

## ZIRCONIUM-CATALYZED CARBOALUMINATION OF ALKYNES AND ENYNES AS A ROUTE TO ALUMINACYCLES AND THEIR CONVERSION TO CYCLIC ORGANIC COMPOUNDS

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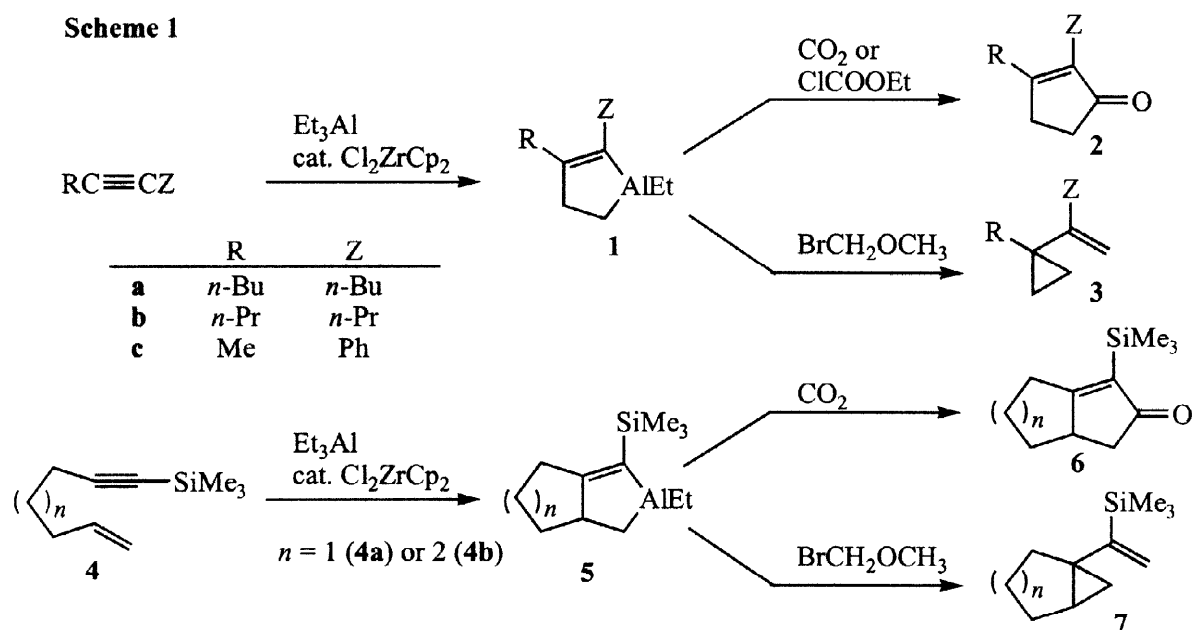
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**Abstract:** Aluminacyclopentenes, obtainable *via* Zr-catalyzed cyclic carboalumination with Et<sub>3</sub>Al and alkynes or enynes, can be converted to the corresponding cyclopentenones and alkenylcyclopropanes by treatment with CO<sub>2</sub> and BrCH<sub>2</sub>OCH<sub>3</sub>, respectively. © 1998 Elsevier Science Ltd. All rights reserved.

Until recently, synthesis of cyclic organic compounds *via* aluminacycles had been very rare.<sup>1,2</sup> In one case, conversion of 1-allylcyclohexene into perhydrindane with *i*-Bu<sub>2</sub>AlH was rationalized in terms of the intermediacy of 1-isobutyl-1-aluminadecalin.<sup>3</sup> Over the past several years, the Zr-catalyzed carboalumination of alkynes has been shown to produce, in some cases, aluminacyclopentenes as the products.<sup>4-6</sup> Also developed recently are conversion of aluminacyclopentanes into cyclobutane<sup>7</sup> and cyclopropane<sup>8</sup> derivatives. In this paper, we report on (a) the preparation of aluminacyclopentenes by the Zr-catalyzed carboalumination of alkynes and enynes and (b) conversion of aluminacyclopentenes into the corresponding cyclopentenones and vinylcyclopropanes by their reactions with CO<sub>2</sub> or its synthetic equivalents and MeOCH<sub>2</sub>Br, respectively (Scheme 1).

