

NOTE

THALLIUM IN ORGANIC SYNTHESIS
IV. A CONVENIENT ONE-STEP SYNTHESIS OF DI-n-ALKYLTHALLIUM-(III) BROMIDES*

ALEXANDER McKILLOP, L. F. ELSOM,

School of Chemical Sciences, University of East Anglia, Norwich, (Great Britain)

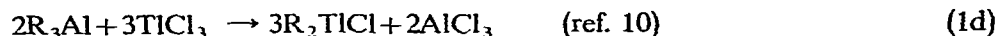
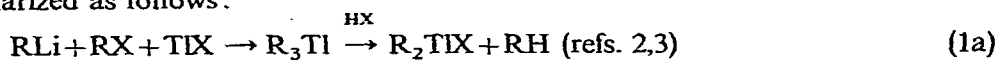
AND

EDWARD C. TAYLOR

Department of Chemistry, Princeton University, Princeton, New Jersey 08540 (U.S.A.)

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Available methods for the preparation of dialkylthallium(III) halides may be summarized as follows:



Method (1a), although apparently straightforward, actually involves the intermediacy of RTl and the formation of the highly pyrophoric and explosive R_3Tl which must be carefully hydrolyzed with strong acid. Method (1b) requires the preparation and use of unstable TlCl_3 and is complicated by concomitant formation of oxidation products of the Grignard reagent by TlCl_3 . Furthermore, low temperatures and extreme care are necessary to keep the reaction under control. Method (1c) has only been used for the preparation of diethylthallium(III) chloride, and method (1d) for the preparation of diethyl, di-n-propyl and diisobutylthallium(III) chlorides. Both methods require the use of preformed pyrophoric organometallic intermediates.

In the course of our studies on the use of thallium derivatives in organic synthesis^{1,11,12}, we examined the reaction of Grignard reagents with thallium(I) bromide¹. Aryl- and sec-alkyl-magnesium bromides gave coupled products, but primary aliphatic Grignard reagents gave di-n-alkylthallium(III) bromides directly**.

* For Part III see ref. 1.

** As far as we are aware, the reaction of aliphatic Grignard reagents with thallium(I) halides has been mentioned only twice before. Menzies and Cope^{13a} in an attempt to prepare triethylthallium(III), observed the formation in poor yield of diethylthallium(III) halides in the reaction of ethylmagnesium halides with thallium(I) halides. Our present studies indicate that their poor yields stemmed from the use of insufficient thallium(I) halide. Okhlobystin *et al.*^{13b} mentioned without any details the reaction of ethylmagnesium bromide with thallium(I) bromide in the presence of added ethyl bromide to give triethylthallium(III).

Yields are only moderate, but this procedure has proven in our hands to be far superior to methods (1a–1d) for the synthesis of di-n-alkylthallium(III) bromides because of manipulative simplicity and the purity of products obtained. Representative results are summarized in Table 1.

TABLE I

ANALYTICAL DATA FOR THE SYNTHESIS OF DI-N-ALKYLTHALLIUM(III) BROMIDES

R ₂ TlBr	Yield, %	m.p. (°C)	Formula	Analysis			
				Calcd.		Found	
				C	H	C	H
(CH ₃) ₂ TlBr	21	295 (dec.) (lit. ⁵ , explodes at 275)	C ₂ H ₆ BrTl	^a			
(C ₂ H ₅) ₂ TlBr	40	> 280 (lit. ⁵ 270)	C ₄ H ₁₀ BrTl	14.03	2.94	13.90	2.87
(C ₃ H ₇) ₂ TlBr	55	188 (dec.)	C ₆ H ₁₄ BrTl	19.45	3.81	19.20	2.40
(C ₄ H ₉) ₂ TlBr	56	212 (dec.) (lit. ⁶ , explodes at 240–250)	C ₈ H ₁₈ BrTl	24.11	4.55	23.89	4.35
(C ₅ H ₁₁) ₂ TlBr	47	248 (dec.)	C ₁₀ H ₂₂ BrTl	28.10	5.19	27.90	5.59
(C ₆ H ₁₃) ₂ TlBr	48	206 (dec.) (lit. ¹⁵ , 205 dec., explodes at 216)	C ₁₂ H ₂₆ BrTl	31.70	5.75	31.42	5.77
(C ₇ H ₁₅) ₂ TlBr	47	210–212 (dec.)	C ₁₄ H ₃₀ BrTl	34.83	6.27	34.87	6.31
(C ₈ H ₁₇) ₂ TlBr	32	205 (dec.)	C ₁₆ H ₃₄ BrTl	37.63	6.71	37.39	7.11
(C ₉ H ₁₉) ₂ TlBr	46	193–194 (dec.)	C ₁₈ H ₃₈ BrTl	40.14	7.11	39.70	6.90
(C ₁₀ H ₂₁) ₂ TlBr	33	194–195 (dec.)	C ₂₀ H ₄₂ BrTl	42.40	7.47	42.10	7.40

^a We have not been able to obtain satisfactory microanalytical data for this compound, perhaps as a result of its thermal instability.

We assume that the initial reaction in these conversions is the formation of an alkylthallium(I). Its subsequent fate is not certain, but we suggest the transient intermediacy of an alkylthallium(III) dibromide which spontaneously disproportionates to give the observed dialkylthallium(III) bromide*.

EXPERIMENTAL

A mixture of 0.135 mole of thallium(I) bromide** and 0.0675 mole of an n-alkylmagnesium bromide in 40 ml of tetrahydrofuran–benzene (1/1) was stirred and refluxed under nitrogen for 5 h, cooled, acidified with dilute hydrochloric acid and filtered. The collected solids were extracted with hot pyridine, filtered to remove metallic thallium, and the filtrate chilled. The colorless, crystalline di-n-alkylthallium(III) bromides so obtained were all recrystallized from pyridine. Details are given in Table I.

* The preparation and actual isolation of simple alkylthallium(III) dihalides by the reaction of thallium(III) tribromide with dialkylthallium(III) halides has been claimed^{14a}. This claim was later shown to be specious^{14b}. Although the alkylthallium(III) dihalides were indeed formed *in situ*, they were shown to undergo spontaneous disproportionation to dialkylthallium(III) halides, the species actually isolated.

** Optimum yields were obtained with a molar ratio of thallium(I) bromide/Grignard reagent of 2/1.

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