] and of silicon-containing compounds, by the procedure in [7]. *N*-Trimethylsilyl-*N*'-phenylurea was synthesized by the procedure in [2].

Reaction of vanadocene with phenylurea. A mixture of 1.12 g of Cp_2V and 0.84 g of phenylurea was heated in 40 ml of toluene for 48 h at 100°C. The solution changed color from violet characteristic of vanadocene to greenish-brown characteristic of the major reaction product, and a precipitate formed. Filtration followed by washing with hot toluene gave 1.10 g (70%) of *N*-(η^5-cyclopentadienylvanadio)-*N*'-phenylurea (I). Found, %: C 57.45; H 4.93; V 20.35. $C_{12}H_{12}N_2OV$. Calculated, %: C 57.38; H 4.82; V 20.28. Cyclopentadiene and hydrogen were detected by GLC. Upon exposure to air for 2 months compound **I** converted to phenylureidovanadium oxide (**II**), dark brown fine crystals. Found, %: C 42.07; H 3.98; V 24.97. $C_7H_7N_2O_2V$. Calculated, %: C 41.60; H 3.49; V 25.21.



Thermoanalytical curve of (*p*-bromophenyl)urea (**IV**).

Reaction of vanadocene with *N*-trimethylsilyl-*N*'-phenylurea was performed in a similar way with 0.58 g of Cp_2V and 2.08 g of *N*-trimethylsilyl-*N*'-phenylurea in 40 ml of THF to obtain 0.75 g (94%) of compound **I**. Cyclopentadiene and $(Me_3Si)_2$ were detected by gas chromatography in the filtrate.

Reaction of *N*-bromosuccinimide with *N*-trimethylsilyl-*N*'-phenylurea. *N*-Bromosuccinimide, 3.55 g, was added to 100 ml of a stirred solution of 4.15 g of *N*-trimethylsilyl-*N*'-phenylurea in THF. After heat release no longer observed (maximal temperature 50°C), the mixture was heated at 100°C for 4 h. Fine white crystals formed and were filtered off. According to DTA and IR data, it contained 1.47 g (74%) of succinimide. The solvent was removed from the filtrate, and the residue was heated in a vacuum (3–4 mm) at 60°C for 1 h to obtain 3.67 g (64%) of *N*-(*p*-bromophenyl)- *N*'-trimethylsilylurea (**III**), sticky reddish amorphous material. Found, %: C 42,63; H 5.30; Br 25.91. $C_{10}H_{15}BrN_2OSi$. Calculated, %: C 41.82; H 5.26; Br 27.82. Hydrolysis of the resulting material in wet ether gave 2.14 g (50%) of (*p*-bromophenyl)urea, mp 212.8°C {published data [8]: mp 220°C.

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