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The conversion of alkynes into substituted cyclopropanes effected by CH_2I_2-R_3Al (R = Me, Et, *i*-Bu)

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ABSTRACT

The reaction of mono- and disubstituted alkynes with CH_2I_2-R_3Al (R = Me, Et, *i*-Bu) was studied. It was found that the reaction of alkynes with CH_2I_2 in the presence of Me_3Al gives β-iodoethyl-substituted cyclopropanes. The use of Et_3Al or *i*-Bu_3Al affords exclusively cyclopropylic organoaluminum compounds.

1. Introduction

Cyclopropane derivatives are members of an important class of biologically active compounds [1–3]. Among the many methods of cyclopropane synthesis, alkene cyclopropanation with diazomethane and Simmons–Smith reaction are the most widely used approaches. New alternative cyclopropanation reagents have been developed on the basis of zinc carbenoids [4]. In addition, it is known that alkenes react with carbenoids of lithium [5], samarium [6,7], aluminum [8–13], indium [14], magnesium [15], cadmium [16], and dysprosium [17] to give cyclopropanes. 1,3-Dienes [4] and terpenoids [8] have been involved in the reaction as well. Earlier attempts to react alkynes with the Simmons–Smith reagent failed [18]. Terminal alkynes gave products of CH_2 insertion into the terminal C–H bond. The reaction with disubstituted alkynes did not proceed selectively and led to the formation of a variety of rearrangement products.

Earlier we tried to react alkynes with carbenoids of lithium, magnesium and aluminum. As a result, we developed a selective method for the preparation of tri- and tetrasubstituted cyclopropanes by the reaction of mono- and disubstituted alkynes with Et_3Al-CH_2I_2 [19–21].

In this paper, we studied the reaction of mono- and disubstituted alkynes with CH_2I_2 in the presence of organoaluminium compounds (OAC) of different structure (Me_3Al, *i*-Bu_3Al, *i*-Bu_2AlH, *i*-Bu_2AlCl, Et_2AlCl) to examine the limitations of the reaction and to develop a general method for the transformation of alkynes into cyclopropane derivatives.

2. Results and discussion

2.1. Preliminary study

4-Octyne was involved in the reaction with CH_2I_2 in the presence of above-mentioned OAC (molar reagent ratio = 1:4:6, CH_2Cl_2, room temperature). These conditions were found in previous work [21] to be optimal for the transformation of 4-octyne into 1,2-diethyl-1,2-dipropylcyclopropane. In the case of dialkylaluminum chlorides (*i*-Bu_2AlCl, Et_2AlCl) and *i*-Bu_2AlH, the conversion of alkyne did not exceed 27% in 24 h (20%, 14% and 27% correspondingly). Apparently, this is the result of a low reaction rate for the formation of aluminum carbenoids from CH_2I_2 [22]. In same time, the reaction of 4-octyne with CH_2I_2 in the presence of Me_3Al proceeded with complete conversion of alkyne and led to selective formation of one product in high yield. The use of Et_3Al or *i*-Bu_3Al gave similar results as well. Thus, only three tested trialkylaluminums favoured the selective conversion of 4-octyne into cyclopropane derivatives.

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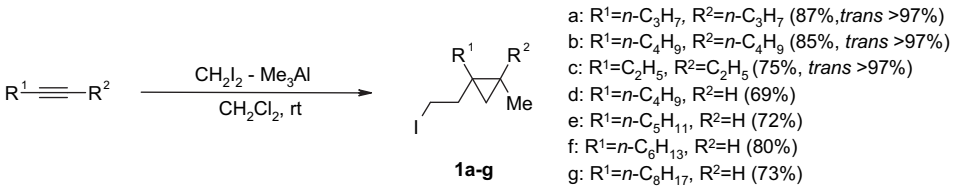
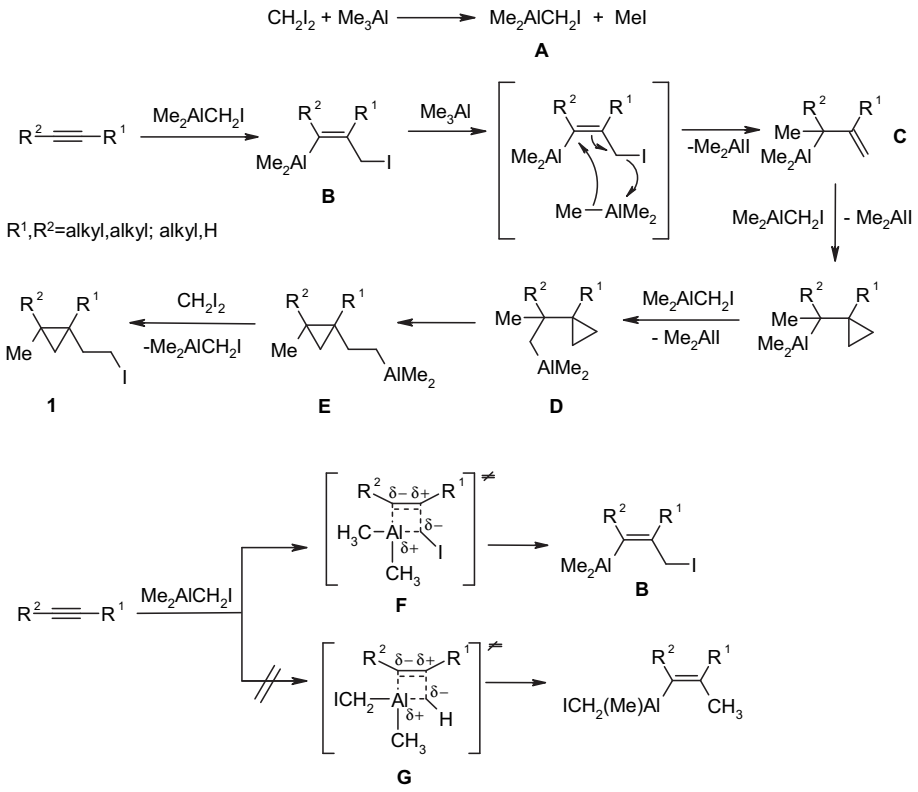


Scheme 1. The reaction of alkynes with CH_2I_2-Me_3Al.



