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Abstract

Full Text

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Interaction of Tropylium Bromide with Tertiary Butyl Alcohol

Earlier we showed (1) that benzyl alcohol interacts with the tropylium ion, with formation of cycloheptatriene and benzaldehyde. It turned out that primary and secondary aliphatic alcohols also interact with tropylium to form cycloheptatriene. We believed that the mechanism of this reaction includes abstraction by the tropylium ion of a hydride ion from the carbon atom bonded to the hydroxyl group of the alcohol.

$$C_6H_5CH_2OH + C_7H_7{}^+\,Br^- \longrightarrow C_6H_5CH(OH)^+ + Br^- + C_7H_8$$

$$C_6H_5CH(OH)^+ \longrightarrow C_6H_5CHO + HBr$$

On the basis of these ideas, we assumed that tertiary alcohols should not interact with tropylium salts. However, it turned out that tert-butyl alcohol, already at room temperature, enters into reaction with tropylium salts with formation of cycloheptatriene, tropone, isobutylene, and tert-butyl bromide. Tropylium bromide is not soluble in tert-butyl alcohol; therefore, in order to study the reaction we were compelled to use aqueous alcohol. In this case, cycloheptatriene, tropone, and, at 65°, isobutylene were isolated in the following ratios:

$$(CH_3)_3COH{+}2\,C_7H_7{}^+\,Br^- \longrightarrow C_7H_8{+}C_7H_6O{+}CH_2{=}C(CH_3)_2{+}\text{polymer}{+}2\,HBr$$

$(CH_3)_3COH$	$2\,C_7H_7{}^+\,Br^-$	C_7H_8	C_7H_6O	$CH_2{=}C(CH_3)_2$
1 mol	2 mol	0.7–0.8 mol	0.6 mol	0.8 mol

The absence of tert-butyl bromide is explained by the fact that at 25° it reacts with water, forming tert-butyl alcohol, while at 65° it eliminates HBr with formation of isobutylene, as was proved by special experiments.

Cycloheptatriene was identified by gas-liquid chromatography, and also by converting it into tropylium (^{2}), followed by precipitation as the chloroplatinate and as cycloheptatrienyl acetylacetonate (^{3}).

Tropone was isolated during distillation of the benzene solution treated with soda. The boiling point and refractive index of the tropone coincided with the literature data (^{4}).

Isobutylene was identified by gas-liquid chromatography. The polymer was isolated by filtration of the reaction mixture and reprecipitated from benzene with petroleum ether. Molecular weight 660 conventional units, which corresponds to seven cycloheptatrienyl residues.

To explain this reaction we propose a mechanism based on the formation of an intermediate oxonium complex, which can decompose in three directions:

[reaction scheme]

1) with cleavage of the tropylium ion—a reaction reverse to the reaction of its formation,
2) with cleavage of the tert-butyl cation, which is stabilized either by addition of the bromide anion with formation of $(CH_3)_3CBr$, or by loss of a proton with formation of isobutylene. The second cleavage product, oxycycloheptatriene, under the action of a molecule of tropylium bromide is converted into tropone and cycloheptatriene.
3) With loss of a proton, tert-butyl tropyl ether is obtained, which can interact with tropylium to form tropone, cycloheptatriene, and the tert-butyl cation.

Taking into account the presence of water in the reaction mixture, the formation of the indicated products could seemingly be explained by two independent processes: the interaction of the tropylium ion with water, leading to oxytropylium, which can form cycloheptatriene and tropone (^{5}), and dehydration of the alcohol under the action of the hydrogen bromide being liberated. However, by special experiments we showed that tropylium, neither at 25° (in the presence of small amounts of tert-butyl alcohol) nor on boiling with water, forms chromatographically detectable amounts

cycloheptatriene. tert-Butyl alcohol at 65° under the action of the hydrobromic acid formed as a result of the reaction does not give isobutylene.

Thus, the proposed scheme of the mechanism is also valid for the aqueous alcohol.

Experimental Part

Reaction of tropylium bromide with aqueous tert-butyl alcohol (homogeneous).

