Organometallic Chemistry

Hydroalumination of alkenes by the $LiAlH_4 \cdot 3AlBr_3$ system

E. V. Gorobets, O. V. Shitikova, S. I. Lomakina, G. A. Tolstikov, and A. V. Kuchin*

Institute of Organic Chemistry, Ural Branch of the Russian Academy of Sciences,
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.
Fax: +7 (347) 234 2914

The hydroalumination of a series of alkenes and some fused aromatic hydrocarbons by the $LiAlH_4 \cdot 3AlBr_3$ system in low-polar solvents was studied. Alkenes with mono-, di-, tri-, and tetraalkyl substituted, mono- and diaryl substituted double bonds and anthracene react at room temperature to give the corresponding dibromoaluminoalkanes in high yields. Benzylidenefluorene, tetraphenylethylene, naphthalene, and phenanthrene do not undergo hydroalumination under these conditions. Camphene, bicyclo[3.2.1]oct-2-ene, and norbornene afford the corresponding organoaluminum compounds with high stereoselectivity. Oxidation and halo- and acyldemetallation of the resulting alkyl- and arylalanes were carried out.

Key words: hydroalumination, alkenes.

The $LiAlH_4 \cdot 3AlBr_3$ system has been used previously for hydroalumination of some alkenes.[1] In the present work we studied the hydroalumination of alkenes having double bonds with various degrees of substitution, the hydroalumination of several fused aromatic systems, and the possibility of functionalizing the resulting organoaluminum compounds (OAC).

Results and Discussion

Dichloroalane $HAlCl_2$, which is able to hydroaluminate alkenes having a vinyl or methylene group when the reaction is catalyzed by boron[2] or titanium[3] compounds, is prepared in ether or THF (*cf.* ref. 4) according to the following reaction:

$$LiAlH_4 + 3AlCl_3 \rightarrow 4HAlCl_2 + LiCl.$$

Other dihaloalanes are prepared in a similar way. Since ether-type solvents form a stable complex with dihaloalanes, the reactivity of the latter in the hydroalumination of alkenes is very low, and a catalyst must be used in order to increase it somewhat. The replacement of ether by dichloroethane makes it possible to prepare $HAlCl_2$ *in situ*, from R_2AlH (R = Et, *i*-Bu) and $AlCl_3$. In this case $HAlCl_2$ is able to hydroaluminate alkenes with di- or trisubstituted double bonds only in the presence of catalysts.[2] $HAlCl_2$ can also be obtained by the reaction of $AlCl_4$ with $LiAlH_4$ without a solvent by mechanical activation and heating (50—150 °C).[5]

By using $AlBr_3$, which is highly soluble in aromatic and aliphatic hydrocarbons, we were able to carry out the reaction with $LiAlH_4$ heterogeneously, in toluene at 80 °C at the 3:1 ratio of the reactants. Elemental analysis of the solution after 2 h showed the presence of only

---

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1637—1642, September, 1993.

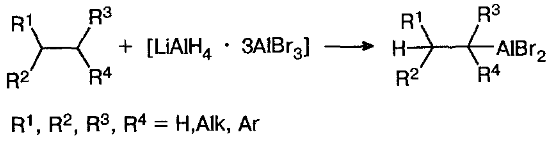
$AlBr_3$, in the same concentration as in the original solution. The hydride hydrogen content was as low as 5 % of the value calculated for $HAlBr_2$ (volumetric analysis). However, the addition of an excess of 1-nonene to the resulting heterogeneous system led to its complete homogenization, as a result of an exothermic reaction, and to the formation of a transparent solution which did not contain hydride hydrogen. The ^1H and ^{13}C NMR spectra showed the presence of a CH_2—Al group. Taking into account the initial ratio between the reactants, and the absence of the LiBr precipitate after the reaction, it may be suggested that the reaction occurs according to the following scheme:

$$4C_7H_{15}CH_2 + [LiAlH_4 \cdot 3AlBr_3] \rightarrow [4C_7H_{15}CH_2CH_2AlBr_2] \cdot LiBr.$$

Further investigations showed that benzene and chlorobenzene, which are much less reactive than toluene in alkylation with alkene, and cyclohexane, which does not undergo alkylation, can be used as solvents for preparing the hydroaluminating system and performing the reaction.

