REACTION OF ALKYLPHENYLACETYLENES WITH THALLIUM(III) ACETATE 1)

Sakae UEMURA,\* Kazuhiro SOHMA, Hideyuki TARA, and Masaya OKANO Institute for Chemical Research, Kyoto University, Uji, Kyoto

The reaction of alkylphenylacetylenes with thallium(III) acetate in acetic acid under mild conditions (at 60-70°C for 1 hr) afforded a mixture of two isomeric acetoxythallated compounds in good yields. The hydrodethallation of these products to give the corresponding vinyl acetates was accomplished with boiling acetic acid.

Although the solvothallation of acetylenes is postulated in hydration<sup>2)</sup> and oxidation<sup>3)</sup> of acetylenes with thallium(III) salts, the intermediate solvothallated compound has not yet been isolated by direct method.<sup>4)</sup> We now report the first example of the direct acetoxythallation of certain acetylenes and the hydrodethallation of acetoxythallated compounds.

The reaction of methylphenylacetylene ( $\underline{1a}$ ) or ethylphenylacetylene ( $\underline{1b}$ ) with Tl(OAc) $_3$  (acetylene:Tl=2:1) in acetic acid at 60-70°C for 1 hr gave an isomeric mixture of  $\underline{2}$  and  $\underline{3}$  in good yield (R=CH $_3$  95%, R=C $_2$ H $_5$  65%; based on the Tl salt charged) where 2 was the major product.

Ph-C 
$$\equiv$$
 C-R  $\xrightarrow{\text{T1 (OAc)}_3}$   $\xrightarrow{\text{Ph}}$  C=C $\stackrel{\text{T1 (OAc)}_2}{R}$  +  $\xrightarrow{\text{Ph}}$  C=C $\stackrel{\text{OAc}}{R}$   $\xrightarrow{\text{1}}$  a:R=CH<sub>3</sub> b:R=C<sub>2</sub>H<sub>5</sub>

The isolation procedure is as follows. After removal of the acetic acid in vacuo, the crude product was taken into chloroform. Concentration in vacuo followed by repeated washings with n-hexane (to remove unreacted acetylene) afforded a mixture of almost pure 2 and 3. The isolation of each isomer from this mixture was achieved For example, a mixture of 2b and 3b on exby the use of appropriate solvents. traction with ether and removal of the ether gave  $\underline{2b}$  (mp 133-135°C), while on careful recrystallization with methanol gave 3b (mp 133-134°C) [Anal. Found: for 2b, C, 37.75; H, 3.72%. for 3b, C, 37.30; H, 3.72%. Calcd. for  $C_{16}H_{19}O_{6}T1$ , C, 37.56; H, 3.74%]. Nmr spectra in CD<sub>3</sub>OD :  $\underline{2b}$ ,  $\tau$  8.85 [C $\underline{H}_3$ CH<sub>2</sub>-, t, 3H,  $J_{\underline{T1-H}}$ =20 Hz], 8.13 [T1(OCOC $\underline{H}_3$ )<sub>2</sub>, s, 6H], 7.83 [OCOC $\underline{H}_3$ , d, 3H,  $J_{T1-H}=13$  Hz], 7.34 [CH $_3$ C $\underline{H}_2$ -, q, 2H,  $J_{T1-H}=1299$  Hz], 2.60 [C<sub>6</sub> $\underline{H}_5$ -, s, 5H];  $\underline{3b}$ , similar to the spectrum of  $\underline{2b}$  except the signals for methyl and methylene protons of ethyl group at  $\tau$  8.66 and 7.32 [J $_{\rm T1-H}$ =116 Hz], respectively, and for aromatic protons being coupled to T1 [ $J_{T1-H}$ =50-120 Hz]. The isolated 2a(mp 169-171°C) through recrystallization from ethanol also showed good analytical

data [Anal. Found: C, 36.28; H, 3.40%. Calcd. for  $C_{15}H_{17}O_{6}T1$ , C, 36.20; H, 3.44%. Nmr (in  $CD_{3}OD$ ):  $\tau$  8.15 [T1( $OCOCH_{3}$ )<sub>2</sub>, s, 6H], 7.85 [ $CH_{3}-C=$ , d, 3H,  $J_{T1(205)-H}=985.5$  and  $J_{T1(203)-H}=976.5$  Hz], 7.82 [ $OCOCH_{3}$ , d, 3H,  $J_{T1-H}=13$  Hz], 2.60 [ $C_{6}H_{5}-$  s, 5H]. Although the attempted isolation of  $\underline{3a}$  in pure state was unfruitful, 5 the crude product was characterized by the presence of allylic methyl proton signal at  $\tau$  7.70 [ $J_{T1-H}=142$  Hz] and aromatic proton signal coupled to T1[ $J_{T1-H}=50-140$  Hz], as in the case of 3b.

When  $\underline{2}$  or  $\underline{3}$  was treated with boiling acetic acid, the formation of the hydrodethallation product, i.e., the corresponding vinyl acetate, was observed. For example,  $\underline{2a}$  afforded trans- $\alpha$ -acetoxy- $\beta$ -methylstyrene ( $\underline{4}$ ) along with propiophenone and its derivative ( $\underline{5}$  and  $\underline{6}$  respectively) on 2 hrs heating, and any traces of cis- $\alpha$ -acetoxy- $\beta$ -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  $\underline{1a}$  with Tl(OAc)<sub>3</sub> 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;  $\beta$ -acetoxy- $\beta$ -methylstyrene (13%),  $\underline{4}$  (44%),  $\underline{5}$  (6%), and  $\underline{6}$  (11%). Here, the former compound may be formed via  $\underline{3a}$ , while the latter three compounds probably come from  $\underline{2a}$ .

## References

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- 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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