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A Controlled Balance between Ionic and Radical Pathways in Reactions of Tributyltin Hydride

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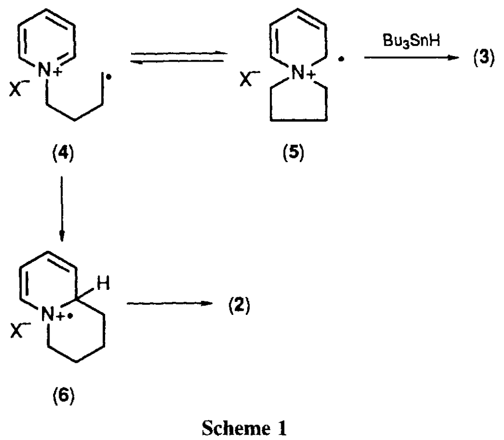
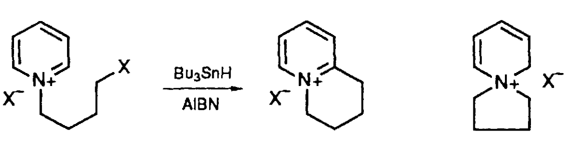
A delicate but controllable balance exists between ionic and radical pathways in the reactions of tributyltin hydride with quaternised haloalkyl pyridinium salts.

We have recently reported[1] the behaviour of a series of iodoalkylpyridinium salts such as (**1a**) in the presence of tributyltin hydride and azoisobutyronitrile (AIBN), which led to the exclusive formation of tetrahydroquinolizinium salts, *e.g.* (**2a**). The curious fact about this reaction was that it only gave the desired product in good yield and purity when a full molar equivalent of AIBN was used. We have now investigated what happens when this condition is not met and the effect of changes of substrate and report a remarkable sensitivity of the reaction to these factors. Thus, when the iodide (**1a**) was treated with tributyltin hydride (1.2 equiv.) and a catalytic quantity (0.1 equiv.) of radical initiator AIBN, the spiro compound (**3a**) was formed, along with the previously observed fused product (**2a**) in a ratio of 1:2. The formation of these two products initially suggested that we were observing a reversible cyclisation[2] of radical (**4**), with the 5-*exo* cyclisation occurring more rapidly and the resulting bicyclic radical (**5**) being trapped by tributyltin hydride when a large concentration of this reagent was present. The ratio of [Bu_3SnH] : [$Bu_3Sn^{\bullet}$] would be expected to fall dramatically in the presence of large amounts of initiator and so in this case the intermediate radical (**5**) would not be trapped so efficiently and, therefore, would more frequently revert to (**4**) which could be diverted to the radical (**6**), the precursor of the observed fused product (Scheme 1). However, although this sounds like a plausible explanation for our observations, radical cyclisations onto nitrogen atoms[3] are rare; this and the following experiments made us sceptical that a radical reaction was the cause of the spirocycle formation. If spiro product formation were the result of the radical process shown then the same ratio of spiro:fused products should result for bromide substrates as for iodides. However, this was not the case. When the bromide (**1b**) was heated under reflux with tributyltin hydride (1.2 equiv.) in the presence of AIBN (0.1 equiv.) in tetrahydrofuran:acetonitrile (1:1), the spiro compound (**3b**) was formed almost exlusively. Only a trace of the tetrahydroquinolizinium salt (**2b**) was detected. When the reaction was repeated under the conditions which led to clean transformation of the iodide (**1a**) into (**2a**) (*i.e.* using 1.2 equiv. of AIBN), the ratio of spiro compound (**3b**) to fused product (**2b**) was 2:1. When the reaction was performed in the complete absence of AIBN, (**3b**) was the only product. This indicated that a non-radical process was playing an important part in determining the products. Accordingly, the tosylate (**7**) was synthesised and subjected to the same cyclisation conditions. Tosylate groups, unlike halides, are not cleaved by tributyltin radicals, and so if the cyclisation requires a carbon



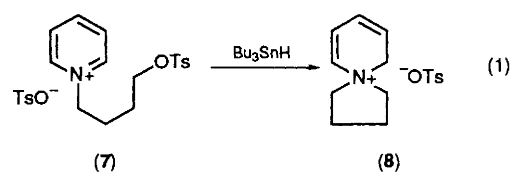
Scheme 1



(**1**) **a**; X = I
b; X = Br

(**2**) **a**; X = I
b; X = Br

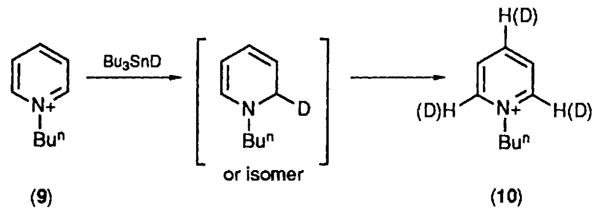
(**3**) **a**; X = I
b; X = Br



(**7**)

(**8**)

Ts = $OSO_2C_6H_4Me$



(9) (10)

Scheme 2

radical then the tosylate should not cyclise. However, cyclisation was indeed seen to give (**8**) in 51% yield [equation (1)]. This could arise by hydride delivery to the pyridinium salt to produce a dihydropyridine; the lone pair of electrons on the nitrogen of this compound could then displace the tosylate in an S_N2 reaction.

The ability of tributyltin hydride to effect hydride delivery to pyridinium rings was further shown when the butylpyridinium compound (**9**) was treated with tributyltin deuteride under these conditions. This led to isolation of the pyridinium compound (**10**) (Scheme 2). Examination of its ^{1}H and ^{2}H NMR spectra showed that extensive deuterium atom substitution had occurred, principally in the α- but also in the γ-positions on the ring. This is consistent with deuteride ion delivery to either of these positions to produce a dihydropyridine, which on work-up easily reoxidizes to a pyridinium salt. We also investigated the reaction of the undeuteriated butylpyridinium salt with tributyltin hydride in a sealed NMR tube. The two possible isomeric dihydropyridines were observed.

Ionic reactions of tributyltin hydride have been witnessed before,[4] but the delicate and controllable balance seen here between an ionic reaction and a radical reaction is unique in the extensive literature of tributyltin hydride.[5]

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