It is known[6] that the problem of hydroboration by means of the complex $HBCl_2 \cdot Et_2O$ has been solved by adding a mixture of alkene and trichloroborane in pentane to the reactant. A stronger Lewis acid (BCl_3) forms a complex with ether, and free dichloroborane is liberated which quickly hydroborates the alkene. We used an analogous approach for preparing the hydroaluminating system (see experimental, method **A**). The hydroaluminating properties of this system are similar to those of the system obtained by direct interaction between $LiAlH_4$ and $AlBr_3$ in benzene (method **B**); the latter system was used throughout in the experiments.

Alkenes with mono-, di-, tri-, or tetrasubstituted double bonds are successfully hydroaluminated to give OAC **1—10** (Table 1) in high yields over 5—30 min. However, in the case of alkenes with tri- and, especially, tetrasubstituted double bonds, in order to increase the yields of OAC it is advantageous to extend the reaction time to 1—2 h and to use more dilute solutions of alkenes, so that the occurence of side reactions of oligomerization and alkylation are reduced.



R^1, R^2, R^3, R^4 = H,Alk, Ar

Cycloolefins are known to undergo hydroalumination with difficulty.[7,8] Only the use of homogeneous catalysis by transition metal[3,9—11] or boron[2] compounds allows hydroalumination to be conducted under mild conditions with i-$BuAlH_2$, i-Bu_2AlCl, $LiAlH_4$, $HAl[N(i\text{-}Pr)_2]_2$, or $HAlCl_2$. Only i-$BuAlH_2$ under drastic conditions[12] and $HAlCl_2$ (see ref. 2) can add to the trisubstituted double bond in α-pinene. Tetrasubstituted double bonds cannot be hydroaluminated at all by the known reactants.

The reactant we prepared exhibits high efficiency and stereoselectivity in hydroalumination of α-pinene, norbornene, and camphene. In each case, only one stereoisomer is obtained, though it has been reported that hydroalumination of norbornene and camphene gives two stereoisomers.[12] Due to minor differences in the spatial environments of the carbon atoms of the double bond in bicyclo[3.2.1]oct-2-ene, its hydroalumination affords two regioisomers, both of which have the aluminum atom in the *exo*-position.

Aryl substituents affect the activity of the double bond of an alkene in the hydroalumination reaction considerably more than alkyl groups. An increase in the number of aryl substituents results in a substantial decrease in the reactivity. Styrene, α-methylstyrene, and indene are hydroaluminated smoothly and give practically none of oligomerization products they are prone to form in the presence of strong Lewis acids. The extent of conversion of 1,1- or 1,2-diphenylethylene under similar conditions does not exceed 72 % or 54 %, respectively, and increasing either the reaction time to 10—20 h or the temperature does not substantially affect the extent of conversion. Unlike stilbene, acenaphthylene, which has a more strained double bond, is smoothly hydroaluminated. Benzylidenefluorene and tetraphenylethylene do not react at all.

A study of the reactivity of naphthalene, phenanthrene, and anthracene showed that only the latter undergoes hydroalumination.

The presence of Al—C bonds in OAC **1—12** and their individuality were proven by the analysis of the ^1H and ^{13}C NMR spectra of these compounds and the products of their hydrolysis as well as by GLC of the latter and comparison with authentic samples. For the identification of OAC **13—17**, the products of their deuterolysis were used. The OAC obtained were subjected to the action of electrophiles: Br_2, I_2, $CuBr_2$, O_2, H_2O, and RCOCl. In all cases except the latter, the OAC were used as solutions in ether or THF. The results of the experiments are given in Table 1.

