<sup>1</sup>H NMR spectra were recorded on a Bruker SXP-4-100 spectrometer at 22 °C. The solutions of the components in  $C_6D_6$  were prepared in a countercurrent of argon. The chemical shifts were determined relative to  $C_6D_6$  and recalculated with respect to tetramethylsilane. The assignment of signals in the <sup>1</sup>H NMR spectra was based on literature data.<sup>6,16</sup> ESR spectra were recorded on an EPR-V spectrometer in the X-range.

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## N-( $\eta^{5}$ -Cyclopentadienylvanadium)benzenesulfonamide

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N-( $\eta^5$ -Cyclopentadienylvanadium)benzenesulfonamide has been synthesized for the first time by treating benzenesulfonamide or N-(tributylstannyl)benzenesulfonamide with vanadocene.

**Key words**: benzenesulfonamide; *N*-(tributylstannyl)benzenesulfonamide; vanadocene; N-( $\eta^5$ -cyclopentadienylvanadium)benzenesulfonamide.

In a continuation of the studies on the chemical properties of organic and organometallic sulfo derivatives<sup>1-6</sup> aimed at the preparation of novel efficient selective catalysts for synthesizing urethanes and biologically active compounds we synthesized the hitherto unknown  $N-(\eta^5$ -cyclopentadienylvanadium)benzenesulfonamide (1). Compound 1 was obtained upon treat-

<sup>†</sup> Deceased.

ment of *N*-(tributylstannyl)benzenesulfonamide with  $bis(n^5$ -cyclopentadienyl)vanadium (Cp<sub>2</sub>V)

$$PhSO_2NHR + Cp_2V \xrightarrow{SH} PhSO_2NHVCp + (1/2) R_2 + CpH,$$
<sup>1</sup>

where  $R = Bu_3Sn$  or H; SH is a hydrogen-containing solvent.

Hexabutyldistannane formed in the reaction was determined by iodometric titration (yield ~40 %), and

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 12, pp. 2107–2109, December, 1993. 1066-5285/93/4212-2021 \$12.50 © 1994 Plenum Publishing Corporation cyclopentadiene was identified by GLC. The color of the reaction solution changed from bright-violet (vanadocene) to dark-brown while compound 1 precipitated.

The same color transformations were also observed when  $Cp_2V$  reacted with unsubstituted benzenesulfonamide. In addition to compound 1 (yield ~80 %), the reaction was found to produce cyclopentadiene (GLC data) and hydrogen.

Compound 1 was formed as lustrous black crystals which oxidize in the air to give benzenesulfonamide. The reaction of sulfonamide 1 with HCl in dioxane results only in VOCl<sub>2</sub> (Cp<sub>2</sub>VCl<sub>2</sub> is not formed). This fact, in combination with the fact of cyclopentadiene evolution in the above reactions, proves that product 1 does not incorporate Cp<sub>2</sub>V fragments.

The IR spectrum of compound 1 displays the following main absorption bands,  $v/cm^{-1}$ : 3200 (N–H); 3095, 1075, 1060, 1005, 795, 750, 720, 690, 590 (C–H, Ph, and Cp); 1230, 1120 (SO<sub>2</sub>); 950 (S–N). An exposure of a sample of 1 in the air for 1–2 days results in a decrease in the intensity of the absorption band at 795 cm<sup>-1</sup> (cyclopentadienyl), a low-frequency displacement of the absorption bands of the N–H group (to 3360 and 3265 cm<sup>-1</sup>) and the SO<sub>2</sub> group (v<sub>as</sub> SO<sub>2</sub> from 1230 to 1330 cm<sup>-1</sup>, v<sub>s</sub> SO<sub>2</sub> from 1120 to 1165 cm<sup>-1</sup>). Longer exposures result in almost complete disappearance of absorption bands of 1. Instead, absorption bands of benzenesulfonamide appear (v/cm<sup>-1</sup>): 3360, 3265, 1660, 1565 (N–H); 1330, 1170 (SO<sub>2</sub>); 3050, 1090, 790, 770, 700, 595, 545 (Ph); 910 (S–N).

The sharp decrease in the frequencies of the absorption bands for  $SO_2$  groups in the IR spectra of compound 1 and, to a somewhat lesser extent, in those of N-(tributylstannyl)benzenesulfonamide (1305 and 1140 cm<sup>-1</sup>, respectively) in comparison to the same absorption bands for the original benzenesulfonamide may be explained by the formation of strong coordination bonds between vanadium or tin atoms and oxygen atoms in the monomeric (A) or dimeric (B) structures. It is likely that compound 1 has no signal in the ESR spectrum (in THF) for the same reason.



