Reaction of Alkoxythallium(III) Compounds of Olefins with Palladium(II) Chloride. Evidence of Tl–Pd Exchange in Oxymetallates

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Summary Treatment of alkoxythallates of styrene with $PdCl_2$ in MeOH gave acetophenone or its alkyl acetal through Tl–Pd transmetallation.

TRANSMETALLATION of Hg with Pd was postulated in the reaction of palladium(II) chloride with oxymercurials.[1,2] We report the first example of transmetallation of Tl with Pd in the oxythallates.

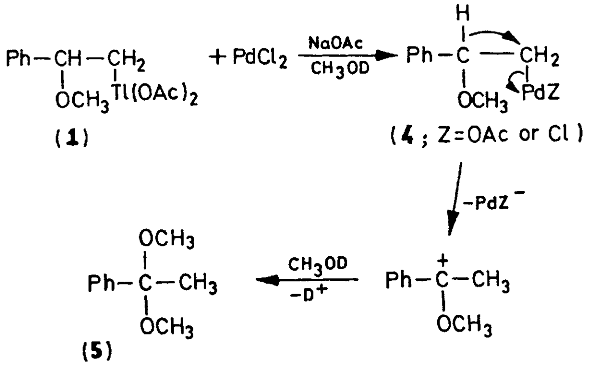
After stirring a mixture of equimolar amounts of alkoxythallium(III) compounds of styrene (1)[3] and palladium(II) chloride in methanol containing sodium acetate at 65° for 10 min, the precipitated metallic palladium was removed and the filtrate was diluted with water and extracted with benzene. The only detectable organic product was acetophenone (2), the yields of which were 73—93% (R^1 = Me, Et, Pr^i, Bu^i; R^2 = Me, Pr^i) (Scheme 1).

$$\mathrm{PhCH(OR^1)\cdot CH_2Tl(OCOR^2)_2 + PdCl_2 \xrightarrow[\text{MeOH}]{\text{NaOAc}}}$$
$$\mathrm{PhCOMe + Pd + Tl^{3+}}$$

SCHEME 1

In the absence of sodium acetate, (1; $R^1 = R^2$ = Me) gave both (2) (48% yield) and 1,1-dimethoxy-2-phenylethane (3) (38%), whilst in the absence of palladium(II) chloride (3) (37%) was the only organic product formed, as reported earlier.[4] These reactions proceeded very rapidly and the yield of (2) was not increased by prolonging the reaction time from 10 min to 5 h. A similar reaction using the mercury analogue of (1; R^1 = Me, Ac) gave a 70—90% yield of (2) in 5 h.

When the filtrate of the reaction mixture was diluted with benzene or n-pentane and then washed with water, 1,1-dimethoxy-1-phenylethane [(5): dimethylacetal of (2)] was obtained instead of (2) in 80% yield [b.p. 98° at 30 Torr;[5] τ 8·47 (s. 3H), 6·82 (s. 6H), and 2·80—2·30 (m. 5H)]. Similarly the ethyl methyl acetal was obtained from (1; R^1 = Me) and ethanol solvent. The same treatment of the reaction mixture of the mercury analogue of (1; R^1 = Me) also afforded (5) in good yield. It is reasonable to consider that (2) is formed by the hydrolysis of (5) by the water added and hydrogen chloride which was formed during the reaction. When this reaction was carried out in MeOD, no deuterium incorporation was observed in (5). This fact could be explained reasonably by Scheme 2.



SCHEME 2.

A reactive oxypalladate (4) formed by Tl–Pd exchange, followed by carbon–palladium bond fission of (4) accompanied by hydride shift, affords a carbonium-ion intermediate which can then react with MeOD. A sequence involving dehydropalladation of (4) giving α-methoxystyrene, followed by the addition of MeOD to the double bond, can be ruled out because of the non-incorporation of deuterium into (5).

Under similar conditions to those described above, the reaction of oxythallates of α-methylstyrene and palladium(II) chloride gives the parent olefin (40% yield) and 2,2-dimethoxy-1-phenylpropane or benzyl methyl ketone (33%), whilst the use of oxymercurials in such reactions affords only the parent olefin (64%) and no ketonic or aldehydic products.

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[3] Detailed description for the preparation of (1) will be reported separately.
[4] H. J. Kabbe, *Annalen*, 1962, **656**, 204.
[5] Lit. b.p. 90° at 20 Torr: M. T. Borgert and P. P. Herrera, *J. Amer. Chem. Soc.*, 1923, **45**, 238.