Alkyl bromides were obtained in the highest yields; it is advisable to treat OAC having primary unbranched hydrocarbon radicals with Br_2, while those with primary branched radicals or especially secondary or tertiary radicals should be treated with $CuBr_2$ in order to suppress the formation of dibromoalkanes. The content of the latter in the bromination products varies from 5 to 20 mol. % depending on the degree of branching of the hydrocarbon radical at the Al atom, while the yields of the target bromides are 64—97 %. However, even the use of $CuBr_2$ did not allow us to reduce the yield of the corresponding dibromides in the bromination of the products of hydroalumination of 2,3-dimethyl-2-butene and cyclohexylidenecyclohexane to less than 65 mol. %, whereas the yield of the target bromides amounted to

Table 1. The products of hydroalumination of alkenes and of the reaction of the resulting OAC with electrophiles (al = $AlBr_2$)

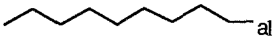
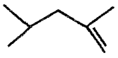
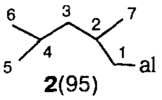
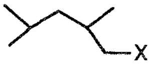
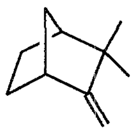
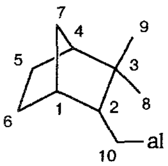
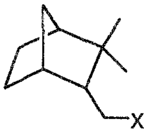
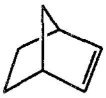
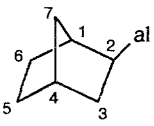
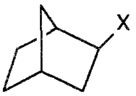
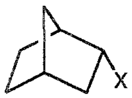
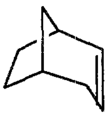
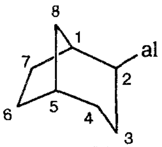
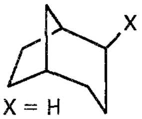
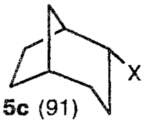
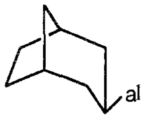
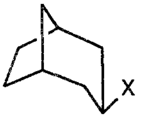
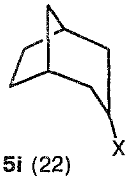
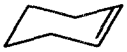
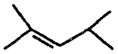
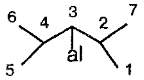
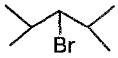
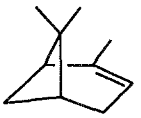
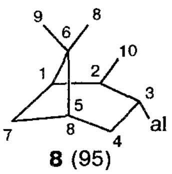
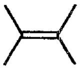
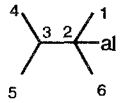
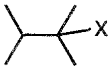
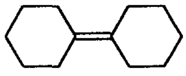
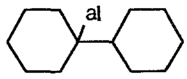
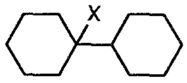
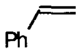
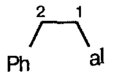
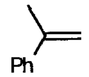
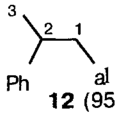
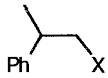
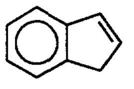
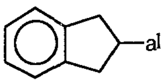
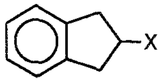
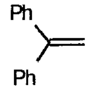
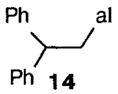
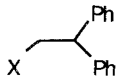
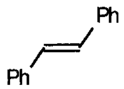
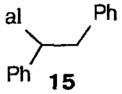
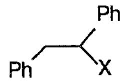
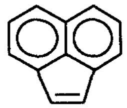
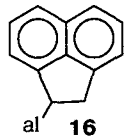
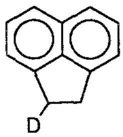
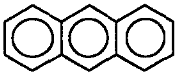
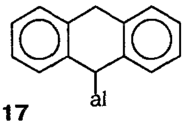
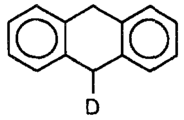
Substrate	OAC (Yield, %)	Electrophile	Product (yield, % (degree of conversion of OAC, %))
	 **1**(100)	H_2O I_2 Br_2 CH_3COCl C_2H_5COCl (*E*)-$CH_3CH=CHCOCl$ O_2(THF) $CuCl_2$ $CuBr_2$	X = H **1a** (95) X = I **1b** (67) X = Br **1c** (85) X = Ac **1d** (80) X = C_2H_5CO **1e** (82) X = (*E*)-$CH_3CH=CHCO$, **1f** (75) X = OH **1g** (78(83))* X = Cl **1h**(18); **1c** (75) **1c** (97) 
	 **2**(95)	I_2 $CuBr_2$ CH_3COCl	X = I **2a** (63) X = Br **2b** (87) X = Ac **2c**(55) 
	 **3** (96)	H_2O $CuBr_2$ $CuCl_2$ $O_2(Et_2O)$	X = H **3a**(95) X = Br **3b** (77) X = Cl **3c** (12) , X = Br **3b** (62) X = OH **3d** (79(79))* 
	 **4** (84)	$CuBr_2$ $O_2(Et_2O)$	 X = Br **4a** (49) X = OH **4c** (49)  **4b** (25) **4d** (9(75))*
	 **5a** (38)	H_2O $CuBr_2$ $O_2(Et_2O)$	 X = H X = Br **5d** (16) X = OH **5f** (5)  **5c** (91) **5e** (16) **5g** (5)
	 **5b** (57)	$CuBr_2$ $O_2(Et_2O)$	 X = Br **5h** (26) X = OH **5j** (48)  **5i** (22) **5k** (9)
	 **6** (95)	$CuBr_2$ O_2 (THF) I_2 CH_3COCl	X = Br **6a** (91) X = **6b** (86(84))* X = I **6c** (28) X = Ac **6d** (18) 
	 **7** (96)	$CuBr_2$	**7a** (74) 
	 **8** (95)	$CuBr_2$ O_2 (THF) H_2O	X = Br **8a** (83 (30))* X = OH **8b** (75(35))* X = H **8c** (89) 
	 **9** (95)	$CuBr_2$ D_2O	X = Br (28) X = D **9b** (62) 

