# SUBSTITUTION REACTIONS WITH THE PARTICIPATION OF ORGANOALUMINUM COMPOUNDS.

## 7.* REACTION OF ORGANOALUMINUM COMPOUNDS WITH MONOCHLORODIMETHYL ETHER

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The reactions of organoaluminum compounds (OACs) with alkyl halides are adequately well studied. The unsaturated allyl and vinyl alkyl halides and the α- or β-halogen-substituted ethers possess high reactivity [1]. Chlorodimethyl ether (CME) reacts with allyl- and propargylaluminum halides with the formation of the corresponding ethers [2]. Ethers containing the halogen atom in the β-position are less reactive, and the yield of the alkylated ethers is low [3]. When CME reacts with Z- or E-alkenyl OACs, unsaturated ethers are formed [4].

The reaction of CME with saturated OACs of varying types was investigated in the present work with the object of developing a method for the synthesis of a new C—C bond and the isolation of ethers. The OACs of the following types were involved in the reaction: $R_3Al$, $R_4AlM$ (M = Li, Na), and $R_2AlCl$ with saturated radicals of differing structure. The reaction of the OACs was performed with excess CME in ether or hydrocarbon solvents on heating. The reaction proceeds by the following scheme:

$$\begin{array}{c} R_3Al + 3ClCH_2OCH_3 \rightarrow R_{3-n}AlCl_n + nCH_3OCH_2R \\ \downarrow H_3{}^+O \\ RH + Al(OH)_3 + nRCH_2OCH_3 \\ (XII)-(XVI) \end{array}$$

The reactivity of the OACs was judged from the ratio of the ether and the hydrocarbon RH formed after hydrolysis. The structure of the ethers was established using IR and PMR spectroscopy. The conditions of the reaction of CME with different types of OACs are presented in Table 1. It follows from the data in Table 1 that the trialkylaluminum compounds give the highest yield of the ethers. The corresponding ate-complexes $R_4AlM$ and the chlorides $R_2AlCl$ react worse, giving the ethers with a lower yield. Therefore, the reactivity of the Al—C bond in the reaction with CME decreases in the series $R_3Al > R_2AlCl > R_4AlM$; this conforms with the data of the work [5] on the reaction of the OACs with methyl α-chloro-α-methoxyacetate.

The most expedient solvents for this reaction are dimethoxyethane (DME) and dioxane. In the cases where the OAC contains the alkylaromatic radical, the alkylation of the aromatic ring by the $CH_2OCH_3$ group with the formation of a mixture of isomeric products is possible. Thus, tri(3-phenylpropyl)aluminum reacts with CME in dioxane at 90°C giving 4-phenylbutyl methyl ether (XVI) with a yield of 30%. The methyl ether of p-propylbenzyl alcohol (XVII) is observed as an impurity (1.5%). The pure ether (XVI) is obtained, albeit in a lower yield, from the ate-complex (X). The dialkyl chloride (XI), which was obtained by mixing 0.5 mole of $AlCl_3$ with 1 mole of the OAC (IX), shows the properties of a strong Lewis acid. As a consequence of this, the reaction with CME results in the detection of the desired ether (XVI) and the mixture of the p-, o-, and m-isomers of the ether (XVII) in an approximately equal quantity with the total yield of 20% (Scheme 1).

The mixed OAC (XVIII), which contains cyclic and aliphatic hydrocarbon radicals, reacts with CME with the formation of the cycloalkyl methyl ethers (XIX) and (XX). An increase in the temperature and an increase of the reaction time leads simultaneously to a small increase

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*For previous communication 6, see [12].

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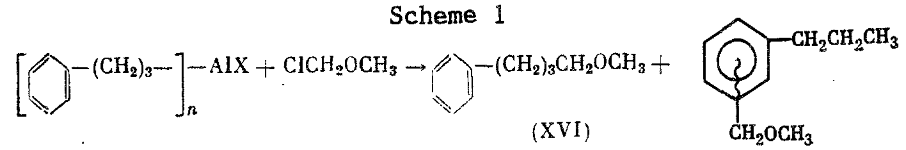
Scheme 1



$n = 3$(IX); X = Li, $n = 4$(X); X = Cl, $n = 2$(XI).

