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Reduction of Acetals with $TiCl_4$–$LiAlH_4$

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The reduction of dialkyl acetals derived from aromatic aldehydes and ketones with $TiCl_4$-$LiAlH_4$ in THF or diethyl ether at room temperature afforded the coupling products, pinacol ethers or olefins, in high yields. On the other hand, when acetals derived from aliphatic aldehydes and ketones were treated with $TiCl_4$–$LiAlH_4$ in diethyl ether, the reductive dealkoxylation took place and the corresponding ethers were isolated in good yields. As to the reaction mechanism we propose that Ti(II) is the reactive species in reductive coupling reaction of acetals derived from aromatic aldehydes and ketones, and that Ti(0)–H_2AlCl complex may be the reactive species in reductive dealkoxylation of acetals derived from aliphatic aldehydes and ketones.

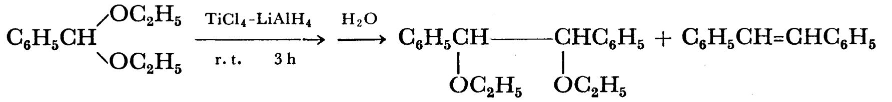
The reactivity of $LiAlH_4$ can be greatly modified by addition of metal salts. $LiAlH_4$–$AlCl_3$ has been found to have an unusual applicability in epoxide reductrion[1)] and in reduction of acetals to the corresponding ethers.[2–7)] Further, $LiAl(OCH_3)_3H$–CuI can effect reductive removal of halo and mesyloxy groups,[8)] and $LiAlH_4$–$TiCl_3$ has been found to be a coupling reagent.[9)] Recently Ashby *et al.* have reported that 1,4-reduction of α,β-unsaturated ketones by using $LiAlH_4$–CuI proceeds with almost complete functional selectivity.

During the course of our investigation on the exploration of various synthetic reaction by the use of $TiCl_4$, we reported in the previous paper[11)] that various olefins were prepared in good ylieds by the treatment of allyl methyl ethers with $TiCl_4$–$LiAlH_4$ in THF or diethyl ether.

Recently, it has been shown[12)] that a low valent titanium compound, prepared from $TiCl_4$ and Zn, reduces aldehydes or ketones to afford the corresponding pinacols or olefins in high yields and that the selectivity of the reaction depends on the reaction conditions.

In the present work the reduction of various acetals using $TiCl_4$ and $LiAlH_4$ was studied, and it was found that reductive coupling or dealkoxylation took place depending on the types of starting acetals and on the solvents employed.

At first the reaction of benzaldehyde diethyl acetal (**1**) with the low valent titanium compound was examined under various conditions. For example, benzaldehyde diethyl acetal (**1**) was added to a mixture of equimolar amounts of $TiCl_4$ and $LiAlH_4$ in THF at room temperature, and after stirring at room temperature for 3 h, the mixture was quenched with aqueous potassium carbonate. Purification by column chromatography (silica gel) gave 1,2-diethoxy-1,2-diphenylethane (**2**) and stilbene (**3**) [trans: 86%, cis: 14%] in 85 and 10% yields, respectively.

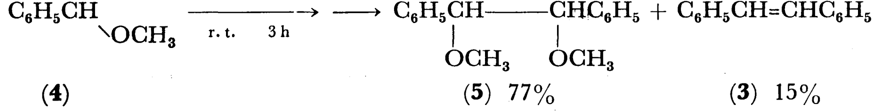


$$\mathrm{C_6H_5CH}\begin{smallmatrix}/\mathrm{OC_2H_5}\\ \backslash\mathrm{OC_2H_5}\end{smallmatrix} \xrightarrow[\text{r.t.}\quad 3\,\text{h}]{\mathrm{TiCl_4\text{-}LiAlH_4}} \xrightarrow{\mathrm{H_2O}} \underset{\mathrm{OC_2H_5}}{\mathrm{C_6H_5CH}}\text{——}\underset{\mathrm{OC_2H_5}}{\mathrm{CHC_6H_5}} + \mathrm{C_6H_5CH{=}CHC_6H_5}$$

(**1**)　(**2**) 85　(**3**) 10%

As shown in Table 1, when the ratio $LiAlH_4$ to $TiCl_4$ was decreased, the yield of products decreased. On the other hand, no difference in yields was observed when molar ratio of $LiAlH_4$ was increased.

The reaction of various acetals derived from aromatic aldehydes or ketones with equimolar amounts of $TiCl_4$–$LiAlH_4$ was tried in THF at room temperature, and the corresponding pinacol ethers and olefins were obtained in high yields as shown in the following equations; (1)-(4).

