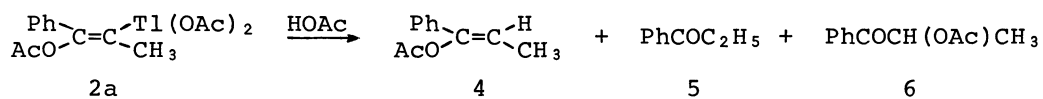


data [Anal. Found: C, 36.28; H, 3.40%. Calcd. for $C_{15}H_{17}O_6Tl$, C, 36.20; H, 3.44%. Nmr (in CD_3OD): τ 8.15 [$Tl(OCOCH_3)_2$, s, 6H], 7.85 [$CH_3-C=$, d, 3H, $J_{Tl(205)-H}=985.5$ and $J_{Tl(203)-H}=976.5$ Hz], 7.82 [$OCOCH_3$, d, 3H, $J_{Tl-H}=13$ Hz], 2.60 [C_6H_5- s, 5H]. Although the attempted isolation of 3a in pure state was unfruitful,⁵⁾ the crude product was characterized by the presence of allylic methyl proton signal at τ 7.70 [$J_{Tl-H}=142$ Hz] and aromatic proton signal coupled to Tl [$J_{Tl-H}=50-140$ Hz], as in the case of 3b.

When 2 or 3 was treated with boiling acetic acid, the formation of the hydrodethallation product, i.e., the corresponding vinyl acetate, was observed. For example, 2a afforded trans- α -acetoxy- β -methylstyrene (4) along with propiophenone and its derivative (5 and 6 respectively) on 2 hrs heating, and any traces of cis- α -acetoxy- β -methylstyrene could not be found. The above results suggest that hydrodethallation may proceed with complete retention and consequently the oxythallation of acetylenes may occur in trans fashion with high stereospecificity.



Further, in the reaction of 1a with $Tl(OAc)_3$ in acetic acid under severe conditions (at 60-70°C for 1 hr and then at 117°C for 2 hr), the following products were formed without isolation of acetoxythallium compounds; β -acetoxy- β -methylstyrene (13%), 4 (44%), 5 (6%), and 6 (11%). Here, the former compound may be formed via 3a, while the latter three compounds probably come from 2a.

References

- 1) Presented at the 26th Annual Meeting of the Chemical Society of Japan, Hiratsuka, April, 1972.
- 2) K. Ichikawa and S. Uemura, Yuki Gosei Kagaku Kyokai Shi, 29, 400 (1971).
- 3) A. McKillop, O. H. Oldenziel, B. p. Swann, E. C. Taylor, and R. L. Robey, J. Amer. Chem. Soc., 93, 7331 (1971).
- 4) Recently, the methoxythallation of allenes to afford vinylthallium compounds has been reported. R. K. Sharma and E. D. Martinez, Chem. Commun., 1129 (1972).
- 5) Elemental analysis of a mixture of 2a and 3a was also satisfactory.

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