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A SELECTIVE AND CONVENIENT SYNTHESIS OF β,β-DIALKYL-SUBSTITUTED ALKENYLBORANES AND ALKENYLZIRCONIUMS VIA CARBOALUMINATION OF ALKYNES[1]

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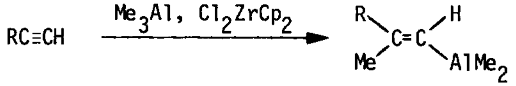
SUMMARY Treatment of (*E*)-2-methyl-1-alkenylalanes (1), readily obtainable via Zr-catalyzed reaction of Me_3Al with 1-alkynes, with *B*-methoxydialkylboranes produces the corresponding alkenylboranes, while sequential treatment of 1 with *n*-BuLi and X_2ZrCp_2 (X = Cl or I) provides the desired monoalkenylzirconium derivatives, the product yields for both reactions being 85-100%.

We have recently reported that the reaction of terminal alkynes with an organoalane and Cl_2ZrCp_2 cleanly produces β,β-dialkyl-substituted alkenylalanes[2] (e.g., 1), readily convertible into various terpenoids.[3]



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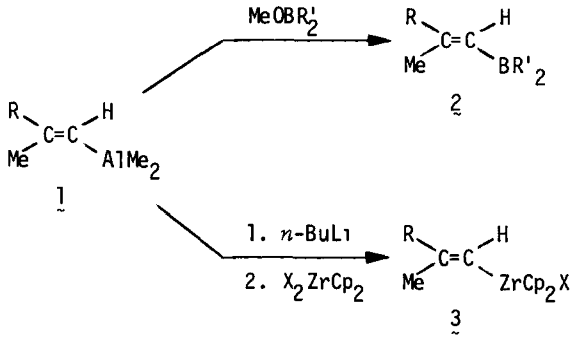
(1)

Their ready availability prompted us to develop indirect routes to various β,β-dialkyl-substituted alkenylmetals, and we have indeed developed a selective synthesis of alkenylmercury derivatives via 1.[4] Herein we report that treatment of 1 with one molar equivalent of a *B*-methoxydialkylborane, e.g., *B*-methoxy-9-borabicyclo[3.3.1]nonane or *B*-methoxydicyclohexylborane, produces 2 in 85 - 100% yields and that treatment of 1, free from Me_3Al and Cl_2ZrCp_2, with one equivlant of *n*-BuLi followed by addition of one equivalent of X_2ZrCp_2 (X = Cl or I) cleanly provides the corresponding monoalkenylzirconium derivatives 3. The reaction of organoalanes with boron compounds to form organoboranes is known. However, direct conversion of alkenylalanes into the corresponding alkenylboranes does not appear to have been reported.[5] Nor does direct conversion of alkenylaluminums into alkenylzirconium derivatives appear to have been documented.



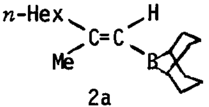
(2)

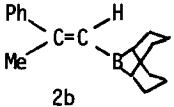
(X = Cl or I)

