Reactions of trialkylalanes with cyclic acetals and orthoformates in CH_2Cl_2 and $ClCH_2CH_2Cl$ as solvents

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Under mild conditions, trialkylalanes (Et_3Al and Bu^i_3Al) in chlorine-containing solvents (CH_2Cl_2 or $ClCH_2CH_2Cl$) react with cyclic acetals and orthoformates to form glycol monoethers and dialkylacetals, respectively, in high yields. The ^1H NMR spectroscopic data demonstrate that CH_2Cl_2 or $ClCH_2CH_2Cl$ interacts with Bu^i_3Al.

Key words: triethylaluminum, triisobutylaluminum, cyclic acetals, orthoformates, reductive alkylation, dichloromethane, 1,2-dichloroethane, ethylene glycol monoethers, butane-1,3-diol monoethers, diastereomers.

The reactions of simplest organoaluminum compounds (OAC) with compounds containing two or three alkoxy groups in the geminal positions (cyclic acetals and orthoesters) find use in organic synthesis, in particular, in selective transformations of protective groups of sugars[1] or in the asymmetric synthesis of carbinols from chiral acetals.[2] These transformations involve the regioselective cleavage of one of the C—O bonds as the key step, which is preceded by coordination of the carbonyl substrate with OAC.[2] The regio- and stereoselectivity of this process depend substantially on the reaction conditions.[2]

It is known that cyclic acetals react with trialkylalanes in hydrocarbon solvents at temperatures no lower than 70 °C to give reductive cleavage and alkylation products.[3] Earlier,[4] we have demonstrated that the use of catalytic amounts of $ZrCl_4$ made it possible to perform the reactions of Bu^i_3Al with 1,3-dioxolanes at 20 °C.

In the present study, we examined the influence of the solvents CH_2Cl_2 and $Cl_2CH_2CH_2Cl_2$ on the regio-, diastereo-, and chemoselectivity of reductive alkylation of cyclic acetals and orthoformates by Et_3Al and Bu^i_3Al. Halohydrocarbons (CH_2Cl_2, $CHCl_3$, and dichloroethane) find application as solvents in the organoaluminum synthesis, particularly, in low-temperature reactions[5] of OAC with carbonyl substrates (data on their influence on the chemoselectivity of the process were published in the literature[6]) as well as in copolymerization of olefins on OAC-containing metal complex catalysts.[7] However, to our knowledge, spectroscopic data on the activating effect of CH_2Cl_2 on the cleavage of cyclic acetals and orthoesters by trialkylalanes are lacking in the literature.

It is known[8] that CH_2Cl_2 cannot be distilled off from an equimolar mixture with Et_3Al at 55 °C, but is virtually completely (78%) recovered after hydrolysis of a mixture with the insignificant formation of MeCl and EtCl. The fact that trimethylaluminum was "partially solvated" with the same solvent was mentioned in the monograph.[9] These data led us to the conclusion that CH_2Cl_2 forms such associates with trialkylalanes thus being able to influence the reactivity of the latter.

Results and Discussion

In the present study, we examined 1,3-dioxolane (**1**), 2-phenyl-1,3-dioxolane (**2**), *cis*-4-methyl-2-phenyl-1,3-dioxane (**3**), triethyl orthoformate (**4**), and tributyl orthoformate (**5**).

We found that compounds **1—5** reacted with Et_3Al or Bu^i_3Al at 20 °C in the presence of no smaller than a fourfold excess of CH_2Cl_2 with respect to trialkylalanes. Thus, Bu^i_3Al in dichloromethane reacted with 1,3-dioxolane (**1**),[6] which is resistant to the action of organoaluminum reagents,[4] (Scheme 1) to give a mixture of products of reductive cleavage **6** and reductive alkylation **9** in a total yield of 44% in a ratio of 2.5 : 1, respectively. 2-Phenyl-1,3-dioxolane (**2**) reacted with Bu^i_3Al to form 2-benzyloxyethanol (**7**) and 2-(3-methyl-1-phenylbutoxy)ethanol (**12**) in 65 and 18% yields, respectively

