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Allyl and 2-Cyclopropylethyl Rearrangements in the Reaction of 1-Alkenylaluminums with Diiodomethane/Triethylaluminum Reagent

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Ilfir R. Ramazanov* Alsu V. Yaroslavova Niyaz R. Yaubasarov Usein M. Dzhemilev

Institute of Petrochemistry and Catalysis of Russian Academy of Sciences, 141 Prospekt Oktyabrya, Ufa 450075, Russian Federation Ilfir.ramazanov@gmail.com



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Abstract The reaction of diiodomethane and triethylaluminum with substituted 1-alkenylaluminums obtained by the Zr-catalyzed carbo- or cycloalumination of mono- or dialkyl-substituted alkynes resulted in the selective formation of di- and tetrasubstituted cyclopropanes. 1-Alkenylaluminums prepared from substituted propargylamines reacted with diiodomethane and triethylaluminum to give substituted allyl-amines. A plausible mechanism for the reaction of the 1-alkenylaluminums with diiodomethane/triethylaluminum is proposed.

Key words alkenylaluminums, aluminum carbenoids, cyclopropanation, rearrangement, allylic amines

We previously developed a method for the preparation of substituted cyclopropanes from alkynes by using trialkylaluminums and CH₂I₂.¹ On the basis of these results, we assumed that the cyclopropanation of 1-alkenylaluminums with the CH₂I₂/Et₃Al reagent might provide cyclopropylaluminums of a different structure. It is known that the reaction of CH₂Br₂/Zn(Cu) reagent with 1-alkenylaluminums prepared by hydroalumination of terminal alkynes affords cyclopropylaluminums in good yields.² However, we failed in our attempts to carry out the reaction of $CH_2Br_2/Zn(Cu)$ reagent with 1-alkenylaluminums prepared by the carboor cycloalumination of mono- and dialkyl-substituted alkynes. We presumed that the interaction of the 1-alkenylaluminums and CH₂I₂/Et₃Al reagent might proceed through a more-complex mechanism, as repeatedly observed in reactions of substituted alkynes with CH₂I₂ and Et₃Al. We therefore decided to investigate the reactions of 1-alkenylaluminums with the CH₂I₂/Et₃Al reagent in an attempt to develop a new method for the synthesis of cyclopropylaluminum compounds.

It is known that the catalytic hydro-,³ carbo-,⁴ and cycloalumination⁵ of alkynes provide a rich set of substituted 1-alkenylaluminums with various structures. The starting materials were the products of the Zr-catalyzed cycloalumination of oct-4-yne, dec-4-yne,^{6,7} N,N-dimethylhept-2-yn-1-amine, or *N*,*N*-dimethylnon-2-yn-1-amine;⁸ the Zr-catalyzed methylalumination of pent-1-yne or hex-1-yne;9 and the Zr-catalyzed hydroalumination of oct-1-yne.¹⁰ First, we studied the reaction of aluminacyclopent-2-enes with the aluminum carbenoid Et₂AlCH₂I, formed in situ by mixing equimolar amounts of CH₂I₂ and Et₃Al. We found that the reaction of the symmetrical dialkyl-substituted alkynes oct-4-yne and dec-5-yne with three equivalents of Et₃Al at 40 °C in hexane for two hours, followed by addition of four equivalents of CH₂I₂ and Et₃Al at room temperature gave, after deuterolysis, the symmetrical dideuterated hydrocarbons 1a and 1b, respectively, which contain a tetrasubstituted cyclopropane fragment (Scheme 1).¹¹ In the ¹³C NMR spectra of the deuterolysis products 1a and 1b, only one set of signals was observed, indicating the formation of a single stereoisomer. Compounds 1a and 1b were identified by comparison with the known properties of their nondeuterated and monodeuterated analogues.¹

