Oxidation by a Cation Radical: Generation of Tropylium Ion by Electron Transfer from Cycloheptatriene and Bitropyl

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Summary Electron transfer from cycloheptatriene and bitropyl to tris-(*p*-bromophenyl)amminium salts is a convenient synthetic route to tropylium salts; the reactions illustrate the utility of stable cation radicals as one-electron oxidants.

STABLE cation radicals ($\mathrm{Ar_3\overset{\cdot+}{N}}$) are readily formed by oxidation of triarylamines[1] and provide convenient one-electron oxidants for suitably active organic molecules.[2] We now report that tris-(*p*-bromophenyl)amminium salts (I)[3] oxidise cycloheptatriene and bitropyl to the corresponding tropylium salt (II), in high yield. Typically, cycloheptatriene (5×10^{-3} M) and (I) (4×10^{-3} M) in CH_2Cl_2, were allowed to react overnight at room temperature. After concentration to half bulk, tropylium hexachloroantimonate (II) was precipitated by addition of diethyl ether [yield 97% based on (I)]. Evaporation of the mother-liquor, followed by extraction with petroleum (30—40°) allowed a quantitative recovery of tri-(*p*-bromophenyl)amine, *i.e.*

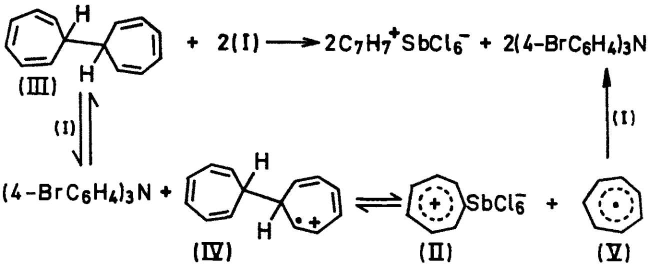
$$\mathrm{C_7H_8 + 2(4\text{-}BrC_6H_4)_3\overset{\cdot+}{N}SbCl_6^- \rightarrow C_7H_7^+SbCl_6^-}$$
$$\mathrm{+\ 2(4\text{-}BrC_6H_4)_3N(+\ HCl + SbCl_5)}$$

The related reaction of (I) with bitropyl (III) was instantaneous at room temperature and is mechanistically significant. Typically (I) (4×10^{-3}M) and (III) (2×10^{-3}M) in CH_2Cl_2 reacted on mixing. After filtration, concentration, and addition of ether, the tropylium salt (II) was precipitated in yields which varied between 70—80%, based on (III). Similar results were obtained when (I) was used as the perchlorate salt, tropylium perchlorate being obtained from both cycloheptatriene and bitropyl.

Chemical one-electron oxidants have not previously been used successfully to generate tropylium ion. Anodic oxidation of bitropyl and cycloheptatriene (presumably involving one-electron transfer) gave a high yield of tropylium ion,[4] but oxidation of (III) with PCl_5[5] yielded mainly bitropylium dication $C_7H_7^+\text{–}C_7H_7^+$.

The mechanism of oxidation by a cation radical could involve direct abstraction of either hydride ion, hydrogen atom, or electron. Hydride ion transfer from bitropyl to triphenylmethyl cation has been shown to give exclusively benzyltropylium ion.[6] Hydrogen atom removal would be expected to give a similar product (in the oxidising conditions), thus one-electron transfer must be the primary step in the oxidation of bitropyl (and by analogy cycloheptatriene) by the amminium salt.

The classical method for generating tropylium ions involves direct hydride abstraction by triphenylmethyl salts.[7] Amminium salts such as (I) are useful alternative oxidants because of their intense visible and e.s.r. spectra, offering convenient probes for monitoring the reactions. The $SbCl_6^-$ salt of (I) is stable indefinitely in the crystalline state, it is conveniently synthesised[3] (and regenerated), and in solution its hydrolytic stability is considerably greater than that of the corresponding triphenylmethyl salt.



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