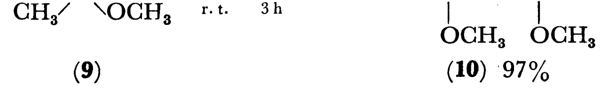


$$\mathrm{C_6H_5CH}\begin{smallmatrix}/\mathrm{OCH_3}\\ \backslash\mathrm{OCH_3}\end{smallmatrix} \xrightarrow[\text{r.t.}\quad 3\,\text{h}]{\mathrm{TiCl_4\text{-}LiAlH_4}} \xrightarrow{\mathrm{H_2O}} \underset{\mathrm{OCH_3}}{\mathrm{C_6H_5CH}}\text{——}\underset{\mathrm{OCH_3}}{\mathrm{CHC_6H_5}} + \mathrm{C_6H_5CH{=}CHC_6H_5} \tag{1}$$

(**4**)　(**5**) 77%　(**3**) 15%

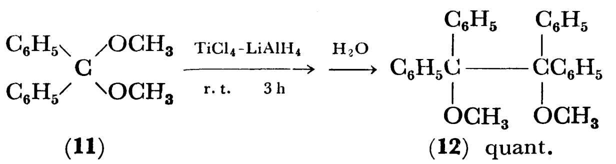
$$p\text{-}\mathrm{CH_3OC_6H_4CH}\begin{smallmatrix}/\mathrm{OC_2H_5}\\ \backslash\mathrm{OC_2H_5}\end{smallmatrix} \xrightarrow[\text{r.t.}\quad 40\,\text{min}]{\mathrm{TiCl_4\text{-}LiAlH_4}} \xrightarrow{\mathrm{H_2O}} p\text{-}\underset{\mathrm{OC_2H_5}}{\mathrm{CH_3OC_6H_4CH}}\text{——}\underset{\mathrm{OC_2H_5}}{\mathrm{CHC_6H_4OCH_3}}\text{-}p \tag{2}$$

(**6**)　(**7**) 98%



$$\begin{smallmatrix}\mathrm{C_6H_5}\backslash & & /\mathrm{OCH_3}\\ & \mathrm{C} & \\ \mathrm{CH_3}/ & & \backslash\mathrm{OCH_3}\end{smallmatrix} \xrightarrow[\text{r.t.}\quad 3\,\text{h}]{\mathrm{TiCl_4\text{-}LiAlH_4}} \xrightarrow{\mathrm{H_2O}} \overset{\mathrm{CH_3}}{\underset{\mathrm{OCH_3}}{\mathrm{C_6H_5C}}}\text{——}\overset{\mathrm{CH_3}}{\underset{\mathrm{OCH_3}}{\mathrm{CC_6H_5}}} \tag{3}$$

(**9**)　(**10**) 97%



$$(C_6H_5)_2C(OCH_3)_2 \xrightarrow[\text{r.t. 3 h}]{TiCl_4\text{-}LiAlH_4} \xrightarrow{H_2O} C_6H_5C(C_6H_5)(OCH_3)\text{—}C(C_6H_5)(OCH_3)C_6H_5 \qquad (4)$$

(11) (12) quant.

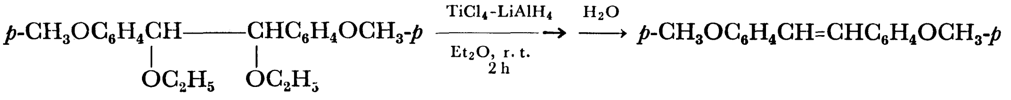
TABLE 1. REDUCTIVE COUPLING OF BENZALDEHYDE DIETHYL ACETAL WITH DIFFERENT RATIO OF THE REAGENTS IN THF

Acetal	Molar ratio		Yield (%)	
	$LiAlH_4$	$TiCl_4$	Pinacol ether	Stilbene
1	0.5	1	41	5
1	1	1	85	10
1	2	1	83	9

As shown in the above equations, pinacol ethers were obtained in high yields by the reaction of acetals derived from aromatic aldehydes and ketones with $TiCl_4$–$LiAlH_4$. The yields of the two kinds of products, pinacol ether and olefins, markedly depended on the solvents used. For example, when *p*-methoxybenzaldehyde diethyl acetal (**6**) was treated with $TiCl_4$–$LiAlH_4$ in THF at room temperature, 4,4′-dimethoxystilbene (**8**) could not be detected and pinacol ether was obtained exclusively. In sharp contrast with this, when diethyl ether was used as solvent, olefins, (**8**) were isolated in 36% yield together with pinacol ether (**7**). However the reductive coupling did not proceed in benzene.

The results are show in Table 2.