Table 1. Continued

Substrate	OAC (Yield, %)	Electrophile	Product (yield, % (degree of conversion of OAC, %))	
	 **10**	$CuBr_2$ D_2O	X = Br **10a** (33) X = D **10b** (66)	
	 **11** (90)	D_2O Br_2	X = D **11a** (67) X = Br **11b** (78)	
	 **12** (95)	D_2O Br_2	X = D **12a** (71) X = Br **12b** (89)	
	 **13**	D_2O $CuBr_2$	X = D **13a** (64) X = Br **13b** (72)	
	 **14**	D_2O $CuBr_2$	X = D **14a** (90(72))* X = Br **14b** (88)	
	 **15**	D_2O $CuBr_2$	X = D **15a** (95(54)) X = Br **15b** (92)*	
	 **16**	D_2O	**16a** (85)	
	 **17**	D_2O	**17a** (82)	

* The yield is based on converted OAC.

28 % and 33 %, respectively. Bromination of OAC **4** and **5a,b** is accompanied by partial inversion of their configuration, OAC **5a,b** giving a mixture of bromides with an equal proportion of *endo-* and *exo-*isomers. Bromination of the OAC obtained from α-pinene occurs stereoselectively and affords isopinocampheyl bromide **8a**. In view of the low stability of the pinane system in the presence of strong Lewis acids, bromination of OAC was carried out under milder conditions, and the degree of its conversion was no more than 30 %. Halogenation by $CuCl_2$ gives alkyl chlorides in rather low yields. The main products in these reactions are the corresponding bromides probably obtained by the reaction of $RAlHal_2$ with $CuBr_2$ or CuBrCl. The formation of these copper halides can be explained by ion exchange processes between $RAlBr_2$ and $CuCl_2$ (see ref. 13). Only OAC with primary hydrocarbon radicals afford the corresponding alkyl iodides in reasonable yields, however, OAC and I_2 should be refluxed in ether for 8—10 h to attain a degree of conversion as high as 75—80 %.

Oxidation of OAC with oxygen in aromatic solvents occurs satisfactorily. Conducting the reaction in diethyl ether gives (after hydrolysis) a considerable amount of the corresponding bromide (up to 23 mol. %) along with the alcohol. The use of THF makes it possible to reduce the content of the bromide in the reaction products to 5—10 mol. %. When the degree of conversion of OAC is 75—84 %, the yields of alcohols amount to 57—72 %, which is somewhat lower than those in the oxidation of similar dichloroaluminioalkanes.[2] Oxidation of the OAC obtained from norbornene and bicyclo[3.2.1]oct-2-ene is accompanied, like bromination, by partial inversion of the configuration, however, in the case of oxidation the degree of inversion is considerably lower.

