Synthesis and transformations of metallacycles
32.* Novel method for the synthesis of cyclopentanols from aluminacyclopentanes

U. M. Dzhemilev, A. G. Ibragimov, L. O. Khafizova, R. R. Gilyazev, and V. A. D´yakonov*

Institute of Petrochemistry and Catalysis, Bashkortostan Republic Academy of Sciences and Ufa Research Center of the Russian Academy of Sciences, 141 prosp. Oktyabrya, 450075 Ufa, Russian Federation. Fax: +7 (347 2) 31 2750. E-mail: ink@anrb.ru

Cyclopentanols were synthesized by a "one-pot" method involving Cp_2ZrCl_2-catalyzed cycloalumination of α-olefins with trialkylalanes followed by the *in situ* reactions of aluminacyclopentanes with esters in the presence of catalytic amounts of Cu, Ni or Pd salts and complexes.

Key words: cyclopentanols, olefins, cycloalumination, aluminacyclopentanes, catalysis, esters.

Cyclopentanols and their derivatives are intermediate products in the synthesis of perfumes and medicines.[2—4] Along with familiar routes to cyclopentanols (reduction of cyclopentanones, hydration of cyclopentenes, *etc.*), reactions of *in situ* formed 1,4-dimagnesium compounds with esters attract attention.[5—7] In these reactions, cyclopentanols have been selectively obtained from compounds containing no cyclopentane fragments. However, 1,4-dimagnesium compounds are not easily accessible, which limits the synthetic value of these reactions.

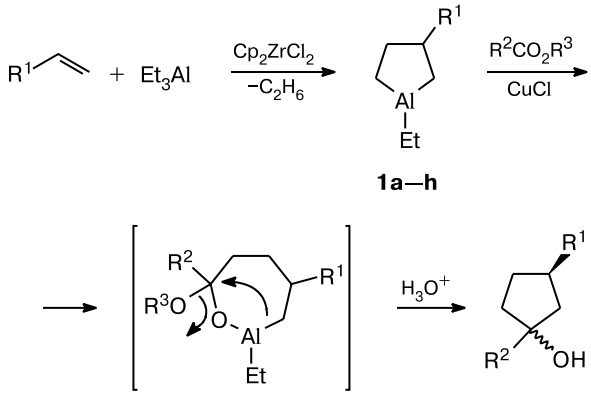
With the aim of developing a "one-pot" method for the synthesis of cyclopentanols from accessible α-olefins and extending the area of application of cyclic organoaluminum compounds (OAC)[8,9] in synthetic practice, we studied the reactions of *in situ* formed aluminacyclopentanes (ACP) with esters in the presence of salts and complexes of transition metals.

Results and Discussion

Trialkylalanes are known[10] to react with esters at elevated temperature (35—80 °C) to give a mixture of primary, secondary, and tertiary alcohols and ketones. Reaction products and their total yield depend on the structure of the starting OAC, the reaction temperature, and the reagent ratio.

We found that ACP **1a,b** prepared *in situ* by Cp_2ZrCl_2-catalyzed cycloalumination of α-olefins (hex-1-ene and oct-1-ene) with Et_3Al react with alkyl formates in the presence of 10 mol.% CuCl (20 °C, 7 h) to selectively give, upon hydrolysis of the reaction mixture, 3-(*n*-alkyl)cyclopentanols **3a,b** in ~75% yield (Scheme 1). Apparently, the reaction mechanism includes generation of an intermediate carbocation center at the orthoester C atom of OAC, its stabilization by intramo-

Scheme 1



1—3	a	b	c	d
R^1	Bu^n	*n*-C_6H_{13}	*n*-C_6H_{13}	*n*-C_6H_{13}
R^2	H	H	Me	Et

1—3	e	f	g	h
R^1		Ph	CH_2Ph	CH_2Ph
R^2	H	H	H	Et

R^3 = Alk

* For Part 31, see Ref. 1.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 130—133, January, 2004.

1066-5285/04/5301-0133

Table 1. Effect of the catalyst nature on the yield of cyclopentanol **3b** (ACP : HCO_2Et = 1 : 3, a catalyst (10 mol.%), hexane, 20 °C, 7 h)

Entry	Catalyst	Yield of **3b** (%)
1	CuCl	76
2	CuI	70
3	$Cu(acac)_2 + 2\ Ph_3P$	37
4	$ZrCl_4$	30
5	$Ni(acac)_2 + 2\ Ph_3P$	43
6	$NiCl_2 + 2\ Ph_3P$	38
7	$PdCl_2 + 2\ Ph_3P$	32
8	$NiCl_2$	25
9	$PdCl_2$	20
10	—	—

lecular ring isomerization into aluminum alkoxides **2**, and hydrolysis of the latter to form target cyclopentanols **3**.

