Cyclopropanation of alkynols with the CH_2I_2—R_3Al system

I. R. Ramazanov,[a] A. V. Yaroslavova,[a] U. M. Dzhemilev,[a] and O. M. Nefedov[b]*

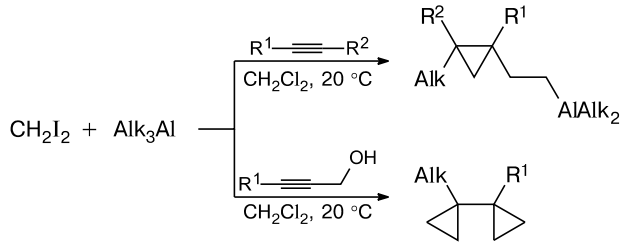
[a]Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, 141 prosp. Oktyabrya, 450075 Ufa, Russian Federation. Fax: +7 (347) 284 2750. E-mail: iramazan@inbox.ru
[b]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (499) 135 5328

Acetylenic alcohols bearing two or three methylene groups between the triple bond and hydroxy group react with CH_2I_2 in the presence of trialkylalanes to give 1,1,2-tri- and 1,1,2,2-tetrasubstituted cyclopropanes.

Key words: cyclopropanes, diiodomethane, alkynols, trialkylaluminums, aluminum carbenoids.

The development of new approaches to the synthesis of cyclopropane compounds is an important task of organic chemistry. We have found earlier that dialkyl(iodomethyl)aluminums generated *in situ* from CH_2I_2 and trialkylalanes react with acetylenes to form cyclopropane compounds,[1—7] and the nature of substituent at the triple bond substantially affect the direction of the reaction. In this process alkyl- and phenyl-substituted acetylenes form tri- and tetrasubstituted cyclopropanes,[2,6] whereas propargyl alcohols produce exclusively bis-cyclopropane derivatives[5] (Scheme 1).

Scheme 1

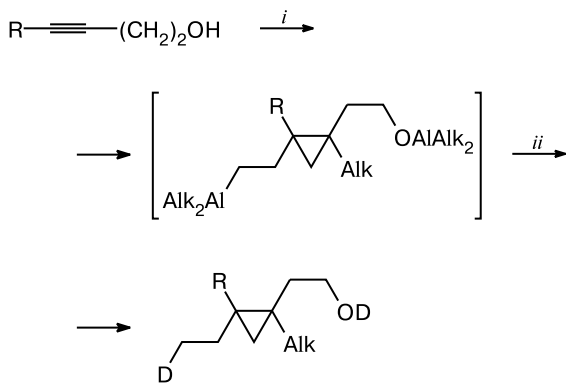


R^1 = alkyl; R^2 = alkyl, Ph, H; Alk = Et, Bu^i

The purpose of the present work was to study the dependence of the direction of the reaction of acetylenic alcohols with an Alk_3Al—CH_2I_2 mixture (usually the molar ratio acetylene : Alk_3Al : CH_2I_2 was 1 : 6 : 4) on the distance between the hydroxyl and acetylenic groups, which made it possible to develop the general method of conversion of functionally substituted acetylenes to compounds of the cyclopropane series.

Preliminary experiments showed that the reaction of non-3-yn-1-ol with CH_2I_2 and Et_3Al (Scheme 2) in dichloromethane at room temperature for 24 h followed by deuterolysis of the reaction mixture afforded 1-(2-deuteroxyethyl)-1-ethyl-2-pentyl-2-(2-deuteroethyl)cyclopropane (**1b**) in 68% yield.

Scheme 2



1a—g

Compound	R	Alk	Compound	R	Alk
1a	Bu^n	Et	**1e**	n-C_5H_{11}	Me
1b	n-C_5H_{11}	Et	**1f**	n-C_8H_{17}	Me
1c	n-$C_{12}H_{25}$	Et	**1g**	n-$C_{12}H_{25}$	Me
1d	Bu^n	Me			

Reagents and conditions: *i*. CH_2I_2 (4 equiv.), Alk_3Al (6 equiv.), CH_2Cl_2, 20 °C; *ii*. D_2O.

One may judge about the structure of an intermediate organoaluminum compound (OAC) from the structure of the product of its deuterolysis (it is difficult to interpret the correlation spectra of OAC because of ligand exchange processes between the aluminum atoms). To identify com-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 306—311, February, 2011.

pound **1b**, we used standard methods of 2D NMR spectroscopy (COSY, HSQC, HMBC, NOESY).

The cyclopropane fragment in the ^{1}H NMR spectrum of compound **1b** is characterized by the AB system of two hydrogen atoms at $\delta_{C(3)H(A)}$ 0.10 and at $\delta_{C(3)H(B)}$ 0.13 with the geminal spin-spin coupling constant (SSCC) $^2J_{H,H}$ = 4.4 Hz (Fig. 1). In the HSQC experiment, these protons correlate with the signal of the carbon atom at $\delta_{C(3)}$ 23.99, while, in the HMBC experiment, it correlates with the signals of the quaternary carbon atoms at $\delta_{C(1)}$ 27.09 and at $\delta_{C(2)}$ 29.37, as well as with the corresponding substituents at the cyclopropane ring.

The ^{13}C NMR spectrum of compound **1b** contains only one set of signals, indicating stereoselective character of the reaction. Unfortunately, we failed to unambiguously determine the stereoconfiguration of the tetrasubstituted cyclopropane formed from an analysis of the NOESY spectrum.

