

NOTE

REACTIONS OF TRIMETHYLLHALLIUM WITH COMPOUNDS CONTAINING AN ACIDIC HYDROGEN

A. G. LEE AND G. M. SHELDRIK

University Chemical Laboratory, Lensfield Road, Cambridge (Great Britain)

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INTRODUCTION

Trimethylthallium has been shown to react with a variety of compounds containing an acidic hydrogen to give methane and the corresponding dimethylthallium derivative. Thus it reacts with hydrogen iodide¹, hydrogen cyanide², acetylacetone³, oximes^{4,5}, cyclopentadiene⁶, manganese carbonyl hydride⁶ and phenyl acetylene^{6,7}. We have found that tris(trimethylsilyl)thallium can react with compounds containing an acidic hydrogen in a variety of different ways⁸ and so we have investigated the scope of these reactions for trimethylthallium.

RESULTS AND DISCUSSION

Reaction of trimethylthallium with halocarbons and related species

Triethylindium has been reported to react with chloroform and bromoform to give diethylindium chloride and bromide respectively⁹ and tris(trimethylsilyl)thallium reacts with chloroform to give bis(trimethylsilyl)thallium chloride⁸. We find that trimethylthallium also reacts with a variety of halomethanes to give the corresponding dimethylthallium halide and methane. It does not react with dichloromethane or carbon tetrachloride at room temperature, but reacts over about ten minutes with chloroform to give dimethylthallium chloride. With dibromomethane there is a slow reaction and with bromoform a fast reaction to give dimethylthallium bromide. With a solution of iodoform in ether and with diiodomethane there is a fast reaction and with iodomethane there is a slow reaction to give dimethylthallium iodide. The nature of the other products of these reactions would seem to be complex.

The order of reactivity of the halomethanes, $I > Br > Cl$ and $CHX_3 > CH_2X_2 > CH_3X$ is similar to that found for the basic hydrolysis of the halocarbons, involving intermediate halocarbon anions^{10,11}.

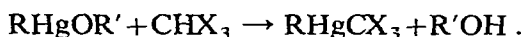
No reaction occurs between trimethylthallium and acetonitrile at room temperature. Unlike the trimethylaluminium/acetonitrile system¹², no stable adduct is formed between the two reagents at room temperature, reflecting the low complexing ability of trimethylthallium. With malononitrile in ether there is immediate formation of a white solid. This solid is not pure Me_2TlCN : the infrared spectrum

shows complex absorption in the cyanide region, and bands attributable to both CN^- ions and covalently bound CN are present. Presumably a mixture of Me_2TlCN and $\text{Me}_2\text{TlCH}(\text{CN})_2$ and decomposition products of the latter could be formed. With CH_2ClCN there is again an immediate reaction, and again the infrared spectrum of the products show complex absorption in the cyanide region.

With nitromethane at room temperature, trimethylthallium immediately gave a white solid which exploded on removal of excess nitromethane. The compound could well have been dimethylthallium nitrite: it was not investigated further.

Reaction of dimethylthallium ethoxide and chloroform

It would seem possible that reactions of trimethylthallium and the halo-methanes go through an intermediate Me_2TlCX_3 . Trihalomethyl derivatives of mercury have been prepared by the reaction of an alkoxide and a halocarbon¹³:



Dimethylthallium ethoxide and chloroform reacted at room temperature to give dimethylthallium chloride in quantitative yield. Some ethanol was also formed. If any trihalomethyl derivatives are formed in the above reactions then they must be very unstable.

Reactions with other compounds

Trimethylthallium reacts with a wide variety of other compounds containing a slightly acidic hydrogen to give methane and the dimethylthallium derivative. Thus it reacts with hydrogen chloride, acetic acid, methanol, ethanol, tert-butyl alcohol, phenol and methanethiol:



Such reactions are, of course, very attractive preparatively as the only product apart from the required thallium derivative is methane.

With diethylamine, as with dimethylamine¹⁴, there was no reaction. The reaction of trimethylthallium and trichlorosilane is complex. A slow reaction to give methane occurs and a white solid is formed, involatile *in vacuo* at room temperature. The weight of this solid is less than the weight of the original trimethylthallium, and thus elimination of more than one methyl group from the thallium must have occurred. The solid has been shown by X-ray powder photography not to contain thallium(I) chloride. This is the only reaction found in which a dimethylthallium derivative seems not to have been formed.

The data so far obtained suggests that the pK_a value of the acidic hydrogen must be less than about 20 for reaction to occur. No reaction occurs with acetonitrile (pK_a 25¹⁵) and with indene (pK_a 20¹⁶) there is a slow reaction.

EXPERIMENTAL

Trimethylthallium was prepared from methylthallium (from methyl iodide and lithium) and thallos iodide in ether¹ and was purified by fractionation in a standard pyrex vacuum line. Chloroform was dried over activated alumina *in vacuo* before

use and acetonitrile was dried by distillation from phosphorous pentoxide. All other reagents used were dried by vacuum distillation through 4A molecular sieve which had been carefully flamed out *in vacuo*. All reactions were carried out *in vacuo* unless otherwise stated.

Reaction with hydrogen chloride

Trimethylthallium (0.22 mmoles) reacted with excess hydrogen chloride (0.22 mmoles consumed) to give methane and dimethylthallium chloride (0.22 mmoles). Dimethylthallium chloride, and all other dimethylthallium compounds prepared, were identified by analysis, IR¹⁷, NMR and mass spectrometry. Details of the NMR and mass spectra are to be published.

Reaction with iodoform

The ethereal solution of trimethylthallium obtained from thallos iodide (24 g) and methylthallium was slowly treated, under dry nitrogen, with a solution of iodoform in ether. The precipitate obtained was washed with ether to remove excess iodoform, and yielded pure dimethylthallium iodide (23 g) in 80% yield. The alternative route to dimethylthallium iodide by reaction with aqueous hydrogen iodide¹ gives a very intractable precipitate.

Reaction with malononitrile

Trimethylthallium reacted immediately with a solution of malononitrile in diethyl ether to give a cream coloured solid. (Found: C, 21.7; H, 1.9; N, 10.0%.) The infrared spectrum in a KBr disc was as follows: 3020 (w), 2925 (m), 2450 (w), 2190 (s), 2160 (s), 2090 (m), 2060 (m), 1680 (m), 1540 (s), 1530 (s), 1430 (sh), 1390 (s), 1350 (w), 1260 (w), 1180 (w), 1160 (w), 1100 (w, br), 810 (s), 790 (s). Bands for the dimethylthallium group can be assigned as 3020 [$\nu_{as}(\text{CH}_3)$], 2925 [$\nu_s(\text{CH}_3)$], 1400 [$\delta_{as}(\text{CH}_3)$], 1180 [$\delta_s(\text{CH}_3)$], 790 [$\rho(\text{CH}_3)$]. Bands in the 2000 cm^{-1} region can be assigned to CN groups.

Reaction of dimethylthallium ethoxide and chloroform

Dimethylthallium ethoxide (0.38 mmoles) and excess chloroform reacted *in vacuo* after one hour at room temperature to give dimethylthallium chloride (0.38 mmoles) and ethanol (identified by IR and NMR).

Reaction of trimethylthallium and ethanol

Trimethylthallium (0.38 mmoles) and excess ethanol were condensed into a flask under vacuum and allowed to warm to room temperature. Methane was rapidly formed. The flask was then cooled to 0° and the methane and excess ethanol pumped off, leaving pure dimethylthallium ethoxide (0.38 mmoles) in quantitative yield.

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