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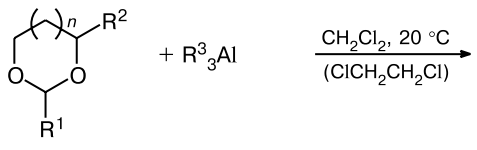
Table 1. Products of reactions of compounds **1—5** with trialkylalanes (20 °C, 2 h)

Starting compound	R_3Al	Substrate : : R_3Al	Solvent	Reaction products (yield (%))
1	Bu^i_3Al	1 : 2	CH_2Cl_2	**6** (31) + **9** (13)
2	Bu^i_3Al	1 : 2	CH_2Cl_2	**7** (65) + **12** (18)
2	Bu^i_3Al	1 : 2	$ClCH_2CH_2Cl$	**7** (38) + **12** (20)
2	Et_3Al	1 : 1	CH_2Cl_2	**10** (98)
3*	Bu^i_3Al	1 : 2	Hexane	**8** (29) + **13** (27)
3	Bu^i_3Al	1 : 2	CH_2Cl_2	**8** (56) +**13** (38)
3*	Et_3Al	1 : 1	Hexane	**11** (98)
3	Et_3Al	1 : 1	CH_2Cl_2	**11** (50)
4	Et_3Al	1 : 1	Hexane	**14** (60)
4	Et_3Al	1 : 1	CH_2Cl_2	**14** (98)
4	Bu^i_3Al	1 : 1	Hexane	**16** (<5)
4	Bu^i_3Al	1 : 1	CH_2Cl_2	**16** (62)
4	Bu^i_3Al	1 : 1	$ClCH_2CH_2Cl$	**16** (20)
5	Et_3Al	1 : 1	CH_2Cl_2	**15** (65)
5	Et_3Al	1 : 1	$ClCH_2CH_2Cl$	**15** (<5)
5	Bu^i_3Al	1 : 1	CH_2Cl_2	**17** (41)
5	Bu^i_3Al	1 : 1	$ClCH_2CH_2Cl$	**17** (<5)

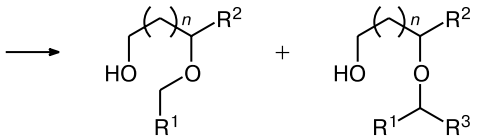
* In the presence of $ZrCl_4$.

(Table 1). It should be noted that reductive alkylation of cyclic acetals by Bu^i_3Al has been carried out earlier[4] only in the presence of $ZrCl_4$ as the catalyst.

Scheme 1



1—3

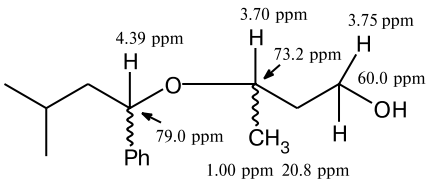


6—8 **9—13**

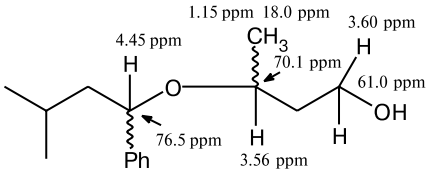
	1	2	3	6	7	8	9	10	11	12	13
R^1	H	Ph	Ph	H	Ph	Ph	H	Ph	Ph	Ph	Ph
R^2	H	H	Me	H	H	Me	H	H	Me	H	Me
R^3	Bu^i	Et	Et	Bu^i	Et	Et	Bu^i	Et	Et	Bu^i	Bu^i
n	0	0	1	0	0	1	0	0	1	0	1

It is known that Et_3Al reacts with cyclic acetals in hexane at 70 °C.[10] The use of CH_2Cl_2 as the solvent made it possible to perform the reaction of Et_3Al with acetal **2** at room temperature and obtain hydroxy ether **10** in quantitative yield.

In *cis*-4-methyl-2-phenyl-1,3-dioxane (**3**), Et_3Al and Bu^i_3Al regioselectively cleave the sterically less hindered O(1)—C(2) bond. Hydroxy ethers **11** and **13** containing two asymmetric centers each are generated as two pairs of diastereomers of 3-(1-phenylpropoxy)butan-1-ol (**11a,b**) and 3-(3-methyl-1-phenylbutoxy)butan-1-ol (**13a,b**), respectively, which are difficult to separate. The ratio (~2 : 1) between the resulting diastereomers **a** and **b** is independent of the nature of trialkylalane. Interestingly, the reactions of acetal **3** with Et_3Al or Bu^i_3Al in the presence of catalytic amounts of $ZrCl_4$ led to a change in the diastereomer ratio (1 : 1 and 3 : 2 for **11a,b** and **13a,b**, respectively).