Acyldemetallation of OAC with primary hydrocarbon radicals without β-branching[1] occurs in 1,2-dichloroethane with both saturated and unsaturated acyl halides and gives the corresponding ketones in good yields. However, the presence of a secondary (**6**) or, to a lesser extent, a β-branched primary radical (**2**) lowers the yield of the target ketone **6d** or **2c** to 18 % and 55 %, respectively, due to the formation of chloroketones (1-acetyl-2-chlorocyclohexane or 4,6-dimethyl-4-chloro-2-heptanone) and unsaturated ketones (1-acetylcyclohexene or 4,6-dimethyl-3-hepten-2-one), which are products of the Kondakov—Darzens reaction of an alkene with acyl halide and of the elimination of HCl from the chloroketone. The alkene is probably formed from the OAC by its interaction with acyl halide due to the high reducing ability of OAC having this structure.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer; for OAC, C_6D_6 was used as the solvent, and the signals from the residual protons and from the carbon atoms in the solvent were used as the standard; for other compounds, $CDCl_3$ was used as the solvent, and TMS was the standard.

GLC was performed on a Chrom 5 chromatograph with a flame ionization detector using helium (40—50 mL per min.) as the carrier gas, and a 1.2 m × 3 mm column packed with 5 % SE-30 on Inerton Super, or on a Shimadzu chromatograph with a flame ionization detector, using helium (0.5 mL per min) as the carrier gas, and a 25 m × 0.2 mm quartz capillary column packed with PEG-20M.

All of the reactions were carried out in absolute solvents in an atmosphere of argon which had been purified by passing it through a 25 % solution of $i\text{-}Bu_2AlH$ in dodecane. We used a 6 *M* filtered solution of $LiAlD_4$ in ether and a 2.6 *M* solution of $AlBr_3$ in benzene which was also prepared in an argon atmosphere and decolorized (if it was orange-colored) by stirring with $LiAlH_4$ (0.1—0.2 g per 0.5 L) at 40—50 °C.

For the preparation of OAC, camphene with $[\alpha]_D^{20}$ −99.1° (*c* 7.8, $CHCl_3$) (ref. 15: −119.1° (c 2.33; C_6H_6) and pinene with $[\alpha]_D^{20}$ +33.0° (*c* 20.0; $CHCl_3$) (ref. 16: +51.1°) were used.

Preparation of the hydroaluminating system $LiAlH_4 \cdot 3AlBr_3$ A. 40 mL of ether was placed in a 100 mL three-neck flask equipped with a magnetic stirrer and a thermometer, and then 6.9 mL of a 2.6 *M* solution of $AlBr_3$ (18 mmol) in benzene and 1 mL of a 6 *M* solution of $LiAlH_4$ (6 mmol) in ether were added with stirring at −10 °C (see ref. 4). The mixture was stirred for 0.5 h at 20 °C. Most of the ether was removed under atmospheric pressure, and the remaining ether and some of the benzene were removed at 10—15 Torr. 10 mL of benzene was added to the resulting complex ($HAlBr_2 \cdot Et_2O$) followed by 9.2 mL of a 2.6 *M* solution of $AlBr_3$ (24 mmol) in benzene at −10 °C; the addition of the latter was accompanied by warming of the mixture. The resulting bluish-white suspension was stirred for 0.5 h at 20 °C.

B. 5 mL of benzene was placed in a 100 mL three-neck flask equipped with a magnetic stirrer and a thermometer, and 1 mL of a 6 *M* ethereal solution of $LiAlH_4$ (6 mmol) was added with stirring. Most of the solvent was removed at 10—15 Torr. 15 mL of benzene and 6.9 mL of a 2.6 *M* solution of $AlBr_3$ (18 mmol) in benzene were added, and the mixture was stirred for 1 h at 20 °C.