Aluminacyclopent-2-enes obtained by the cycloalumination of substituted propargylamines reacted well with the CH_2I_2/Et_3AI reagent to give, after deuterolysis, the dideuterated enamines **2a** and **2b** in 80 and 88% yield, respectively. The reaction of the CH_2I_2/Et_3AI reagent with 1-alkenylaluminums prepared by Zr-catalyzed methylalumination of 1-alkynes gave, after deuterolysis, the monodeuterated hydrocarbons **3a** and **3b** containing monosubstituted cyclopropane fragments in 66 and 70% yield, respectively. However, the use of Me₃AI instead of Et₃AI (Scheme 1) led only to the formation of the iodo-substituted cyclopropane **4** in 83% yield. Diisobutyl(pentyl)aluminum, prepared by the



hydroalumination of dec-1-yne with DIBAL-H did not react with the CH_2I_2/Et_3Al reagent, and (1*E*)-dec-1-ene- d_1 was exclusively isolated from the reaction mixture after deuterolysis. Generally, confusion is caused by both an unexpected structure of the reaction products and the sharp differences in in the behavior of the various 1-alkenvlaluminums.

Therefore, the reaction of 1-alkenylaluminums with CH₂I₂ and Et₃Al proceeds in an unusual way. It is obvious that diethyl(iodomethyl)aluminum is formed in the first stage of the reaction (Scheme 2).^{12,13} Subsequent interaction between the aluminum carbenoid and the substituted alkenylaluminum A might proceed by three possible pathways: (a) cyclopropanation of the C=C double bond, (b) insertion of a methylene group into the $Al-C(sp^2)$ bond, or (c) insertion of a methylene group into the $Al-C(sp^3)$ bond. However, it is known that the reaction of the 1-alkenylaluminum prepared from Et₃Al and but-1-yne, with an equimolar amount of CH₂N₂ in toluene-anisole at -78 °C occurs predominantly at the Al-C(sp²) bond to give methylene-insertion and allyl-rearrangement products sequentially.¹⁴ According to the proposed mechanism (Scheme 2), the 1alkenylaluminum A reacts with the aluminum carbenoid Et₂AlCH₂I to give the product of methylene insertion into Al-C(sp²) bonds (intermediate **B**). Intermediate **B** then undergoes allylic rearrangement to form intermediate C.

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According to the results of Hoberg,¹⁴ methylene insertion into the bond between the aluminum atom and the guaternary carbon atom of the intermediate **C** can occur to give the homoallylic aluminum compound **D**. The ease of the insertion might be due to the higher electron density on the quaternary carbon atom. Previously, we have used this hypothesis to explain the conversion of terminal and disubstituted alkynes into tri- and tetrasubstituted cyclopropanes under the action of Et₃Al and CH₂I₂.¹ The subsequent reaction of intermediate **D** with one equivalent of the aluminum carbenoid (Et₂AlCH₂I) gives compound E, which contains a 1.1-disubstituted cyclopropane fragment. However, in the case of substituted propargyl amines, the C=C double bond of intermediate **D** is insufficiently reactive to give cyclopropanes. The driving force for the subsequent 2-cyclopropylethyl rearrangement of intermediate **E** is the greater thermodynamic stability of the resulting substituted cyclopropane **F**.



The proposed scheme fully describes the formation of all three types of deuterolysis products **1–3**. Plausible mechanisms for the formation of products **1a**, **2a**, **3a**, and **4** are given in the Supporting information. We have previously obtained compounds of a similar structure by the reaction of mono- or disubstituted alkynes with trialkylaluminums (Et₃Al or Me₃Al) and CH₂I₂.¹ The formation of the intermediates **D–F** fits perfectly into the scheme proposed in the early study, where the first organometallic version of the 2-cyclopropylethyl rearrangement was observed. To the best of our knowledge, an earlier attempt to observe the rearrangement of 2-cyclopropylethyl organomagnesium compounds of various structures resulted in failure.¹⁵

The reason why the 2-cyclopropylethyl rearrangement does not occur in the case of terminal alkynes remains unclear. We assume that the presence of an equimolar amount of a zirconocene complex in the reaction mixture might affect the 2-cyclopropylethyl rearrangement process through the formation of stable Zr–Al bimetallic complexes.