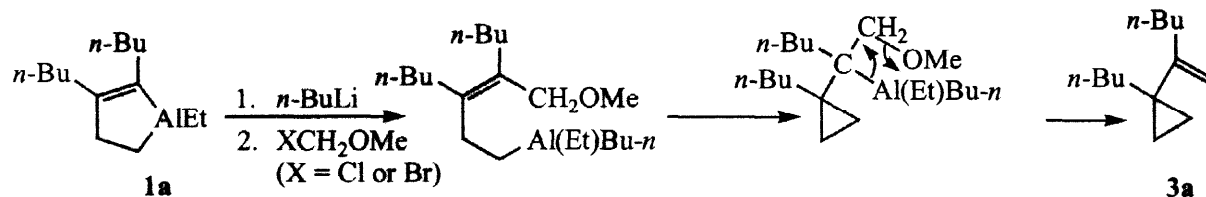
The above-mentioned recent finding that the Zr-catalyzed carboalumination of alkynes<sup>9</sup> with Et<sub>3</sub>Al and higher trialkylalanes can give aluminacyclopentenes (1)<sup>5-6</sup> prompted us to seek various ways of converting 1 into both cyclic and acyclic organic products. One of the most obvious reagents to be considered was carbon monoxide. Curiously, however, the literature appears to be devoid of reports on the reaction of organoalanes with CO.<sup>1,2,10,11</sup> Indeed, treatment of **1a** (R = *n*-Bu) with 10 atm of CO at 23 °C for 24 h did not lead to carbonylation of **1a**. After deuterolysis of the reaction mixture, (*Z*)-5-deuteriomethyl-6-deuterio-5-decene (>95% D in both positions) was obtained in 90% yield. Evidently, little or no migratory insertion takes place. Fortunately, more favorable results were obtained with carbonic acid derivatives and CO<sub>2</sub> itself. Thus, treatment of **1a** with 3 equiv

of  $\text{ClCOOEt}^{12}$  (65%),  $\text{CO(OEt)}_2$  (34%), or even  $\text{ClCOCOC}l$  (34%) produced the desired 2,3-di(*n*-butyl)-2-cyclopentenone (**2a**) in the yields indicated in parentheses. However, by far the best results were obtained with dry  $\text{CO}_2^{13}$  at 0 to 23 °C, which led to a 76% yield (> 95% by NMR) of **2a**. Similarly, treatment of **1b** with  $\text{CO}_2$  produced **2b** in 72% yield. Conversion of aluminacycles to the corresponding cyclic ketones *via* treatment with  $\text{CO}_2$  appears to be novel, although not unexpected, and it makes the development of the carbonylation of aluminacycles with CO unnecessary.



In search for other carbon-carbon bond formation reactions of **1**, **1a** was first converted to the corresponding “ate” complex by its treatment with *n*-BuLi and then reacted with an excess (6 equiv) of paraformaldehyde in one case and  $\text{ClCH}_2\text{OME}$  in another. Whereas the reaction with paraformaldehyde provided, after protonolysis, the expected (*E*)-2-(*n*-butyl)-3-ethyl-2-hepten-1-ol in 56% yield, that with  $\text{ClCH}_2\text{OME}$  produced unexpectedly 1-(*n*-butyl)-1-(2-hexenyl)cyclopropane (**3a**) in 30% yield. Ate complexation proved to be unnecessary for the latter reaction. Furthermore, the use of  $\text{BrCH}_2\text{OME}$  improved the yield of **3a** to 62%. Similarly, **3b** ( $R = n\text{-Pr}$ ) was obtained in 56% yield, and 1-phenylpropyne (**1c**) was converted to 1-(1'-phenylethenyl)-1-(*n*-propyl)cyclopropane (**3c**) in 52% yield along with a minor amount of 1-phenyl-1-(2'-propenyl)cyclopropane. The results indicate that, as in the corresponding reaction of acyclic alkenylaluminates,<sup>12</sup> the alkenyl group must selectively react with methoxymethyl halides but that the allyl ether thus formed must undergo homoallyl-cyclopropylcarbinyl rearrangement and deoxyalumination (Scheme 2). This reaction adds to the growing list of trapping cyclopropylcarbinylmetals *via*  $\beta$ -elimination to give alkenylcyclopropanes.<sup>14</sup>