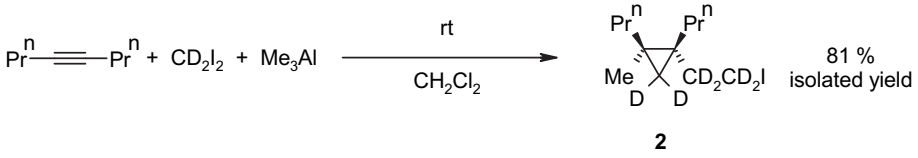
Scheme 2. The proposed mechanism of the transformation of alkynes into β-iodoethyl-substituted cyclopropanes.

2.2. The reaction of alkynes with CH_2I_2-Me_3Al

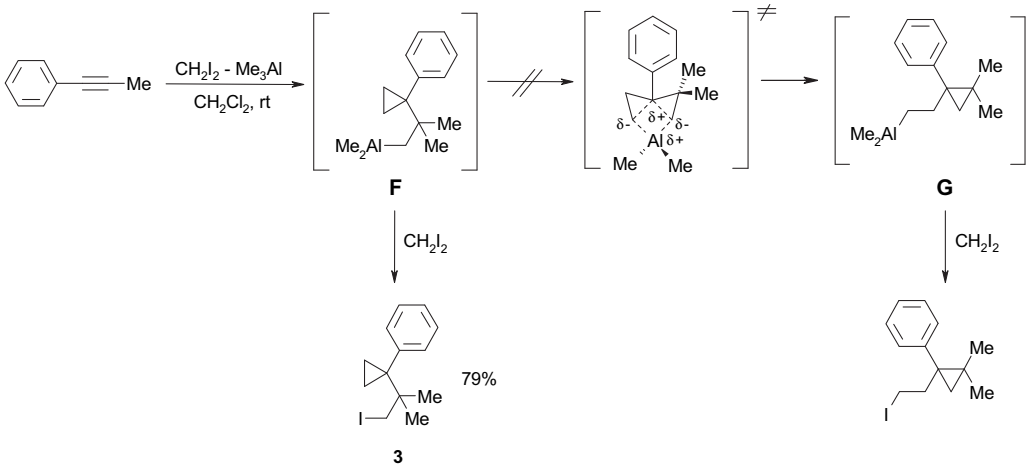
Among the cyclopropane-containing natural compounds, methyl-substituted cyclopropanes occupy a special place [23]. Therefore the transformation of alkynes into substituted methylcyclopropanes is of particular interest.

We found that the reaction of 4-octyne with CH_2I_2 and Me_3Al in CH_2Cl_2 for 8 h at room temperature gave 1-(2-iodoethyl)-2-methyl-1,2(*Z*)-dipropylcyclopropane **1a** in 87% GC and 72% isolated yield (Scheme 1). The treatment of the reaction mixture with D_2O did not afford the deuterio-substituted product, which shows the absence of Al–C bonds in the structure of the compound. The best results were obtained in halogen-containing solvents (dichloromethane, dichloroethane) and hydrocarbons (hexane, pentane). The use of ether solvents (diethyl ether, THF) inhibits the cyclopropanation process. Carrying out the reaction at different temperatures (0, 20, 60 °C) has little effect on the composition of the reaction products. Assignment of signals in the NMR spectra of the compound **1a** was carried out using 2D NMR spectrometry (COSY, HSQC, HMBC) [24] and was based on the spectral parameters of the previously synthesized 1,2-diethyl-1,2-dipropylcyclopropane [19,20]. *Trans*-configuration of substituents at the cyclopropane cycle was established by a NOESY experiment [25].

The products of the reaction of disubstituted (3-hexyne, 5-decyne) and terminal (1-hexyne, 1-heptyne) alkynes with CH_2I_2-Me_3Al were identified in same way. While the *trans*-configuration



Scheme 3. The reaction of 4-octyne with CD_2I_2-Me_3Al.

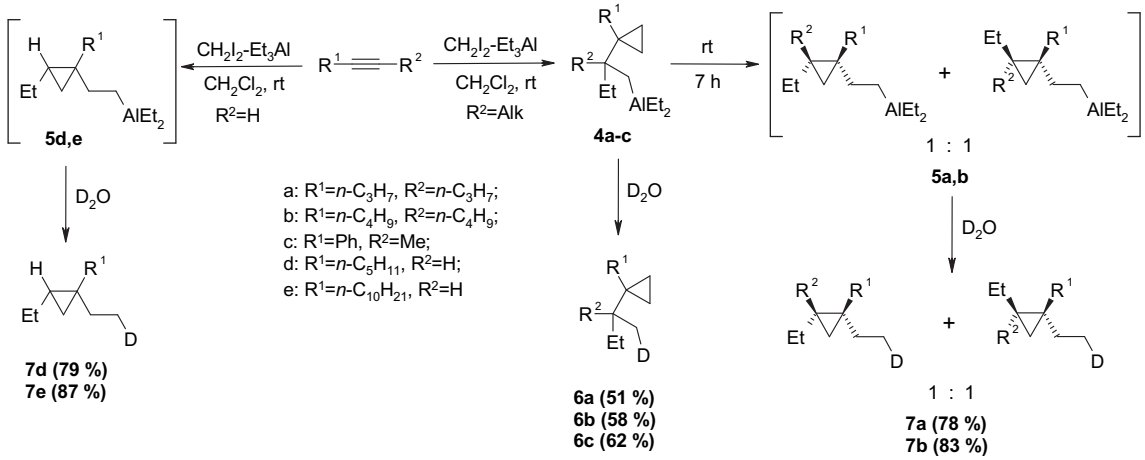


Scheme 4. The reaction of 1-phenyl-1-propyne with CH_2I_2-Me_3Al.