In situ formed ACP **1** react with esters of organic acids (acetic and propionic) or with acetyl chloride or bromide to give 1,3-dialkylcyclopentanols **3c,d** (see Scheme 1).

The longer the alkyl substituent at the carbonyl C atom in the ester, the lower the yields of the corresponding cyclopentanols. Among the salts and complexes of transition metals (Cu, Ni, Pd, and Zr) we used in the cyclization, copper compounds proved to be most active (Table 1). The reactions were carried out in hexane because the yields of the target products in other (aromatic and ethereal) solvents were lower (Table 2).

The developed "one-pot" synthesis opens a convenient route to cyclopentanols, their structures being mainly determined by the starting olefins. Under our reaction conditions (10 mol.% CuCl, 20 °C, 7 h, hexane), cyclopentanols **3e—h** and **5a,b** were obtained from vinylcyclohexene, styrene, allylbenzene, and dicyclopentadiene (in the last case, the reaction proceeds through OAC **4a,b** (Scheme 2)).

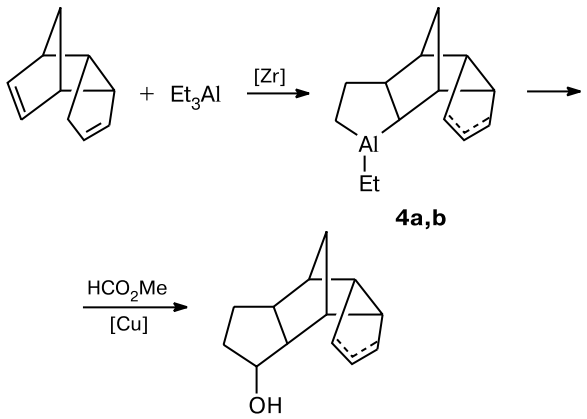
The reactions of *in situ* formed[11] *trans*-3,4-dialkylaluminacyclopentanes **6** with alkyl carboxylates afford cyclopentanols **7**, in which the alkyl substituents are also *trans* (Scheme 3).

Thus, our "one-pot" method for the synthesis of cyclic alcohols involves cycloalumination of olefins with tri-

Table 2. Effect of the solvent nature on the yield of cyclopentanol **3b** (ACP : HCO_2Et = 1 : 3, CuCl (10 mol.%), 20 °C, 7 h)

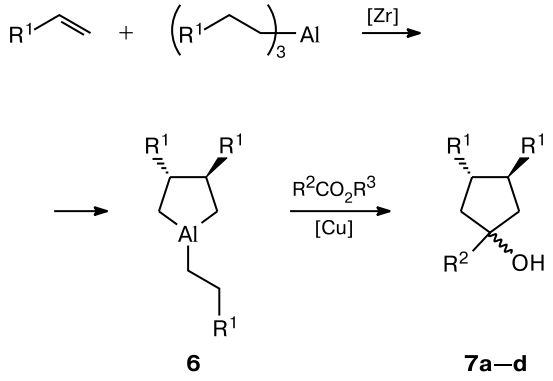
Entry	Solvent	Yield of **3b** (%)
1	Hexane	76
2	Toluene	54
3	Benzene	52
4	THF	10
5	Ether	9

Scheme 2



4, 5: Δ^3 (**a**), Δ^4 (**b**)

Scheme 3



7	**a**	**b**	**c**	**d**
R^1	Bu^n	n-C_6H_{13}	Bu^n	Bu^n
R^2	H	H	Me	Et

R^3 = Alk; [Zr] = $ZrCl_4$, Cp_2ZrCl_2

alkylalanes followed by the *in situ* reaction of the resulting aluminacyclopentanes with alkyl carboxylates in the presence of transition metal salts or complexes to give, upon hydrolysis of the reaction mixture, desired cyclopentanols.