13a



13b

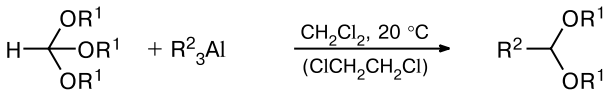
The structures of the regio- and diastereomers were established based on analysis of the chemical shifts in the ^1H and ^{13}C NMR spectra and analysis of the two-dimensional C—H correlation spectrum. The ^{13}C NMR spectra of diastereomer **13a** have two doublets at δ 73.2 and 79.0 belonging to two methine C atoms of the ether fragment and a triplet at δ 60.0 assigned to the C(1) atom bound to the OH group. In the case of the cleavage of the C(2)—O(3) bond, the spectrum should contain two doublets at δ ~65.0—68.0 characteristic of the CHMeOH fragment rather than signals at δ 60.0 and 61.0 belonging to the CH_2OH fragment. The assignment of the diastereomers was made based on the upfield shifts of the signals of the C(2) and C(4) atoms due to the 1,3-*syn* interaction.[11]

The use of 1,2-dichloroethane instead of CH_2Cl_2 in the reaction of dioxolane **2** with Bu^i_3Al led to a decrease in the total yield of hydroxy ethers **7** and **12** to 58% with a simultaneous increase in the percentage of reductive alkylation product **12** to 34% (see Table 1).

As expected, orthoformates in CH_2Cl_2 exhibited higher reactivity than cyclic acetals. The best results were obtained with the use of Et_3Al. Thus, ethyl orthoformate **4** reacted with an equimolar amount of Et_3Al at room temperature to give (after alkaline hydrolysis of the reaction mixture) propionaldehyde diethylacetal **14** (Scheme 2) in

virtually quantitative yield (see Table 1). It should be noted that this reaction proceeded very smoothly without any formation of by-products even in the presence of a threefold excess of Et_3Al. In particular, the reaction did not give rise to products of further reduction, *viz.*, ethers and hydrocarbons. Hence, trialkylalanes offer advantages over organomagnesium compounds, which are traditionally used in the synthesis of aldehydes from orthoformates according to the Chichibabin—Bodroux reaction.[12,13]

Scheme 2



4, 5 **14—17**

	4	**5**	**14**	**15**	**16**	**17**
R^1	Et	Bu^n	Et	Bu^n	Et	Bu^n
R^2	Et	Et	Et	Et	Bu^i	Bu^i

In the case of Bu^i_3Al, the yields of isovaleraldehyde acetals **16** and **17** were no higher than 62 and 20% in dichloromethane and 1,2-dichloroethane, respectively. The use of hexane as the solvent led to a decrease in the yields of acetals **14** and **16** (see Table 1).

It was assumed[9,14] that halohydrocarbon solvents facilitate the transformation of OAC from the dimeric form to the more active monomeric form. However, the observed activating effect of chlorohydrocarbons observed under the conditions of our experiments cannot be attributed only to the above-mentioned fact, because one would not expect substantial changes in the course of reactions of Bu^i_3Al (which exists predominantly in the monomeric form regardless of the nature of the solvent[9,15]) with cyclic acetals and orthoformates. The possibility of the formation of alkylhaloalanes, which also cleave acetals and ketals under mild conditions,[16] as well as the generation of superelectrophilic complexes of the $CCl_4/AlCl_3$ type, which promote the formation of carbon-carbon bonds,[17] can be neglected, because the percentage of alkylation products in the reaction of Et_3Al with CH_2Cl_2 in the absence of transition metal complexes or high temperatures is very low.