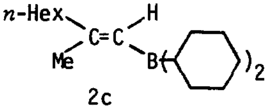
The following procedure for the preparation of (E)-B-(2-methyl-1-octenyl)-9-borabicyclo-[3 3.1]nonane (2a) is representative of the Al-to-B conversion. 1-Octyne (1.10 g, 10 mmol) was carbometallated at 25°C with Me$_3$Al (1.44 g, 1.9 ml, 20 mmol) and Cl$_2$ZrCp$_2$ (0.73 g, 2.5 mmol) in 1,2-dichloroethane (20 ml), as described previously.[2] After 3-6 hr the volatile compounds were evaporated by heating the reaction mixture to 50-60°C at $\leq$0.5 mm Hexane was added portionwise (4 x 5 ml) to the residue, and the supernatant solution was transferred into another flask by means of a double-tipped needle. The ^{1}H NMR spectrum of the hexane solution showed a singlet at 5.43 ppm for the alkenyl proton No signal for the Zr-bound cyclopentadienyl group was discernible, indicating that all Zr-containing compound had been removed. To an aliquot of this solution containing 1 mmol of the alkenylalane was added 1 mmol (0 152 g, 0.16 ml) of B-methoxy-9-borabicyclo[3 3.1]nonane[6] at 25°C, and the resultant mixture was stirred for 1 hr. Examination by ^{1}H NMR indicated the complete disappearance of the signal at 5.43 ppm and the appearance of a singlet at 5.98 ppm attributable to the alkenyl proton of 2a. The yield of 2a by ^{1}H NMR was 100% A sample of 2a free from any Al-containing byproduct was obtained by evaporating volatile compounds at 90-100°C and $\leq$0.5 mm ^{1}H NMR (C$_6$H$_6$, Me$_4$Si) δ 0 96 (t, J = 6 Hz, 3 H), 1.2-1.6 (m, 12 H), 1 9-2.3 (m, 15 H), 6.19 (s, 1 H) ppm, ^{13}C NMR (C$_6$H$_6$, Me$_4$Si) δ 14.29, 21.32, 23.01, 23 81, 28 39, 29.52, 32.15, 33.90, 43.86, 130 (broad), 162.09 ppm.

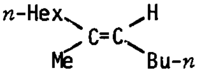
To further characterize the alkenylborane product as well as to demonstrate its synthetic utility 2a was converted into (E)-6-methyl-5-dodecene[7] (4) in 77% GLC yield (~ 60% isolated yield) by treating 2a sequentially with one equivalent each of n-BuLi and iodine in THF (-70°C to room temperature). As reported by Levy,[8] the alkene product 4 obtained by the Zweifel olefin synthesis via deiodoboration[9] run in the absence of an excess of a base is the E-isomer ($\geq$98% E)· bp 47-48°C (0.5 mm), ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 0.87 (t, J = 6 Hz, 6 H), 1.1-1 5 (m, 12 H), 1.57 (s, 3 H), 1.94 (t, J = 6 Hz, 4 H), 5.10 (t, J = 8 Hz, 1 H) ppm; ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 14 10, 15.88, 22.43, 22.76, 27.70, 28.09, 29.07, 31.91, 32.24, 39.85, 124.62, 135.16 ppm

The reaction of 2a with methyl vinyl ketone[10] (3 equiv) also proceeded smoothly at 0-25°C (6-8 min) to give 5[7] in 75% GLC yield (60% isolated yield): bp 95-96°C (0 5 mm), IR (neat) 1720 cm^{-1}, ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 0.88 (t, J = 6 Hz, 3 H), 1 1-1.5 (m, 8 H), 1 61 (s, 3 H), 1 98 (t, J = 6 Hz, 2 H), 2.13 (s, 3 H), 2 2-2.6 (m, 4 H), 5.08 (t, J = 8 Hz, 1 H) ppm; ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 14.11, 15 90, 22.57, 22 68, 27 94, 28 99, 29 89, 31.84, 39 71, 43.82, 122 40, 136.76, 208.60 ppm The stereospecificity observed in this reaction was also $\geq$98%, strongly supporting the assignment of the E geometry to 2. The corresponding reaction of alkenylalanes is known.[11] However, the maximum GLC yield of 5 in this reaction was limited to 56%.


2a


2b


2c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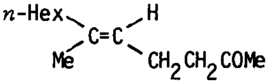
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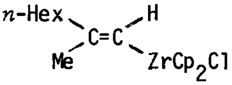
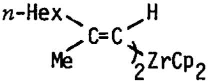

3a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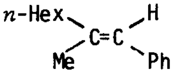
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In the above alkenylborane reactions the product yields were essentially unaffected by the presence of the Al-containing byproducts, e.g , Me_2AlOMe, so that their removal by evaporation may be omitted for such synthetic purposes.