Experimental

Reactions with organometallic compounds were carried out in a flow of dry argon. Solvents were dried and distilled immediately before use. Commercially available 95% Et_3Al was used. Reaction products were analyzed on a Chrom-5 chromatograph in a helium flow (column 1200×3 mm, 5% SE-30). IR spectra were recorded on an IR75 spectrometer (thin film). Mass spectra were recorded on a MX-1306 spectrometer (70 eV, 200 °C). ^1H and ^{13}C NMR spectra were recorded on Jeol FX-90 Q in-

strument (89.55 (^{1}H) and 22.5 MHz (^{13}C)) in $CDCl_3$. The yields of the products were determined by GLC.

CuCl-catalyzed reactions of 3-substituted 1-ethyl-ACP with esters (general procedure). Cp_2ZrCl_2 (0.5 mmol), hexane (3 mL), an olefin (10 mmol), and Et_3Al (12 mmol) were placed in a glass reaction vessel under dry argon at 0 °C. The reaction mixture was warmed to ~20 °C and stirred for 12 h. At −15 °C, CuCl (1 mmol) was added and then an ester (30 mmol) was slowly added dropwise. The reaction mixture was allowed to warm to ~20 °C, stirred for 8 h, and hydrolyzed with aqueous 8—10% HCl. The organic material was extracted with ether or hexane, and the extracts were dried with $CaCl_2$. The products were isolated by column chromatography (silica gel L 40/100 μm, hexane—Et_2O (10 : 1) as the eluent).

3-(*n*-Butyl)cyclopentanols (3a)*. Yield 76%, R_f 0.45. Found (%): C, 75.82; H, 12.63. $C_9H_{18}O$. Calculated (%): C, 76.00; H, 12.76. IR, ν/cm^{-1}: 3355, 2985, 2950, 2840, 1730, 1450, 1385, 1230, 1030, 925, 730. ^{1}H NMR, δ: 0.90 (t, 3 H, Me, J = 6.0 Hz); 1.15—1.52 (m, 6 H, CH_2); 1.78—2.35 (m, 7 H, CH, CH_2 (ring)); 4.29 (m, 1 H, C<u>H</u>—OH). ^{13}C NMR, δ: 14.50 (C(9)); 22.74 (C(8)); 30.28 (C(7)); 30.78, 30.86 (C(4)); 32.08, 32.79 (C(6)); 35.97, 36.05 (C(5)); 37.84, 37.98 (C(3)); 39.95 (C(2)); 76.47, 76.82 (C(1)). MS, m/z: 124 $[M - 18]^+$.

3-(*n*-Hexyl)cyclopentanols (3b)*. Yield 75%, R_f 0.46. Found (%): C, 77.39; H, 12.84. $C_{11}H_{22}O$. Calculated (%): C, 77.58; H, 13.02. IR, ν/cm^{-1}: 3380, 2990, 2950, 2840, 1720, 1460, 1380, 1185, 1030, 950, 720. ^{1}H NMR, δ: 0.91 (t, 3 H, Me, J = 6.0 Hz); 1.18—1.51 (m, 10 H, CH_2); 1.78—2.35 (m, 7 H, CH, CH_2 (ring)); 4.30 (m, 1 H, C<u>H</u>—OH). ^{13}C NMR, δ: 14.06 (C(11)); 22.62 (C(10)); 29.46 (C(8)); 28.49 (C(7)); 30.57, 30.66 (C(4)); 31.87 (C(9)); 32.20, 32.96 (C(6)); 35.77, 35.86 (C(5)); 36.52, 37.90 (C(3)); 39.62 (C(2)); 76.55, 76.95 (C(1)). MS, m/z (I_{rel} (%)): 152 $[M - 18]^+$ (5.26), 112 (1.52), 85 (2.48), 71 (2.63), 67 (100), 57 (16.28), 43 (31.01), 29 (27.50).

3-(*n*-Hexyl)-1-methylcyclopentanols (3c)*. Yield 68%, R_f 0.59. Found (%): C, 78.02; H, 13.01. $C_{12}H_{24}O$. Calculated (%): C, 78.19; H, 13.13. IR, ν/cm^{-1}: 3350, 2990, 2950, 2840, 1720, 1460, 1380, 1235, 1100, 1030, 1000, 925, 900, 730, 700. ^{1}H NMR, δ: 0.90 (t, 3 H, Me, J = 6.0 Hz); 1.20—1.58 (m, 10 H, CH_2); 1.33 (s, 3 H, Me); 1.61—2.51 (m, 7 H, CH, CH_2 (ring)). ^{13}C NMR, δ: 14.07 (C(11)); 22.67 (C(10)); 28.52, 28.78 (C(12)); 29.50, 29.56 (C(7), C(8)); 31.19, 31.45 (C(4)); 31.90 (C(9)); 36.52, 36.98 (C(6)); 38.41, 39.06 (C(3)); 40.75, 41.59 (C(5)); 48.23, 48.62 (C(2)); 79.74, 79.96 (C(1)). MS, m/z: 184 $[M]^+$.

