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Abstract

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INTERACTION OF THE TROPYLIUM ION WITH ETHYLENE OXIDE

In previous papers (^{1,2}) we showed that the tropylium ion reacts with primary, secondary, and tertiary alcohols with the formation of cycloheptatriene. The hydride transfer that occurs in this process, for primary and secondary alcohols, can take place by two mechanisms: I, directly from the alcohol molecule to the tropylium ion,

$$\begin{aligned}&\mathrm{R(R')C(H)OH} + \mathrm{C_7H_7^+Br^-} \longrightarrow \mathrm{R(R')C{=}O} + \mathrm{C_7H_8} + \mathrm{HBr},\\ &\mathrm{R} = \mathrm{H},\ \mathrm{Alk}\end{aligned} \qquad \text{(I)}$$

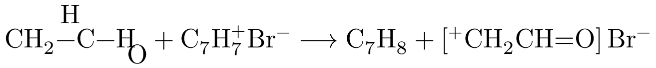
II, through the intermediate formation of an oxonium compound (IIA), which then, eliminating a proton, is converted into an alkyltropyl ether (IIB). Transfer of a hydride ion from this ether to another tropylium ion and the transformations accompanying it constitute the final stage of the reaction (IIB).

$$\begin{aligned}&\mathrm{R_3C{-}OH} + \mathrm{C_7H_7^+Br^-} \rightleftharpoons \mathrm{R_3C{-}OH^+{-}C_7H_7\,Br^-} \qquad \text{(A)}\\ &\mathrm{R_3C{-}OH^+{-}C_7H_7\,Br^-} \longrightarrow \mathrm{R_3C{-}O{-}C_7H_7} + \mathrm{HBr} \qquad \text{(B)}\\ &\mathrm{R_3C{-}O{-}C_7H_7} + \mathrm{C_7H_7^+Br^-} \longrightarrow\\ &\qquad\qquad \mathrm{R_3CBr} + \mathrm{C_7H_6O} + \mathrm{C_7H_8} \qquad \text{(V)}\end{aligned} \qquad \text{(II)}$$

By mechanism I, reactions of a tropylium salt with primary and secondary alcohols can proceed. In this case aldehydes (ketones) and cycloheptatriene should be obtained.

By mechanism II proceeds the reaction between a tropylium salt and a tertiary alcohol. In this case tropone, cycloheptatriene, and an alkyl halide are formed.

In the present work we were interested in the question of whether the tropylium ion is capable of reacting with simple ethers. The experiments performed showed that diisopropyl ether and ethylene oxide react with tropylium bromide, and that cycloheptatriene is formed in the process. We carried out a detailed study of this reaction using ethylene oxide as an example. According to the considerations set forth above, it could be expected that the reaction would proceed either with direct abstraction of a hydride ion from the ethylene oxide molecule (scheme III):



$$\mathrm{CH_2{-}\overset{H}{C}{-}\underset{O}{H} + C_7H_7^{+}Br^{-} \longrightarrow C_7H_8 + [^{+}CH_2CH{=}O]\,Br^{-}} \qquad \text{(III)}$$

either with the intermediate formation of an oxonium compound (IVA), followed by abstraction of a hydride ion from the ether molecule (2) (IVB). It could be

$$\text{(IV)}\quad \mathrm{CH_2-CH_2\ O\ +\ C_7H_7^{+}Br^{-}} \rightleftharpoons \left[\begin{array}{c} \mathrm{H_2C-CH_2} \\ \mathrm{O^{+}} \\ | \\ \mathrm{H-C_7H_7} \end{array}\right]\mathrm{Br^{-}} \quad \text{(A)}$$

$$1 \rightarrow \mathrm{BrCH_2CH_2O-C_7H_7H} \quad (2) \quad \text{(B)} \qquad (1)$$

$$\begin{aligned} &\mathrm{BrCH_2CH_2-O-C_7H_7H + C_7H_7^{+}Br^{-} \rightarrow BrCH_2CH_2Br+} \\ &\quad \mathrm{BrCH_2CH_2Br + H_2O \rightarrow BrCH_2CH_2OH} \\ &\quad \mathrm{+C_7H_6O + C_7H_8} \quad \text{(V)} \end{aligned}$$

\end{equation}

be expected that β-bromoethyltropyl ether (2) would be comparatively stable with respect to the tropylium ion, since the halogen atom, possessing a considerable negative inductive effect, should lower the electron density on the oxygen atom and thereby decrease the hydride mobility of the hydrogen.

