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Reaction of Triaryloxonium Salts with Bases *via* Dehydroarenes

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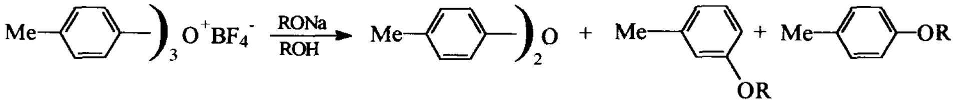
Abstract. Tri-*p*-tolyloxonium tetrafluoroborate reacts with NaOH in water yielding a mixture of *m*- and *p*-cresols (1:1), use of MeOH as solvent results in a mixture of *m*- and *p*-methoxytoluenes (1.5:1). This result proves this reaction to proceed *via* 3,4-dehydrotoluene. © 1997 Elsevier Science Ltd.

Diazotized anthranilic acid and *o*-phenyliodoniobenzoate are well-known sources of dehydrobenzene.[1,2] Formation of dehydroarenes (3-12%) has been also established by thermolysis of diaryliodonium acetates.[3] It is also known that the reaction of diaryliodonium salts with strong bases also proceeds 27-30% *via* dehydroarenes.[4]

It has been shown earlier, that triphenyloxonium salts are extremely stable compounds with very high decomposition temperatures and are very inert towards nucleophiles. They readily undergo decomposition in the presence of bases.[5] However until now these facts could not be explained. We supposed that the unusual inertness of these salts was caused by purely steric reasons: Ph_3O^+ cation possesses a propeller-like structure,[6] and its α-carbon atoms are unavailable for nucleophilic attack. However, reaction of these salts with bases *via* dehydrobenzene should proceed more readily, since the Ph_2O^+ group exhibits a strong σ-electron-withdrawing effect, and *ortho*-protons of phenyl cycles are sterically available.

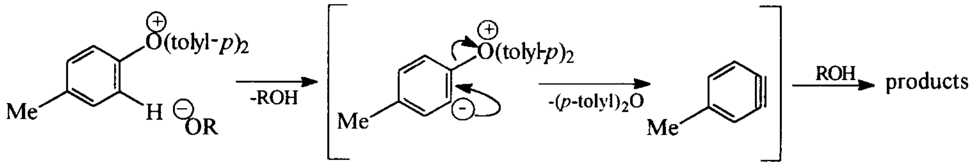
Indeed, in this paper we have shown that the thermolysis of triphenyloxonium acetate prepared *in situ* from the tetrafluoroborate **1** and potassium acetate at 80°C, in benzene gave dehydrobenzene in 95% yield, measured by trapping with tetraphenylcyclopentadienone.[7]

We have also shown that tri-*p*-tolyloxonium tetrafluoroborate **2**[8] reacted with NaOH in water yielding a mixture of *p*- and *m*-cresols (1:1),[9] and with NaOH or with MeONa in MeOH produced a mixture of *p*- and *m*-methoxytoluenes in 1:1.5 ratio. [10] In both cases the conversion was nearly 100%:



R = H 1 : 1
R = Me 1.5 : 1

The obtained results clearly demonstrate that triaryloxonium salts react with bases *via* dehydroarenes.



Reaction products were identified using ^1H and ^{13}C NMR spectroscopy. Isomer ratios in the above reactions were determined according to integral intensities of proton peaks in ^1H NMR spectra.

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7. 0.1 g (0.3 mmol) of **1**, 0.115 g (0.3 mmol) of tetraphenylcyclopentadienone and 0.035 g (0.36 mmol) of freshly fused potassium acetate were stirred in boiling benzene (5 ml) under dry argone for 24 h. Standard work-up[3] gave the 1,2,3,4-tetraphenylnaphtalene (m.p. 201-202°C, cf. ref.[11]) in 95% yield. The compound was detected by the comparison of its mass spectrum ($[M]^+$ 432) with that from the NIST databank.
8. Prepared analogously to [12]. M. p. 234-234.5°C. Found %: C 64.56; H 5.68. $C_{21}H_{21}BF_4O\cdot 0.75H_2O$. Calc.%: C 64.72; H 5.82. ^1H NMR [300 MHz, $CO(CD_3)_2$]: $\delta = 2.42$ (s, 9H, CH_3); 7.53-8.02 (m, 12H, AA'XX' spin system).
9. 0.37 g (1 mmol) of **2**, 2 ml of 5N NaOH (10 mmol) and 2 ml of water were refluxed for 15 h, usual treatment yielded 1:1 mixture of *p*- and *m*-cresols. ^1H NMR [300 MHz, CCl_4/MeCN-d_3 (4:1)]: $\delta = 2.27$ (s, 3H, *p*-CH_3); 2.30 (s, 3H, *m*-CH_3).
10. 0.113 g (0.3 mmol) of **2**, 0.48 ml of 6.25N NaOH (3 mmol) and 4 ml of MeOH were refluxed for 10 h, diluted with water and extracted with ether. According to GC/MS data, the ethereal extract contained 52.7% of di-*p*-tolyloxide ($[M]^+$ 198) and 47.3% of mixture of *p*- and *m*-methoxytoluenes ($[M]^+$ 122). ^1H NMR [300 MHz, CCl_4/MeCN-d_3 (4:1)]: $\delta = 2.34$ (s, 3H, *p*-CH_3); 2.38 (s, 3H, *m*-CH_3).
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