Synthesis and transformations of metallacycles
21.* A novel method for the synthesis of 1,1-dialkylcyclopropanes

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A regioselective method for the synthesis of 1,1-dialkylcyclopropanes was developed. The method is based on the reaction of 2,3-dialkyl-1-ethylalumacyclopent-2-enes with an excess of dialkyl sulfates (Me_2SO_4 or Et_2SO_4). A plausible reaction mechanism was suggested.

Key words: organoaluminum compounds, alumacyclopentenes, dialkyl sulfates, substituted cyclopropanes.

Previously, we reported on the preparation of cyclopropanes by the reaction of 3-alkyl-1-ethylalumacyclopentanes with allyl chloride in the presence of Ni complexes.[2,3]

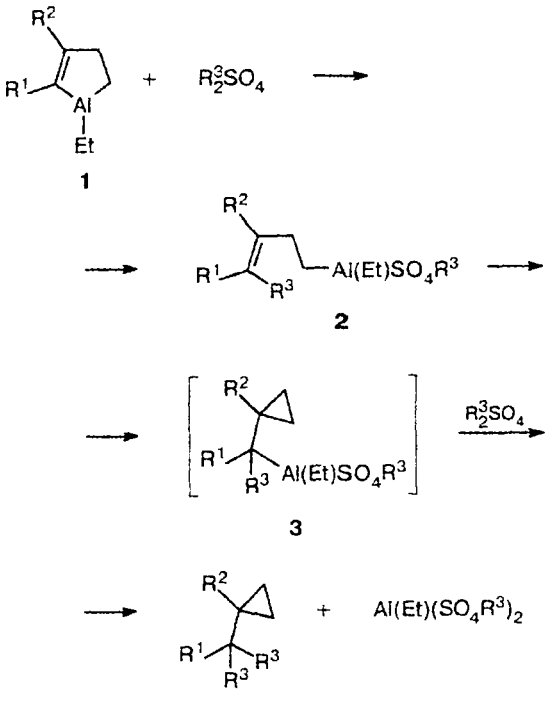
In continuation of the study of skeletal rearrangements in the series of five-membered organoaluminum compounds (OAC),[4–6] as well as for the purpose of extending the area of application of the above-mentioned reaction and developing preparative methods for the synthesis of substituted cyclopropanes, we investigated the reactions of 2,3-dialkyl-1-ethylalumacyclopent-2-enes (ACP) with dialkyl sulfates.

It turned out that the alkylation of alumacyclopentenes **1** with dimethyl (or diethyl) sulfate occurs with selective cleavage of the vinylic C—Al bond to give homoallylic OAC **2**. The latter undergo *in situ* intramolecular carboalumination and, upon additional alkylation, are transformed into 1,1-disubstituted cyclopropanes **4** (Scheme 1).

The influence of the reaction conditions and the solvent nature on the overall yield and the composition of the reaction products was studied with a reaction of 1-ethyl-2,3-di(*n*-butyl)alumacyclopent-2-ene (**1b**) (prepared *in situ* from dec-5-yne and Et_3Al) with an excess of Me_2SO_4 as an example. It was established that 1-butyl-1-(2-methylhexan-2-yl)cyclopropane (**4b**) is formed in 80% yield (with respect to dec-5-yne) at –20 °C over 12 h (Scheme 2). The optimum molar ratio of disubstituted acetylene to Me_2SO_4 is 1 : 4. With a smaller amount of Me_2SO_4 or with a shorter reaction time, the reaction mixture contains, along with 1,1-disubstituted cyclopropane **4b**, an intermediate product **2b** in considerable amount (up to 50% with respect to dec-5-yne). The nature of the solvent (tetrahydrofuran, hexane, cyclohexane, benzene, toluene, or diethyl ether) does not influence the yield and ratio of the reaction products of ACP with dimethyl sulfate; however, in the stage of preparing ACP, the solvents should be aliphatic (hexane or cyclohexane) or aromatic (benzene or toluene) hydrocarbons.[7]

The relatively low yield of compound **4c** is due to the presence of product **2c** (25%) in the reaction mixture

Scheme 1



* For Part 20, see Ref. 1.

