

SYNTHESIS AND REACTIONS OF 2, 3-
DICHLOROTHIANAPHTHENE-1-OXIDE

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Oxidation of 2, 3-dichlorothianaphthene affords 2, 3-dichlorothianaphthene-1-oxide. This reacts with methanol, ethanol, and piperidine to give 2-chloro-3-methoxy-, 2-chloro-3-ethoxy-, 2, 3-diethoxy-, and 2-chloro-3-piperidinothianaphthene-1-oxide.

Sulfoxides of the thianaphthene series have been little investigated [1]. The present paper describes the oxidation of 2, 3-dichlorothianaphthene (I) to the 1-oxide (II), and the reaction of the latter with methanol, ethanol, and piperidine.

From the structure of the reaction product of methanol with the sulfoxide II, it may be concluded that the methoxy group combines with the carbon atom in the 3-position, followed by elimination of hydrogen chloride to give 2-chloro-3-methoxythianaphthene-1-oxide (III). Reaction of II with ethanol yields, in addition to 2-chloro-3-ethoxythianaphthene-1-oxide (IV), 2, 3-diethoxythianaphthene-1-oxide (V). The formation of V may be explained by the addition of a second molecule of ethanol to IV, followed by dehydrochlorination.

The structures of the compounds obtained were confirmed by their IR spectra. The spectra of all the compounds showed bands at 1033-1080 cm^{-1} due to the SO group, 1561-1605 cm^{-1} (C=C), 3060-3076 cm^{-1} (aromatic C-H). The spectra of III, IV, and V displayed bands due to asymmetric (1268, 1288, and 1289 cm^{-1} , respectively) and symmetric (1015, 1015, and 1018 cm^{-1} , respectively) stretching vibrations of the =C-O-C group. In the spectrum of 2-chloro-3-thianaphthene-1-oxide (VI), a band occurs at 1285 cm^{-1} , due to stretching of the =C-N group, and at 1260 cm^{-1} (C-N).

EXPERIMENTAL

The IR spectra were taken on an IKS-14 spectrophotometer with LiF and NaCl prisms, as pastes in Vaseline oil and as solutions in CCl_4 . Thin-layer chromatography was carried out on grade II alumina, with iodine as developer.

2, 3-Dichlorothianaphthene-1-oxide (II). To a solution of 5 g (0.025 mole) of I [2] in 15 ml of acetic anhydride and 5 ml of acetic acid was added at 30° 3.3 g (0.027 mole) of 28% hydrogen peroxide, and the mixture was heated to 60° and stirred until a spot due to the sulfone appeared on the chromatogram (2-3 h). The mixture was then cooled and diluted with water, and the precipitate was filtered off and recrystallized from alcohol. The mixture was then dissolved in benzene and separated chromatographically on alumina, using benzene as an eluent. There was thus obtained 0.5 g of I, 0.9 g of 2, 3-dichlorothianaphthene-1, 1-dioxide, and 3 g (56%) of II, mp 94-95°, R_f 0.4 (1:1 ether-hexane). Found: C 43.5; H 2.7%. $\text{C}_8\text{H}_4\text{Cl}_2\text{OS}$. Calculated: C 43.83; H 2.8%.

2-Chloro-3-methoxythianaphthene-1-oxide (III). To a solution of 1.1 g (0.005 mole) of II in 20 ml of methanol was added 0.12 g (0.05 mole) of potassium hydroxide, and the mixture was boiled for 1 h. After removal of the solvent, the residue was diluted with water, and the solid was filtered off and recrystallized

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from methanol, then purified as described for II above to give 0.5 g (46%) of III, mp 142-142.5°, R_f 0.75 (ether). Found: C 49.9; H 3.5%. $C_9H_7ClO_2S$. Calculated: C 50.5; H 3.3%.

Oxidation of III with hydrogen peroxide in acetic acid gave 2-chloro-3-methoxythianaphthene-1,1-dioxide, mp 152-153° [1].

2-Chloro-3-ethoxy- (IV) and 2, 3-diethoxythianaphthene-1-oxide (V). To an alcoholic solution of sodium ethoxide, prepared from 0.12 g (0.005 g-atom) of sodium, was added 1.1 g (0.005 mole) of II, and the mixture was boiled for 1 h. After removal of the solvent, the residue was treated with water, and the solid was filtered off and recrystallized from alcohol, giving 0.5 g (42%) of V, mp 98-99°, R_f 0.63 (ether). Found: C 60.2; H 5.7%. $C_{12}H_{14}O_3S$. Calculated: C 60.5; H 5.9%. and 0.1 g (8%) of IV, mp 107-108°, R_f 0.65 (ether-benzene, 1:1). Found: C 52.7; H 3.6%. $C_{10}H_9ClO_2S$. Calculated: C 52.6; H 4.0%.

2-Chloro-3-piperidinothianaphthene-1-oxide (VI). To a solution of 1.4 g (0.0064 mole) of II in 30 ml of 85% alcohol was added 1.4 g (0.019 mole) of piperidine, and the mixture was boiled for 1 h 30 min. After removal of the solvent, the product was filtered off, washed with water, dried, dissolved in benzene, and worked up as described for II. There was obtained 0.25 g (15%) of VI, mp 86.5-87.5°, R_f 0.59 (ether). Found: C 59.5; H 3.4%. $C_{13}H_{14}ClNOS$. Calculated: C 60.1; H 3.6%.

LITERATURE CITED

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