The Al-to-B transmetallation appears to be quite general. Thus, no difficulty was encountered in preparing 2b and 2c in 100 and 87% yields, respectively, from the corresponding alkenylalanes and *B*-methoxydialkylboranes. The ^1H NMR signals for the alkenyl protons in 2b and 2c appear at 6.65 and 5.70 ppm, respectively, in hexane.

The transmetallation involving Al and Zr presents an intriguing case. Alkenylalanes (1) do not react with Cl_2ZrCp_2 to produce 3.[2] In fact, alkenylzirconium derivatives are known to react with $AlCl_3$ or dialkylchloroalanes to give alkenylalanes.[12] Despite these facts, we reasoned that the Al-to-Zr transmetallation should be promoted by increasing the alkenyl transferability through ate complexation and have indeed found that a complete alkenyl transfer from Al to Zr occurs in the reaction of lithium alkenylaluminates with X_2ZrCp_2 (X = Cl or I). The following is representative of the Al-to-Zr transmetallation. (*E*)-2-Methyl-1-octenyldimethylalane (1a) was prepared as described above and converted into the corresponding aluminate by adding one equivalent of *n*-BuLi. This was then added to a suspension of Cl_2ZrCp_2 (1 equiv) in THF at -78°C The reaction mixture was warmed slowly to room temperature and evaporated under reduced pressure. The ^1H NMR spectrum of the product dissolved in 1,2-dichloroethane shows a singlet at 6.11 ppm along with very minor singlets at 6.35 and 5 98 ppm. The peak at 6.35 ppm is due to Cl_2ZrCp_2. That the peak at 5.98 ppm is due to the dialkenylated product 6 has been established by an independent synthesis of 6 by the reaction of Cl_2ZrCp_2 with (*E*)-1-lithio-2-methyl-1-octene generated by treating (*E*)-1-iodo-2-methyl-1-octene[13] with *n*-BuLi (1 equiv) at -78°C to -60°C. The yield of 3a by ^1H NMR was ca 95% The ^1H and ^{13}C NMR spectra of 3a in C_6D_6 display the following signals ^1H NMR (C_6D_6, Me_4Si) δ 0.89 (t, J = 6 Hz, 3 H), 1.1-1.5 (m, 8 H), 1.97 (s, 3 H), 2.23 (t, J = 7 Hz, 2 H), 5.91 (s, 10 H) ppm, ^{13}C NMR (C_6D_6, Me_4Si) δ 14.27, 22.94, 24.46, 28.67, 29.45, 32 13, 44.01, 112.53, 133 (broad), 173.32 ppm. In the ^1H NMR spectrum, the alkenyl proton signal is not readily discernible. The assignment of the *E* geometry to 3a has been supported by conversion of 3a by its treatment with iodine into (*E*)-1-iodo-2-methyl-1-octene which is identical in all respects with an authentic sample obtained by treating 1a with iodine.[13] As expected, 3a smoothly reacted with iodobenzene in the presence of 5 mol % of $Pd(PPh_3)_4$ and $ZnCl_2$[14] (1 equiv) in THF at room temperature to give 7 in 89% yield.[15] Since neither toluene nor *n*-butylbenzene was produced, the alkylaluminum derivatives, e g , *n*-$BuMe_2Al$, do not compete for iodobenzene with 3a compound. Interestingly, treatment of the transmetallation product containing 3a and the trialkylalane byproducts with 1-2 molar equiv of $AlCl_3$ at room temperature induces the known Zr-to-Al transmetallation,[12] as evidenced by (a) complete disappearance of the Cp signal at 6.10 ppm for 3a as well as by reappearance of the Cp signal at 6.36 ppm for Cl_2ZrCp_2 and a broad singlet at 5 1 ppm[16] for alkenylalanes. The results clearly establish the clean-cut reversibility of the transmetallation between organoaluminum and organozirconium compounds

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