After deuterolysis, the reactions of oct-3-yn-1-ol and dodec-3-yn-1-ol with CH_2I_2 and Et_3Al afford tetrasubstituted cyclopropanes **1a,c** (see Scheme 2).

On going from Et_3Al to Me_3Al, the formation of the corresponding products **1d—g** proceeds more slowly, and 2—3 days are needed for completion of the reaction. It is interesting that an analogous reaction of dialkyl-substituted acetylenes with a mixture of CH_2I_2 and Me_3Al affords 2-iodoethyl derivatives of cyclopropane, which are formed due to the Al—I exchange between cyclopropyl-containing OAC and CH_2I_2 (see Ref. 6). Probably, in the case of homopropargyl alcohols, intramolecular coordination prevents this exchange (Scheme 3).

However, in the case of oct-3-yn-1-ol, with an increase in the amount of CH_2I_2 introduced into the reaction to the ratio acetylene : CH_2I_2 : Me_3Al = 1 : 8 : 6 the equilibrium can be shifted toward the formation of organoiodine derivative **2** in 52% yield (see Scheme 3).

Thus, unlike propargyl alcohols, homopropargyl alcohols form tetrasubstituted cyclopropane structures similar to those observed earlier in the reaction with nonfunctionalized acetylenes.

We believe that the initial steps of the reaction are analogous in both cases (with propargyl and homopropargyl alcohols). Dialkyl(iodomethyl)aluminum[8] generated *in situ* carboaluminates acetylenic alcohol to form iodine-containing alkenylalane **A** (see Ref. 9 and Scheme 4). Subsequent rearrangement involving trialkylalane affords unsaturated OAC **B**. The subsequent cyclopropanation of the double bond[10] affords cyclopropane-containing OAC **C**. In the case of propargyl alcohols, alumoxane is eliminated to form vinylcyclopropane **D**. In the case of homopropargyl alcohols, the elimination step is hindered and methylene is inserted into the Al—C bond. The further rearrangement of derivative **E** affords cyclopropane-containing OAC **F**, whose deuterolysis gives **1**.

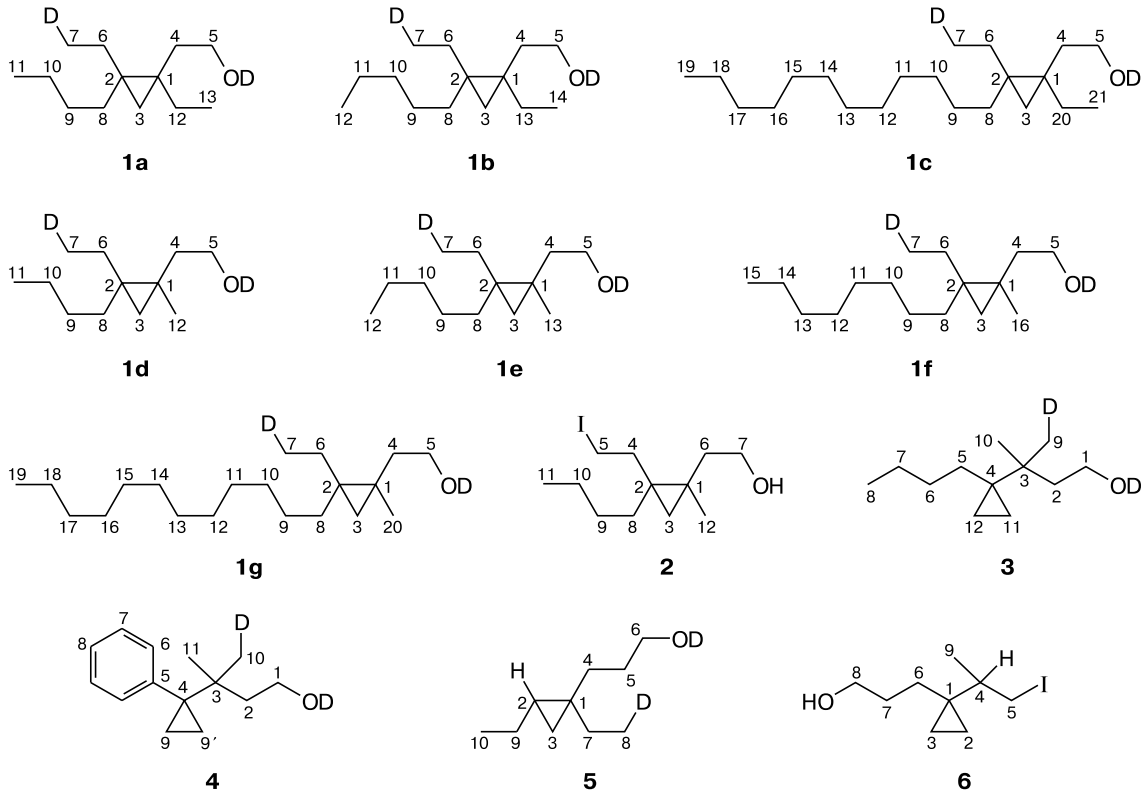
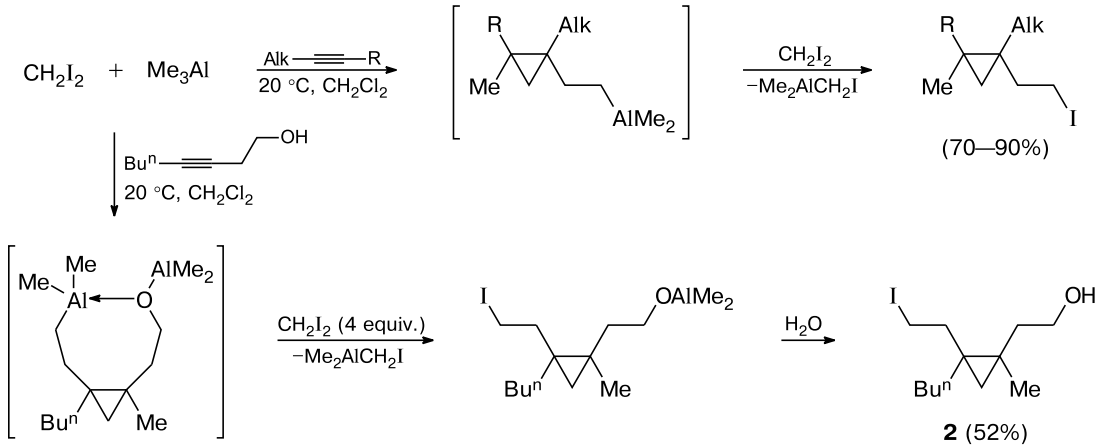


