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Aluminum carbenoids in allene cyclopropanation

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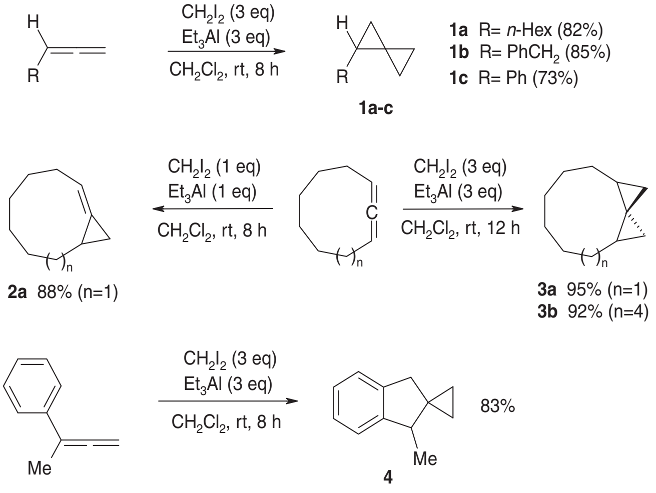
ABSTRACT

The reactions of aluminum carbenoids with alkyl- and phenyl-substituted allenes and cyclic allenes are studied. An efficient method for the synthesis of substituted spiropentanes was developed. 1,2-Cyclononadiene was selectively converted into bicyclo[7.1.0]dec-1-ene. An unusual transformation of α-methylphenylallene into a spiroindane derivative under the action of $Et_3Al–CH_2I_2$ was found.

Earlier, we reported that alkynes react with CH_2I_2 and trialkylaluminums (Me_3Al, Et_3Al, and *i*-Bu_3Al) to give substituted cyclopropanes.[1] It was found that the structures of the products and the mechanism of their formation depended strongly on the nature of the multiple bonds. In the case of alkenes, the reaction proceeds as a one-stage methylene transfer process to afford the product of cyclopropanation.[2] Contrary to this, the reaction of alkynes with $CH_2I_2–R_3Al$ (R = Me, Et and *i*-Bu) proceeds via a sequence of rearrangements. According to the scheme proposed for the reaction, carboalumination of the triple bond by aluminum carbenoids occurs in the first stage. Thus, alkenes and alkynes show a curious difference in behavior toward aluminum carbenoids. This prompted us to investigate the reaction of aluminum carbenoids with allenes which contain both sp^2- and sp-hybridized carbon atoms. In order to develop a general method for the selective preparation of alkylidenecyclopropanes and spiropentanes, the influence of the nature of the substituent on the allene moiety, the degree of substitution, and the structure of allene have been studied. It should be noted that in the literature there is a single example of the exhaustive cyclopropanation of 3,4-pentadien-1-ol using $Me_3Al–CH_2I_2$.[3]

It was found that the monosubstituted allenes (*n*-hexylallene, benzylallene, and phenylallene) reacted with CH_2I_2 and Et_3Al (in a molar ratio of 1:3:3) in CH_2Cl_2 at room temperature for eight hours to give the substituted spiropentanes **1a–c** in high yields (GC) (Scheme 1).[4] When using one equivalent of CH_2I_2 and Et_3Al, a mixture of mono- and bis-cyclopropanation products was formed. The yield of **1a** did not change significantly when *i*-Bu_3Al was used instead of Et_3Al. In contrast to this, the reaction was sluggish with $Me_3Al–CH_2I_2$. The structures of spiropentanes **1a–c** were established by 1D and 2D NMR spectroscopy.[5]

The cyclopropanation of cyclic allenes (1,2-cyclononadiene, 1,2-cyclotridecadiene) proceeded in the same way (Scheme 2). In the case of 1,2-cyclononadiene, the product of mono-cyclopropanation (bicyclo[7.1.0]dec-1-ene) (**2a**) was obtained in high yield when using an equimolar ratio of reagents, apparently due to steric hindrance of the second cyclopropanation. The reaction with three equivalents of CH_2I_2 and Et_3Al gave tricyclo[8.1.0.0^{1,3}]undecane (**3a**) with the R^*R^* configuration at the chiral centers.[6] Due to molecular symmetry, the two cyclopropyl methylene groups are magnetically equivalent. The cyclopropanation of 1,2-cyclotridecadiene using equimolar amounts of CH_2I_2 and Et_3Al lacked selectivity with the preferential formation of the exhaustive cyclopropanation product **3b**.