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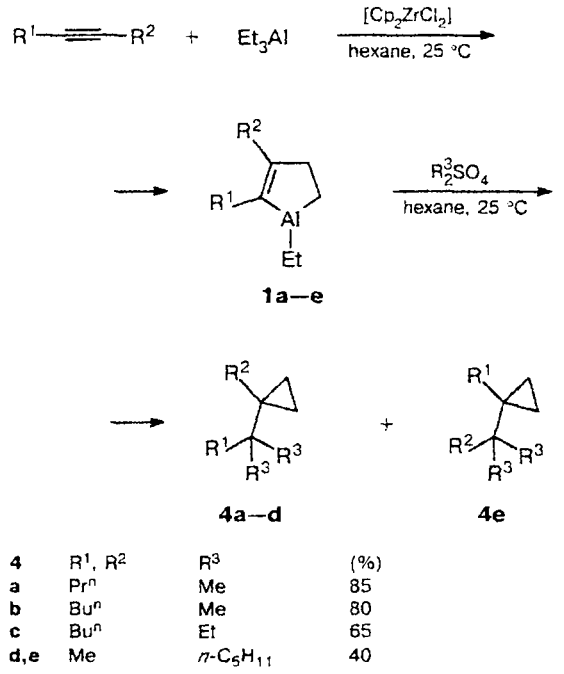
Scheme 2



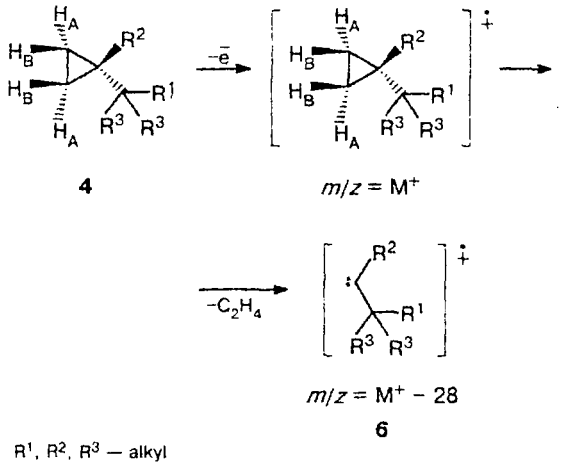
4	R^1, R^2	R^3	(%)
a	Pr^n	Me	85
b	Bu^n	Me	80
c	Bu^n	Et	65
d,e	Me	*n*-C_5H_{11}	40

(the formation of **2c** was proved by identification of its hydrolysis product, 5,6-dibutyldec-5-ene **5**). In the case of regioisomeric mixture of ACP (**1d** : **1e** – 1 : 1), a mixture of substituted cyclopropanes **4d,e** with the same component ratio was formed.

To confirm the reaction scheme proposed, we studied the reaction mixture of equimolar amounts of Me_2SO_4, ACP **1b**, and Et_2O by ^{13}C NMR spectroscopy. The role of Et_2O is to form a stable etherate with ACP, which decelerates the interligand exchange involving OAC and makes resonance lines of ACP more pronounced. After 1 h, the signals for ACP **1b** disappear almost completely, and the signals corresponding to compound **2b** are observed instead. The rearrangement of compound **2b** and the formation of 1,1-dialkylcyclopropane **4b** was completed over 5 h; at the same time, ^{13}C NMR spectra showed no signals for intermediate **3b**. The results obtained suggest that the rate-limiting stage is the rearrangement **2b** → **3b**, and the alkylation of **3b** is a fast reaction. The structure of OAC **2c** was confirmed by identification of its hydrolysis product, *viz.*, alkene **5**.

Analysis of the ^1H NMR spectra of 1,1-dialkylcyclopropanes **4a—e** reveals the presence of an AA'BB' system of the cyclopropane fragment (Scheme 3). The chemical shifts of the signals for H_A and H_B in compound **4b** are δ 0.33 and 0.12, respectively, *i.e.*, they differ by 0.21 ppm. The chemical nonequivalence of H_A and H_B in 1,1-dialkylcyclopropanes **4** is due to their unequal shielding with alkyl substituents. According to the calculation of shielding constants by the GIAO method with the 3-21G (RHF/3-21G(GIAO)//3-21G) basis, H_B in 1-*tert*-butyl-1-ethylcyclopropane is more shielded (by *ca.* 0.2 ppm) than H_A, which agrees well with the experimental values.