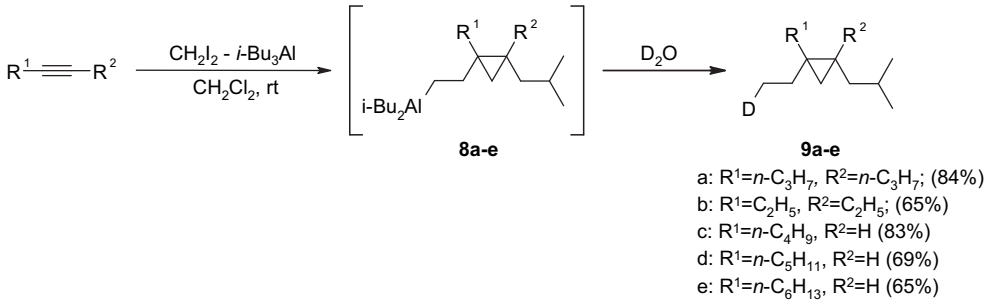
of the compounds **1a**–**c** was unequivocally established by NOESY experiment, the stereo configuration of trisubstituted cyclopropanes **1d**–**g** could not be determined by NMR spectroscopy.

We suggest that the scheme of the transformation is similar to that was proposed earlier for the reaction of alkynes with CH_2I_2-Et_3Al (Scheme 2) [21]. We assume that mechanistically the generation of dimethyl(iodomethyl)aluminum Me_2AlCH_2I **A** occurs initially [8] followed by carboalumination of the alkyne with the formation of iodo-containing alkenylaluminum **B** (Scheme 2) [26]. Me_2AlCH_2I is more electrophilic than Me_3Al and therefore its reaction with alkyne has lower activation energy. As far as transition state **F** is more stable than **G** (according to charge distribution), the carboalumination proceeds via iodomethyl transfer and gives **B** as reaction intermediate. Further rearrangement under the action of Me_3Al affords unsaturated organoaluminium compound **C**. Cyclopropanation of the double bond [11] and CH_2–insertion into Al–C bond gives OAC **D**, which then rearranges to **E**. Finally, the Al–I exchange leads to the formation of iodo-containing cyclopropane **1**.

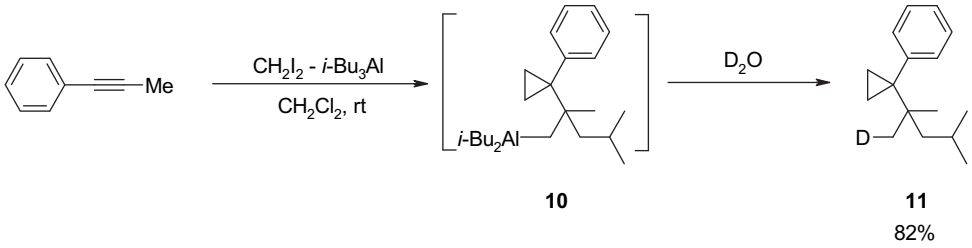
We carried out the reaction of 4-octyne with CD_2I_2 and Me_3Al to confirm the proposed mechanism (Scheme 3) and obtained the



Scheme 5. The reaction of alkynes with CH_2I_2-Et_3Al.



Scheme 6. The reaction of alkynes with CH_2I_2-*i*-Bu_3Al.



Scheme 7. The reaction of 1-phenyl-1-propyne with CH_2I_2-*i*-Bu_3Al.

corresponding deuterated cyclopropane **2**. The positions of the deuterium atoms in the product **2** were determined by comparison of its ^1H and ^{13}C NMR spectra with those of **1a** and were as expected.

Another indirect evidence for the proposed mechanism may come from the findings that the reaction of 1-phenyl-1-propyne with CH_2I_2-Me_3Al affords 1,1-disubstituted cyclopropane **3** (Scheme 4). Perhaps the further rearrangement of **F** to **G** was hindered mainly by unfavorable steric factors in the transition state.

According to the mechanism, one of its stages is alkyne carboalumination by dimethyl(iodmethyl)aluminum. It is known that many transition metal complexes catalyze the carboalumination process [27–29]. However, the use of catalytic amounts of Cp_2ZrCl_2 or Cp_2TiCl_2 in the reaction had no effect on the reaction rate, the conversion of alkynes, and the composition of the products.

As mentioned above, the initial stage of reaction is the generation of aluminum carbenoid from Me_3Al and CH_2I_2. It is known that metallation by organometallic compounds may be subjected to other polyhalomethanes, such as CHI_3, $CHBr_3$, CH_2Br_2, CH_2BrI [8,30]. In this context, we studied the reaction of 4-octyne with Me_3Al in the presence of various polyhalomethanes instead of CH_2I_2. It was found that the product **1a** forms in 45% yield with CH_2BrI. The reaction did not proceed with CHI_3, $CHBr_3$ or CH_2Br_2.

Thus, contrary to Simmons–Smith reagent, the reaction of alkynes with aluminum carbenoid smoothly proceeds to give cyclopropanes. According to DFT study of ethylene cyclopropanation by metal carbenoids, the mechanism depends on metal nature [31]. The increase in ionic character of the metal-carbon bond facilitates carboalumination process over methylene transfer at the first stage of the reaction. Aluminum is more electropositive element than zinc (measured by Pauling's scale) and therefore its tendency to carboalumination is more pronounced compared to traditional Simmons–Smith reagents.

2.3. The reaction of alkynes with CH_2I_2-Et_3Al

The reaction of alkynes with CH_2I_2-Et_3Al was discussed in detail in our earlier papers [21]. The Scheme 5 shows typical yields of the products in the reaction with terminal and disubstituted alkynes.

