$ZrCl_4$-Catalyzed scission of ethylene acetals with organoaluminum compounds

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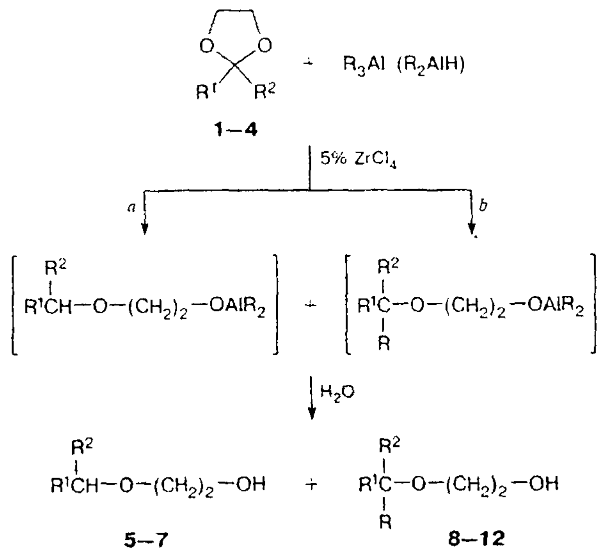
Ethylene acetals and ethylene ketals undergo reductive scission under the action of Bu^i_2AlH in the presence of catalytic amounts of $ZrCl_4$. With Et_3Al and Bu^i_3Al, reductive alkylation also occurs.

Key words: organoaluminum compounds, cyclic acetals, zirconium complexes, catalysis by metal complexes.

It is known[1–3] that the C—O bond in ethylene acetals and ethylene ketals is cleaved under the action of Bu^i_2AlH or Bu^i_3Al at 60—110 °C. Subsequent hydrolysis of the corresponding aluminates affords ethylene glycol monoethers (route *a* in Scheme 1).

Scheme 1



1: $R^1 = R^2 = H$; **2, 5**: $R^1 = H$, $R^2 = Pr^i$; **3, 6**: $R^1 = H$, $R^2 = Ph$; **4, 7**: $R^1 + R^2 = —(CH_2)_5—$; **8**: $R = Et$, $R^1 = H$, $R^2 = Pr^i$; **9**: $R = Bu^i$, $R^1 = R^2 = H$; **10**: $R = Bu^i$, $R^1 = H$, $R^2 = Pr^i$; **11**: $R = Bu^i$, $R^1 = H$, $R^2 = Ph$; **12**: $R = Bu^i$, $R^1 + R^2 = —(CH_2)_5—$

As part of continuing studies of catalytic conversions of organoaluminum compounds (OAC), we found that this process in the presence of $ZrCl_4$ (5 mol.%) in hydrocarbon solvents (hexane or benzene) at room temperature was completed in 20—40 min. Ether-type solvents totally suppress this process, which is typical of conversions of OAC catalyzed by zirconium complexes.[4] The other zirconium compounds tested by us, *viz.*, $ZrOCl_2 \cdot 6H_2O$, $Zr(acac)_4$, and Cp_2ZrCl_2, do not exhibit analogous catalytic activity. In the presence of $TiCl_4$, the reaction mixture is resinified.

With Bu^i_3Al, reduction of the initial dioxolanes **2—4** is accompanied by their reductive alkylation (route *b* in Scheme 1). In the absence of a catalyst, this reaction is typical of only *n*-alkylalanes, in particular, of Et_3Al.[5] The total yield of the corresponding reaction products was no less than 70%. The exception is formaldehyde acetal (**1**), which gave only a product of reductive alkyla-

Table 1. Products of the reactions of 1,3-dioxolanes with organoaluminum compounds

Initial acetal	OAC	Reaction products (ratio)	Total yield (%)
1	Bu^i_3Al	**9**	10
2	Bu^i_3Al	**5**, **10** (3:1)	76
2	Bu^i_2AlH	**5**	98
2	Et_3Al	**8**	98
3	Bu^i_3Al	**6**, **11** (4:1)	68
3*	Bu^i_3Al	**6**, **11** (1:1)	20
4	Bu^i_3Al	**7**, **12** (5:1)	60

* Acetal : OAC = 1 : 4.