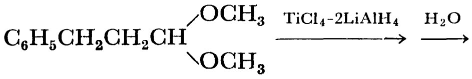
Further, it was found that pinacol ether (**7**) reacted with two molar amounts of $TiCl_4$–$LiAlH_4$ in diethyl ether at room temperature to afford the corresponding olefins (**8**) in 57% yield.



$$p\text{-}CH_3OC_6H_4CH(OC_2H_5)\text{—}CH(OC_2H_5)C_6H_4OCH_3\text{-}p \xrightarrow[\text{Et}_2\text{O, r.t. 2 h}]{TiCl_4\text{-}LiAlH_4} \xrightarrow{H_2O} p\text{-}CH_3OC_6H_4CH{=}CHC_6H_4OCH_3\text{-}p$$

(**7**) (**8**) 57%

On the other hand, the reduction of acetals derived from aliphatic aldehydes and ketones such as 3-phenylpropanal dimethyl acetal (**13**) with $TiCl_4$–$LiAlH_4$ did not take place in THF. But when, the acetal (**13**) was treated with $TiCl_4$ and two molar amounts of $LiAlH_4$ in diethyl ether, the acetal was reduced to the corresponding ether, 1-methoxy-3-phenylpropane (**14**), in 87% yield.



$$C_6H_5CH_2CH_2CH(OCH_3)_2 \xrightarrow{TiCl_4\text{-}2LiAlH_4} \xrightarrow{H_2O} C_6H_5CH_2CH_2CH_2OCH_3$$

(**13**)

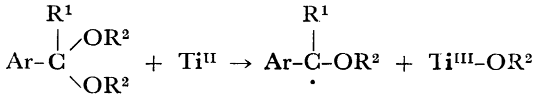
(**14**) 87%

The generality of the reaction was examined by the use of various acetals such as 3-phenylpropanal diethyl acetal, benzylacetone dimethyl acetal, benzylacetone diethyl acetal, cyclohexanone dimethyl acetal, cyclohexanone ethylene acetal, and in all cases the corresponding ethers were obtained in good yield (see Table 3).

Although a detailed understanding of the reaction mechanism must wait knowledge of the nature of the reagent, Eq. 5, shows a possible explanation for the observation of a black precipitate and gas evolution in the first step of this reaction.

$$TiCl_4 + LiAlH_4 \longrightarrow TiCl_2 + LiCl + H_2AlCl + H_2 \quad (5)$$

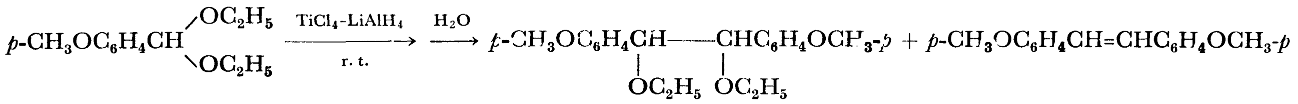
McMurry[9] has suggested that Ti(II) is the reactive species in reductive coupling reactions. Recently, Corey[15] has proposed that Ti(II) is the reactive species in the intermolecular and intramolecular pinacolic coupling reaction of aldehydes and ketones. Based on these assumptions a possible mechanism of the reductive coupling reaction is proposed (Scheme 1).



$$Ar\text{-}C(R^1)(OR^2)_2 + Ti^{II} \rightarrow Ar\text{-}\dot{C}(R^1)\text{-}OR^2 + Ti^{III}\text{-}OR^2 \qquad (6)$$

Scheme 1.

TABLE 2.



$$p\text{-}CH_3OC_6H_4CH(OC_2H_5)_2 \xrightarrow[\text{r.t.}]{TiCl_4\text{-}LiAlH_4} \xrightarrow{H_2O} p\text{-}CH_3OC_6H_4CH(OC_2H_5)\text{—}CH(OC_2H_5)C_6H_4OCH_3\text{-}p + p\text{-}CH_3OC_6H_4CH{=}CHC_6H_4OCH_3\text{-}p$$

(**6**) (**7**) (**8**)

Solvent	Molar ratio			Reaction time (min)	Yield (%)		Recovery (%)
	(**7**)	$LiAlH_4$	$TiCl_4$		(**7**)	(**8**)	(**6**)
Benzene	1	1	1	120	0	0	91
THF	1	1	1	40	98	0	—
Ether	1	1	1	60	58	36	—
	1	2	1	60	53	42	—
	1	3	1	60	38	54	—

