Acetoxythallation of Terminal Acetylenes

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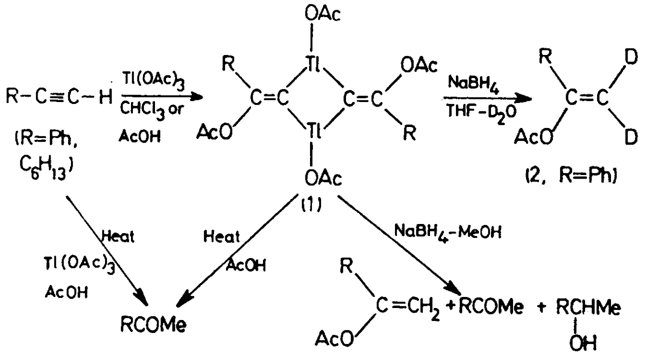
Summary The reaction of terminal acetylenes with $Tl(OAc)_3$ in chloroform gives a new type of oxythallation adduct; this was shown to be one of the intermediates in the thallium(III) salt-catalysed conversion of terminal acetylenes into ketones.

It has been reported that thallium(III) salts are catalysts for the conversion of terminal acetylenes into ketones.[1] Although this reaction was assumed to proceed by oxythallation,[2] the intermediate oxythallation adduct has never been isolated. During a study of the acetoxythallation of alkylphenylacetylenes[3] we have now isolated new organothallium(III) compounds which we have shown are such intermediates.

The reaction of phenylacetylene or oct-1-yne with $Tl(OAc)_3$ (acetylene : Tl = 2 : 1) in $CHCl_3$ or AcOH at 20 or 0 °C for 1 h, followed by evaporation, gave an almost colourless oil which was washed several times with n-hexane to afford a white amorphous solid (80—95% yield). Although we have not yet succeeded in obtaining a single crystal for *X*-ray analysis, we tentatively assign structure (**1**) on the basis of the reactions in the Scheme and the following data:‡ (**1**; R = Ph): m.p. 140—142 °C (decomp.); δ (CD_3OD): 1·71 (3H, s, TlOAc), 2·0 (3H, s, =COAc), 7·2—



Scheme

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‡ Satisfactory elemental analyses were obtained.

7·7 (3H, m, Ph), and 7·8—8·2 (2H, m, Ph); i.r. (Nujol and hexachlorobutadiene): 1765 ($\nu_{C=O}$), 1625 ($\nu_{C=C}$), 1540 (ν_{asCOO}), 1395 (ν_{sCOO}), 1185 (ν_{C-O}), 770 (Ph), and 700 (Ph) cm^{-1}; *m/e*: 249 and 247 ($TlCO_2^+$), 221 and 219 (TlO^+), and 205 and 203 (Tl^+);[4] *M* (cryoscopy in benzene): 835 (calc. 847). Compound (**1**; R = C_6H_{13}) had m.p. 100—102 °C (decomp.)‡

The formation of (**1**) may be explained by assuming a concerted intermolecular acetoxythallation between two alkynylthallium diacetates which can be produced by replacement of the acidic hydrogen of acetylene by $-Tl(OAc)_2$. Several instances of a four-membered M–C–M–C ring are known; *e.g.* for M = Al,[5] Be,[5] Nb,[6] and Ta[6]. Application of this reaction to mercury(II) acetate gave the bis-alkynylmercury compound quantitatively.

Reduction ($NaBH_4$) of (**1**; R = Ph) in tetrahydrofuran–D_2O at 0 °C for 1 h afforded a 75% yield of (**2**; R = Ph) together with some acetophenone and phenylacetylene. The formation of (**2**; R = Ph) supports the assignment of structure (**1**), namely the presence of two C–Tl bonds on the same carbon atom.[3] Similar treatment of (**1**; R = C_6H_{13}) in MeOH gave mainly octan-2-one (27%) and octan-2-ol (24%) together with a small amount of 2-acetoxyoct-1-ene (5%). We confirmed in separate experiments that vinyl esters were converted into ketones and alcohols under similar conditions.

Heating of (**1**; R = Ph or C_6H_{13}) under reflux in AcOH for 1 h gave acetophenone and octan-2-one in 65 and 26% yield, respectively. With equimolar amounts of $Tl(OAc)_3$ and (**1**), the yield of ketone increased to 90 and 68% respectively. When phenylacetylene or oct-1-yne (2 mol. equiv.) were heated in AcOH under reflux for 1 h in the presence of $Tl(OAc)_3$ (1 mol. equiv.), without isolation of (**1**), acetophenone or octan-2-one were formed in 90 and 82% yield respectively. Under similar conditions without the $Tl(OAc)_3$ hardly any ketone was obtained. These results show that (**1**) is clearly one of the intermediates in this conversion of terminal acetylenes into ketones.

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