4 g (0.0234 mole) of tropylium bromide, recrystallized by Doering’ s method

(6), was dissolved in 15 ml of water, mixed with 41 g (0.554 mole) of tert-butyl alcohol, and heated in a flask with a reflux condenser connected to a gas burette (filled with a saturated solution of sodium chloride) at 65° until gas evolution ceased (30 h). Benzene was added to the reaction liquid; it was washed well with water; the benzene layer was separated, and the aqueous layer was extracted repeatedly with benzene; the combined benzene extracts were dried with magnesium sulfate. A 1/175 portion of the benzene solution was washed with saturated calcium chloride solution and dried with calcium chloride. Then phosphorus pentachloride was added, and the mixture was left overnight. The precipitate that formed was filtered off and decomposed with alcohol. Ether was added to the alcoholic solution, and tropylium hexachloroplatinate was precipitated with an alcoholic solution of chloroplatinic acid. The precipitate was filtered off, washed with ether, dried, and weighed. Weight 0.0133 g, i.e., the yield of cycloheptatriene was 0.72 g (78% of theory).

A portion of the benzene solution was treated in the same way, but the precipitate with phosphorus pentachloride was decomposed with water. To the aqueous solution was added a solution of acetylacetone in pyridine. After recrystallization from petroleum ether, m.p. 125.1-125.6°. A mixed sample with cycloheptatrienylacetylacetone gave no depression. Literature data: 124.7-125.2° (3). The remaining portion of the benzene solution was treated with sodium carbonate solution, washed with water, and distilled. Yield of tropone 0.64 g (61% of theory), b.p. 92-93°/5 mm, n_D^{20} 1.6083. Literature data: b.p. 104-105.5°/10 mm, n_D^{25} 1.6070 (4).

On distilling the benzene solution without preliminary treatment with sodium carbonate, a white crystalline substance was isolated, which in its properties resembled tropylium bromide: it is readily soluble in water and alcohol, insoluble in ether, and sublimes (7).

In the course of the reaction, 420 ml (81% of theory) of a gas that decolorized bromine water was evolved. By gas-liquid chromatography it was shown to be isobutylene.

Reactions were carried out analogously under modified conditions: 1) at 21-30°; 2) with the addition of 11.5 g of glacial acetic acid at 60-67°; 3) with the addition of 11.5 g of glacial acetic acid at 21-30°. In all cases cycloheptatriene and tropone were obtained in similar yields: 70-80% cycloheptatriene, 60% tropone. At 20-30° all the isobutylene dissolved in the alcohol. The presence of isobutylene in the alcohol was shown by gas-liquid chromatography.

Reaction of tropylium bromide with anhydrous tert-butyl alcohol (heterogeneous).

1 g (0.0058 mole) of recrystallized tropylium bromide and 10 g (0.013 mole) of tert-butyl alcohol were stirred vigorously for 60 h at 26° in a flask connected to a gas burette. The precipitate was filtered off, washed with dry carbon tetrachloride, and dried. Weight 0.8 g; it dissolves in alcohol and forms a precipitate with chloroplatinic acid. The solution that did not give a precipitate

with chloroplatinic acid was distilled in vacuo while the receiver was cooled with liquid nitrogen. Me-

The presence in the distillate of cycloheptatriene, tropone, isobutylene, and *tert*-butyl bromide was proved by gas–liquid chromatography.

Reaction of tropylium bromide with water in the presence of a very small amount of *tert*-butyl alcohol. 1.24 g (0.007 mole) of recrystallized tropylium bromide was dissolved in 8 ml of distilled water; 0.09 g (0.0012 mole) of *tert*-butyl alcohol was added to the solution, and it was left to stand at room temperature. After 170 h the reaction mixture was extracted with ether; the ether solution was dried over magnesium sulfate and distilled in vacuo. Cycloheptatriene was not detected in the distillate (gas–liquid chromatography method).

Cycloheptatriene was also not detected when tropylium bromide was boiled with water for 1.5 h. Thus, under our conditions tropylium bromide does not form cycloheptatriene in appreciable amounts.

Hydrolysis of *tert*-butyl bromide. 0.4 g of *tert*-butyl bromide was heated at 28° for 30 h in a solution of 7 ml of water and 16 ml of *tert*-butyl alcohol. After this the solution contained only insignificant traces of *tert*-butyl bromide, as shown by gas–liquid chromatography.

In the reaction of tropylium bromide with *tert*-butyl alcohol, a dark polymeric substance always precipitated (about 15% by weight of the tropylium bromide taken); it was soluble in benzene and was reprecipitated from benzene with petroleum ether. The molecular weight (by the cryoscopic method) was 650–700 conventional units; carbon content, 80%.

Analysis by gas–liquid chromatography was carried out on a Khrom-1 instrument on polyethylene glycol-1500 and polyethylene glycol adipinate on diatomaceous brick, in a stream of nitrogen at 46° for the low-boiling components and at 80–100° for the determination of cycloheptatriene and tropone.

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