We assumed that the formation of associates of chlorohydrocarbons with trialkylalanes, which further react with cyclic acetals and orthoformates, plays a decisive role in the observed activating effect. The possibility of the existence of such associates was confirmed by the published data.[8,9]

With the aim of examining these assumptions, we studied the ^1H NMR spectra of solutions of mixtures of CH_2Cl_2 and Bu^i_3Al in cyclohexane-d_{12} and benzene-d_6 used in different ratios. In the spectra of the CH_2Cl_2—Bu^i_3Al mixture in C_6D_{12} (Fig. 1, Table 2), the

Table 2. Chemical shifts in the ^1H NMR spectra (δ) for a Bu^i_3Al—CH_2Cl_2 mixture at different molar ratios of the components (20 °C)

Solvent	Bu^i_3Al : : CH_2Cl_2	δ (^3J/Hz)			
		Bu^i_3Al			CH_2Cl_2
		CH_3 (d)	CH_2 (d)	CH (m)	
C_6D_6	0 : 1	—	—	—	4.44 (s)
	1 : 0	1.11 (6.8)	0.29 (6.8)	2.04	—
	1 : 1	1.00 (6.9)	0.29 (6.9)	1.95	4.90 (br.s)
	1 : 4	1.02 (6.9)	0.33 (6.9)	1.97	4.65 (br.s)
C_6D_{12}	0 : 1	—	—	—	5.16 (s)
	1 : 1	1.00 (7.0)	0.35 (7.0)	1.97	5.20 (br.s)
	1 : 4	1.00 (7.0)	0.35 (7.0)	1.97	5.21 (br.s)

signal of the protons of CH_2Cl_2 at a Bu^i_3Al : CH_2Cl_2 molar ratio of 1 : 4 (see Fig. 1, *a*) is observed as a broadened singlet ($\Delta W_{1/2}$ = 21 Hz) at δ 5.21. As the Bu^i_3Al : CH_2Cl_2 ratio was decreased to 1 : 1 (see Fig. 1, *b*), the signal of CH_2Cl_2 was substantially broadened ($\Delta W_{1/2}$ = 60 Hz) and slightly shifted upfield. By contrast, in none of the cases, did changes in the chemical shifts as well as in character of signals of the methyl, methylene, and methine groups of the hydrocarbon fragment of Bu^i_3Al occur.

The addition of diethyl ether, which is a Lewis base, to an equimolar Bu^i_3Al—CH_2Cl_2 mixture to the ratio Bu^i_3Al : CH_2Cl_2 : Et_2O = 1 : 1 : 1 led, apparently, to a partial decomposition of the initial associates, as evidenced by the appearance of a signal at lower field (δ_H = 5.21) corresponding to free CH_2Cl_2 along with two broadened peaks ($\Delta W_{1/2}$ = 18 Hz) assigned to associates formed by CH_2Cl_2 with Bu^i_3Al (see Fig. 1, *c*).

It should be noted that Bu^i_3Al did not react with cyclic acetals in the presence of CH_2Cl_2 upon a tenfold dilution of the reaction mixture with benzene. The spectroscopic data also confirmed decomposition of associates of Bu^i_3Al with CH_2Cl_2 under the reaction conditions used.

It is known that the signal of CH_2Cl_2 is shifted upfield due to intermolecular interaction with benzene because of the magnetic anisotropy of the latter.[18] Dissolution of CH_2Cl_2 in C_6D_6 in a ratio of 1 : 5 led to a shift of the signal for the protons of CH_2Cl_2 to δ 4.40, whereas the line width (0.5 Hz) was retained. The addition of Bu^i_3Al to the reaction solution caused a downfield shift and substantial broadening of the signal for the protons of CH_2Cl_2, *i.e.*, benzene and Bu^i_3Al compete for the association with CH_2Cl_2.

If the Bu^i_3Al : CH_2Cl_2 : C_6D_6 ratio is 1 : 4 : 20, the line width of CH_2Cl_2 is ~30 Hz. If the ratio is 1 : 1 : 5, this line width reaches 140 Hz and the center of the signal is shifted downfield to δ 4.90, whereas the spin-spin coupling constants of doublets for the protons of the CH_3, CH_2, and CH groups of the Bu^i_3Al molecule remain virtually unchanged (~7 Hz), the line widths of these signals