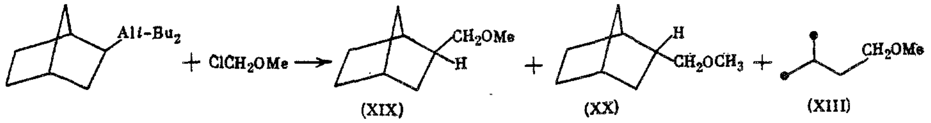


TABLE 1. Influence of the Type of OAC and the Conditions on the Yield of the Products of the Reaction with CME

| OAC | Solvent | T, °C (time, h) | Ratio of products after hydrolysis, % GLC | |
|---|---|---|---|---|
| | | | RH | $RCH_2OCH_3$ |
| $Et_3Al$ (I) | DME | 60(2) | 10 | 90 |
| $Et_4AlNa$ (II) | THF | 60(5) | 75 | 25 (XII) |
| $Et_2AlCl$ (III) | DME | 80(2) | 75 | 25 |
| $i$-$Bu_3Al$ (IV) | Dioxane | 90(2) | 15 | 85 (XIII) |
| $Hex_3Al$ (V) | Same | 90(2) | 10 | 90 |
| Same | Hexane | 60(5) | 50 | 50 (XIV) |
| $Hex_4AlLi$ (VI) | THF | 60(5) | 75 | 25 |
| $Hex_2AlCl$ (VII) | Dioxane | 90(2) | Resinification | |
| Same Same | Same | 60(5) | 50 | 50 |
| $Oct_3Al$ (VIII) | » | 90(2) | 10 | 90 (XV) |
| $(Ph(CH_2)_3)_3Al$ (IX) | » | 90(5) | 70 | 30 |
| $(Ph(CH_2)_3)_4AlLi$ (X) | THF | 60(5) | 90 | 10 (XVI) |
| $(Ph(CH_2)_3)_2AlCl$ (XI) | Dioxane | 60(5) | 80 | 20 |

in the yield of the requisite ethers and the formation of the secondary dimeric hydrocarbons R—R. The amount of the methyl (3-methyl)butyl ether (XIII) is significantly less than the stoichiometrically calculated amount.

After its reaction with CME, diisobutylnorbornylaluminum (XVIII) forms the 1:1 mixture of the exo- and endo-ethers (XIX) and (XX). This follows from the PMR spectral data; there are two signals of the angular protons in the region of 2.05 m and 2.33 s ppm, two singlets of the $OCH_3$ methyl groups at 3.20 ppm, a doublet at 3.55 ppm (J = 6 Hz), and a multiplet from 3.64 to 4.07 ppm for the $CH_2O$ groups of the ethers of the endo- and exo-configuration. The assignment of the signals was performed by analogy with the isomeric 10-isocamphanols, the stereochemistry of which was established earlier [6]. There is a characteristic absorption band for the ether group at 1120 $cm^{-1}$ in the IR spectrum of the mixture of the ethers (XIX) and (XX).

It is known from previous investigations that the hydroalumination of norbornene goes through from the exo-side with the formation of the exo-OAC (XVIII) [7]. Therefore, the configuration of the nucleophilic center in the reagent is not retained in the substitution reaction, or the initially formed ether (XIX) isomerizes by the action of the Lewis acid $R_nAlX_{3-n}$ and heating to give the ether (XX).

## EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer. The PMR spectra were recorded on a Tesla BS-487B (60 MHz) instrument for the solutions of the substances in $CCl_4$ relative to TMS. The GLC was performed on a Khrom-5 instrument with a column 1.2 m × 3 mm, 5% SE-30 on Chromaton N-AW-DMCS, and the He gas carrier (50 ml/min).

The OACs (VI) and (X) were obtained by the catalytic hydroalumination of the corresponding olefins with $LiAlH_4$ by the method of [8]. The OACs (V), (VIII), and (IX) were obtained by the transalkylation of the corresponding olefins by the method of [9]. The OAC (XVIII) was obtained by the thermal hydroalumination of norbornene by diisobutylaluminum hydride at 50°C for 2 h. Monochlorodimethyl ether (CME) was obtained according to [10]. The solvents were dehydrated over Na and $LiAlH_4$.

General Method for the Reaction of Trialkylalanes with Monochlorodimethyl Ether. To the solution of the OAC (0.01 mole) in dimethoxyethane or dioxane was added, dropwise, CME (0.045 mole, ~1 M solution in the same solvent) in an atmosphere of Ar at 25°C. The mixture warmed up weakly in proportion to the addition. After the addition of all the CME, the mixture was heated for 2-5 h at 60-90°C (cf. Table 1). It was cooled prior to dilution with ether and hydrolysis with dilute HCl (1:1), extraction with ether, washing with water, and drying with $MgSO_4$. After the evaporation of the solvent, the residue was analyzed by the method of GLC.

