Regio- and stereo-selective hydroalumination of disubstituted acetylenes with Et_3Al catalysed by $(\eta^5\text{-}C_5H_5)_2TiCl_2$

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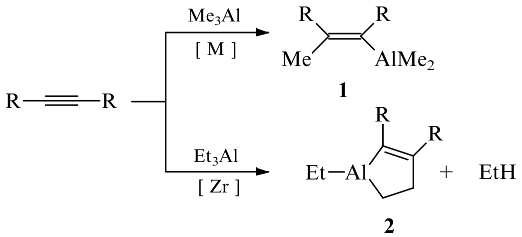
A novel regio- and stereo-selective method for the hydroalumination of disubstituted acetylenes in 1-[(*E*)-alkenyl]-1,1-diethylalanes with Et_3Al catalysed by $(\eta^5\text{-}C_5H_5)_2TiCl_2$ is reported.

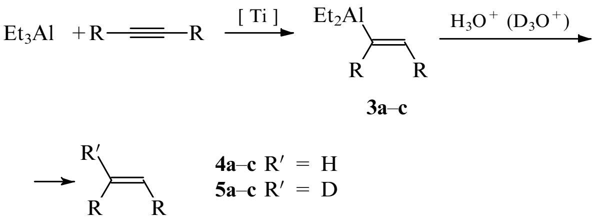
The reaction of trialkylalanes with disubstituted acetylenes in the presence of catalytic amounts of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ or $(\eta^5\text{-}C_5H_5)_2TiCl_2$ proceeds with high regio- and stereo-selectivity *via* carbo-[1,2] or cyclo-metallation[3–5] to give alkenylalanes **1** or substituted aluminacyclopent-2-enes **2**, respectively; the route and selectivity of these reactions depends mainly on the nature of the catalysts central atom, the organometallic reagent and its structure, and the solvent.



M = Ti, Zr
R = Ph, alkyl

This paper describes the hydrometallation of 1,2-disubstituted acetylenes with Et_3Al catalysed by $(\eta^5\text{-}C_5H_5)_2TiCl_2$, performed by us for the first time.

Et_3Al was found to hydroaluminate disubstituted acetylenes in the presence of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ at 22–23 °C for 6–8 h to give the (*E*)-alkenylalanes **3a–c** in yields of 75–90%.



4a–c R′ = H
5a–c R′ = D

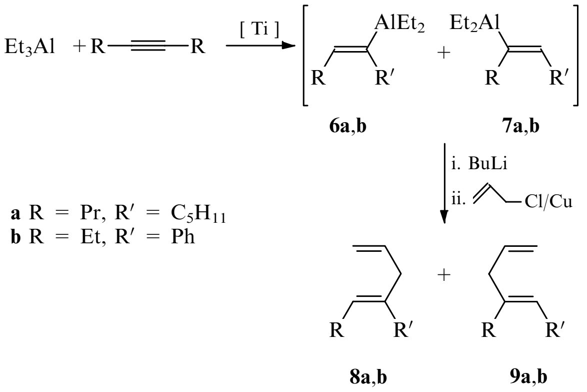
a R = Pr (90%)
b R = Bu (88%)
c R = Ph (78%)

The highest yields of compounds **3a–c** were obtained by using 5 mol% of $(\eta^5\text{-}C_5H_5)_2TiCl_2$, a two-fold excess of Et_3Al with respect to the initial acetylene, followed by a hydroalumination process without a solvent (for oct-4-yne and dec-5-yne) or in benzene for diphenylacetylene.[†] The structure of the alkenylalanes was assigned by NMR spectroscopy. The ^{13}C NMR spectrum of alkenylalane **3a** showed a broad singlet at δ 150.08 that was assigned to the sp^2 hybridized C-4 atom bonded to the aluminium atom. A doublet at δ 145.3 was assigned to carbon atom C-5, δ 1.10–32.06 signals were assigned to saturated carbon atoms.[‡]

The hydrolysed **4a–c** and deuteriolysed **5a–c** products were identified by comparison with known compounds.[6] The *cis*-isomer content in the hydrocarbon mixture obtained was 96%.

Hydroalumination of the asymmetric disubstituted acetylenes proceeded under the given conditions to give regioisomers. Thus, regioisomers **6a** and **7a** were formed by treating dec-4-yne with Et_3Al in the presence of 5 mol% of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ (*ca.* 1 : 1). The analogous reaction with phenylethylacetylene gave **6b** and **7b** (*ca.* 9 : 1). The ratio of regioisomers **6a**,**b** and **7a**,**b** were assigned by spectroscopy and determined by cross-coupling products **8a**,**b** and **9a**,**b**.[§] *cis*-4,5-Disubstituted alka-1,4-dienes **8a**,**b** and **9a**,**b** were identified by comparison with known samples.[7]

Thus, a novel hydrometallating reagent Et_3Al–$(\eta^5\text{-}C_5H_5)_2TiCl_2$ was developed to give diethylalkenylalanes and the corresponding (*Z*)-alkenes and *cis*-4,5-disubstituted alka-1,4-dienes from disubstituted acetylenes under mild conditions with high selectivity.



a R = Pr, R′ = C_5H_{11}
b R = Et, R′ = Ph

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[†] *Synthetic procedure:* A 50 ml flask equipped with a magnetic stirrer under argon at 0 °C was charged with oct-4-yne (1.10 g, 10 mmol), Et_3Al (2.28 g, 20 mmol) and $(\eta^5\text{-}C_5H_5)_2TiCl_2$ (0.10 g, 0.5 mmol). The reaction mixture was stirred for 8 h at 22–23 °C, treated with 5% HCl and then neutralised with water to give (*Z*)-oct-4-ene **4a** (1.0 g, 90% yield).

[‡] *Spectroscopic data*: **3a** ^{13}C NMR ($CDCl_3$) 15.53 (C-1), 16.10 (C-2), 32.06 (C-3), 150.08 (C-4), 145.31 (C-5), 25.00 (C-6), 19.71 (C-7), 15.53 (C-8), −1.10 (C-9), 9.98 (C-10).

[§] *Synthetic procedure*: An equimolar amount of BuLi with respect to Et_3Al was added to a solution of (*E*)-alkenylalane (10 mmol) in 10 ml absolute THF at 0 °C. The reaction mixture was stirred for 0.5 h and then allyl chloride was added (Et_3Al : allyl chloride = 1 : 3) along with 5 mol% CuCl. The resultant mixture was heated to room temperature and stirred for 5 h. A mixture of regioisomers **8a**,**b** and **9a**,**b** was obtained in 60–75% yield.

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