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Preliminary communication

Acetoxythallation of dialkylacetylenes

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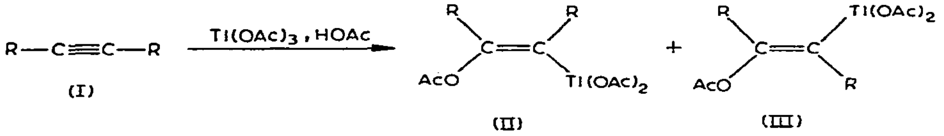
Although oxythallation of olefins[1] and allenes[2] has been reported, no examples of corresponding adducts of acetylenes are known. We have found that dialkylacetylenes react with a molar equivalent of thallium(III) acetate sesquihydrate in glacial acetic acid containing 4.5 mole equivalents of acetic anhydride to give stable acetoxythallation products. In a recent communication analogous methoxythallation compounds were postulated as intermediates in the oxidation of alkylarylacetylenes with thallium(III) nitrate in methanol[3].



(a : R = CH_3; b: R = C_2H_5)

Dimethylacetylene Ia gave a mixture of IIa and IIIa in 70% yield. The structure of the *trans* compound IIIa (m.p. 172–173°)* obtained by two recrystallizations of the mixture from chloroform–petroleum ether is based on its NMR spectrum ($CDCl_3$, TMS) in which the protons in the methyl group on the carbon atom α to the thallium appeared as a doublet at δ 1.96, J(Tl–H) 997 Hz, the methyl *cis* to thallium as a doublet at δ 2.12, J(Tl–H) 144 Hz, the acetoxy as a singlet at δ 2.12 and the acetate protons as a singlet at δ 2.00. From a comparison of the NMR spectra of the mixture and of IIIa the assignments of the bands due to the *cis* isomer IIa could be made: the protons in the methyl group on the carbon atom α to thallium showed a doublet at δ 2.11, J(Tl–H) 1078 Hz, the methyl *trans* to thallium a doublet at δ 2.09, J(Tl–H) 66 Hz, the acetoxy a singlet at δ 2.06 and the acetate protons a singlet at δ 2.00. A mixture of IIa and IIIa was obtained even when the reaction was carried out in the dark with freshly distilled Ia. In these spectra the lines

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*Compounds IIIa and IIIb gave satisfactory analytical data.

due to ^{203}Tl—^{1}H coupling were not resolved from those due to ^{205}Tl—^{1}H coupling interaction. The structural assignments are based upon the relationship $J(cis) > J(trans)$ for Tl—H coupling interaction for the protons in methyl groups *cis* or *trans* to thallium[4].

Diethylacetylene Ib gave IIIb (yield 87%, m.p. 157–158°). In its NMR spectrum ($CDCl_3$, TMS) the protons in the methylene group on carbon atom α to thallium appeared as a doublet of quartets at δ 2.38, J(Tl—H) 1338 Hz J(H—H) 7 Hz, the protons in the methylene group *cis* to thallium as a doublet of quartets* at δ 2.45, J(Tl—H) 126, J(H—H) 7 Hz, the protons in the aliphatic methyl groups as a multiplet at δ 1.06, the acetoxy protons as a singlet at δ 2.32 and the acetate protons as a singlet at δ 2.00.

Further work on the mechanism of acetoxythallation reaction is in progress.

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*In the 60 MHz spectrum the right hand peak of the doublet was buried under the multiplet due to methyl groups. The δ and J values were obtained by a comparison of the spectra obtained at 60 and 100 MHz.