2.4. The reaction of alkynes with CH_2I_2-*i*-Bu_3Al

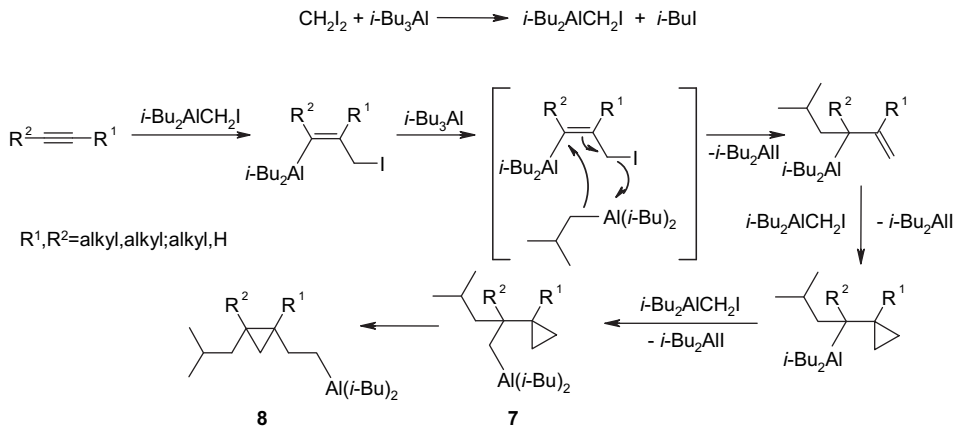
In preliminary experiments, we have found that 4-octyne reacts with CH_2I_2 and *i*-Bu_3Al to give OAC **8a**. Deuterolysis of the latter affords deutero-containing tetrasubstituted cyclopropane **9a** in 84% GC and 70% isolated yield (Scheme 6).

The structure of the compound **9a** was established by comparing its 1D and 2D NMR spectra with the spectral parameters of previously obtained substituted cyclopropane **7a** [21]. ^{13}C NMR spectrum of the compound **9a** shows only one set of signals that probably evidences the formation only one stereo-isomer, but, despite the use of NOESY technique, we could not determine the stereo-configuration of formed tetrasubstituted cyclopropane. The interpretation of the 2D spectra of **8a** was complicated by the process of the ligand exchange between the aluminum atoms of OAC.

The reaction of 3-hexyne with CH_2I_2-*i*-Bu_3Al followed by deuterolysis resulted in the formation of 1,1,2,2-tetrasubstituted cyclopropane **9b**. Terminal alkynes (1-hexyne, 1-heptyne, 1-octyne) reacted with CH_2I_2 and *i*-Bu_3Al to give OAC **8c**–**e**.

In contrary, the reaction with 1-phenyl-1-propyne gave OAC **10** containing 1,1-disubstituted cyclopropane moiety (Scheme 7). The same behavior of this alkyne was observed earlier with CH_2I_2-Me_3Al and CH_2I_2-Et_3Al systems.

Thus, it is obvious that the reaction of mono- and disubstituted alkynes with CH_2I_2-*i*-Bu_3Al proceeds in the same way as with CH_2I_2-Et_3Al (Scheme 8).



Scheme 8. The proposed mechanism of the transformation of alkynes into cyclopropylic OAC.