1-Ethyl-3-(*n*-hexyl)cyclopentanols (3d)*. Yield 60%, R_f 0.52. Found (%): C, 78.51; H, 13.04. $C_{13}H_{26}O$. Calculated (%): C, 78.72; H, 13.21. IR, ν/cm^{-1}: 3350, 2990, 2950, 2840, 1720, 1450, 1380, 1230, 1030, 920, 730. ^{1}H NMR, δ: 0.83—1.02 (m, 6 H, Me); 1.20—1.57 (m, 12 H, CH_2); 1.61—2.51 (m, 7 H, CH, CH_2 (ring)). ^{13}C NMR, δ: 8.49, 8.72 (C(13)); 14.00 (C(11)); 22.68 (C(10)); 28.48, 29.49 (C(7), C(8)); 30.86, 31.38 (C(4)); 31.87 (C(9)); 34.41, 34.47 (C(12)); 36.33, 36.37 (C(6)); 36.95, 37.14 (C(5)); 38.02, 38.57 (C(3)); 46.00, 46.45 (C(2)); 82.31, 82.80 (C(1)). MS, m/z: 198 $[M]^+$.

3-Cyclohexenylcyclopentanols (3e)*. Yield 65%, R_f 0.68. Found (%): C, 79.28; H, 10.70. $C_{11}H_{18}O$. Calculated (%): C, 79.46; H, 10.91. ^{1}H NMR, δ: 1.60—2.21 (m, 14 H, CH, CH_2); 4.28 (m, 1 H, C<u>H</u>—OH); 5.15—5.75 (m, 2 H, CH=CH). ^{13}C NMR, δ: 25.26 (C(10)); 27.60, 27.82 (C(4)); 28.52 (C(11)); 30.73 (C(7)); 35.32, 35.68 (C(6)); 37.32, 37.68 (C(5)); 39.16, 39.39 (C(3)); 43.07, 43.50 (C(2)); 75.81, 76.18 (C(1)); 126.50 (C(8)); 127.18 (C(9)). MS, m/z (I_{rel} (%)): 166 $[M^+]$ (0.72), 148 (17.79), 134 (0.57), 122 (1.06), 108 (1.91), 94 (8.55), 81 (39.84), 80 (100), 58 (1.29), 44 (1.95), 30 (1.00), 29 (18.01).

3-Phenylcyclopentanols (3f)*. Yield 64%, R_f 0.52. Found (%): C, 81.23; H, 8.52. $C_{11}H_{14}O$. Calculated (%): C, 81.44; H, 8.70. IR, ν/cm^{-1}: 3380, 3015, 2990, 2950, 2840, 1710, 1490, 1450, 1395, 1180, 750, 700. ^{1}H NMR, δ: 1.45—2.25 (m, 6 H, CH_2); 3.10—3.25 (m, 1 H, C<u>H</u>—Ph); 4.40 (m, 1 H, C<u>H</u>—OH); 7.00—7.50 (m, 5 H, Ph). ^{13}C NMR, δ: 28.91, 29.20 (C(4)); 32.65, 33.49 (C(5)); 35.65, 36.01 (C(3)); 43.95, 44.25 (C(2)); 73.51, 73.75 (C(1)); 126.04 (C(9)); 127.08 (C(7)); 127.53 (C(8), C(10)); 128.48 (C(11)); 141.62 (C(6)). MS, m/z (I_{rel} (%)): 162 $[M]^+$ (31.87), 145 (9.42), 144 (100), 143 (52.88), 118 (25.89), 104 (53.75), 90 (2.04), 77 (29.56), 29 (17.74).