It is well known that ethylene oxide readily adds electrophilic agents at oxygen, with subsequent cleavage of the C–O bond. Therefore it seemed likely to us that the reaction between ethylene oxide and tropylium might proceed by mechanism (IV). In this case the reaction should proceed in two stages–the interaction of an ethylene oxide molecule first with one molecule of tropylium bromide, with formation of β-bromoethyltropyl ether (2), and then the interaction of β-bromoethyltropyl ether (2) with a second molecule of tropylium bromide. In carrying out the reaction between ethylene oxide and tropylium bromide, cycloheptatriene and tropone were isolated in approximately equal molecular amounts, with an overall yield of 71%, as well as ethylene bromohydrin.

The formation not only of cycloheptatriene but also of tropone and ethylene bromohydrin indicates that the reaction proceeds by mechanism IV, through formation of β-bromoethyltropyl ether (2), followed by abstraction of a hydride ion from the seven-membered ring (IVB). For complete certainty it was necessary to isolate β-bromoethyltropyl ether. For this purpose we attempted to stop the reaction at the stage of ether formation; to do so, benzene was added to the reaction mixture (to remove the ether from the sphere of interaction with tropylium bromide), and the reagents were added in the reverse order: an aqueous solution of tropylium bromide was added to a solution of ethylene oxide. Under these conditions we did indeed obtain β-bromoethyltropyl ether (2). However, we were unable to stop completely the second stage of the reaction, and we obtained β-bromoethyltropyl ether as a mixture with tropone. After treatment of the mixture with water and subsequent distillation, we succeeded in isolating ether (2) in practically pure form. β-Bromoethyltropyl ether has the following properties*:

a) The IR spectra showed intense absorption bands in the region of 577 cm^{-1} —vibrations of the C—Br bond—and 1121 cm^{-1}—vibrations of the bonds C—O—C. b) The NMR spectra showed peaks characteristic of the protons of a seven-membered ring, and a multiplet of the A_2B_2 type, characteristic of the protons of the CH_2—CH_2 group. c) On interaction of ether (2) with tropylium bromide, cycloheptatriene, tropone, and ethylene bromohydrin are formed, which is in agreement with reaction equation IVB. d) On treatment with a dilute alcoholic solution of chloroplatinic acid, a precipitate of tropylium chloroplatinate is formed. This reaction is analogous to the well-known reaction between ditropylium ether and chloroplatinic acid. e) On interaction with an aqueous solution of silver nitrate, free silver is formed. Ditropylium ether also reduces $AgNO_3$ to silver. By contrast, cycloheptatriene, tropone, and tropylium bromide do not reduce the silver ion to elemental silver under these conditions. This reaction indicates an increased hydride mobility of hydrogen in tropylium ethers, which is characteristic of these substances.

The high hydride mobility of the hydrogen atom in tropylium ethers is probably the reason why the interaction of tropylium salts with alcohols and simple ethers can proceed through the intermediate formation of tropylium ethers.

Experimental Part

Interaction of tropylium bromide with diisopropyl ether. 0.1 g of tropylium bromide was boiled with 5 ml of diisopropyl ether for one hour; then the reaction products boiling up to 30°/8 mm were distilled off. The formation of cycloheptatriene was shown by gas-liquid chromatography.

Interaction of tropylium bromide with ethylene oxide (addition of ethylene oxide to a solution of tropylium bromide).

a) **In aqueous solution.** Ethylene oxide was passed for 5 hours, with vigorous stirring, through a solution of 5.5 g (0.032 mole) of recrystallized tropylium bromide in 100 ml of distilled water. The solution had a neutral reaction and gave no precipitate with chloroplatinic acid. The solution was extracted with benzene. The fraction boiling up to 80° contains ethylene

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* The IR spectra were taken at the Institute of Chemical Physics by L. B. Senyavina. The NMR spectra were

oxide and benzene and contains no halide (Beilstein test). The fraction boiling up to 25°/8 mm contains benzene, cycloheptatriene, and ethylene bromohydrin.

PCl_5 was added to 0.092 part of the benzene fraction. The precipitate was filtered off, decomposed with alcohol, ether was added, and tropylium was precipitated with an alcoholic solution of H_2PtCl_6. The weight of tropylium chloroplatinate was 0.2921 g, which corresponds to a cycloheptatriene yield of 0.98 g (0.011 mole) (67% of theoretical).

Part of the benzene solution was treated in the same way, but the precipitate with phosphorus pentachloride was decomposed with water. After addition of acetylacetone in pyridine to the aqueous solution and recrystallization from petroleum ether, cycloheptatrienylacetylacetone was obtained, m.p. 124.5—125.0°. Lit.: 124.7—125.2° (3). A mixed sample showed no depression.