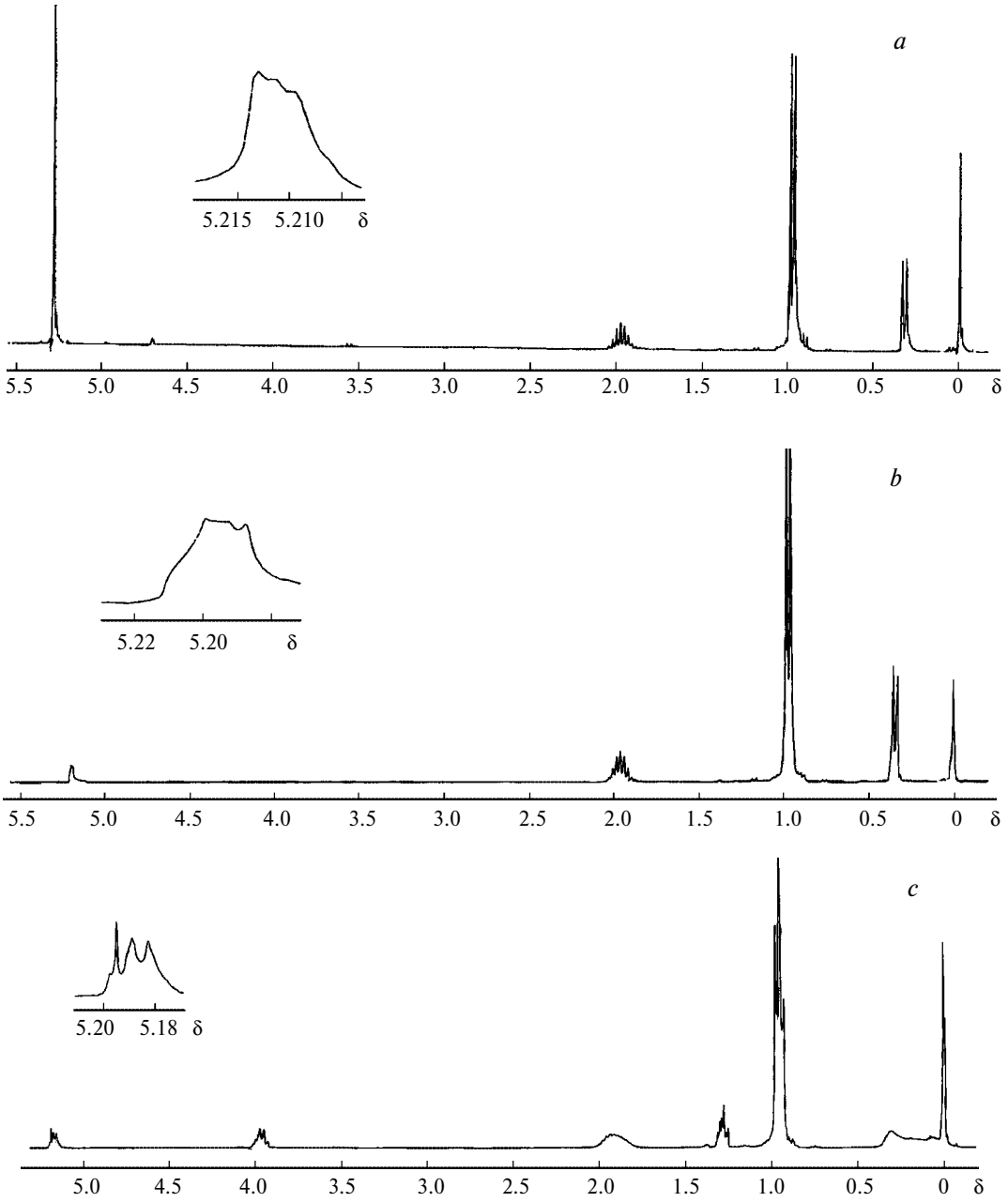


Fig. 1. ^{1}H NMR spectra of the $Bu^i_3Al—CH_2Cl_2$ mixture in a molar ratio of 1 : 4 (*a*) and 1 : 1 (*b*) and of the 1 : 1 mixture after dilution with Et_2O (*c*) (C_6D_{12}, 20 °C).

being <0.5 Hz. Analogous changes are observed for the signal of the protons of the methylene group of 1,2-dichloroethane in C_6D_6 upon the addition of Bu^i_3Al. Interestingly, in the spectrum in 1,2-dichloroethane, changes are observed not only in the resonances of the solvent but also in the resonances of the hydrocarbon fragment of Bu^i_3Al. The isobutyl group of the Bu^i_3Al molecule gives two groups of resonances, which indicates that Bu^i_3Al in solution coexists in two states. The spin-spin coupling constants of the doublets for the methyl and methine protons of Bu^i_3Al remain within the range of 7 Hz.