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The formation of iodo-substituted cyclopropane 4 can be explained by the same reason that iodocyclopropanes are formed in the reaction of mono- and disubstituted alkynes with Me₃Al and CH₂I₂.¹ The rate of generation of the aluminum carbenoid in the case of Me₃Al is much lower than that in the reaction of CH₂I₂ with Et₃Al. Gas chromatography showed that when equimolar amounts of CH₂I₂ and Et₃Al reacted in a solution of dichloromethane at room temperature, CH₂I₂ was not detected in the reaction mixture after five minutes because it was completely converted into the aluminum carbenoid. In the case of Me₂Al, the conversion of CH₂I₂ was only 73% after two hours. This result can be explained by the lower concentration of monomeric Me₃Al compared with that of Et₃Al, due to the greater propensity of Me₃Al to form the dimer (Me₃Al)₂.¹⁶ Consequently, the cyclopropane-containing organoaluminum intermediate G reacts with residual CH₂I₂ to give the iodocyclopropane **4**.

Therefore, in an attempt to clarify the mechanism of interaction of alkynes with trialkylaluminums and CH₂I₂, we studied the reaction of 1-alkvnvlaluminums with the CH₂I₂/Et₃Al reagent. During the study, we found analogies to the work of Hoberg, who studied the reactions of aluminum carbenoids. The reaction that we discovered represents an interesting modification of the transformation of (Z)-but-1-en-1-yldiethylaluminum under the action of CH₂N₂.¹⁴ Our results clarified the mechanism of the reaction of alkynes with trialkylaluminums and CH₂I₂. At the same time, in our opinion, the observed allyl and 2-cyclopropylethyl rearrangements of organoaluminums merit further investigation.

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Supporting Information

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(1a)Dec-5-yne (0.14 g, 1 mmol) and Et₃Al (0.18 mL, 1.2 mmol) were added to a suspension of Cp₂ZrCl₂ (0.015 g, 0.05 mmol) in hexane (5 mL) under argon at 40 °C. After 2 h, CH₂I₂ (0.32 mL, 4 mmol) and Et₃Al (0.60 mL, 4 mmol) were added at 0 °C, and the mixture was stirred for 18 h at rt. The mixture was diluted with hexane (5 mL) and then D₂O (3 mL) was added dropwise while the reaction flask was cooled in an ice bath. The precipitate was collected on a filter paper, and the aqueous layer was extracted with $Et_2O(3 \times 5 \text{ mL})$. The organic layers were combined, washed with brine (10 mL), dried (CaCl₂), and concentrated in vacuo to give the crude product as a colorless oil, which was distilled through a microcolumn at 2 mm Hg to give a colorless oil; yield: 0.15 g (71%); bp 98-100 °C (2 mm Hg). ¹H NMR (400 MHz, CDCl₃): δ = 0.85–0.95 [m, 10 H, C(1,10)H₃, C(12,14)H₂D], 1.25– 1.42 [m, 18 H, C(2-4, 7-9)H₂, C(11,13,15)H₂]. 13 C NMR (100 MHz, $CDCl_3$): $\delta = 0.89$ [2 C, J = 19 Hz, C(12,14)], 14.21 [2 C, C(1,10)], 23.26 [2 C, C(2,9)], 24.13 [2 C, C(11,13)], 24.27 [C(15)], 29.23 [2 C, C(3,8)], 30.02 [2 C, C(5,6)], 30.77 [2 C, C(4,7)]. MS: m/z (%) = 212 (9) [M]⁺, 182 (58) [M - C₂H₄D]⁺, 155 (57) [M -C₄H₉]⁺. Anal. calcd for C₁₅H₂₈D₂: C, 84.8. Found: C, 84.6.

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