PREPARATIVE SYNTHESIS OF ISOPRENE OXIDE

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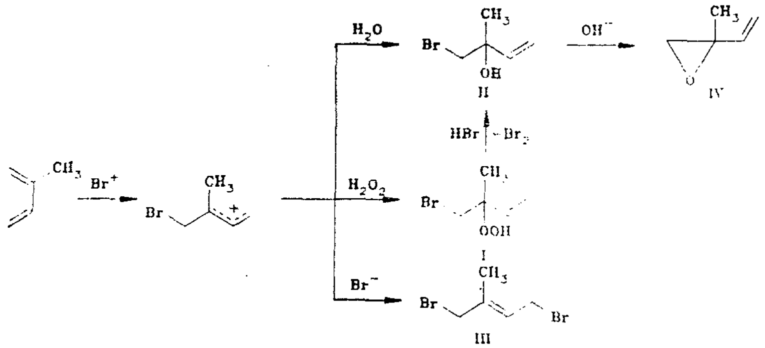
The reaction of isoprene, hydrogen peroxide, and commercial hydrobromic acid gives 1-bromo-2-methyl-3-buten-2-ol, the low-temperature dehydrobromination of which gives isoprene oxide in high yield.

2-Vinyl-2-methyloxirane is a source of isoprenoid synthons in fine organic synthesis. It is usually obtained by oxidation of isoprene by per acids [1], but a more convenient and safer method, including the dehydrohalogenation of the corresponding halohydrins [2], has not been widely used because of the limited availability of the halohydrins.

We have shown that one of such halohydrins, 1-bromo-2-methyl-3-buten-2-ol, can be facilely obtained and converted to isoprene oxide in high yield, using only the readily available compounds isoprene, hydrogen peroxide, and commercial hydrobromic acid.

Apparently, in the presence of H_2O_2, the Br^- anion is oxidized to Br^+, which undergoes addition at the more nucleophilic double bond of isoprene with the formation of an allyl carbocation. The latter is stabilized by addition of the nucleophiles contained in the solution, with, as was shown with model systems [3, 4], the carbocation reacting more preferentially with the more nucleophilic H_2O_2 than with H_2O or HBr. The obtained bromine hydroperoxide I is facilely reduced by HBr to bromohydrin in II and bromine.

It is of interest to note that the attack of the bromide anion occurs not at the tertiary carbon atom, but at the primary carbon atom of the allyl carbocation with the formation of 1,4-dibromo-2-methyl-2-butene (III).



The yield of the mixture of bromohydrin II and dibromide III (16:1 ratio) was 44%. During its dehydrobromination by alkali, oxide IV (89% yield) was obtained, and this oxide was facilely distilled off from dibromide III, which remained unchanged.

EXPERIMENTAL

The proton NMR spectra were recorded with a Perkin—Elmer R-12B instrument (60 MHz) in CCl_4, and the internal standard was HMDS. The reaction products were identified by GLC with an LKhM-80-1 instrument with a katharometer with packed columns with dimensions 3 × 300 and 3 × 2000 mm with Chromaton coated with 15% PEGA and Apiezon L with carrier-gas (helium) velocity 40-60 ml/min at 100-150°C.

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Preparation of a Mixture of 1-Bromo-2-hydroxy-2-methyl-3-butene (II) and 1,4-Dibromo-2-methyl-2-butene (III). To a mixture of 6.8 g (0.1 mole) of isoprene and 24.9 g (0.11 mole) of a 30% H_2O_2 solution, 20.2 g (0.1 mole) of a 40% HBr solution was added with intense stirring for 2 h at a rate such that the temperature of the mixture did not rise above 40°C. After warming ceased, the stirring was continued at the same temperature for 3 h more. The excess H_2O_2 was decomposed with a 10% aqueous Na_2SO_3 solution. The organic layer was separated, the aqueous one was extracted with ether, and it was dried with $MgSO_4$. The ether was removed, and 6.9 g (42%) of bromohydrin II with bp 59-62°C (14 torr), n_D^{20} 1.4952, and d_4^{20} 1.3998 [5] and 0.6 g (2.6%) of dibromide III with bp 95-97°C (14 torr), n_D^{20} 1.5620, and d_4^{20} 1.7943 [6] were recovered by distillation in vacuo. Proton NMR spectrum (CCl_4) of bromohydrin II: 1.34 (3H, singlet, CH_3); 2.69 (1H, singlet, OH); 3.42 (2H, singlet , CH_2Br); 5.14 and 5.36 (2H, double doublet, ^3J = 2 Hz, ^3J = 10.4 Hz, ^3J = 17.3 Hz, $=CH_2$); 5.95 (1H, quartet, ^3J = 10.4 Hz, ^3J = 17.3 Hz, =CH).

2-Vinyl-2-methyloxirane (IV). A. To 4 g (0.1 mole) of sodium hydroxide in 50 ml of ether, 5 g (0.03 mole) of bromohydrin II was added dropwise for 30 min. The mixture warmed to 30°C, at this temperature it was stirred for 3 h and then cooled to 20°C, the precipitate was filtered, the ether was removed, and 2.2 g (89%) of isoprene oxide IV with bp 80-81°C (650 torr), n_D^{20} 1.4260, and d_4^{20} 0.8549 was recovered by distillation [7].

B. The untreated reaction mixture, obtained from 6.8 g (0.1 mole) of isoprene, 24.9 g (0.11 mole) of a 30% H_2O_2 solution, and 20.2 g (0.1 mole) of a 40% HBr solution, was added with stirring to a 50% aqueous NaOH solution (12 g, 0.3 mole). The mixture was stirred for 4 h at 30°C and then extracted with ether, and the extract was washed with acidified water and dried with $MgSO_4$. After removal of the ether by distillation, 3 g (36%) of isoprene oxide IV with bp 80-81°C (650 torr), n_D^{20} 1.4260, d_4^{20} 0.8548 and 0.5 g (2.2%) of dibromide III with bp 93-95°C (13 torr), n_D^{20} 1.5615, and d_4^{20} 1.1794 [6] were recovered by distillation.

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