Broadening and shifts of the signals for the methylene protons of CH_2Cl_2 and 1,2-dichloroethane observed in the ^{1}H NMR spectra in the presence of Bu^i_3Al disappear upon dilution with benzene or addition of diethyl ether. This is indicative of the formation of unstable associates of OAC with halohydrocarbons through nonbonded interactions, which apparently leads to activation of the Al—C bonds and then to the reactions with cyclic acetals and orthoethers,.

To summarize, the use of CH_2Cl_2 and $ClCH_2CH_2Cl$ as solvents allows one to cleave cyclic acetals and ortho-

formates by trialkylalanes under mild conditions in high yields. The ^1H NMR spectroscopic data provide evidence for the formation of associates of Bu^i_3Al with CH_2Cl_2 and $ClCH_2CH_2Cl$.

Experimental

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer in $CDCl_3$, C_6D_{12}, and C_6D_6 with Me_4Si as the internal standard. The GLC-mass spectra were obtained on a Hewlett Packard 5890 instrument (evaporator temperature was 280 °C, linear programming of the thermostat temperature from 50 to 280 °C with a rate of 5 °C min^{-1}, 50 m×0.25 mm Ultra capillary column, helium as the carrier gas, energy of ionizing electrons was 70 eV). The GLC analysis was carried out on a Chrom-5 chromatograph (flame ionization detector, 1200×5 mm stainless steel column, 5% SE-30 on Inerton N-AW DMCS (0.125—0.160), helium as the carrier gas).

The experiments were carried out under dry argon. The solvents CH_2Cl_2 and $ClCH_2CH_2Cl$ were distilled from P_2O_5 under argon immediately before use. Triethyl- and triisobutylaluminum were purchased from the Redkinskii pilot-production plant (Russia). The starting acetals **1—3** and orthoformates **4** and **5** were synthesized according to known procedures,[13,19,20] distilled under a stream of argon over NaOH, and stored under an inert atmosphere.

***cis*-4-Methyl-2-phenyl-1,3-dioxane (3).** ^1H NMR ($CDCl_3$), δ: 1.35 (d, 3 H, CH_3, J = 6.2 Hz); 1.56 (dq, 1 H, CH_2, J = −14.5 Hz, J = 1.3 Hz); 1.84 (ddt, 1 H, CH_2, J = −14.5 Hz, J = 12.9 Hz, J = 5.1 Hz); 4.00 (m, 2 H, CHO and CH_2O); 4.28 (dd, 1 H, CH_2O, J = −11.5 Hz, J = 5.1 Hz, J = 1.3 Hz); 5.54 (s, 1 H, OCHO); 7.30—7.60 (m, 5 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 23.0 (CH_3); 32.5 (CH_2); 66.3 (CH_2O); 73.0 (CHO); 101.4 (O—CH—O); 124.0—140.0 (CH and C, Ar).

The vicinal spin-spin coupling constant between the H(4) and H(5a) protons (12.9 Hz) is indicative of the axial orientation of the H(4) proton and, consequently, of the equatorial orientation of the Me substituent at the C(4) atom. The fact that the equatorial orientation of the Ph substituent in the second position is preferential one was established based on the direct spin-spin coupling constant $J_{C(2),H(2)}$ = 159.3 Hz and taking into account that this constant increased by 1 Hz as the temperature of the sample was increased by 55 °C.[21]

Reactions of cyclic acetals with trialkylalanes (general procedure). Trialkylalane (20 or 40 mmol) was added dropwise to a solution of cyclic acetal (20 mmol) in a chlorine-containing solvent (80 mmol) stirred at 0 °C. The temperature of the reaction mixture was increased to 20 °C. The reaction mixture was stirred at this temperature for 2 h, diluted with Et_2O (20 mL), cooled to −10 °C, and decomposed with a 5% aqueous solution of NaOH (40 mL). The organic layer was separated, dried with $MgSO_4$, and analyzed by GLC. The yields of the reaction products are given in Table 1.