Fig. 1. Numeration of atoms in the ^{1}H and ^{13}C NMR spectra of compounds **1a—g** and **2—6**.

Scheme 3

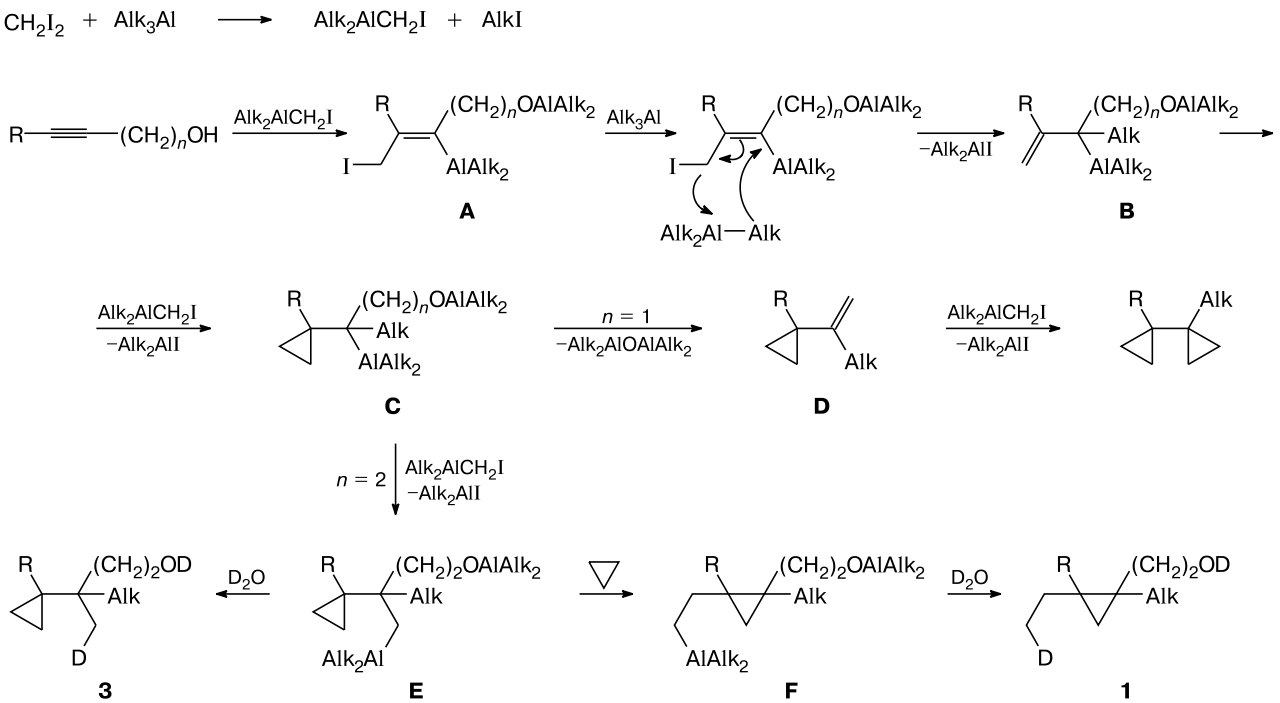


R = H, alkyl

The proposed mechanism is confirmed by the structure of deuterated derivative **3**, which was isolated in 15% yield by the deuterolysis of intermediate OAC **E**, which was obtained after 24 h in the reaction of oct-3-yn-1-ol, CH_2I_2, and Me_3Al at the reactant ratio 1 : 4 : 6 (see Scheme 4). An indirect proof for this mechanism is an experiment involving phenyl-substituted homopropargyl alcohol, 4-phenylbut-3-yn-1-ol, which reacts with Me_3Al and CH_2I_2 followed by deuterolysis and affords individual 1,1-disubstituted cyclopropane **4** in 60% yield (Scheme 5). We obtained an analogous product when involved methylphenylacetylene in the reaction under study.[6]