The reaction of the ate-complexes and dialkylaluminum chlorides with CME was performed with a 5:1 and 3:1 ratio of the components correspondingly.

Methyl Propyl Ether (XII). This compound had the bp 39°C, cf. [11, p. 400].

Methyl 3-Methylbutyl Ether (XIII). This compound had the bp 90°C, cf. [11, p. 354].

Methyl Heptyl Ether (XIV). This compound had the bp 150°C, cf. [11, p. 414]. The PMR spectrum (δ, ppm) was as follows: 0.90 t (3H, $CH_3$, J = 6 Hz), 1.33 m (10H, $CH_2$), 3.25 s (3H, $CH_3O$), and 3.28 t (2H, $CH_2O$, J = 5 Hz). The IR spectrum (ν, $cm^{-1}$) was characterized at 1120 (C–O).

Methyl Nonyl Ether (XV). The PMR spectrum (δ, ppm) was as follows: 0.90 t (3H, $CH_3$, J = 7 Hz), 1.26 m (14H, $CH_2$), 3.23 s (3H, $CH_3O$), and 3.28 t (2H, $CH_2O$, J = 5 Hz). The IR spectrum (ν, $cm^{-1}$) was characterized at 1130 (C–O).

Methyl 4-Phenylbutyl Ether (XVI). The PMR spectrum (δ, ppm) was as follows: 1.58 m (4H, $CH_2$), 2.55 t (2H, $CH_2$–Ph, J = 7 Hz), 3.303 s (3H, $CH_3O$), 3.28 t (2H, CH–O, J = 6 Hz), and 7.06 s (5H, $C_6H_5$). The IR spectrum (ν, $cm^{-1}$) was as follows: 715, 765 (C–H, Ph), and 1130 (C–O).

The Methyl Ether of Norisocamphanol (XIX), (XX). To the solution of 2.4 g of the OAC (XVIII) in 10 ml of dioxane was added, dropwise, the solution of 3.6 g of CME in 10 ml of dioxane at 25°C. The mixture was heated for 2 h at 80°C; it was treated by the general method after cooling. The 1:1:1 ratio of (XIII)[(XIX) + (XX)]:norbornane was noted on the basis of GLC. The mixture was separated by column chromatography on silica gel using hexane and the 1:1 mixture of hexane:EA as the eluents. The 1:1 ratio of the mixture of (XIX) and (XX) was obtained in the yield of 0.6 g (30%).

## CONCLUSIONS

The reaction of monochlorodimethyl ether with different organoaluminum compounds is only a convenient method for the isolation of alkyl methyl ethers in the case of trialkylalanes.

## LITERATURE CITED

1. G. A. Tolstikov and V. P. Yur'ev, Organoaluminum Synthesis [in Russian], Nauka, Moscow (1979).
2. M. Gandemar, Bull. Soc. Chim. France, 1475 (1963).
3. D. B. Miller, J. Org. Chem., 31, 908 (1966).
4. G. Zwaifel and R. A. Lynd, Synthesis, 816 (1976).
5. H. Reinheckel, H. Grob, K. Haage, and G. Sonnek, Chem. Ber., 101, 1736 (1968).
6. A. V. Kuchin, L. I. Akhmetov, V. P. Yur'ev, and G. A. Tolstikov, Zh. Obshch. Khim., 49, 1567 (1979).
7. R. Schimpf and P. Heimbach, Chem. Ber., 103, 2122 (1970).
8. F. Sato, S. Sato, and M. Sato, J. Organomet. Chem., 122, 25 (1976).
9. H. Ziegler, H. Martin, and F. Krupp, Liebigs Ann. Chem., 629, 14 (1960).
10. B. A. M. Kazanskii, Syntheses of Organic Preparations [in Russian], Vol. 1, IL, Moscow (1949), p. 278.
11. Beilsteins Handbuch der Organischen Chemie, Vol. 1, Springer-Verlag, Berlin (1958).
12. G. A. Tolstikov, T. B. Romanova, R. R. Muslukhov, and A. V. Kuchin, Izv. Akad. Nauk SSSR, Ser. Khim., 1331 (1987).