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tion (**9**) in a yield of no more than 10%, while the reaction of compound **1** with OAC in the absence of a catalyst did not occur.[5] It appeared that the composition of the resulting mixture depended on the structures and the ratio of the initial reagents (Table 1). Thus the presence of bulky substituents (R^1 and R^2) at the C(2) atom of dioxolanes **2—4** hinders their reductive alkylation, while acetal **1** gives exclusively alkylation product **9**. Analogously, when Et_3Al, containing less bulky substituents, was used instead of $Bu^i{}_3Al$ in the reaction with 2-isopropyl-1,3-dioxolane (**2**), alkylation product **8** was obtained in virtually quantitative yield. Note that analogous regularities were also observed in the reactions of acetals with organomagnesium compounds.[6]

Experimental

All experiments were performed in an atmosphere of dry argon. Organoaluminum compounds were used as 30% solutions in hexane. The initial ethylene acetals **1—4** were synthesized according to a known procedure,[7] distilled under argon, and stored in an inert atmosphere over metallic sodium. The physicochemical constants of compounds **1—4** coincide with the published data.[8] The solvents were distilled in an inert atmosphere over $Bu^i{}_2AlH$ immediately before use. The GLC analysis was performed on a Chrom-5 chromatograph (flame ionization detector, 5% SE-30 on Chromaton N-AW as the stationary phase, 1200×5-mm column, temperature programming from 50 to 300 °C, decane as the internal standard). The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer in $CDCl_3$ with Me_4Si as the internal standard. Ethylene glycol monoethers **5—12** were isolated by vacuum distillation on a Fisher MMS-155 microcolumn.

Reactions of ethylene acetals with OAC (general procedure). Anhydrous $ZrCl_4$ (0.2 mmol) was added to a solution of an organoaluminum compound (4 mmol) in hexane at -20 °C. Then 1,3-dioxolane **1—4** (2 mmol) was added dropwise with intense stirring over 30 min. The reaction mixture was diluted with an equal volume of ether, cooled to −10 °C, decomposed with water (4 mL) with stirring, and treated with 5% HCl until the precipitate dissolved. The organic layer was separated, dried with $MgSO_4$, and analyzed by GLC. The yields and the ratios of products **5—12** are given in Table 1. The compounds synthesized were identified based on the data of elemental analysis and ^1H and ^{13}C NMR spectroscopy. 2-*iso*-Butoxyethanol[9] (**5**) (b.p. 39—40 °C (4 Torr), $n_D{}^{20}$ 1.4129), 2-benzyloxyethanol[5] (**6**) (b.p. 98 °C (3 Torr), $n_D{}^{20}$ 1.5269), 2-cyclohexyloxyethanol[10] (**7**) (b.p. 76 °C (4 Torr), $n_D{}^{20}$ 1.4606), and 2-(3-methylbutoxy)ethanol[5] (**9**) (b.p. 66 °C (10 Torr), $n_D{}^{20}$ 1.4370) were identified by comparing with the published data. The physicochemical constants of 2-(2-methylpentan-3-yloxy)ethanol (**8**), 2-(2,5-dimethylhexan-3-yloxy)ethanol (**10**), 2-(3-methyl-1-phenylbutoxy)ethanol (**11**), and 2-(1-isobutylcyclohexyloxy)ethanol (**12**) are given in Table 2.