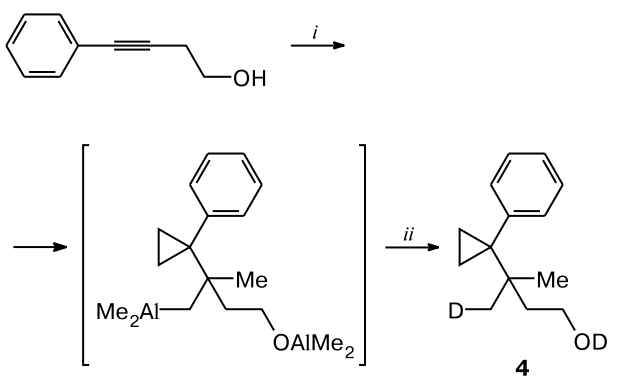
According to Scheme 4, the structure of the product formed is determined in the step of addition of dialkyl-

Scheme 4



R = alkyl, Alk = Et, Me
3: R = Bu^n, Alk = Me

Scheme 5



Reagents and conditions: *i*. CH_2I_2 (4 equiv.), Me_3Al (6 equiv.), CH_2Cl_2, 20 °C, 48 h; *ii*. D_2O.

(iodomethyl)aluminum to acetylene, *i.e.*, it depends on regioselectivity of carboalumination of acetylenic alcohol. It is known that the carboalumination of acetylenes proceeds through the four-centered transition state[11] in which the metal atom is coordinated to the carbon atom of the triple bond having the highest π-electron density. Therefore, the NBO analysis of occupancies of molecular orbitals was performed for a series of acetylenic compounds by the B3LYP/6-31G* method (Table 1).

According to the data obtained (see Table 1), in *n*-butyl-substituted alcohols bearing one or two methylene groups between the acetylenic and hydroxyl functions, the maximum electron density is localized on the carbon atom at the functionally substituted group. In addition, the formation of one regioisomer can be favored by intramolecular coordination of the aluminum atom with the oxygen atom in intermediate **A**. Charge separation between the sp-hybridized carbon atoms is insignificant in phenyl-substituted acetylene and, most likely, the coordination effect determines regioselectivity of the carboalumination step. The character of triple bond polarization in pent-4-yn-1-ol is opposite to that in alkyl-substituted acetylenic alcohols, thus favoring the addition of the aluminum atom to the terminal carbon atom of the acetylene bond.

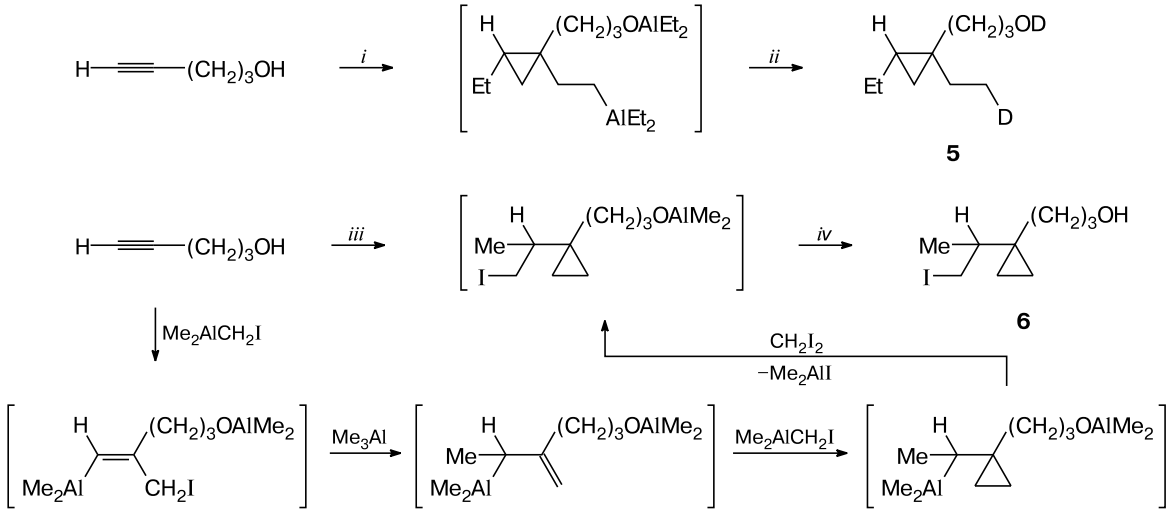
Table 1. The values of charges q(C) and q(C*) on the carbon atoms of the triple bond in acetylenes $R^1—C≡C^*—R^2$ calculated by the B3LYP/6-31G* method

R^1	R^2	q(C)	q(C*)
		a.u.	
n-Bu	$CH_2O(←AlMe_3)AlMe_2$	0.04	−0.08
n-Bu	$(CH_2)_2O(←AlMe_3)AlMe_2$	0.0	−0.04
Ph	$(CH_2)_2O(←AlMe_3)AlMe_2$	−0.02	0.0
H	$(CH_2)_3O(←AlMe_3)AlMe_2$	−0.24	−0.02

Note. Occupancies of molecular orbitals are analyzed by the NBO method.

