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SOME PROPERTIES OF THE ADDUCT OF BENZENESULFINYL CHLORIDE WITH MYRCENE

Α.	Μ.	Moiseenkov, V. V. Veselovskii,	UDC 541.12.034.2:542.955:
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At high pressure, PhSOC1 reacts with isoprene (Ia) to give Z-chlorosulfoxide (IIa) [1]. The replacement of (Ia) by triene (Ib) leads to the analogous result: at 5 kbar, myrcene forms labile chlorosulfoxide (IIb) whose structure was confirmed by spectral analysis and conversion to stable products. Thus, the PMR spectrum of chloride (IIb) has characteristic signals for the trans- and cis-CH<sub>3</sub> groups of the isopropylidene fragment at  $\delta \sim 1.6$  and 1.7 ppm. The signals for the CH<sub>2</sub>S protons form an AB spectrum with  $J_{AB} = 12$  Hz which coincides with that found for isoprene derivative (IIa) [1].



The acetolysis of chlorosulfoxide (IIb) by KOAc in acetic acid leads to acetate (III). The reduction of (III) by  $LiAlH_4$  gives hydroxysulfide (IV). The hydrolysis of (IV) gives hydroxy derivative (V).

The structures of (III)-(V) were confirmed by their physical data and elemental analysis results. Treatment of hydroxysulfoxide (V) by  $Na/NH_3$  gave geraniol (VI) in about 70% yield. The formation of about 10% nerol may be attributed to the partial isomerization of the trisubstituted C=C bond in the allyl carbanion arising under the Birch reduction conditions.

# EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer in  $CHCl_3$ . The PMR spectra of the solutions in  $CDCl_3$  were taken on a Tesla BS-497 spectrometer at 100 MHz and Bruker WM-250 spectrometer relative to TMS. The mass spectra were taken on a Varian MAT CH-6 spectrometer at 70 eV. The R<sub>f</sub> values were given for Silufol silica gel plates.

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1057

<u>1-Chloro-3-phenylsulfinylmethyl-7-methylocta-2Z,6-diene (IIb).</u> A solution of 1.4 g (8.7 mmoles) PhSOC1 [2] and 1.36 g (10 mmoles) (Ib) in 6 ml CHCl<sub>3</sub> was maintained in a teflon ampul at 5 kbar and 25°C for 4 h and treated with 50 ml ether and 10 ml water. The aqueous layer was neutralized with NaHCO<sub>3</sub> and extracted with ether. The combined organic layer was washed with water, dried over MgSO<sub>4</sub> and evaporated in vacuum. The residue (2.5 g) was subjected to chromatography on 70 g silica gel. Gradient elution from hexane to ether gave 0.75 g (29%) (IIb) as an oil with R<sub>f</sub> 0.56 (3:2 ether-hexane). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 790, 1050, 1090, 1355, 1380, 1445, 1670, 2870-3020. PMR spectrum ( $\delta$ , ppm): 1.56 and 1.67 br. s (6H, CH<sub>3</sub>), 2.1 m (4H, CH<sub>2</sub>), 3.59 (2H, CH<sub>2</sub>S, J<sub>AB</sub> = 12 Hz,  $\Delta\delta$  0.26), 3.9 m (2H, CH<sub>2</sub>Cl), 5.01 br. t (1H, HC<sup>6</sup>, J = 7 Hz), 5.75 br. t (1H, HC<sup>2</sup>, J = 7.5 Hz), 7.6 m (5H, C<sub>6</sub>H<sub>5</sub>).