Scheme 1. Cyclopropanation of allenes.

The reaction of α-methylphenylallene with three equivalents of CH_2I_2 and Et_3Al in CH_2Cl_2 at room temperature for eight hours gave 1′-methylspiro(cyclopropane-1,2′-indane) (**4**) in 83% yield.[7] Deuterolysis of the reaction mixture did not result in the formation of a deutero-substituted compound.

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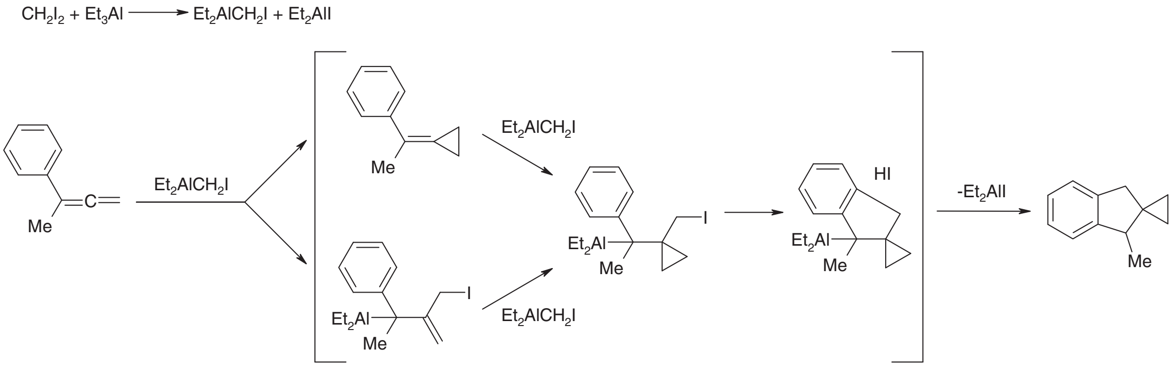

Scheme 2. The reaction of α-methylphenylallene with CH_2I_2–Et_3Al.

Scheme 2 shows two possible routes for the formation of compound **4**. Investigation of the mechanism of this unusual transformation and its scope is the subject of further research.

Earlier, Me_3Al–CH_2I_2 was preferably used for the cyclopropanation of 3,4-pentadien-1-ol.[3] It was noted that the use of Et_3Al and *i*-Bu_3Al instead of Me_3Al led to the rapid decomposition of aluminum carbenoids formed in situ. Contrary to this, in the case of alkyl- and phenyl-substituted and cyclic allenes, we obtained cyclopropanation products in high yield using only CH_2I_2–Et_3Al and CH_2I_2–*i*-Bu_3Al, whereas the reaction with CH_2I_2–Me_3Al was slow. We observed the same difference between trialkylaluminums earlier in the reactions with propargyl alcohols.[1b] The low activity of Me_3Al may be the result of its greater tendency to form stable complexes.[8] In addition, the importance of the procedure should be emphasized.[9]

Despite the fact that the cyclopropanation of allenes with metal carbenoids and CH_2N_2 is a well known method to prepare spiropentanes and methylenecyclopropanes, we have revealed herein some features of the reactions of aluminum carbenoids with alkyl- and aryl-substituted allenes and cyclic allenes. Unlike zinc carbenoids,[10] aluminum carbenoids reacted not only with alkyl-substituted allenes, but also with phenylallene. It should be noted that the reaction of phenylallene with CH_2N_2/Pd(acac)$_2$ gave only the mono-cyclopropanation product, benzylidenecyclopropane, in 49% yield.[11a] Interestingly, according to the published data,[11a,b] 1,2-cyclononadiene reacted with CH_2N_2 in the presence of a palladium catalyst with the formation of **2a** in 85% yield. Further reaction of the latter with CH_2N_2 gave **3a** in only 15% yield.