Hydroalumination of 1-nonene. A solution of 2.9 g (23 mmol, 4.0 mL) of 1-nonene in 15 mL of benzene was added dropwise with stirring to the reaction system obtained from 6 mmol of $LiAlH_4$ and 18 mmol of $AlBr_3$ according to procedure **B**. The reaction mixture warmed up to 30—40 °C. The reaction was complete within 5—10 min and was accompanied by the formation of a transparent solution of OAC.

Hydroalumination of the other alkenes was carried out in a similar way. For the preparation of OAC **4,7,9—17** solutions of 23 mmol of alkene in 35—40 mL of the solvent were used.

^{13}C NMR, δ: (**2**): 20.75 (C-1); 22.06 (C-5); 22.45 (C-6); 23.98 (C-7); 25.34 (C-4); 27.7 (C-2); 50.40 (C-3). (**3**): 13.40 (C-10); 20.19 (C-6); 22.01 (C-8); 24.93 (C-5); 32.01 (C-9); 37.24 (C-7); 37.98 (C-3); 44.88 (C-1); 46.73 (C-2); 49.08 (C-4). (**4**): 29.39 (C-2); 29.57 (C-5); 32.55 (C-6); 34.65 (C-3); 37.48 (C-4); 38.47 (C-1); 39.65 (C-7). (**5a**): 20.82 (C-3); 29.81 (C-6); 32.02 (C-2); 33.07 (C-7); 33.24 (C-4); 36.10 (C-5); 37.37 (C-1); 40.68 (C-8). (**5b**): 18.57 (C-3); 29.62 (C-6,7); 34.65 (C-2,4); 36.79 (C-1,5); 40.26 (C-8). (**7**): 23.88 (C-1,5); 24.19 (C-6,7); 28.47 (C-2,4); 46.50 (C-3). (**8**): 22.38 (C-8); 22.85 (C-3); 23.48 (C-10); 28.08 (C-9); 28.43 (C-4); 33.74 (C-7); 37.73 (C-2); 39.13 (C-6); 41.39 (C-5); 48.37 (C-1). (**9**): 20.34 (C-4,5); 22.30 (C-1,6); 30.38 (C-2); 36.87 (C-3). (**11**): 17.33 (C-1); 30.19 (C-2). (**12**): 27.30 (C-2); 27.52 (C-3); 37.05 (C-1).

^1H NMR, δ: (**9**): 1.17 (d, ^3J = 6.8 Hz, 6 H, CH_3); 1.22 (s, 6 H, CH_3); 1.88 (sept, ^3J = 6.8 Hz, 1 H, CH); (**11**): 1.22 (t, ^3J = 8.0 Hz, CH_2Al); 3.08 (t, ^3J = 8.0 Hz, 2 H, CH_2Ph); (**12**): 1.08 (m, CH_2Al); 1.44 (d, ^3J = 6.9 Hz, 3 H, CH_3); 3.17 (m, 1 H, CH).

Reaction of OAC 12 with Br_2. 30 mL of ether was added with stirring at 0 °C to a solution of 23 mmol of OAC **12** in benzene and a solution of 3.8 g (24 mmol, 1.2 mL) of Br_2 in 10 mL of benzene was added dropwise at −20 °C accompanied by decoloration of the solution. Alter 0.5 h the reaction mixture was hydrolyzed. The usual workup gave 3.8 g (89 %) of 1-bromo-2-phenylpropane.

Reaction of OAC 7 with $CuBr_2$. All the solvent was removed from a solution of 23 mmol of OAC **7** in benzene with stirring at 50→1 Torr. 50 mL of THF was added to the cooled (solid CO_2) residue and then 10.7 g (48 mmol) of finely pulverized $CuBr_2$ was added at −78 °C. The mixture was heated to 50 °C for 2 h. After hydrolysis and the usual workup the main bulk of the solvents (THF, ether) was evaporated, and the residue (6 mL) was distilled (35 Torr) to afford 2.9 g (74 %) of 3-bromo-2,4-dimethylpentane.