To check this assumption, we involved pent-4-yn-1-ol in the reaction with CH_2I_2 and Et_3Al in dichloromethane. The deuterolysis of the reaction mixture gave substituted cyclopropane **5** in 56% yield (Scheme 6). Using Me_3Al instead of Et_3Al and increasing the amount of CH_2I_2 involved in the reaction to the ratio acetylene : CH_2I_2 : Me_3Al = 1 : 8 : 6, we succeeded to obtain iodine-containing 1,1-disubstituted cyclopropane **6** in 35% yield. In the COSY spectrum, the doublet of the

Scheme 6



Reagents and conditions: *i*. CH_2I_2 (4 equiv.), Et_3Al (6 equiv.); *ii*. D_2O; *iii*. CH_2I_2 (8 equiv.), Me_3Al (6 equiv.); *iv*. H_2O.

methyl group has a cross-peak with the multiplet of the hydrogen atom at C(5), which interacts in turn with the methylene group of the iodomethyl fragment. The HMBC spectrum additionally exhibits the interaction between the methyl group and the C(1) atom of the cyclopropane ring.

Thus, the results obtained undoubtedly have synthetic prospects and the approach based on analysis of charge separation in the starting acetylenes is not rigid but qualitatively correctly describes regioselectivity of carboalumination of disubstituted acetylenes.

Experimental

Commercially available reagents were used. Prior to use CH_2Cl_2 was distilled above P_2O_5. GLC analysis was performed on a Carlo Erba chromatograph (Ultra-1 glass capillary column (Hewlett Packard) 25000×0.2 mm, flame-ionization detector, temperature of the thermostat during temperature programming 50 → 170 °C, helium as a carrier gas). Mass spectra were measured on a Finnigan 4021 instrument (electron impact ionization energy 70 eV, temperature of the ionization chamber 200 °C). Elemental analysis was carried out on a Carlo Erba analyzer, model 1106. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer (100 MHz (^{13}C) and 400 MHz (^{1}H)), using $SiMe_4$ and signals of residual protons of $CDCl_3$ as internal standards. The yields of products were determined by GC using an internal standard. Thin layer chromatography was carried out on Silufol UV-254 plates in an ethyl acetate—petroleum ether (1 : 4) system. Nonempirical calculations were performed using the GAMESS program.[12]

Cyclopropanation of alkynols (general procedure). A 25-mL glass reactor was successively loaded on cooling to 0 °C and stirring under argon with CH_2Cl_2 (5 mL), alkynol (2 mmol), Alk_3Al (12 mmol), and CH_2I_2 (0.64 mL, 8 mmol). The reaction mixture was stirred at room temperature for a specified time (24 h in the synthesis of **1a—c**, **3**, and **5** or 2 days in the synthesis of **1d—g** and **4**). Then the mixture was cooled to 0 °C and D_2O (3 mL) was added. Precipitated aluminum deuteroxide was filtered off. The aqueous layer was extracted with diethyl ether, and the extract was combined with the organic layer, dried with anhydrous $CaCl_2$, and concentrated *in vacuo*. Individual products (**1a—g**, **3**, **4**, and **5**) were isolated by chromatography on a column with silica gel using an EtOAc—petroleum ether (1 : 10 → 1 : 3) system as an eluent.

1-Butyl-1-(2-deuteroethyl)-2-(2-deuteroxyethyl)-2-ethylcyclopropane (1a). Transparent oily liquid. The yield was 63%, R_f = 0.40. Found (%): C, 77.26. $C_{13}H_{24}D_2O$. Calculated (%): C, 77.93. ^{1}H NMR ($CDCl_3$), δ: 0.05—0.20 (m, 2 H, C(3)H_2); 0.8—1.1 (m, 8 H, C(7)H_2D, C(11)H_3, C(13)H_3); 1.15—1.8 (m, 7 H, C(6)H_a, C(8)H_a, C(9)H_2, C(10)H_2, C(12)H_a); 1.9—2.1 (m, 3 H, C(6)H_b, C(8)H_b, C(12)H_b); 2.3—2.4 (m, 2 H, C(4)H_2); 3.55—3.8 (m, 2 H, C(5)H_2). ^{13}C NMR ($CDCl_3$), δ: 10.81 (C(7), J = 19.03 Hz); 11.22 (C(13)); 14.18 (C(11)); 23.98 (C(3)); 24.53 (C(12)); 24.86 (C(6)); 29.23 (C(9)); 29.43 (C(10)); 30.03 (C(8)); 39.74 (C(4)); 61.59 (C(5)).

1-(2-Deuteroxyethyl)-2-(2-deuteroethyl)-1-ethyl-2-pentylcyclopropane (1b). Transparent oily liquid. The yield was 68%, R_f = 0.63. Found (%): C, 77.98. $C_{14}H_{26}D_2O$. Calculated (%): C, 78.44. ^{1}H NMR, δ: 0.10—0.13 (m, 2 H, C(3)H_2, J = 4.4 Hz); 0.89 (t, 3 H, C(12)H_3, J = 7.2 Hz); 0.90 (t, 2 H, C(7)H_2D, J = 7.6 Hz); 0.92 (t, 3 H, C(14)H_3, J = 7.6 Hz); 1.21—1.50 (m, 6 H, C(2)H_2, C(8)H_2, C(11)H_2); 1.38—1.46 (m, 2 H, C(10)H_2); 1.40—1.52 (m, 4 H, C(6)H_2, C(13)H_2). ^{13}C NMR, δ: 10.81 (C(7), J = 19.05 Hz); 11.04 (C(14)); 14.11 (C(12)); 22.73 (C(11)); 23.99 (C(3)); 24.60 (C(6)); 24.86 (C(13)); 26.64 (C(2)); 27.09 (C(1)); 29.37 (C(9)); 30.53 (C(10)); 32.42 (C(8)); 37.56 (C(4)); 61.59 (C(5)).