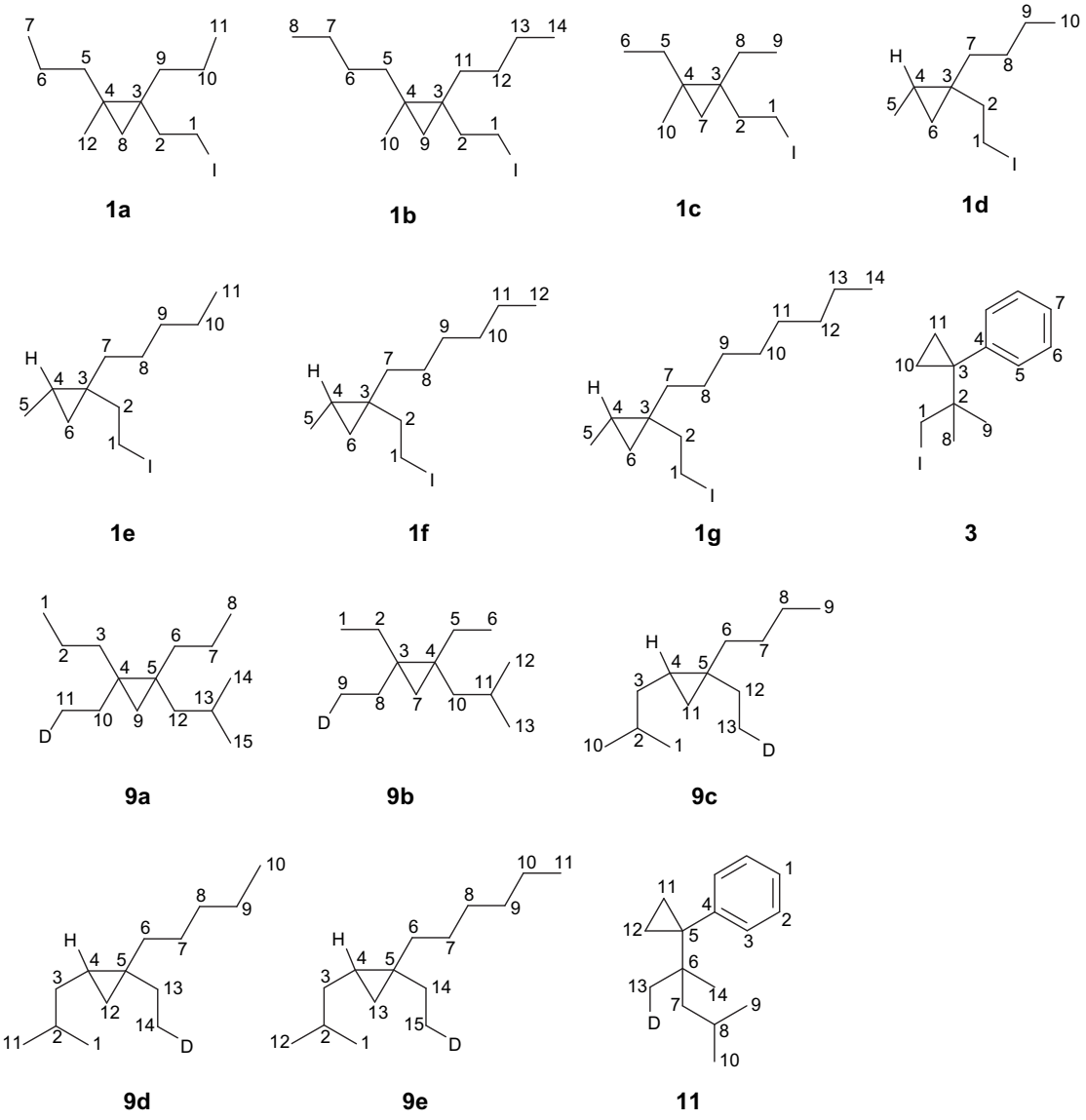


Fig. 1. The numbering of atoms in the ^{13}C and ^{1}H NMR spectra of the compounds **1a**–**g**, **3**, **9a**–**e** and **11**.

2.5. The study of the relative reactivity of trialkylaluminums and alkynes in the reaction

We studied the kinetics of the reaction of 4-octyne with CH_2I_2 and various trialkylaluminums (Me_3Al, Et_3Al, *i*-Bu_3Al) in CH_2Cl_2 at 0 °C. It was found that the relative reactivity of trialkylaluminums decreases in the row $Et_3Al > i\text{-}Bu_3Al > Me_3Al$ ($k_{rel}(Et_3Al) = 1$, $k_{rel}(i\text{-}Bu_3Al) \approx 0.3$, $k_{rel}(Me_3Al) \approx 0.2$). A low activity of Me_3Al can be the result of its greater tendency to form stable associates [32]. In case of *i*-Bu_3Al, probably steric factors play an important role in the reaction. The study of the relative reactivity of alkynes showed that dialkylsubstituted alkynes react with CH_2I_2-Et_3Al faster than terminal alkynes (k_{rel}(4-octyne) = 1, k_{rel}(1-octyne) ≈ 0.7).

3. Conclusions

Contrary to alkenes, the reaction of alkynes with CH_2I_2-R_3Al (R = Me, Et, *i*-Bu) does not proceed as one-stage cyclopropanation but the sequence of rearrangements. Thus, the reaction of mono- and disubstituted alkynes with CH_2I_2 in the presence of Me_3Al leads to the selective formation of β-iodoethyl-substituted cyclopropanes, but the use of Et_3Al or *i*-Bu_3Al affords exclusively cyclopropylic OAC.

4. Experimental

4.1. General procedures

The reagents were obtained from Aldrich or Acros. Dichloromethane was distilled over P_2O_5. Mass spectra were obtained on a Finnigan 4021 instrument. Nuclear Magnetic Resonance spectroscopy was performed on a Brucker Avance-400. The ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$. The chemical shifts are reported in ppm relative to tetramethylsilane (TMS) as the internal standard. The yields of the products were calculated from GC peak areas by the corrected area normalization method with undecane as the internal standard. Boiling points were determined by the Sivolobov method [33]. The numbering of atoms in the ^{13}C and ^{1}H NMR spectra of the compounds **1a**–**g**, **3**, **9a**–**e** and **11** is shown in Fig. 1.

4.2. Synthesis of substituted cyclopropanes

To a solution of 3 mmole of alkyne and diiodomethane (0.97 mL, 12 mmol) in CH_2Cl_2 (5 mL), 18 mmol of trialkylaluminium (Me_3Al or *i*-Bu_3Al) (*caution: organoaluminums are pyrophoric and can ignite on contact with air, water or any oxidizer*) 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 a 7 wt% aq. solution of HCl (in case of the reaction with Me_3Al) or 15 wt% solution DCl in D_2O (in case of the reaction with *i*-Bu_3Al). The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were then washed with saturated $NaHCO_3$ solution and dried over anhydrous $CaCl_2$. The solvent was removed under reduced pressure and the residue distilled.

4.2.1. 1-(2-Iodoethyl)-2-methyl-1,2-dipropylcyclopropane (**1a**)

Bp 125–127 °C (10 mm Hg). ^{1}H NMR δ 0.15–0.2 (m, 2H, C(8)H$_2$), 0.90 (t, $^3J_{CH}$ = 7.2 Hz, 3H, C(7)H$_3$), 0.91 (t, $^3J_{CH}$ = 6.8 Hz, 3H, C(11)H$_3$), 1.10 (s, 3H, C(12)H$_3$), 1.1–1.5 (m, 8H, C(5)H$_2$, C(6)H$_2$, C(9)H$_2$, C(10)H$_2$), 1.8–1.9 (m, 1H, C(2)H$_a$), 2.1–2.2 (m, 1H, C(2)H$_b$), 3.05–3.15 (m, 1H, C(1)H$_a$), 3.15–3.25 (m, 1H, C(1)H$_b$). ^{13}C NMR δ 3.10 (C(1)), 14.52 and 14.55 (C(7) and C(11)), 19.79 (C(12)), 20.20 and 20.36 (C(6) and C(10)), 24.47 (C(4)), 25.69 (C(8)), 30.28 (C(3)), 33.24 (C(9)), 38.12 (C(2)), 38.23 (C(5)). MS (*m*/*z*, %): 294 (M$^+$, 10), 251 ([M − C_3H_7]$^+$, 47), 209 (51), 195 (42), 155 (46), 139 (78), 97 (83), 55 (100). Anal. Calcd. for $C_{12}H_{23}I$: C, 48.99; H, 7.88. Found: C, 48.68; H, 7.92.