Thus, compared to other cyclopropanation agents, aluminum carbenoids show useful activity toward allenes.

Acknowledgments

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References and notes

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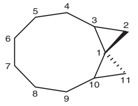
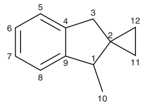
4. *Synthesis of 1-hexylspiro[2.2]pentane* (**1a**): To a solution of *n*-hexylallene (3 mmol) and diiodomethane (0.73 mL, 9 mmol) in CH_2Cl_2 (15 mL), Et_3Al (9 mmol) (**Caution**: *organoaluminums are pyrophoric and can ignite on contact with air, water, or any oxidant*) was added at 0 °C under an argon atmosphere. The mixture was stirred at room temperature for 8 h. The reaction was terminated by dilution with CH_2Cl_2 (10 mL) followed by treatment with an aq solution of HCl (7 wt %). The aqueous layer was extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were then washed with satd $NaHCO_3$ and dried over anhydrous $CaCl_2$. The solvent was removed under reduced pressure and the residue was distilled to give 0.34 g (74% isolated yield) of **1a**. Bp 87–90 °C (15 Torr).
5. ^1H and ^{13}C NMR spectra were recorded as $CDCl_3$ solutions on a Bruker Avance 400 (400.13 MHz for ^1H and 100.62 MHz for ^{13}C) spectrometer.
6. ^1H NMR spectral parameters of compounds **2a** were identical to published data.[11a] ^{13}C NMR of **3a** (δ, ppm): 12.45 (2C, C(2, 11)), 19.36 (2C, C(3, 10)), 19.75 (C(1)), 25.10 (2C, C(6, 7)), 27.33 (2C, C(5, 8)), 29.21 (2C, C(4, 9)). ^1H NMR of **3a** (δ, ppm): 0.45–0.5 (m, 2H, C(2, 11)H_a), 0.7–0.8 (m, 2H, C(2, 11)H_b), 1.15–1.3 (m, 4H, C(4, 9)H_a, C(3, 10)H), 1.3–1.45 (m, 4H, C(5–8)H_a), 1.45–1.7 (m, 4H, C(5–8)H_b), 2.15–2.25 (m, 2H, C(4–9)H_b).



7. The ^1H NMR spectrum of **4** in $CDCl_3$ solution shows four multiplets for the cyclopropyl hydrogen atoms at 0.4–0.8 ppm. The doublet signal of the methyl group has a cross-peak with the quartet for the hydrogen atom at C(1) in the COSY spectrum. The quaternary carbon atoms of the benzene moiety are magnetically non-equivalent due to the lack of symmetry in the molecule. The HMBC spectrum shows the interaction between the carbon atom at 148.92 ppm and the doublet assigned to the methyl group. ^{13}C NMR (δ, ppm): 8.75 (C(11)), 12.52 (C(12)), 16.82 (C(10)), 26.92 (C(2)), 41.70 (C(3)), 44.45 (C(1)), 123.40 and 124.15 (C(5, 8)), 126.20 (2C, C(6, 7)), 142.42 (C(4)), 148.92 (C(9)). ^1H NMR (δ, ppm): 0.4–0.5 (m, 1H, C(11)H_a), 0.55–0.6 (m, 1H, C(12)H_a), 0.6–0.7 (m, 1H, C(12)H_b), 0.75–0.8 (m, 1H, C(11)H_b), 1.12 (d, 3H, $J = 6.8$ Hz, C(10)H_3), 2.85–3.05 (m, 3H, C(1)H, C(3)H_2), 7.1–7.35 (m, 4H, Ar). MS (*m*/*z*, %): 158 (5) $[M]^+$, 143 (5) $[M-CH_3]^+$, 141 (6), 131 (13), 130 (100), 129 (40), 128 (27), 115 (40). Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.7; H, 8.6.



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