1-(2-Deuteroxyethyl)-2-(2-deuteroethyl)-2-dodecyl-1-ethylcyclopropane (1c). Transparent oily liquid. The yield was 62%, R_f = 0.58. Found (%): C, 78.97. $C_{21}H_{40}D_2O$. Calculated (%): C, 80.70. ^{1}H NMR, δ: 0.05—0.2 (m, 2 H, C(3)H_2); 0.85—1.0 (m, 8 H, C(7)H_2D, C(19)H_3, C(21)H_3); 1.2—1.35 (m, 23 H, C(6)H_a, C(8)H_a, C(9)H_2—C(18)H_2, C(20)H_a); 1.35—1.5 (m, 3 H, C(6)H_b, C(8)H_b, C(20)H_b); 1.6—1.8 (m, 2 H, C(4)H_2); 3.65—3.75 (m, 2 H, C(5)H_2). ^{13}C NMR, δ: 10.8 (C(7), J = 19.5 Hz); 11.22 (C(21)); 14.12 (C(19)); 22.69 (C(18)); 23.99 (C(20)); 24.54 (C(6)); 24.86 (C(3)); 26.99 (C(14)); 29.35 (C(9)); 29.65 (C(10)); 29.68 (C(11)); 61.61 (C(5)); 29.74 (C(12)); 29.74 (C(13)); 29.74 (C(15)); 29.74 (C(16)); 30.59 (C(17)); 31.92 (C(8)); 33.56 (C(4)).

1-Butyl-1-(2-deuteroethyl)-2-(2-deuteroxyethyl)-2-methylcyclopropane (1d). Transparent oily liquid. The yield was 71%, R_f = 0.6. Found (%): C, 77.15. $C_{12}H_{22}D_2O$. Calculated (%): C, 77.35. ^{1}H NMR, δ: 0.05—0.3 (m, 2 H, C(3)H_2); 0.85—1.0 (m, 5 H, C(7)H_2D, C(11)H_3); 1.11 (s, 3 H, C(12)H_3); 1.2—1.8 (m, 10 H, C(4)H_2, C(6)H_2, C(8)H_2—C(10)H_2); 3.74 (t, 2 H, C(5)H_2, J = 6.8 Hz). ^{13}C NMR, δ: 11.07 (C(7), J = 19.0 Hz); 14.16 (C(11)); 19.84 (C(12)); 23.19 (C(10)); 24.40 (C(6)); 25.10 (C(3)); 29.13 (C(9)); 31.10 (C(8)); 38.64 (C(4)); 61.64 (C(5)).

1-(2-Deuteroxyethyl)-2-(2-deuteroethyl)-1-methyl-2-pentylcyclopropane (1e). Transparent oily liquid. The yield was 75%, R_f = 0.53. Found (%): C, 77.16. $C_{13}H_{24}D_2O$. Calculated (%): C, 77.93. ^{1}H NMR, δ: 0.05—0.3 (m, 2 H, C(3)H_2); 0.85—0.95 (m, 5 H, C(7)H_2D, C(12)H_3); 1.12 (s, 3 H, C(13)H_3); 1.15—1.55 (m, 10 H, C(6)H_2, C(8)H_2—C(11)H_2); 1.67 (t, 2 H, C(4)H_2, J = 7.2 Hz); 3.76 (t, 2 H, C(5)H_2, J = 7.2 Hz). ^{13}C NMR, δ: 10.82 (C(7), J = 20.0 Hz); 14.12 (C(12)); 19.88 (C(13)); 22.70 (C(11)); 24.42 (C(6)); 25.11 (C(3)); 26.56 (C(9)); 31.37 (C(8)); 32.40 (C(10)); 38.67 (C(4)); 61.69 (C(5)).

1-(2-Deuteroxyethyl)-2-(2-deuteroethyl)-1-methyl-2-octylcyclopropane (1f). Transparent oily liquid. The yield was 83%, R_f = 0.43. Found (%): C, 80.21. $C_{16}H_{30}D_2O$. Calculated (%): C, 79.27. ^{1}H NMR, δ: 0.05—0.2 (m, 2 H, C(3)H_2); 0.85—0.95 (m, 5 H, C(7)H_2D, C(15)H_3); 1.11 (s, 3 H, C(16)H_3); 1.2—1.8 (m, 18 H, C(4)H_2, C(6)H_2, C(8)H_2—C(14)H_2); 3.7—3.8 (m, 2 H, C(5)H_2). ^{13}C NMR, δ: 11.05 (C(7), J = 19.5 Hz); 14.19 (C(15)); 19.72 (C(16)); 22.53 (C(14)); 24.48 (C(6)); 25.13 (C(3)); 27.08 (C(10)); 29.45 (C(11)); 29.66 (C(12)); 30.19 (C(9)); 31.42 (C(8)); 31.96 (C(13)); 38.64 (C(4)); 61.75 (C(5)).