4.2.2. 1-(2-Iodoethyl)-2-methyl-1,2-dibutylcyclopropane (**1b**)

Bp 156–157 °C (10 mm Hg). ^{1}H NMR: δ 0.15–0.2 (m, 2H, C(9)H$_2$), 0.90 (t, $^3J_{CH}$ = 7.2 Hz, 3H, C(8)H$_3$), 0.91 (t, $^3J_{CH}$ = 6.8 Hz, 3H, C(14)H$_3$), 1.10 (s, 3H, C(10)H$_3$), 1.2–1.45 (m, 12H, C(5)H$_2$, C(6)H$_2$, C(7)H$_2$, C(11)H$_2$, C(12)H$_2$, C(13)H$_2$) 1.8–1.9 (m, 1H, C(2)H$_a$), 2.1–2.2 (m, 1H, C(2)H$_b$), 3.05–3.15 (m, 1H, C(1)H$_a$), 3.15–3.25 (m, 1H, C(1)H$_b$). ^{13}C NMR δ 3.15 (C(1)), 14.16 (2C, C(8), C(14)), 19.85 (C(10)), 23.13 and 23.15 (C(7) and C(13)), 24.62 (C(4)), 25.66 (C(9)), 29.31 and 29.47 (C(6) and C(12)), 30.41 (C(3)), 30.64 (C(11)), 35.66 (C(5)), 38.13 (C(2)). MS (*m*/*z*, %): 322 (M$^+$, 1). Anal. Calcd. for $C_{14}H_{27}I$: C, 52.18; H, 8.44. Found: C, 52.14; H, 8.65.

4.2.3. 1-(2-Iodoethyl)-2-methyl-1,2-diethylcyclopropane (**1c**)

Bp 105–107 °C (15 mm Hg). ^{1}H NMR δ 0.15 (s, 2H, C(7)H$_2$), 0.90 (t, $^3J_{CH}$ = 6.8 Hz, 3H, C(6)H$_3$), 0.92 (t, $^3J_{CH}$ = 7.6 Hz, 3H, C(9)H$_3$), 1.10 (s, 3H, C(10)H$_3$), 1.25–1.55 (m, 4H, C(5)H$_2$, C(8)H$_2$), 1.8–1.95 (m, 1H, C(2)H$_a$), 2.1–2.25 (m, 1H, C(2)H$_b$), 3.05–3.15 (m, 1H, C(1)H$_a$), 3.15–3.25 (m, 1H, C(1)H$_b$). ^{13}C NMR δ2.99 (C(1)), 11.21 и 11.36 (C(6) и C(9)), 19.25 (C(10)), 23.45 (C(8)), 25.16 (C(7)), 25.94 (C(4)), 28.50 (C(5)), 31.62 (C(3)), 37.41 (C(2)). Anal. Calcd. for $C_{10}H_{19}I$: C, 45.13; H, 7.20. Found C, 45.27; H, 7.00.

4.2.4. 1-(2-Iodoethyl)-2-methyl-1-butylcyclopropane (**1d**)

Bp 106–109 °C (12 mm Hg). ^{1}H NMR δ −0.15–(−0.05) (m, 1H, C(6)H$_a$), 0.4–0.5 (m, 1H, C(6)H$_b$), 0.6–0.7 (m, 1H, C(4)H), 0.90 (t, $^3J_{CH}$ = 7.4 Hz, 3H, C(10)H$_3$), 1.06 (d, $^3J_{CH}$ = 6.4 Hz, 3H, C(5)H$_3$), 1.1–1.4 (m, 6H, C(7)H$_2$, C(8)H$_2$, C(9)H$_2$), 1.65–1.9 (m, 2H, C(2)H$_2$), 3.15–3.25 (m, 2H, C(1)H$_2$). ^{13}C NMR δ 2.86 (C(1)), 13.69 (C(5)), 14.15 (C(10)), 17.87 (C(4)), 19.03 (C(6)), 23.09 (C(9)), 24.82 (C(3)), 29.02 (C(8)), 29.02 (C(8)), 29.16 (C(7)), 42.33 (C(2)). MS (*m*/*z*, %): 266 (M$^+$, 1). Anal. Calcd. for $C_{10}H_{19}I$: C, 45.13; H, 7.20. Found: C, 45.31; H, 7.35.

4.2.5. 1-(2-Iodoethyl)-2-methyl-1-amylcyclopropane (**1e**)

Bp 97–100 °C (3 mm Hg). ^{1}H NMR δ −0.15–(−0.05) (m, 1H, C(6)H$_a$), 0.4–0.5 (m, 1H, C(6)H$_b$), 0.55–0.7 (m, 1H, C(4)H), 0.89 (t, $^3J_{CH}$ = 7.6 Hz, 3H, C(11)H$_3$), 1.04 (d, $^3J_{CH}$ = 6.0 Hz, 3H, C(5)H$_3$), 1.1–1.4 (m, 8H, C(7)H$_2$, C(8)H$_2$, C(9)H$_2$, C(10)H$_2$), 1.65–1.9 (m, 2H, C(2)H$_2$), 3.10–3.25 (m, 2H, C(1)H$_2$). ^{13}C NMR δ 2.88 (C(1)), 13.74 (C(5)), 14.14 (C(11)), 17.89 (C(4)), 19.08 (C(6)), 22.72 (C(10)), 24.84 (C(3)), 26.49 (C(8)), 29.44 (C(7)), 32.27 (C(9)), 42.32 (C(2)). Anal. Calcd. for $C_{11}H_{21}I$: C, 47.15; H, 7.55. Found: C, 47.27; H, 7.35.