The reactions of OAC **1—6**, **9**, **10**, **13—15** with $CuBr_2$ were carried out in a similar way. In the reaction of OAC **13** (from α-pinene) with $CuBr_2$ the temperature was raised from −78 to −20 °C over 1 h, and the mixture was stirred for 1.5 h at −20 °C.

Acyldemetallation of 1-dibromoaluminiononane (1). A solution of 2 g (26 mmol, 1.8 mL) of acetyl chloride in 5 mL of dichloroethane was added dropwise at −20°C to a stirred solution of 24 mmol of OAC **1** in 25 mL of dichloroethane. The mixture was stirred for 1 h at −20 °C and for 0.5 h at 25 °C. After hydrolysis and the usual workup, 3.3 g (80 %) of 2-undecanone was isolated by column chromatography on SiO_2 (CH_2Cl_2 as the eluent).

The reactions of OAC **2** and **6** with acetyl chloride were carried out in a similar way, the total yields of ketones were 64 % and 55 %, respectively.

Reaction of 1-dibromoaluminononane (1) with crotonoyl chloride. A solution of 24 mmol of OAC **1** in 25 mL of dichloroethane was added dropwise at −30 °C to a stirred solution of 2.7 g (26 mmol) of crotonoyl chloride in 20 mL of dichloroethane. The mixture was stirred for 1 h at −30 °C and for 1 h at 25 °C. After hydrolysis and the usual workup, 3.5 g

(75 %) of (*E*)-2-tridecen-4-one was isolated by chromatography on SiO_2 (CH_2Cl_2 as the eluent).

^{13}C NMR spectra of the products of the reactions of OAC with electrophiles, δ: **(2a)**, 18.08 (C-1); 20.76 (C-7); 22.39 (C-5); 25.33 (C-4); 32.38 (C-2); 45.89 (C-3). **(2b)**: 18.89 (C-7); 22.44 (C-6); 23.11 (C-5); 25.28 (C-4); 32.71 (C-2); 41.80 (C-1); 44.32 (C-3). **(3b)**: 19.71 (C-6); 20.36 (C-8); 24.48 (C-5); 32.25 (C-9); 33.19 (C-10); 36.36 (C-3); 36.60 (C-7); 41.75 (C-1); 49.70 (C-4); 52.76 (C-2). **(3c)**: 19.99 (C-6); 20.46 (C-8); 24.56 (C-5); 32.30 (C-9); 36.81 (C-7); 37.88 (C-3); 40.91 (C-1); 44.21 (C-10); 49.71 (C-4); 52.74 (C-2). **(5d)**: 27.54 (C-7); 28.09 (C-6); 28.14 (C-3); 28.72 (C-4); 34.32 (C-5); 34.41 (C-8); 43.60 (C-1); 58.39 (C-2). **(5e)**: 25.8 (C-7); 28.14 (C-6); 29.38 (C-3); 31.22 (C-4); 33.18 (C-5); 39.92 (C-8); 44.72 (C-1); 58.39 (C-2). **(5h)**: 28.32 (C-6,7); 37.18 (C-1,5); 38.83 (C-8); 44.95 (C-2,4); 48.19 (C-3). **(5i)**: 28.48 (C-6,7); 34.33 (C-1,5); 37.77 (C-8); 41.79 (C-2,4); 47.16 (C-3). **(7a)**: 19.70 (C-1,5); 21.72 (C-6,7); 32.36 (C-2,4); 75.89 (C-3). **(8a)**: 20.28 (C-10); 23.88 (C-8); 27.98 (C-9); 35.25 (C-7); 38.57 (C-6); 40.88 (C-4); 43.36 (C-5); 49.37 (C-2); 49.49 (C-1); 52.52 (C-3). **(3d)**: 20.17 (C-6); 20.35 (C-8); 24.46 (C-5); 32.48 (C-9); 36.54 (C-3); 36.98 (C-7); 39.69 (C-1); 49.03 (C-4); 52.50 (C-2); 60.43 (C-10). **(1d)**: 13.77 (C-13); 17.76 (C-1); 22.45 (C-12); 23.95 (C-6); 29.11 (C-7,9); 29.24 (C-10); 31.66 (C-11); 39.75 (C-5); 131.7 and 141.4 (C-2,3); 199.5 (C-4). **(3a)**: 11.48 (C-10); 20.02 (C-6); 21.48 (C-8); 24.88 (C-5); 32.30 (C-9); 36.80 (C-3); 37.26 (C-7); 44.11 (C-2); 44.81 (C-1); 49.23 (C-4).