1-(2-Deuteroxyethyl)-2-(2-deuteroethyl)-2-dodecyl-1-methylcyclopropane (1g). Transparent oily liquid. The yield was 80%, R_f = 0.55. Found (%): C, 78.14. $C_{20}H_{38}D_2O$. Calculated (%): C, 80.46. ^{1}H NMR, δ: 0.05—0.2 (m, 2 H, C(3)H_2); 0.85—0.95 (m, 5 H, C(7)H_2D, C(19)H_3); 1.11 (s, 3 H, C(20)H_3); 1.2—1.35 (m, 22 H, C(6)H_a, C(8)H_a, C(9)H_2—C(18)H_2); 1.4—1.55 (m, 2 H, C(6)H_b, C(8)H_b); 1.6—1.75 (m, 2 H, C(4)H_2); 3.7—3.8 (m, 2 H, C(5)H_2). ^{13}C NMR, δ: 11.01 (C(7), J = 19.3 Hz); 14.12 (C(19)); 19.85 (C(20)); 22.69 (C(18)); 24.42 (C(6)); 25.11 (C(3)); 26.89 (C(14)); 29.35 (C(16)); 29.65 (C(15)); 29.68 (C(13)); 29.70 (C(11)); 29.70 (C(12)); 30.19 (C(10)); 31.92 (C(17)); 31.34 (C(8)); 31.42 (C(9)); 38.63 (C(4)); 61.68 (C(5)).

1-Butyl-1-(2-deuteromethyl-4-deuteroxybut-2-yl)cyclopropane (3). Transparent oily liquid. The yield was 15%, R_f = 0.62. Found (%): C, 78.11. $C_{12}H_{22}D_2O$. Calculated (%): C, 77.35. ^{1}H NMR, δ: 0.22 (t, 2 H, C(11)H_a, C(12)H_a, J = 5.2 Hz); 0.41 (t, 2 H, C(11)H_b, C(12)H_b, J = 5.2 Hz); 0.83 (s, 5 H, C(9)H_2D, C(10)H_3); 0.90 (t, 3 H, C(8)H_3, J = 7.2 Hz); 1.05—1.15 (m, 2 H, C(6)H_2); 1.2—1.3 (m, 2 H, C(7)H_2); 1.45—1.55 (m, 2 H, C(5)H_2); 1.70 (t, 2 H, C(2)H_2, J = 7.6 Hz); 3.76 (t, 2 H, C(1)H_2, J = 7.6 Hz). ^{13}C NMR, δ: 6.94 (2 C, C(11), C(12)); 14.15 (C(8)); 23.51 (C(7)); 25.06 (t, C(9), J = 20 Hz); 25.38 (C(10)); 28.95 (C(6)); 32.19 (C(5)); 43.28 (C(2)); 60.12 (C(1)).

3-Deuteromethyl-3-deuteroxy-3-(1-phenylcyclopropyl)butane (4). Transparent oily liquid. The yield was 60%, R_f = 0.6. Found (%): C, 81.03. $C_{14}H_{18}D_2O$. Calculated (%): C, 81.50. ^{1}H NMR, δ: 0.64—0.88 (m, 4 H, C(9)H_2, C(9′)H_2, AA′BB′ system); 0.87 (s, 6 H, C(10)H_3, C(11)H_3); 1.56 (t, 2 H, C(2)H_2, J = 7.6 Hz); 3.79 (t, 2 H, C(1)H_2, J = 7.6 Hz). ^{13}C NMR, δ: 8.91 (2 C, C(9), C(9′)); 24.61 (C(10), J = 20 Hz); 24.90 (C(4)); 24.92 (C(11)); 28.05 (C(4)); 34.33 (C(3)); 43.33 (C(2)); 60.14 (C(1)); 126.14 (C(8)); 127.32 (2 C, C(7), C(7′)); 144.92 (C(5)); 132.23 (2 C, C(6), C(6′)).

1-(2-Deuteroethyl)-1-(3-deuteroxypropyl)-2-ethylcyclopropane (5). Transparent oily liquid. The yield was 56%, R_f = 0.51. Found (%): C, 76.24. $C_{10}H_{18}D_2O$. Calculated (%): C, 75.89. ^{1}H NMR, δ: –(0.2—0.1) (m, 1 H, C(3)H_a); 0.3—0.4 (m, 1 H, C(3)H_b); 0.4—0.5 (m, 1 H, C(2)H); 0.87 (t, 3 H, C(8)H_3, J = 7.2 Hz); 0.95 (t, 3 H, C(10)H_3, J = 7.4 Hz); 0.9—1.05 (m, 1 H, C(7)H_a); 1.25—1.5 (m, 5 H, C(7)H_b, C(9)H_2, C(5)H_2); 1.5—1.7 (m, 2 H, C(4)H_2); 3.64 (t, 2 H, C(6)H_2, J = 6.6 Hz). ^{13}C NMR, δ: 10.55 (C(8)); 14.48 (C(10)); 18.21 (C(3)); 22.35 (C(9)); 24.30 (C(1)); 25.84 (C(5)); 26.25 (C(2)); 30.07 (C(4)); 30.19 (C(7)).

Synthesis of β-iodoethyl-substituted cyclopropanes (general procedure). A 25-mL glass reactor was successively loaded on cooling to 0 °C and stirring under argon with CH_2Cl_2 (5 mL), alkynol (2 mmol), Me_3Al (12 mmol), and CH_2I_2 (1.28 mL, 16 mmol). The reaction mixture was stirred for 2 days at room temperature and then cooled to 0 °C. Water (10 mL) was added and aluminum hydroxide precipitated was filtered off. The further treatment of the reaction mixture and isolation of the product were carried out analogously to the above described procedure of synthesis of substituted cyclopropanes.