Scheme 3



R^1, R^2, R^3 — alkyl

It is noteworthy that the mass spectra (EI, 70 eV) of cyclopropanes **4a—e** contain no molecular ion. The MNDO calculation of the electronic structure of a carbenium radical ion **6** shows that the positive charge in the molecule is predominantly localized on the carbenium C atom. The presence of a *tert*-alkyl group at the positively charged C atom stabilizes radical ion **6** (*i.e.*, favors fragmentation of 1,1-disubstituted cyclopropane **4** with elimination of ethylene) (see Scheme 3).

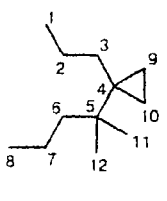
Thus, the mass spectra of 1,1-disubstituted cyclopropanes **4a—e** contain the $[M - C_2H_4]^{\cdot +}$ radical cation rather than the molecular ion.

Experimental

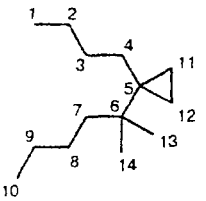
Reactions with organoaluminum compounds were carried out in an atmosphere of dry argon. Solvents were distilled over $LiAlH_4$ immediately before use. The reaction products were analyzed on a Khrom-5 chromatograph (flame ionization detector, PEG-6000 or SE-30 as the stationary phase, column 2000×3 mm, operating temperature 50—170 °C). Mass spectra were obtained on a Finnigan 4021 instrument (EI, 70 eV), ionization chamber temperature 200 °C. ^1H and ^{13}C NMR spectra were recorded on Jeol FX-90Q (22.5 (^{13}C) and 90 MHz (^1H)) and Bruker AM-300 (75.46 (^{13}C) and 300 MHz (^1H)) spectrometers. $SiMe_4$ and $CDCl_3$ were used as the internal standards in recording the ^1H and ^{13}C NMR spectra, respectively, of compounds **2a—e** and **5**; the ^{13}C NMR spectra of OAC were referenced to C_6D_{12}. The ^{13}C NMR spectra of 1,1-dialkylcyclopropanes were recorded in the COM, NOE, and INEPT regimes. The numbering of C atoms is given in Scheme 4.

Synthesis of 1,1-dialkylcyclopropanes. Et_3Al (5 mmol) was added to a mixture of disubstituted acetylene (2 mmol) and Cp_2ZrCl_2 (0.028 g, 0.01 mmol) in 5 mL of dry hexane in an atmosphere of argon at 0 °C. The reaction mixture was stirred at

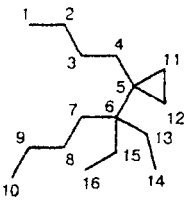
Scheme 4



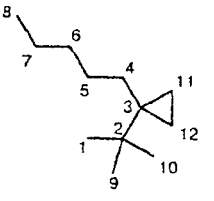
4a



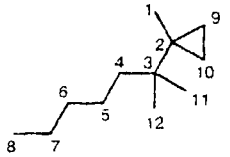
4b



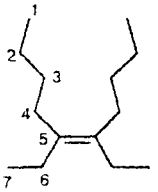
4c



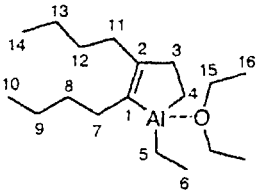
4d



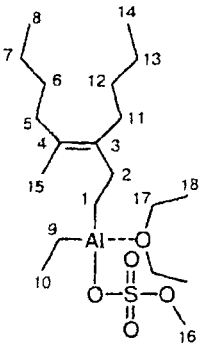
4e



5



1b · Et_2O



2b · Et_2O

~20 °C for 10 h. Then dialkyl sulfate (8 mmol) was added dropwise at 0 °C, and stirring was continued at 20 °C for 12 h. After addition of 5 mL of hexane, the reaction mixture was subjected to hydrolysis with 10% HCl. The products were extracted from the organic layer with ether, washed with Na_2CO_3 until a neutral reaction, and dried with $CaCl_2$.