2-Methoxyethanol (**6**), 2-benzyloxyethanol (**7**), 3-benzyloxybutan-1-ol (**8**), 2-(3-methylbutoxy)ethanol (**9**), 2-(1-phenylpropoxy)ethanol (**10**), 3-(1-phenylpropoxy)butan-1-ol (**11**), and 2-(3-methyl-1-phenylbutoxy)ethanol (**12**) were identified by comparing their physicochemical constants with the published data.[3,4,22—24]

3-(3-Methyl-1-phenylbutoxy)butan-1-ol (13) was separated by chromatography on a column with silica gel (40/100 μm), hexane—AcOEt (4 : 1) as the eluent. B.p. 125 °C (1 Torr), n_D^{20} 1.4551. Found (%): C, 76.28; H, 10.25. Calculated (%): C, 76.23; H, 10.24.

3-(3-Methyl-1-phenylbutoxy)butan-1-ol (13a). ^1H NMR ($CDCl_3$), δ: 0.85 (d, 6 H, $C\underline{H}_3CH$, J = 6.5 Hz); 1.00 (d, 3 H, $C\underline{H}_3CHO$, J = 6.2 Hz); 1.53 (m, 1 H, $CH_3C\underline{H}$); 1.48—1.80 (m, 4 H, $CHC\underline{H}_2$); 3.00 (br.s, 1 H, OH); 3.70 (m, 1 H, $CH_3C\underline{H}O$); 3.75 (m, 2 H, $C\underline{H}_2OH$); 4.39 (t, 1 H, CH—Ar, J = 6.2 Hz, J = 7.6 Hz); 7.22 (m, 5 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 20.8 ($\underline{C}H_3CH$); 22.5 and 22.9 ($\underline{C}H_3CH$); 24.4 ($CH_3\underline{C}H$); 38.0 ($CH\underline{C}H_2CH_2$); 47.5 ($CH\underline{C}H_2CH$); 60.0 ($\underline{C}H_2OH$); 73.2 ($CH_3\underline{C}HO$); 79.0 (CH—Ar); 126.6 (CH, Ar); 128.2 (CH, Ar); 127.3 (CH, Ar); 144.1 (C, Ar).

3-(3-Methyl-1-phenylbutoxy)butan-1-ol (13b). ^1H NMR ($CDCl_3$), δ: 0.85 (d, 6 H, $C\underline{H}_3CH$, J = 6.5 Hz); 1.15 (d, 3 H, CH_3CHO, J = 6.2 Hz); 1.53 (m, 1 H, $CH_3C\underline{H}$); 1.48—1.80 (m, 4 H, $CHC\underline{H}_2$); 3.00 (br.s, 1 H, OH); 3.56 (m, 1 H, $CH_3C\underline{H}O$); 3.60 (m, 2 H, $C\underline{H}_2OH$); 4.45 (t, 1 H, CH—Ar, J = 6.2 Hz, J = 7.6 Hz); 7.22 (m, 5 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 18.0 ($\underline{C}H_3CH$); 22.2 and 23.1 ($\underline{C}H_3CH$); 24.5 ($CH_3\underline{C}H$); 38.5 ($CH\underline{C}H_2CH_2$); 47.0 ($CH\underline{C}H_2CH$); 61.0 ($\underline{C}H_2OH$); 70.1 ($CH_3\underline{C}HO$); 76.5 (CH—Ar); 126.9 (CH, Ar); 128.5 (CH, Ar); 127.7 (CH, Ar); 142.7 (C, Ar).

Reactions of orthoformates with trialkylalanes (general procedure). A solution of Bu^i_3Al or Et_3Al (20 mmol) was added dropwise to a solution of orthoester (20 mmol) in a chlorine-containing solvent (80 mmol) at −20 °C. The reaction mixture was warmed to 20 °C and stirred at this temperature for 2 h. Then the reaction mixture was cooled to −20 °C and decomposed with a 10% aqueous solution of NaOH (20 mL). The organic layer was separated, dried with $MgSO_4$, and analyzed by GLC using heptane as the internal standard. The yields of the reaction products are given in Table 1.

Propionaldehyde diethylacetal (**14**), propionaldehyde dibutylacetal (**15**), isovaleraldehyde diethylacetal (**16**), and isovaleraldehyde dibutylacetal (**17**) were identified by comparing with samples synthesized according to a procedure described earlier.[25]

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