Table 2. Spectral data and selected physicochemical characteristics of the synthesized ethylene glycol monoethers

Compound	B.p. /°C (*p*/Torr)	$n_D{}^{20}$	$\frac{\text{Found}}{\text{Calculated}}$ (%) C	H	Molecular formula	^1H NMR, δ, *J*/Hz	^{13}C NMR, δ
8	72 (10)	1.4279	$\underline{65.70}$ 65.71	$\underline{12.20}$ 12.41	$S_8H_{18}O_2$	0.73 (d, 3 H, CH_3, *J* = 6.8); 0.77 (d, 3 H, CH_3, *J* = 6.9); 0.80 (t, 3 H, CH_3, *J* = 7.1); 1.25—1.42 (m, 2 H, CH_2); 1.70 (octet, 1 H, CH, *J* = 6.6); 2.83 (q, 1 H, CHO, *J* = 6.5); 3.00 (br.s, 1 H, OH); 3.42 (t, 2 H, CH_2O, *J* = 4.6); 3.56 (t, 2 H, CH_2O, *J* = 4.6)	9.68 (CH_3); 18.0 (CH_3); 18.09 (CH_3); 22.85 (CH_2); 30.22 (CH); 61.82 (CH_2OH); 70.86 (CH_2O); 86.24 (CHO)
10	65—70 (4)	1.4315	$\underline{68.99}$ 68.92	$\underline{12.77}$ 12.72	$S_{10}H_{22}O_2$	0.80 (d, 6 H, CH_3, *J* = 6.7); 0.86 (d, 6 H, CH_3, *J* = 6.7); 1.15 (m, 1 H, CH_2); 1.38 (m, 1 H, CH_2); 1.70—1.80 (m, 1 H, CH); 1.80—1.90 (m, 1 H, CH); 3.10—3.20 (m, 1 H, CHO); 3.48 (br.s, 1 H, OH); 3.61 (t, 2 H, CH_2O, *J* = 4.7); 3.69 (t, 2 H, CH_2O, *J* = 4.7)	17.17 (CH_3); 17.71 (CH_3); 21.79 (CH_3); 23.35 (CH_3); 24.24 ($\underline{C}H-CH_2$); 30.19 ($\underline{C}H-CH$); 39.26 (CH_2); 61.52 (CH_2OH); 70.60 (CH_2O); 82.50 (CH—O)
11	105 (3)	1.5118	$\underline{74.90}$ 74.96	$\underline{9.62}$ 9.68	$C_{13}H_{20}O_2$	0.74 (d, 3 H, CH_3, *J* = 2.66); 0.76 (d, 3 H, CH_3, *J* = 2.66); 1.25 (m, 1 H, CH_2); 1.53 (m, 1 H, CH_2); 1.62 (m, 1 H, CH); 3.32 (br.s, 1 H, OH); 3.33 (t, 2 H, CH_2O, *J* = 4.55); 3.60 (t, 2 H, CH_2O, *J* = 4.55); 4.28 (dd, 1 H, CH—Ar, *J* = 5.88, *J* = 6.12); 7.0—7.2 (m, 5 H, Ar)	22.48 (CH_3); 24.13 (CH_3); 47.11 (CH_2); 61.15 (CH_2OH); 71.17 (CH_2O); 80.50 ($\underline{C}H$—Ar); 126.03 (CH, arom.); 127.24 (2 CH, arom.); 127.82 (2 CH, arom.); 142.43 ($\underline{C}$, arom.)
12	110 (4)	1.4649	$\underline{71.97}$ 71.95	$\underline{12.00}$ 12.08	$S_{12}H_{24}O_2$	0.75 (d, 6 H, 2 CH_3, *J* = 6.6); 1.00—1.25 (m, 4 H, 2 CH_2); 1.30—1.55 (m, 7 H, 3 CH_2, CH); 1.60—1.80 (m, 2 H, $C\underline{H}_2-CH$); 3.10—3.25 (m, 2 H, CH_2O); 3.40—3.55 (m, 2 H, CH_2O)	21.35 (CH_2 of the ring); 25.54 (2 CH_2 of the ring); 34.49 (2 CH_2 of the ring); 22.59 (2 CH_3); 24.59 (CH); 44.59 (CH_2); 60.67 (CH_2OH); 61.76 (CH_2O); 75.34 (C—O)

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