<u>1-Acetoxy-3-phenylsulfinylmethyl-7-methylocta-22,6-diene (III)</u>. A sample of (IIb) was obtained from 11.1 g (0.069 mole) PhSOC1 and 20 g (0.146 mole) (I) by the above procedure and without further purification was treated with 20 g (0.203 mole) KOAc in 50 ml acetic acid with stirring at 25°C. After 20 h, 10 ml ether and 40 ml hexane were added. The residue was filtered off and washed with ether. The filtrate was evaporated in vacuum and 30 ml CCl<sub>4</sub> was added to the residue. After the removal of an additional amount of salt, the solution was evaporated in vacuum and the oily residue (16 g) was subjected to chromatography on 350 g silica gel. Gradient elution from hexane to ether (up to 50% ether) gave 8.82 g (40% relative to PhSOC1) (III) as an oil with R<sub>f</sub> 0.36 (3:2 ether-hexane). IR spectrum (v, cm<sup>-1</sup>): 790, 1040, 1090, 1240, 1380, 1445, 1730, 2910, 3010. PMR spectrum ( $\delta$ , ppm): 1.52 and 1.60 br.s (6H, CH<sub>3</sub>), 1.95 s (3H, CH<sub>3</sub>CO), 2.0 m (4H, CH<sub>2</sub>), 3.58 (2H, CH<sub>2</sub>S, J<sub>AB</sub> = 12.5 Hz,  $\Delta\delta$  0.22), 4.32 d (2H, CH<sub>2</sub>O, J = 7 Hz), 4.97 br. t (1H, HC<sup>6</sup>, J = 6 Hz), 5.60 br. t (1H, HC<sup>2</sup>, J = 7 Hz), 7.5 m (5H, C<sub>6</sub>H<sub>5</sub>). Found: C, 67.74; H, 7.27; S, 9.90%. Calculated for C<sub>18</sub>H<sub>2</sub>4O<sub>3</sub>S: C, 67.46; H, 7.55; S, 10.00%.

<u>l-Hydroxy-3-phenylthiomethyl-7-methylocta-22,6-diene (IV)</u>. A sample of 0.15 g (3.96 mmoles) LiAlH<sub>4</sub> was added to a solution of 0.98 g (3.06 mmoles) (III) in 15 ml THF with stirring at 10°C under argon. Stirring was continued at 10-25°C for 35 min. The mixture was decomposed with 1:1 Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O-Cellite [3]. The precipitate was filtered off and washed on the filter with ether. The combined filtrate was evaporated in vacuum and the oily residue (0.9 g) was subjected to chromatography on 30 g silica gel. Gradient elution from hexane to ether (up to 30% ether) gave 0.53 g (66%) (IV) as an oil with R<sub>f</sub> 0.40 (1:1 ether-hexane). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1000, 1220, 1375, 1580, 1660, 2850-3020, 3450, 3570, 3610. PMR spectrum ( $\delta$ , ppm): 1.58 and 1.65 br. s (6H, CH<sub>3</sub>), 2.2 m (4H, CH<sub>2</sub>), 3.51 s (2H, CH<sub>2</sub>S), 3.82 d (2H, CH<sub>2</sub>O, J = 7 Hz), 5.1 m (1H, HC<sup>6</sup>), 5.49 br. t (1H, HC<sup>2</sup>, J = 7 Hz), 7.4 m (5H, C<sub>6</sub>H<sub>5</sub>). Found: S, 11.77%; M<sup>+</sup> 262. Calculated for C<sub>16</sub>H<sub>22</sub>OS: S, 12.22%, mol. wt. 262.4.

 $\frac{1-\text{Hydroxy-3-phenylsulfinylmethyl-7-methylocta-22,6-diene (V)}{\text{Mmoles}}. A solution of 2.7 g (8.45 mmoles) (III) and 0.2 ml 50% H_2SO_4 in 15 ml methanol was stirred at 25°C for 20 h, neutralized with NaHCO_3 and treated with 100 ml ether and 10 ml water. The aqueous layer was separated and extracted with ether. The residue (2.4 g) was subjected to chromatography on 80 g silica gel. Gradient elution from hexane to ether gave 1.7 g (72.5%) (V) as an oil with Rf 0.52 (ether). IR spectrum (<math>\nu$ , cm<sup>-1</sup>): 860, 890, 930, 960, 1000, 1040, 1090, 1220, 1380, 1430,1450, 1480, 1520, 1660, 2930, 3020, 3380, 3680. PMR spectrum ( $\delta$ , ppm): 1.56 and 1.66 br. s (6H, CH<sub>3</sub>), 2.0 m (4H, CH<sub>2</sub>), 3.61 (2H, CH<sub>2</sub>S, J<sub>AB</sub> = 13 Hz,  $\Delta\delta$  0.35), 3.9 m (2H, CH<sub>2</sub>O), 5.0 m (1H, HC<sup>6</sup>), 5.89 br. t (1H, HC<sup>2</sup>, J = 8 Hz), 7.6 m (5H, C<sub>6</sub>H<sub>5</sub>). Found: C, 69.0; H, 8.03; S, 11.56%, M<sup>+</sup> 278. Calculated for C<sub>16</sub>H<sub>22</sub>O<sub>2</sub>S: C, 69.03; H, 7.97; S, 11.49%, mol. wt. 278.4.