3-Benzylcyclopentanols (3g)*. Yield 69%, R_f 0.53. Found (%): C, 81.57; H, 8.98. $C_{12}H_{16}O$. Calculated (%): C, 81.77; H, 9.15. IR, ν/cm^{-1}: 3380, 2990, 3015, 2995, 2950, 1715, 1600, 1490, 1450, 1400, 1180, 750, 700. ^{1}H NMR, δ: 1.58—2.25 (m, 7 H, CH, CH_2); 2.62 (d, 2 H, C<u>H</u>$_2$—Ph, J = 5.6 Hz); 4.28 (m, 1 H, C<u>H</u>—OH); 7.00—7.48 (m, 5 H, Ph). ^{13}C NMR, δ: 30.34, 30.54 (C(4)); 32.09, 32.39 (C(5)); 38.78, 39.36 (C(3)); 39.72, 40.33 (C(5)); 41.60, 42.06 (C(2)); 76.38, 76.57 (C(1)); 126.00 (C(10)); 128.24 (C(8), C(12)); 128.42 (C(9), C(11)); 141.38 (C(7)).

3-Benzyl-1-ethylcyclopentanols (3h)*. Yield 55%, R_f 0.64. Found (%): C, 82.09; H, 9.23. $C_{14}H_{20}O$. Calculated (%): C, 82.30; H, 9.87. IR, ν/cm^{-1}: 3360, 3015, 2960, 2905, 1710, 1600, 1490, 1450, 1400, 730, 700. ^{1}H NMR, δ: 0.92 (t, 3 H, Me, J = 6.0 Hz); 1.10—2.20 (m, 9 H, CH, CH_2); 2.38—2.90 (m, 1 H, C<u>H</u>—Ph); 6.98—7.50 (m, 5 H, Ph). ^{13}C NMR, δ: 8.62, 8.82; 30.73, 31.38; 34.57; 38.60, 39.64; 39.90, 41.01; 42.24, 42.83; 45.69, 46.34; 82.27, 82.76; 125.68, 128.21, 128.73, 141.74.

Tetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridec-3-en-11-ol (5a) and tetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridec-4-en-11-ol (5b) (~1 : 1). Yield 65%, R_f 0.51. Found (%): C, 81.95; H, 9.49. $C_{13}H_{18}O$. Calculated (%): C, 82.06; H, 9.53. ^{1}H NMR, δ: 1.08—2.48 (m, 14 H, CH_2, CH); 5.48—5.66 (m, 2 H, CH=CH); 4.34 (m, 1 H, C<u>H</u>—OH). ^{13}C NMR, δ: <u>**5a**</u>: 26.53 (C(9)), 31.97 (C(13)), 33.17 (C(5)), 38.02 (C(1)), 39.65 (C(10)), 40.72 (C(7)), 41.72 (C(6)), 42.16 (C(8)), 45.51 (C(12)), 53.29 (C(2)), 75.42 (C(11)), 130.14 (C(4)), 132.51 (C(3)); <u>**5b**</u>: 26.53 (C(9)), 31.57 (C(13)), 32.97 (C(3)), 36.17 (C(12)), 38.02 (C(1)), 39.65 (C(10)), 41.41 (C(7)), 42.16 (C(8)), 43.78 (C(2)), 51.92 (C(6)), 75.30 (C(11)), 130.76 (C(4)), 132.23 (C(5)).

Reactions of *trans*-3,4-disubstituted 1-alkyl-ACP with esters. A solution of a corresponding R_3Al (10 mmol) was prepared according to a known procedure and placed in a glass reaction vessel under argon.[10] Copper(I) chloride (1 mmol) was added at −15 °C, and then an ester (30 mmol) was slowly added dropwise. The reaction was carried out and the reaction products were isolated as described above for 3-substituted 1-ethyl-ACP.

***trans*-3,4-Dibutylcyclopentanol (7a).** Yield 75%, R_f 0.61. Found (%): C, 78.53; H, 13.01. $C_{13}H_{26}O$. Calculated (%): C, 78.72; H, 13.21. IR, ν/cm^{-1}: 3350, 2985, 2845, 1725, 1450, 1385, 1230, 1030, 925, 730. ^{1}H NMR, δ: 0.86—0.90 (m, 6 H, Me); 1.15—1.30 (m, 12 H, CH_2); 1.65—2.35 (m, 6 H, CH, CH_2 (ring)); 4.30 (m, 1 H, C<u>H</u>—OH). ^{13}C NMR, δ: 14.12 (C(9), C(13)); 22.66 (C(8), C(12)); 29.85 (C(7), C(11)); 34.35 (C(6), C(10)); 39.10 (C(3), C(4)); 42.02 (C(2), C(5)); 73.25 C(1).

* A mixture of *cis*- and *trans*-isomers (~2 : 1).