Scheme 2



The Zr-catalyzed cyclic carboalumination as well as the reactions with  $\text{CO}_2$  and  $\text{BrCH}_2\text{OCH}_3$  are also applicable to the cases of enynes, such as 7-(trimethylsilyl)-1-hepten-6-yne (**4a**) and 8-(trimethylsilyl)-1-octen-7-yne (**4b**). Treatment of **4a** and **4b** with  $\text{Et}_3\text{Al}$  (2.5 equiv) and 12.5 mol % of  $\text{Cl}_2\text{ZrCp}_2$  led to the formation of **5a** and **5b** in 60 and 55% yields, respectively, by GLC analysis of the protonolysis products. The reaction of **5a** and **5b** with  $\text{CO}_2$  gave **6a** and **6b** in 50 and 51% yields, respectively, while the reaction of **5a** with  $\text{BrCH}_2\text{OCH}_3$  provided **7a** in 47% yield. Although these transformations are stoichiometric in Al, it is catalytic in Cp-bearing Zr, which makes the use of chiral Cp derivatives for asymmetric conversion of **4** into **6** and **7** an attractive proposition. We are currently pursuing this aspect.

The following procedures for the conversion of **4a** into **6a** and that of **1a** into **3a** are representative. **Zr-catalyzed bicyclization of 7-(trimethylsilyl)-1-hepten-6-yne with  $\text{Et}_3\text{Al}$  followed by treatment with  $\text{CO}_2$  to provide 2-(trimethylsilyl)bicyclo[3.3.0]oct-1(2)-en-3-one.** To a suspension of  $\text{Cp}_2\text{ZrCl}_2$  (0.074 g, 0.25 mmol) in toluene (5 mL) was added  $\text{Et}_3\text{Al}$  (1.9 M in toluene, 2.7 mL, 5 mmol) at 23 °C. After 5 min 7-(trimethylsilyl)-1-hepten-6-yne (**4a**) (0.332 g, 2.0 mmol) was added, and the reaction mixture was stirred for 65 h. Analysis of a protonolyzed aliquot by GLC indicated the formation of **5a** in 60% yield. After cooling the reaction mixture to 0 °C,  $\text{CO}_2$  was slowly bubbled through *via* a 17 gauge needle. The reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$  and poured on 3N HCl and ether at 0 °C. The organic layer was washed with aqueous  $\text{NaHCO}_3$ , dried over  $\text{MgSO}_4$ , and concentrated. Chromatographic purification (pentane and then 4:1 pentane-ether) afforded **6a**<sup>15</sup> as a pale yellow oil (0.194 g, 1.0 mmol, 50%). **Generation of 1a by Zr-catalyzed cyclic carboalumination of 5-decyne with  $\text{Et}_3\text{Al}$  followed by its treatment with  $\text{BrCH}_2\text{OCH}_3$ .** Generation of **1a** in 95% yield was performed as reported previously<sup>6</sup> from 5-decyne (0.36 mL, 2 mmol),  $\text{Et}_3\text{Al}$  (0.82 mL, 6 mmol), and  $\text{Cp}_2\text{ZrCl}_2$  (59 mg, 0.2 mmol) in hexanes (4 mL). At -78 °C  $\text{BrCH}_2\text{OCH}_3$  (90%, 0.20 mL, 2.2 mmol) was added, and the mixture was stirred overnight at 23 °C. After the usual workup, purification by column chromatography (pentane) provided 1-(1'-butylethenyl)-1-butylcyclopropane (0.224 g, 62% yield):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ )  $\delta$  0.34 (dd,  $J = 6$  and 4 Hz, 2 H), 0.53 (dd,  $J = 6$  and 4 Hz, 2 H), 0.8-1.0 (m, 6 H), 1.2-1.5 (m, 10 H), 2.06 (t,  $J = 8$  Hz, 2 H), 4.74 (s, 2 H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ )  $\delta$  12.07, 14.07, 14.14, 22.77, 22.82, 26.25, 29.51, 30.37, 33.90, 36.65, 109.38, 151.66.

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