An alcoholic solution of sulfuric-acid 2,4-dinitrophenylhydrazine was added to part of the benzene solution; no precipitate formation was observed.

The remaining part of the benzene extract was distilled.* 0.3 g (15% of theoretical) of ethylene bromohydrin was obtained. B.p. 24—25°/2 mm, n_D^{20} 1.4937. Lit.: b.p. 48.5°/13 mm; 54.5°/14 mm; n_D^{20} 1.4915 (4). The residue (tropone) was distilled at 73—75°/2 mm, weight 1.3 g (0.012 mole, 75% of theoretical). After redistillation, the tropone had the following constants: b.p. 74—74.5°/2 mm, n_D^{20} 1.6156. Lit.: b.p. 68°/1 mm, n_D^{20} 1.6172 (5). Cycloheptatriene and ethylene bromohydrin were found in the benzene fraction by gas–liquid chromatography.

When the experiment was carried out at 40°, cycloheptatriene (40%) and a mixture of β-bromoethyl tropylium ether with tropone were formed. Isolation under these conditions mixture of tropone with ether, and not pure tropone, makes it possible to assume that increasing the reaction temperature increases the rate of ether formation to a greater extent than the cleavage of a hydride ion from it.

b) **In a water–benzene mixture.** To an aqueous solution of 5.5 g of tropylium bromide, 50 ml of benzene was added, and, with gentle stirring, ethylene oxide was passed through for 5 h (until the tropylium bromide disappeared from the aqueous solution). The aqueous layer, which had a neutral reaction, was extracted with benzene. The benzene fraction was distilled in the same way as in case a), and the yield of cycloheptatriene was determined (35% of theoretical).

On distillation of the residue, a fraction of 2.5 g was obtained, boiling at 78—83°/2 mm, n_D^{20} 1.5802. After repeated distillation the fraction contained 21.1% halide, on the basis of which the content of tropone and β-bromoethyl tropyl ether in the mixture was calculated (58% ether and 42% tropone).

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* In all experiments, distillation of the high-boiling products was carried out in a stream of nitrogen.

Reaction of tropylium bromide with ethylene oxide (addition of tropylium bromide to ethylene oxide). To a solution of 50 g (0.14 mole) of ethylene oxide in 50 ml of water and 30 ml of benzene, with stirring, a solution of 5.8 g (0.034 mole) of tropylium bromide was added over 6 h (at 30—40°), the benzene layer being replaced four times with fresh benzene. The return condenser was cooled with solid CO_2. The subsequent procedure was as in experiments a) and b). The yield of cycloheptatriene was 17%. The residue, 3.6 g, was distilled in the interval 73—80°/2 mm, n_D^{20} 1.5642. The ether content in the mixture with tropone was approximately 70% (from the precipitate of tropylium chloroplatinate).

The obtained fraction was washed repeatedly with distilled water and distilled. B.p. 72—72.5°/1 mm, n_D^{25} 1.5510.

Found, %: C 51.77; H 5.24; Br 37.36
Calculated, %: C 50.25; H 5.16; Br 37.15

Reaction of a mixture of tropone and β-bromoethyl tropyl ether with tropylium bromide. A 1 g portion of the fraction boiling at 73—83°/2 mm in 5 ml of benzene and a solution of 0.8 g of recrystallized tropylium bromide in 8 ml of distilled water were stirred vigorously in a flask connected to a gas burette at room temperature for 10 h. No gas (vinyl bromide) was evolved. The aqueous layer was extracted with benzene. The distilled residue gives no precipitate with a dilute solution of H_2PtCl_6 and does not reduce silver nitrate. By gas-liquid chromatography, in addition to tropone, cycloheptatriene and ethylene bromohydrin were detected in it.

Gas-liquid chromatographic analysis was carried out on a "Khrom-1" instrument at 100° (analysis for cycloheptatriene) and on a "Willy Giede" chromatograph at 120° (analysis for ethylene bromohydrin) on polyethylene glycol-1500 on diatomaceous brick. Tropone was analyzed on a "Willy Giede" chromatograph on liquid cow' s butter at 80—100°.

Using diisopropyl ether and ethylene oxide as examples, it has been shown that the tropylium ion is capable of reacting with simple ethers with the formation of cycloheptatriene. It has been established that the reaction of tropylium bromide with ethylene oxide proceeds in two stages: 1) addition of a molecule of tropylium bromide to a molecule of ethylene oxide; 2) cleavage of a hydride ion from the molecule of the β-bromoethyl tropyl ether formed, under the action of a second molecule of tropylium bromide. As a result of the reaction, cycloheptatriene, tropone, and ethylene bromohydrin are formed.

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Note: Figure translations are in progress. See original paper for figures.