The ^{13}C NMR chemical shifts of compounds **4a—d**, **5f, g, j, k**, and **8b, c** agree with those reported previously.[17,18]

From OAC **3** and **8**, derivatives with the following $[\alpha]_D^{20}$ values ($CHCl_3$) were obtained: **3a,** *endo*-isocamphane, +7.5° (*c* 12.5); **3b,** bromo-*endo*-isocamphane, −18.0° (*c* 24.5); **3c,** *endo*-isocamphanol, +5.1° (*c* 28.5); **8a,** isopinocampheyl bromide, −22.9° (*c* 11.8); **3b,** isopinocampheol −21.3° (*c* 9.2) (ref. 19: −32.8° (*c* 10.0, C_6H_6).

References

1. E. V. Gorobets, A. V. Kuchin, L. M. Halilov, and G. A. Tolstikov, *Metallorgan. Khim.*, 1991, **4**, 198 [*J. Organomet. USSR*, 1991, **4** (Engl. Transl.)]
2. K. Maruoka, H. Sano, K. Shinoda, S. Nakai, and H. Yamamoto, *J. Am. Chem. Soc.*, 1986, **108**, 6036.
3. F. Sato, S. Sato, H. Kodama, and M. Sato, *J. Organometal. Chem.*, 1977, **142**, 71.
4. E. C. Ashby and J. Prather, *J. Am. Chem. Soc.*, 1966, **88**, 729.
6. H. C. Brown and N. Ravindran, *J. Am. Chem. Soc.*, 1976, **98**, 1798.
7. L. I. Zakharkin, V. V. Gavrilenko, and V. V. Golubev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1966, 142 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1966, **15**, No. 1 (Engl. Transl.)].
8. K. Ziegler, H. Gellert, H. Martin, K. Nagel, and J. Shneider, *Liebigs Ann. Chem.*, 1954, **589**, 91.
9. G. A. Tolstikov, U. M. Dzhemilev, O. S. Vostrikova, and A. G. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 669 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1982, **31**, *596.* (Engl. Transl.)].
10. U. M. Dzhemilev, O. S. Vostrikova, A. G. Ibragimov, G. A. Tolstikov, and L. M. Zelenova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 476 (in Russian).
11. E. C. Ashby and S. A. Noding, *J. Org. Chem.*, 1979, **44**, 4364.
12. A. V. Kuchin, L. I. Akhmetov, V. P. Yur'ev, and G. A. Tolstikov, *Zh. Obshch. Khim.*, 1979, **49**, 1567 [*J. Gen. Chem.*, 1979, **49** (Engl. Transl.)].
13. V. V. Gavrilenko, L. I. Zakharov, V. M. Smagin, and V. K. Golubev, *Zh. Obshch. Khim.*, 1978, **48**, 2073 [*J. Gen. Chem.*, 1978, **48** (Engl. Transl.)].
14. G. Giacome, L. Lardicci, and F. Palla, *J. Org. Chem.*, 1984, **49**, 310.
15. G. W. Hana and H. Koch, *Chem. Ber.*, 1978, **111**, 2527.
16. F. H. Thurber and R. C. Thielke, *J. Am. Chem. Soc.*, 1931, **53**, 1030.
17. J. K. Whitesell and M. A. Mintor, *Stereochemical Analysis of Alicyclic Compounds by C-13 NMR Spectroscopy*, Chapman and Hall Ltd, London—New York, 1987, 231.
18. J. Coxon, G. Hydes, and P. Steel, *J. Chem. Soc. Perkin Trans. 2*, 1984, 1351.
19. G. Zweifel and H. C. Brown, *J. Am. Chem. Soc.*, 1964, **86**, 393.

Received December 30, 1992