4.2.6. 1-(2-Iodoethyl)-2-methyl-1-hexylcyclopropane (**1f**)

Bp 109–111 °C (3 mm Hg). ^{1}H NMR δ −0.15–(−0.05) (m, 1H, C(6)H$_a$), 0.4–0.5 (m, 1H, C(6)H$_b$), 0.55–0.7 (m, 1H, C(4)H), 0.89 (t, $^3J_{CH}$ = 7.6 Hz, 3H, C(12)H$_3$), 1.06 (d, $^3J_{CH}$ = 6.4 Hz, 3H, C(5)H$_3$), 1.1–1.45 (m, 10H, C(7)H$_2$, C(8)H$_2$, C(9)H$_2$, C(10)H$_2$, C(11)H$_2$), 1.6–1.7 (m, 2H, C(2)H$_a$), 1.8–1.9 (m, 1H, C(2)H$_b$), 3.15–3.25 (m, 2H, C(1)H$_2$). ^{13}C NMR δ 2.83 (C(1)), 13.68 (C(5)), 14.08 (C(12)), 17.87 (C(4)), 19.04 (C(6)), 22.67 (C(11)), 24.85 (C(3)), 26.78 (C(8)), 29.47 (C(9)), 29.72 (C(7)), 31.90 (C(10)), 42.32 (C(2)). Anal. Calcd. for $C_{12}H_{23}I$: C, 48.99; H, 7.88. Found: C, 48.76; H, 7.59.

4.2.7. 1-(2-Iodoethyl)-2-methyl-1-octylcyclopropane (**1g**)

Bp 112–113 °C (1 mm Hg). ^{1}H NMR δ −0.15–(−0.05) (m, 1H, C(6)H$_a$), 0.4–0.5 (m, 1H, C(6)H$_b$), 0.5–0.7 (m, 1H, C(4)H), 0.89 (t, $^3J_{CH}$ = 7.6 Hz, 3H, C(14)H$_3$), 1.06 (d, $^3J_{CH}$ = 6.5 Hz, 3H, C(5)H$_3$), 1.1–1.4 (m, 14H, C(7)H$_2$, C(8)H$_2$, C(9)H$_2$, C(10)H$_2$, C(11)H$_2$, C(12)H$_2$, C(13)H$_2$), 1.7–1.8 (m, 2H, C(2)H$_a$), 1.8–1.9 (m, 1H, C(2)H$_b$), 3.15–3.25 (m, 2H, C(1)H$_2$). ^{13}C NMR δ 2.77 (C(1)), 13.69 (C(5)), 14.10 (C(14)), 17.88 (C(4)), 19.38 (C(6)), 22.67 (C(13)), 23.48 (C(3)), 26.81 (C(8)), 29.46 (C(7)), 29.34 and 29.65 and 30.07 (C(9), C(10), C(11)), 31.90 (C(12)), 42.33 (C(2)). Anal. Calcd. for $C_{14}H_{27}I$: C, 52.18; H, 8.44. Found: C, 52.01; H, 8.65.

4.2.8. 1-[1-(2-Iodo-1,1-dimethylethyl)cyclopropyl]benzene (**3**)

Bp 118–120 °C (5 mm Hg). ^{1}H NMR δ 0.7–0.95 (m, 4H, C(10)H$_2$, C(11)H$_2$), 1.06 (s, 6H, C(8)H$_3$, C(9)H$_3$), 3.23 (s, 2H, C(1)H$_2$), 7.15–7.25 (m, 5H, Ph). ^{13}C NMR δ 9.57 (2C, C(10), C(11)), 23.80 (C(1)), 25.56 (2C, C(8), C(9)), 27.83 (C(3)), 29.74 (C(2)), 126.61 (C(7)), 127.6 (2C, C(6), C(6′)), 132.00 (2C, C(5), C(5′)), 144.08 (C(4)). MS (*m*/*z*, %): 300 (M$^+$, 1). Anal. Calcd. for $C_{13}H_{17}I$: C, 52.02; H, 5.71. Found: C, 52.10; H, 5.64.

4.2.9. 1-(2-deutereoethyl)-2-iso-butyl-1,2-dipropylcyclopropane (**9a**)

Bp 96–99 °C (15 mm Hg). ^{1}H NMR δ 0–0.1 (m, 2H, C(9)H$_2$), 0.9–1.1 (m, 14H, C(1)H$_3$, C(8)H$_3$, C(14)H$_3$, C(15)H$_3$, C(11)H$_2$D), 1.2–1.6 (m, 12H, C(2)H$_2$, C(3)H$_2$, C(6)H$_2$, C(7)H$_2$, C(10)H$_2$, C(12)H$_2$), 1.65–1.75 (m, 1H, C(13)H). ^{13}C NMR δ 11.33 (t, $^1J_{CD}$ = 19.05 Hz, C(11)), 14.96 (C(1),C(8)) 20.24 (C(2)) and 20.27 (C(7)), 22.78 (C(15)) and 23.74 (C(14)), 24.49 (C(10)), 25.40 (C(9)), 26.23 (C(13)), 34.13 (C(3)) and 34.87 (C(6)), 40.22 (C(12)). MS (*m*/*z*, %): 211 (M$^+$, 1)). Anal. Calcd. for $C_{15}H_{29}D$: C, 85.22; H, 13.83; D, 0.95. Found: C, 84.09.

4.2.10. 1-(2-deutereoethyl)-2-iso-butyl-1,2-diethylcyclopropane (**9b**)

Bp 83–85 °C (15 mm Hg). ^{1}H NMR δ 0.06 (s, 2H, C(7)H$_2$), 0.75–1.05 (m, 15H, C(1,6,12,13)H$_3$, C(9)H$_2$D, C(10)H$_a$), 1.15–1.4 (m, 3H, C(2,5,8)H$_a$), 1.4–1.55 (m, 4H, C(2,5,8,10)H$_b$), 1.65–1.8 (m, 1H, C(11)H). ^{13}C NMR δ 11.31 (t, $^1J_{CD}$ = 19.04 Hz, C(9)), 11.34 (C(1)) 11.37 (C(6)), 22.79 (C(12)), 23.61 (C(8)), 23.73 (C(13)), 24.17 (C(2)), 24.99 (C(7)), 25.09 (C(5)), 26.19 (C(11)), 28.7 (C(3)), 29.5 (C(4)), 39.39 (C(10)). MS (*m*/*z*, %): 183 (M$^+$, 1). Anal. Calcd. for $C_{13}H_{25}D$: C, 85.16; H, 13.74; D, 1.10. Found: C, 84.69.