<u>Geraniol (VI)</u>. A solution of 0.8 g (2.87 mmoles) (V) in 8 ml ether was added to a solution of 0.66 g (28.7 mg-at) Na in 20 ml NH<sub>3</sub> vigorously stirred at  $-70^{\circ}$ C over 5 min. The mixture was stirred for 20 min at  $-70^{\circ}$ C and decomposed by excess NH<sub>4</sub>Cl. Ammonia was evaporated and the residue was treated with 10 ml water and extracted with ether. The usual work-up of the extract gave 0.7 g product which was subjected to chromatography on 20 g silica gel. Gradient elution from hexane to ether (up to 30% ether) gave 0.32 g (72%) (IV) which was identical to an authentic sample as indicated by gas-liquid chromatography and PMR spectroscopy containing about 10% nerol (as indicated by gas-liquid chromatography and PMR spectroscopy).

#### CONCLUSION

The reaction of PhSOC1 with myrcene at high pressure leads to the cis-1,4 addition product.

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# REACTION OF PHENYLBORIC ANHYDRIDE WITH

### HEXAMETHYLCYCLOTRISILAZANE

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The synthesis of borazines, as a rule, is based on the reaction of halogen-containing boron compounds with organic and organosilicon amines [1, 2] and cyclosilazanes [3]. The use of esters of organoboron acids for the synthesis of borazines presupposes their initial conversion to amino derivatives with subsequent heating at 280-295°C [4].

We selected phenylboric anhydride (PBA), which is a relatively stable and readily available anhydride, as the starting compound. A studied was carried out on the reaction of PBA with hexamethylcyclotrisilazane in the presence of 1% KOH, starting at 180°C and raising the temperature gradually over 4 h to 280°C.



Up to 40% triphenylborazine was isolated from the solid products by recrystallization from heptane. Methane, benzene, hexamethylcyclotrisiloxane, and the mixed silazasiloxane ring (I) were found in the liquid and gaseous reaction products.

Thus, this reaction proceeds with cleavage of the B-O and Si-N bonds, such that an oxygen atom in PBA is replaced by an NH group of the silazane with the formation of borazine, siloxane and silazaoxane rings. In addition, a side-reaction occurs, in which a B-C bond is broken, as indicated by the finding of benzene in the reaction products.

# EXPERIMENTAL

A mixture of 2.19 g (0.01 mole) hexamethylcyclotrisilazane, 3.12 g (0.01 mole) PBA and 0.05 g (1%) KOH was heated for 4 h at from 180 to  $280^{\circ}$ C, collecting the liquid and gaseous products. We obtained 65 ml (30 mole %) CH<sub>4</sub> and 0.6 ml of a liquid containing hexamethyl-cyclotrisiloxane, benzene (30 mole %) and mixed silazasiloxane as indicated by gas-liquid chromatography on an LKhM-8MD chromatography using a 3 m × 4 mm column packed with 5% SE-30 on Inertone AW-HMDS with 0.2-0.25 particles using a 30 ml/min helium gas carrier flow rate and katharometer detector. The residue was extracted with benzene. The solvent was removed and the residue was recrystallized from heptane to give 1.2 g (40%) triphenylborazine with mp

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1059