***trans*-3,4-Di(*n*-hexyl)cyclopentanol (7b).** Yield 74%, R_f 0.60. Found (%): C, 80.03; H, 13.19. $C_{17}H_{34}O$. Calculated (%): C, 80.24; H, 13.47. ^{1}H NMR, δ: 0.88—0.91 (m, 6 H, Me); 1.15—1.30 (m, 20 H, CH_2); 1.65—2.35 (m, 6 H, CH, CH_2 (ring)); 4.30 (m, 1 H, C<u>H</u>—OH). ^{13}C NMR, δ: 14.15 (C(11), C(17)); 22.54 (C(10), C(16)); 26.15 (C(7), C(13)); 29.42 (C(8), C(14)); 31.72 (C(9), C(15)); 34.31 (C(6), C(12)); 39.02 (C(3), C(4)); 41.45 (C(2), C(5)); 72.18 (C(1)).

***trans*-3,4-Di(*n*-butyl)-1-methylcyclopentanol (7c).** Yield 73%, R_f 0.68. Found (%): C, 78.98; H, 13.11. $C_{14}H_{28}O$. Calculated (%): C, 79.18; H, 13.29. ^{1}H NMR, δ: 0.83—0.95 (m, 6 H, Me); 1.14—1.29 (m, 12 H, CH_2); 1.32 (s, 3 H, Me); 1.65—2.35 (m, 6 H, CH, CH_2 (ring)). ^{13}C NMR, δ: 14.12 (C(9), C(13)); 22.69 (C(8), C(12)); 26.92 (C(14)); 31.93 (C(7), C(11)); 34.53 (C(6), C(10)); 38.15 (C(3), C(4)); 41.94 (C(2), C(5)); 72.83 (C(1)).

***trans*-3,4-Di(*n*-butyl)-1-ethylcyclopentanol (7d).** Yield 69%, R_f 0.71. Found (%): C, 79.37; H, 13.20. $C_{15}H_{30}O$. Calculated (%): C, 79.58; H, 13.36. ^{1}H NMR, δ: 0.86—0.92 (m, 9 H, Me); 1.24—1.62 (m, 14 H, CH_2); 1.67—2.54 (m, 6 H, CH, CH_2 (ring)). ^{13}C NMR, δ: 8.80 (C(15)); 14.11 (C(9), C(13)); 22.69 (C(8), C(12)); 29.95 (C(7), C(11)); 32.42 (C(14)); 33.90 (C(6), C(10)); 37.41 (C(3), C(4)); 38.44 (C(2), C(5)); 76.65 (C(1)).

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 02-03-97903a and 03-03-33050a).

References

1. A. G. Ibragimov, L. O. Khafizova, G. N. Gil´fanova, L. R. Yakupova, A. L. Borisova, and U. M. Dzhemilev, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 2302 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 2434].
2. J. S. Cha and O. O. Kwon, *J. Org. Chem.*, 1997, **62**, 3019.
3. K. V. Lebedeva, V. A. Minyailo, and Yu. B. Pyatnova, *Feromony nasekomykh* [*Insect Pheromones*], Nauka, Moscow, 1984, 189 pp. (in Russian).
4. I. N. Bratus, *Khimiya dushistykh veshchestv* [*The Chemistry of Perfumes*], Pishchevaya prom-st´, Moscow, 1979, 304 pp. (in Russian).
5. V. G. Granik, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 1291 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 1356].
6. C. D. Nenitzescu and I. Necsoiu, *J. Am. Chem. Soc.*, 1950, **72**, 3483.
7. A. G. Ibragimov, E. V. Gribanova, L. M. Khalilov, L. M. Zelenova, and U. M. Dzhemilev, *Zh. Org. Khim.*, 1985, **21**, 259 [*J. Org. Chem. USSR*, 1985, **21** (Engl. Transl.)].
8. U. M. Dzhemilev and A. G. Ibragimov, *Usp. Khim.*, 2000, **69**, 134 [*Russ. Chem. Rev.*, 2000, **69**, 121 (Engl. Transl.)].
9. U. M. Dzhemilev and A. G. Ibragimov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 816 [*Russ. Chem. Bull.*, 1998, **47**, 786 (Engl. Transl.)].
10. G. A. Tolstikov and V. P. Yur´ev, *Alyuminiiorganicheskii sintez* [*Organoaluminum Synthesis*], Nauka, Moscow, 1979, 290 pp. (in Russian).
11. U. M. Dzhemilev, A. G. Ibragimov, A. B. Morozov, R. R. Muslukhov, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 1607 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 1425 (Engl. Transl.)].

Received July 30, 2003