4.2.11. 1-(2-deutereoethyl)-2-iso-butyl-1-butylcyclopropane (**9c**)

Bp 92–95 °C (5 mm Hg). ^{1}H NMR δ (−0.2)–(−0.1) (m, 1H, C(11)H$_a$), 0.35–0.4 (m, 1H, C(11)H$_b$), 0.4–0.5 (m, 1H, C(4)H), 0.7–1.2 (m, 14H, C(1)H$_3$, C(9)H$_3$, C(10)H$_3$, C(13)H$_2$D, C(3)H$_a$, C(6)H$_a$, C(12)H$_a$), 1.2–1.4 (m, 7H, C(3)H$_b$,C(6)H$_b$, C(12)H$_b$, C(7)H$_2$, C(8)H$_2$), 1.55–1.65 (m, 1H, C(2)H). ^{13}C NMR δ 10.82 (t, $^1J_{CD}$ = 19.0 Hz, C(13)),. 14.46 (C

(9)), 19.02 (C(11)), 22.71 (C(4)), 22.79 (C(1)) and 23.48 (C(10)), 23.48 (C(8)), 24.20 (C(5)), 29.32 (C(2)), 29.32 (C(7)), 30.01 (C(6)), 30.72 (C (12)), 38.63 (C(3)). MS (*m*/*z*, %): 183 (M^+, 1), 155 ([M − 28]$^+$, 13), 154 ([M − 29]$^+$, 39), 153 ([M-C_2H_4D]$^+$, 100), 125 ([M − 58]$^+$, 8). Anal. Calcd. for $C_{13}H_{25}D$: C, 85.16; H, 13.74; D, 1.10. Found: C, 85.01.

*4.2.12. 1-(2-deutereoethyl)-2-iso-butyl-1-amylcyclopropane (**9d**)*

Bp 115–117 °C (1 mm Hg). ^{1}H NMR: δ (−0.2)–(−0.1) (m, 1H, C (12)H_a), 0.3–0.4 (m, 1H, C(12)H_b), 0.4–0.5 (m, 1H, C(4)H), 0.7–1.1 (m, 14H, C(1)H_3, C(10)H_3, C(11)H_3, C(14)H_2D, C(3)H_a, C(6)H_a, C(13) H_a), 1.2–1.4 (m, 9H, C(3)H_b, C(6)H_b, C(13)H_b, C(7)H_2, C(8)H_2, C(9) H_2), 1.55–1.65 (m, 1H, C(2)H). ^{13}C NMR: δ 10.16 (t, $^1J_{CD}$ = 19.0 Hz, C (14)), 14.35 (C(10)), 19.02 (C(12)), 22.69 (C(4)), 22.78 (C(11)), 23.01 (C(9)), 23.18 (C(1)), 23.87 (C(5)), 26.72 (C(7)), 29.32 (C(2)), 30.27 (C (6)), 30.63 (C(13)), 32.68 (C(8)), 38.63 (C(3)). MS (*m*/*z*, %): 197 (M^+, 1). Anal. Calcd. for $C_{14}H_{27}D$: C, 85.19; H, 13.79; D, 1.02. Found: C, 84.26.

*4.2.13. 1-(2-deutereoethyl)-2-iso-butyl-1-hexylcyclopropane (**9e**)*

Bp 125–126 °C (1 mm Hg). ^{1}H NMR: δ (−0.2)–(−0.1) (m, 1H, C (13)H_a), 0.35–0.4 (m, 1H, C(13)H_b), 0.4–0.5 (m, 1H, C(4)H), 0.7–1.4 (m, 25H, C(1)H_3, C(11)H_3, C(12)H_3, C(15)H_2D, C(3)H_2, C(6)H_2, C(14) H_2, C(7)H_2, C(8)H_2, C(9)H_2, C(10)H_2), 1.55–1.65 (m, 1H, C(2)H). ^{13}C NMR: δ 10.85 (t, $^1J_{CD}$ = 19.05 Hz, C(15)), 14.09 (C(11)), 18.81 (C(13)), 22.65 (C(4)), 22.70 (C(10)), 22.72 (C(1)), 22.98 (C(12)), 23.90 (C(5)), 26.82 (C(7)), 29.69 (C(6)), 29.84 (C(2)), 29.95 (C(8)), 30.17 (C(14)), 32.03 (C(9)), 38.41 (C(3)). MS (*m*/*z*, %): 211 (M^+, 1). Anal. Calcd. for $C_{15}H_{29}D$: C, 85.22; H, 13.83; D, 0.95. Found: C, 84.57.

*4.2.14. 1-1-[1-(deuteromethyl)-1,3-dimethylbutyl] cyclopropylbenzene (**11**)*

Bp 123–126 °C (1 mm Hg). ^{1}H NMR: δ 0.5–0.75 (m, 4H, cyclopropyl), 0.8–1.1 (m, 11H, $(CH_3)_2$CH, CH_3, CH_2D), 1.17 (d, 2H, $^3J_{CH}$ = 6.9 Hz, CH_2), 1.5–1.7 (m, 1H, CH), 7.15–7.25 (m, 5H, Ph). ^{13}C NMR: δ 8.98 (2C, C(11), C(12)), 24.10 (t, $^1J_{CH}$ = 19.1 Hz, C(13)), 24.15 (C(14)), 25.03 (2C, C(8), C(9)), 25.59 (C(10)), 49.23 (C(7)), 126.01 (C (1)), 127.21 (2C, C(2), C(2′)), 132.65 (2C, C(3), C(3′)). MS (*m*/*z*, %): 189 ([M − 28]$^+$, 18). Anal. Calcd. for $C_{14}H_{23}D$: C, 88.24; H, 10.89; D, 0.87. Found: C, 88.14.

4.2.15. The study of the kinetics of the reaction

The procedure described above was used. The reaction temperature was kept all the time at 0 °C. Examination was carried out using GC after 5, 10, 15, 30, 60, 90, 120, 180, 240 and 480 min. Relative reaction rates were estimated using $\tau_{1/2}$ of alkyne calculated for each case.

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