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Bimolecular Nucleophilic Substitution in the Decomposition of Monoalkylthallium(III) Halides

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Summary The predominant mechanism of decomposition of monoalkylthallium(III) halides in pyridine solution involves bimolecular displacement of thallium(I) by attack of halide ion or pyridine on the alkyl group; hence, mono-neopentylthallium(III) halides are relatively stable.

Though monoalkylthallium(III) carboxylates are readily prepared,[1,2] nearly all attempts to prepare monoalkylthallium(III) halides have failed.[3] Even the addition of halide ion to solutions of monoalkylthallium(III) carboxylates rapidly results in the formation of thallium(I) halide and alkyl halide.[1] This instability has been attributed[4] to the formation of alkyl carbonium ions, which if correct, would mean that mononeopentylthallium(III) halides would not only be no more stable than other n-alkylthallium(III) halides, but would give rearranged alkyl halides on decomposition.

We report here that, despite the fact that most monoalkylthallium(III) halides cannot be prepared by the reaction of the more stable di-alkylthallium(III) halides with halogens,[5] mononeopentylthallium(III) halides are not only formed under these conditions, they are also stable and decompose eventually without rearrangement.

In typical experiments, dimethylthallium(III) chloride was dissolved in the minimum of pyridine and its ^{1}H n.m.r. spectrum was measured. One mole of pyridinium perbromide was added and the spectrum was measured again at intervals. The methyl doublet (τ 8·36; J 425 Hz) was replaced by a singlet (τ 5·13) corresponding to the formation of the methylpyridinium ion. In contrast, when the same experiment was carried out with di-neopentylthallium(III) chloride, the methyl doublet (τ 8·83; J 31 Hz) and the methylene doublet (τ 7·54; J 415 Hz) of the di-neopentylthallium(III) halide were replaced by the methyl doublet (τ 8·85; J 67 Hz) and the methylene doublet (τ 7·25; J 712 Hz) of the mono-neopentylthallium(III) halide, together with the methyl singlet (τ 9·05) and the methylene singlet (τ 6·71) of neopentyl bromide. After 3 days at 25°, no decomposition of the mono-neopentylthallium(III) halide was apparent, but after 5 days at 65° it had largely decomposed to more neopentyl bromide. No rearranged alkyl halides or alkylpyridinium ions could be detected.

The mono-neopentylthallium(III) compound was isolated from the reaction of equivalent quantities of di-neopentylthallium(III) chloride and pyridinium perbromide in dichloromethane solution.

The stability of the mono-neopentylthallium(III) halide must be because the predominant mechanism of decomposition involves S_N2 displacement of thallium(I) by attack of halide ion on the neopentyl group. Such S_N2 displacements of neopentyl compounds are known to be extremely slow.[6] The absence of rearrangement[6] of the neopentyl group during the decomposition also rules out reaction *via* the S_N1 mechanism, and the very much greater rate of decomposition of the methylthallium(III) halide than of the mono-neopentylthallium(III) halide rules out a reaction involving the rate-determining homolysis of the carbon–thallium bond and a concerted reductive elimination of the alkyl halide.

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