1-(2-Methylpentan-2-yl)-1-propylcyclopropane (4a), yield 85%, b.p. 84—87 °C (15 Torr). ^{13}C NMR, δ: 15.06 (q, C(1)); 17.79 (t, C(2)); 43.48 (t, C(3)); 24.88 (s, C(4)); 35.22 (s, C(5)); 35.42 (t, C(6)); 20.13 (t, C(7)); 15.26 (q, C(8)); 7.06 (t, C(9), C(10)); 25.21 (q, C(11), C(12)). ^1H NMR, δ: 0.14 (m, 2 H, BB′); 0.35 (m, 2 H, AA′); 0.73 (s, 6 H, $C(11)H_3$, $C(12)H_3$); 0.83—0.88 (m, 6 H, $C(1)H_3$, $C(8)H_3$); 1.01—1.52 (m, 8 H, $C(2)H_2$, $C(3)H_2$, $C(6)H_2$, $C(7)H_2$). MS, *m/z*: 140 $[M - C_2H_4]^+$. Found (%): C, 85.34; H, 14.16. $C_{12}H_{24}$. Calculated (%): C, 85.71; H, 14.29.

1-Butyl-1-(2-methylhexan-2-yl)cyclopropane (4b), yield 80%, b.p. 103 °C (9 Torr). ^{13}C NMR, δ: 14.28 (C(1)); 23.75 (C(2)); 26.75 (C(3)); 40.68 (C(4)); 24.96 (C(5)); 35.01 (C(6)); 32.56 (C(7)); 29.24 (C(8)); 23.89 (C(9)); 14.35 (C(10)); 6.97 (C(11), C(12)); 25.21 (C(13), C(14)). ^1H NMR (300 MHz), δ: 0.12 (2 H, BB′, $^3J_{BB'.cis}$ = 9.5 Hz, $^2J_{AB.gem}$ = −5.4 Hz, $^3J_{AB'.trans}$ = 5.5 Hz); 0.33 (2 H, AA′, $^3J_{AA'.cis}$ = 9.5 Hz, $^2J_{AB.gem}$ = −5.4 Hz, $^3J_{AB'.trans}$ = 5.5 Hz); 0.70 (s, 6 H, $C(13)H_3$, $C(14)H_3$); 0.83—0.93 (m, 6 H, $C(1)H_3$, $C(10)H_3$); 1.05—1.57 (m, 12 H, $C(2)H_2$—$C(4)H_2$, $C(7)H_2$—$C(9)H_2$). MS, *m/z*: 168 $[M - C_2H_4]^+$. Found (%): C, 85.47; H, 14.06. $C_{14}H_{28}$. Calculated (%): C, 85.71; H, 14.29.

1-Butyl-1-(3-ethylheptan-3-yl)cyclopropane (4c), yield 65%, b.p. 128 °C (3 Torr). ^{13}C NMR, δ: 14.28 (C(1)); 23.79 (C(2)); 28.85 (C(3)); 33.34 (C(4)); 20.72 (C(5)); 38.99 (C(6)); 32.36 (C(7)); 26.12 (C(8)); 23.97 (C(9)); 14.28 (C(10)); 5.31 (C(11), C(12)); 25.99 (C(13), C(15)); 8.50 (C(14), C(16)). ^1H NMR, δ: 0.10 (m, 2 H, BB′); 0.40 (m, 2 H, AA′); 0.76 (t, 6 H, $C(14)H_3$, $C(16)H_3$, J = 7.81 Hz); 1.17—1.34 (m, 10 H, $C(1)H_3$, $C(10)H_3$, $C(13)H_3$, $C(15)H_3$); 1.40—1.62 (m, 12 H, $C(2)H_2$—$C(4)H_2$, $C(7)H_2$—$C(9)H_2$). MS, *m/z*: 196 $[M - C_2H_4]^+$. Found (%): C, 85.17; H, 13.85. $C_{16}H_{32}$. Calculated (%): C, 85.71; H, 14.29.

1-*tert*-Butyl-1-pentylcyclopropane (4d), yield 40%, b.p. 93 °C (24 Torr). ^{13}C NMR, δ: 27.70 (C(1)); 34.07 (C(2)); 21.50 (C(3)); 40.90 (C(4)); 24.06 (C(5)); 33.17 (C(6)); 22.89 (C(7)); 14.24 (C(8)); 27.70 (C(9), C(10)); 7.74 (C(11), C(12)). ^1H NMR, δ: 0.05 (m, 2 H, BB′); 0.43 (m, 2 H, AA′); 0.82 (s, 9 H, $C(1)H_3$, $C(9)H_3$, $C(10)H_3$); 0.82—1.50 (m, 11 H, $C(4)H_2$—$C(7)H_2$, $C(8)H_3$). MS, *m/z*: 140 $[M - C_2H_4]^+$. Found (%): C, 85.93; H, 14.11. $C_{12}H_{24}$. Calculated (%): C, 85.71; H, 14.29.

