SYNTHESIS OF 3-CARENE THIOXIDES

O. N. Nuretdinova, G. A. Bakaleinik,
and B. A. Arbuzov

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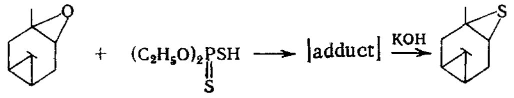
The method of obtaining alkylene thioxides, used by us previously to obtain propylene sulfide [1], proved to be suitable for the synthesis of more complex thioxides. Thus, thioxides were obtained from the 3-carene trans- and cis-oxides, the spatial structure of which we will report later. The thioxide obtained from 3-carene trans-oxide was designated as (I), and that from the cis-oxide as (II).

The synthesis of the thioxides was run in two steps: first the oxide-diethyldithiophosphoric acid adduct was obtained, which without prior purification was then treated with alkali in alcohol.



The chromatographically pure thioxides (I) and (II) were isolated by chromatographing the vacuum-distilled compounds on silica gel.

Thioxides (I) and (II) differ but slightly in the density and refractive index, but they show a large difference in the NMR spectra and optical rotation. They decompose when stored at ~20°, with the formation of sulfur and 3-carene (heating accelerates this process). Here thioxide (I) tends to decompose more than thioxide (II). The reaction of thioxides (I) and (II) with hexaethylphosphorus triamide (HEPTA) also results in the cleavage of sulfur and the formation of 3-carene.

EXPERIMENTAL METHOD

Synthesis of 3-Carene Thioxides.* With stirring, to 2.3 g of 3-carene trans-oxide in 20 ml of ether was added 2.8 g of diethyldithiophosphoric acid in 30 ml of ether. The mixture was refluxed for 15 min, the solvent was removed in vacuo, the adduct was dissolved in 20 ml of alcohol, and to the stirred solution was added 0.84 g of KOH in 30 ml of alcohol. The mixture was heated at 90-95° for 15 min, cooled, 150 ml of petroleum ether (bp 40-60°) was added, and the ether solution was washed with water twice, dried over $CaCl_2$, and distilled. We obtained 1.82 g (70%) of 3-carene thioxide (I) with bp 37-39° (0.1 mm); d_4^{20} 0.9983; n_D^{20} 1.5100; α_D^{27} −37.6° (neat). After purification on a SiO_2 column (petroleum ether equals eluant), thioxide (I) had the following constants: d_4^{20} 0.9951; n_D^{20} 1.5151; α_D^{27} −44.3°. Found: S 18.98%. $C_{10}H_{16}S$. Calculated: S 19.02%. NMR spectrum (in C_6H_6, δ, ppm): 0.82 s, 0.96 s, 1.58 s (protons of CH_3 groups). In a similar manner, from 1.52 g of 3-carene cis-oxide and 1.86 g of diethyldithiophosphoric acid we obtained 1.23 g (73%) of 3-carene thioxide (II) with bp 43-46° (0.15 mm); d_4^{20} 1.0105; n_D^{20} 1.5141; α_D^{27} +10.7°. After purification on a SiO_2 column, thioxide (II) had the constants: d_4^{20} 0.9983; n_D^{20} 1.5175, α_D^{27} +14.5°. Found: S 18.63%. $C_{10}H_{16}S$. Calculated: S 19.02%. NMR spectrum (in C_6H_6, δ, ppm): 0.65 s, 0.95 s, 1.40 s (protons of CH_3 groups).

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*The method is not suitable for obtaining pinene thioxides.

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The separation of sulfur is observed when thioxide (I) is stored for a month at ~20°, while distillation of the filtrate gave 3-carene with bp 51-53° (15 mm); d_4^{20} 0.8631; n_D^{20} 1.4720; α_D^{27} +14.3°. The IR spectrum of the obtained 3-carene was identical with that of an authentic specimen.

Reaction of 3-Carene Thioxides (I) and (II) with HEPTA. The temperature of the reaction mixture rose from 27 to 62° when 2.6 g of thioxide (I) was mixed with 3.8 g of HEPTA. After the temperature had dropped to 27° the mixture was heated at 100° for 15 min and then distilled. We obtained: 1) 1.1 g (52%) of 3-carene with n_D^{20} 1.4710; d_4^{20} 0.8680; α_D^{27} +14.9°; 2) 3.1 g (72%) of hexaethylthiophosphoric triamide with bp 107° (0.1 mm); n_D^{20} 1.5010; $\delta_{^{31}P} = -78$ ppm.

The temperature of the mixture rose from 27 to 42° when 1.35 g of thioxide (II) was mixed with 2 g of HEPTA. We obtained 0.5 g (50%) of 3-carene and 1.5 g (66%) of hexaethylthiophosphoric triamide.

CONCLUSIONS

The 3-carene thioxides were obtained from the 3-carene trans- and cis-oxides, and some of their chemical properties were studied.

LITERATURE CITED

1. O. N. Nuretdinova and B. A. Arbuzov, Izv. Akad. Nauk SSSR, Ser. Khim., 145 (1970).