A DTA study of compound 1, benzenesulfonamide, and its tributylstannyl analog showed that under the conditions of the analysis, benzenesulfonamide (Fig. 1, curve 1) melts at 158 °C, while N-(tributylstan-



**Fig. 1.** Thermograms for benzenesulfonamide (1), N-(tributylstannyl)benzenesulfonamide (2), and N-( $\eta^5$ -cyclopentadienylvanadium)benzenesulfonamide (3).

nyl)benzenesulfonamide (curve 2) melts at 42 °C. This is in good agreement with the literature data<sup>7,8</sup> (m.p. 156 °C and 43-46 °C, respectively). The compounds specified do not decompose at these temperatures. The thermogram for compound 1 displays no anomalies at temperatures below ~270 °C (see Fig. 1, curve 3). This indicates that the sample does not contain the starting compounds or side products. Above 277 °C, the DTA curve deflects upwards due to the onset of melting and drops abruptly at 282 °C due to the decomposition of the compound.

## Experimental

IR spectra were recorded on a Specord 75-IR spectrophotometer for suspensions in vaseline oil placed between KBr plates. The ESR study was performed on a Bruker ER-200D-SRC spectrometer in the X-range at a working frequency of 9.4 GHz. Chromatography was performed on a Tsvet-69A chromatograph with a catharometer as the detector, Chromaton-N-AW as the support, and Reoplex-400 as the stationary phase; the column length was 2 m. The temperatures of the column thermostat, catharometer, and evaporator were 70 °C, 120 °C, and 150 °C, respectively. DTA was performed on an instrument based on PRT-1000M. The temperature measurement error did not exceed 0.7 %. The heating rate was 5 (or 10) °C/min, and the thermocouple sensitivity was 6.9 mV cm<sup>-1</sup>. All operations were performed in evacuated apparatus or in sealed evacuated two-section tubes equipped with glass filters. The samples for the analyses were prepared in vacuo or in an atmosphere of dry purified argon.

*N*-(Tributylstannyl)benzenesulfonamide was synthesized by a procedure in Ref. 8. Found (%): C, 48.78; H, 7.63; S, 6.94; Sn, 26.41.  $C_{18}H_{33}NO_2SSn$ . Calculated (%): C, 48.45; H, 7.45; S, 7.19; Sn, 26.60. IR, v/cm<sup>-1</sup>: 3235 (N-H); 1305, 1140 (SO<sub>2</sub>) (Refs. 5, 9, 10); 1280, 1235, 1070, 1035, 1000, 960, 880, 870, 675, 590, 560 (Bu<sub>3</sub>Sn) (Ref. 11); 1090, 750, 720, 690, 615 (Ph). *N*-( $\eta^5$ -Cyclopentadienylvanadium)benzenesulfonamide (1). *A*. A mixture of *N*-(tributylstannyl)benzenesulfonamide (1.72 g) and Cp<sub>2</sub>V (0.70 g) (molar reagent ratio 1:1) in toluene (30 mL) was kept for 1 h at 120–125 °C (oil bath) in an evacuated sealed tube. The resulting black precipitate was filtered off and washed with toluene to give 0.6 g of compound 1 (yield 57 %) as very fine lustrous black crystals. Found (%): C, 48.31; H, 4.02; N, 5.22; S, 12.40; V, 19.26. C<sub>11</sub>H<sub>11</sub>NO<sub>2</sub>SV. Calculated (%): C, 48.53; H, 4.07; N, 5.14; S, 11.78; V, 18.71. 0.44 g of (Bu<sub>3</sub>Sn)<sub>2</sub> (yield 39 %) was determined by iodometric titration<sup>12</sup> of the reaction solution. This was also identified by

the reaction with AlCl<sub>3</sub> (cf. Ref. 12). CpH was qualitatively determined by GLC.
B. In a similar way, the reaction of benzenesulfonamide (0.64 g) and Cp<sub>2</sub>V (0.74 g) (molar reagent ratio 1:1, 20-25 °C, 30 days) in toluene (30 mL) afforded 0.91 g of compound 1 (yield 82 %) as a fine lustrous brownish-black powder. CpH in

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identified by mass spectrometry.

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## Tributyl- or tribenzylbismuth—copper diacetate system as an alkylating reagent for alcohols

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Tributyl- and tribenzylbismuth react with aliphatic alcohols in the presence of copper diacetate to give dialkyl ethers, with yields of 0.10-0.25 moles per mole of the organobismuth compound.

Key words: tributyl- and tribenzylbismuth; copper diacetate; dialkyl ethers.

The substitution of a phenyl group for the active hydrogen atom in alcohols or amines by the action of triphenylbismuth in the presence of copper diacetate (molar ratio 1:2) occurs at 50 °C according to the following equation:<sup>1,2</sup>

 $ROH + Ph_{3}Bi + 2 Cu(OAc)_{2} \rightarrow ROPh + PhH +$  $+ PhBi(OAc)_{2} + 2 CuOAc (1)$ 

R = Me, Et, Bu, Pr<sup>i</sup>, cyclo-C<sub>6</sub>H<sub>11</sub>, C<sub>5</sub>H<sub>11</sub><sup>i</sup>