1-Butyl-2-(2-hydroxymethyl)-1-(2-iodoethyl)-2-methylcyclopropane (2). Transparent oily liquid. The yield was 52%, R_f = = 0.45. Found (%): C, 44.52; H, 7.01. $C_{12}H_{23}IO$. Calculated (%): C, 46.46; H, 7.47. ^{1}H NMR, δ: 0.22—0.28 (m, 2 H, C(3)H_2, AB system); 0.91 (t, 3 H, C(11)H_3, J = 7.2 Hz); 1.13 (s, 3 H, C(12)H_3); 1.24—1.35 (m, 4 H, C(9)H_2, C(10)H_2); 1.28—1.42 (m, 2 H, C(8)H_2); 1.67 (t, 2 H, C(6)H_2, J = 7.2 Hz); 1.93—2.13 (m, 2 H, C(4)H_2); 3.11—3.21 (m, 2 H, C(5)H_2); 3.76 (t, 2 H, C(7)H_2, J = 7.6 Hz). ^{13}C NMR, δ: 2.93 (C(5)); 13.96 (C(11)); 19.93 (C(12)); 21.73 (C(2)); 22.97 (C(10)); 24.99(C(3)); 29.57 (C(1)); 29.70 (C(9)); 31.07 (C(8)); 37.38 (C(4)); 38.39 (C(6)); 61.35 (C(7)).

1-(3-Hydroxypropyl)-1-(1-iodoprop-2-yl)cyclopropane (6). Transparent oily liquid. The yield was 35%, R_f = 0.49. Found (%): C, 40.80; H, 6.09. $C_9H_{17}IO$. Calculated (%): C, 40.31; H, 6.39. ^{1}H NMR, δ: 0.29—0.46 (m, 4 H, C(2)H_2, C(3)H_2); 1.08 (d, 3 H, C(9)H_3, J = 6.8 Hz); 1.29 (m, 1 H, C(6)H_a); 1.40 (m, 1 H, C(4)H); 1.51 (m, 2 H, C(7)H_2); 1.57 (m, 1 H, C(6)H_b); 3.09 (m, 1 H, C(5)H_a); 3.39 (m, 1 H, C(5)H_b); 3.61 (t, 2 H, C(8)H_2, J = 6.0 Hz). ^{13}C NMR, δ: 10.47 (C(2)); 11.27 (C(3)); 12.71 (C(5)); 17.63 (C(9)); 23.16 (C(1)); 28.64 (C(6)); 29.89 (C(7)); 43.16 (C(4)); 63.19 (C(8)).

The authors are grateful to Prof. L. M. Khalilov, Head of the Laboratory of Structural Chemistry of the Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, for help in recording and interpreting ^{1}H and ^{13}C NMR spectra.

This work was financially supported by the Ministry of Science and Education of the Russian Federation (Program for State Support of the Leading Scientific Schools of the Russian Federation, Grant NSh-4105.2010.3) and the Division of Chemistry and Materials Science of the Russian Academy of Sciences (Program No. 1).

References

1. I. R. Ramazanov, M. P. Luk´yanova, A. Z. Sharipova, A. G. Ibragimov, U. M. Dzhemilev, O. M. Nefedov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2001, 1338 [*Russ. Chem. Bull.*, *Int. Ed.*, 2001, **50**, 1406].
2. U. M. Dzhemilev, I. R. Ramazanov, A. G. Ibragimov, L. I. Dyachenko, M. P. Lukyanova, O. M. Nefedov, *J. Organomet. Chem.*, 2001, **636**, 91.
3. I. R. Ramazanov, L. K. Dilmukhametova, L. M. Khalilov, U. M. Dzhemilev, O. M. Nefedov, *Tetrahedron Lett.*, 2008, **49**, 6058.
4. I. R. Ramazanov, L. K. Dil´mukhametova, U. M. Dzhemilev, O. M. Nefedov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2009, 1311 [*Russ. Chem. Bull., Int. Ed.*, 2009, **58**, 1349].
5. I. R. Ramazanov, A. V. Yumagulova, U. M. Dzhemilev, O. M. Nefedov, *Tetrahedron Lett.*, 2009, **50**, 4233.
6. I. R. Ramazanov, L. K. Dilmukhametova, U. M. Dzhemilev, O. M. Nefedov, *J. Organomet. Chem.*, 2010, **695**, 1761.
7. I. R. Ramazanov, A. V. Yaroslavova, L. M. Khalilov, U. M. Dzhemilev, O. M. Nefedov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2010, 1623 [*Russ. Chem. Bull., Int. Ed.*, 2010, **59**, 1668].
8. D. B. Miller, *Tetrahedron Lett.*, 1964, **17**, 989.
9. H. Hoberg, *Lieb. Ann. Chem.*, 1962, **656**, 1.
10. K. Maruoka, Y. Fukutani, H. Yamamoto, *J. Org. Chem.*, 1985, **50**, 4412.
11. J. J. Eisch, W. C. Kaska, *J. Am. Chem. Soc.*, 1966, **88**, 2976.
12. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. J. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.

Received May 17, 2010 ;
in revised form October 26, 2010