1-Methyl-1-(2-methylheptan-2-yl)cyclopropane (4e), yield 40%, b.p. 93 °C (24 Torr). ^{13}C NMR, δ: 21.85 (C(1)); 26.18 (C(2)); 32.45 (C(3)); 33.69 (C(4)); 26.99 (C(5)); 32.97 (C(6)); 22.89 (C(7)); 14.24 (C(8)); 9.82 (C(9), C(10)); 24.65 (C(11), C(12)). ^1H NMR, δ: 0.15 (m, 2 H, BB′); 0.39 (m, 2 H, AA′); 0.73 (s, 6 H, $C(11)H_3$, $C(12)H_3$); 0.94 (s, 3 H, $C(1)H_3$); 0.82—1.50 (m, 11 H, $C(4)H_2$—$C(7)H_2$, $C(8)H_3$). MS, *m/z*: 140 $[M - C_2H_4]^+$. Found (%): C, 85.93; H, 14.11. $C_{12}H_{24}$. Calculated (%): C, 85.71; H, 14.29.

5,6-Diethyldec-5*Z*-ene (5), yield 25%, b.p. 113 °C (14 Torr). ^{13}C NMR, δ: 14.15 (C(1)); 24.43 (C(2)); 31.06 (C(3)); 31.64 (C(4)); 134.46 (C(5)); 23.19 (C(6)); 13.89 (C(7)). ^1H NMR, δ: 0.66—0.96 (m, 12 H, $C(1)H_3$, $C(7)H_3$); 1.00—1.23 (m, 8 H, $C(2)H_2$, $C(3)H_2$); 1.30 (q, 4 H, $C(6)H_2$, J = 7.1 Hz); 1.90 (t, 4 H, $C(4)H_2$, J = 7.3 Hz). MS, *m/z*: 196 $[M]^+$. Found (%): C, 85.32; H, 13.61. $C_{14}H_{28}$. Calculated (%): C, 85.71; H, 14.29.

^{13}C NMR spectroscopic study of the reaction. Et_3Al (5 mmol) was added in an atmosphere of argon to a mixture of disubstituted acetylene (2 mmol) and Cp_2ZrCl_2

(0.028 g, 0.01 mmol) in 5 mL of dry hexane at 0 °C. The reaction mixture was stirred at 20 °C for 10 h. After the completion of the reaction, the hexane was removed from the reaction mixture under reduced pressure. The resulting product was transferred in an atmosphere of argon to an NMR tube, and equimolar (with respect to alumacyclopentene) amounts of Et_2O and Me_2SO_4 were added successively at 0 °C. The ^{13}C NMR spectra of the reaction mixture were recorded 30, 60, 90, 120, 240, and 480 min after the start of the reaction.

Complex of 2,3-di(*n*-butyl)-1-ethylalumacyclopent-2-ene (1b) with Et_2O. ^{13}C NMR, δ: 146.87 (C(1)); 159.42 (C(2)); 35.73 (C(3)); 1.78 (C(4)); 0.35 (C(5)); 9.91 (C(6)); 31.96 (C(7)); 33.19 (C(8)); 23.83 (C(9)); 14.40 (C(10)); 32.80 (C(11)); 35.34 (C(12)); 23.96 (C(13)); 14.40 (C(14)); 67.01 (C(15)); 9.91 (C(16)).

Complex of 2b with Et_2O. ^{13}C NMR, δ: 1.33 (C(1)); 34.69 (C(2)); 124.89 (C(3)); 139.78 (C(4)); 31.76 (C(5)); 32.41 (C(6)); 23.83 (C(7)); 14.40 (C(8)); 0.68 (C(9)); 8.42 (C(10)); 31.57 (C(11)); 28.58 (C(12)); 23.57 (C(13)); 14.40 (C(14)); 17.98 ((C15)); 58.88 (C(16)); 67.14 (C(17)); 9.91 (C(18)).

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