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Preliminary communication

Alkylation of dialkylthallium halides with Grignard reagents in diethyl ether solution

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Generally, trialkylthallium compounds are prepared by treating an alkyllithium reagent with a dialkylthallium halide in an ether or alkane solvent (Eq. 1)[1-3]. A few years ago Okhlobystin *et al.*[4] discovered that trialkylthallium compounds could also be synthesized from a dialkylthallium halide and a Grignard reagent in tetrahydrofuran (Eq. 2). Originating from these relatively few studies of trialkylthallium compounds is a myth that Grignard reagents in diethyl ether will not alkylate a dialkylthallium halide[1]. The apparent lack of experimental support for this belief[1,2,4] prompts the communication of some observations made during a mechanistic study of electrophilic aliphatic substitution on organothallium compounds[5].

$$R_2TlX + RLi \rightarrow R_3Tl + LiX \quad (1)$$

$$R_2TlX + RMgX \xrightarrow{THF} R_3Tl + MgX_2 \quad (2)$$

During the preparation of a series of dialkylthallium halides from thallic chloride and excess (greater than 2 equivalents) of Grignard reagent in diethyl ether at low temperature (−60°) the following observations were made: (1) The addition of a third equivalent of Grignard reagent changed the reaction mixture from a white suspension to a colored solution (yellow to gray-black), (2) Addition of aqueous acid precipitated a white solid, later identified as a dialkylthallium halide. A reasonable interpretation of these observations is that a trialkylthallium compound is formed as an intermediate. Dialkylthallium halides are known to be insoluble in diethyl ether while trialkylthallium compounds are miscible with ether. Also, trialkylthallium compounds are known to form colored solutions and to undergo hydrolysis to the R_2TlX stage[1].

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Another set of observations consistent with intermediate trialkylthallium formation is the following: (1) Methylmagnesium bromide was observed to react with either a diethyl ether suspension of diphenylthallium chloride or diethylthallium bromide to form a solution, (2) The products from these reactions, after the usual aqueous mineral acid work-up, were shown by NMR spectra to consist of a mixture which included, respectively, methylphenylthallium halide or methylethylthallium halide. These unsymmetrical products are derived from acid cleavage of the most labile alkyl group of the trisubstituted intermediates, methyldiphenylthallium or methyldiethylthallium.

Another possible explanation for the above observations is that the alkyl group of the Grignard reagent is exchanging with an alkyl group of the dialkylthallium halide. As a test of the hypothesis that trialkylthallium compounds existed as intermediates in the above cases, the following reaction was carried out. Under a dry nitrogen atmosphere a slight excess of ethylmagnesium bromide was added to a suspension of dry diethylthallium bromide in diethyl ether at −10° to 0° resulting in a yellow to black solution. After the mixture had warmed to room temperature, a reduced pressure (about 0.1 mm) bulb-to-bulb distillation removed solvent and all volatiles from a solid residue. Diethyl ether was removed from the distillate at atmospheric pressure, leaving behind a colored liquid residue. A reduced pressure distillation of the residue resulted in a 50% yield of viscous yellow liquid, b.p. 25–30° at 0.2 mm. The physical properties[3] and a low temperature (−40°) NMR[★] spectrum[6] identified the yellow liquid as triethylthallium.

Dry thallic chloride was found to react with an excess of ethyl Grignard at −60°, forming a colored solution. Work-up as described above resulted in the isolation of a very small amount of triethylthallium. At this time the poor yield of trialkylthallium compound obtained from thallic chloride and Grignard reagent cannot be explained.

Thus, contrary to the popular myths[1], alkylation of dialkylthallium halides is not limited to alkyllithium reagents. Grignard reagents in either of the common ether solvents, diethyl ether or tetrahydrofuran, have sufficient carbanion character to alkylate a dialkylthallium halide.

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