TABLE 3. REDUCTION OF ACETALS DERIVED FROM ALIPHATIC ALDEHYDES AND KETONES WITH $TiCl_4$-$2LiAlH_4$

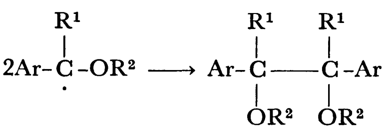
Acetal	Ether	Yield (%)	Bp (°C/mmHg)
$C_6H_5CH_2CH_2CH(OCH_3)_2$ (**13**)	$C_6H_5CH_2CH_2CH_2OCH_3$ (**14**)	87	98—100/20[a]
$C_6H_5CH_2CH_2CH(OC_2H_5)_2$ (**15**)	$C_6H_5CH_2CH_2CH_2OC_2H_5$ (**16**)	76	104—107/20[b]
$C_6H_5CH_2CH_2CCH_3(OCH_3)_2$ (**17**)	$C_6H_5CH_2CH_2CHCH_3OCH_3$ (**18**)	69	100—102/12
$C_6H_5CH_2CH_2CCH_3(OC_2H_5)_2$ (**19**)	$C_6H_5CH_2CH_2CHCH_3OC_2H_5$ (**20**)	67	106—110/12
cyclo-$C_6H_{10}(OCH_3)_2$ (**21**)	cyclo-$C_6H_{11}OCH_3$ (**22**)	72	127—129/760[c]
cyclo-$C_6H_{10}\begin{matrix}\diagup OCH_2\\ \vert\\ \diagdown OCH_2\end{matrix}$ (**23**)	cyclo-$C_6H_{11}OCH_2CH_2OH$ (**24**)	75	100—101/14[d]

a) Lit,[13] 92—94 °C/12 mmHg. b) Lit,[14] 90—95°C/10 mmHg. c) Lit,[3] 122 °C/754 mmHg. d) Lit,[3] 100 °C/14 mmHg.

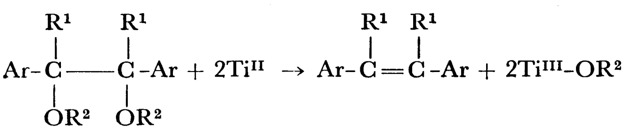
TABLE 4. PHYSICAL PROPERTIES AND ANALYTICAL DATA OF THE PRODUCTS

Product	IR (cm^{-1})	NMR (δ)	Found (%) (Calcd) C	H
2	b) 700 1100	c) 1.14(t, J=7 Hz, 3H), 3.40(q, J=7 Hz, 2H) 4.38(s, 1H), 7.07(s, 5H)	79.81 (79.96)	8.15 (8.20)
5		c) 3.08(s, 3H), 4.10(s, 1H), 7.22(s, 5H)	79.20 (79.31)	7.52 (7.49)
7	b) 1090 1245	d) 1.14(t, J=7 Hz, 3H), 3.35(q, J=7 Hz, 2H) 3.66(s, 3H), 4.23(s, 3H), 6.72(q, J=9 Hz, 4H)	72.58 (72.70)	8.05 (7.93)
10	b) 700 1110 1118	c) 1.67(s, 3H), 3.08(s, 3H), 6.60—7.12(m, 5H)	79.79 (79.96)	8.23 (8.20)
12		c) 3.11(s, 3H) 6.90—7.70(m, 10H)	85.02 (85.24)	6.81 (6.64)
14	a) 1090	c) 1.80(m, 2H), 2.60(m, 2H), 3.26(s, 3H), 3.30(t, J=6 Hz, 2H), 7.17(s, 5H)		
16		c) 1.20(t, J=7 Hz, 3H), 1.92(m, 2H), 2.67(m, 2H), 3.49(q, J=7 Hz, 4H), 7.29(s, 5H)		
18	a) 1090	c) 1.10(d, J=6 Hz, 3H), 1.72(m, 2H), 2.65(m, 2H), 3.21(m, 3H), 3.27(s, 3H), 7.19(s, 5H)	80.31 (80.44)	9.92 (9.83)
20	a) 1095	c) 1.10(d, J=6 Hz, 3H), 1.70(m, 2H), 2.62(m, 2H), 3.39(m, 3H), 7.17(s, 5H)	80.62 (80.85)	10.23 (10.18)
22	a) 1080	c) 1.42(m, 10H), 3.28(s, 3H), 3.34(m, 1H)		
24	a) 3450 1110	c) 1.53(m, 10H), 2.75(m, 1H),[e] 3.55(m, 5H)		

a) Neat, b) KBr disk, c) in CCl_4, d) in $CDCl_3$, e) exchanged with D_2O.



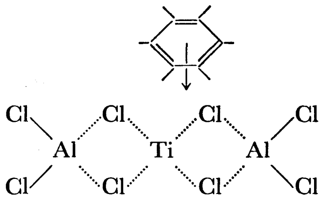
$$2Ar\text{-}\overset{R^1}{\overset{|}{C}}\text{-}OR^2 \longrightarrow Ar\text{-}\underset{OR^2}{\underset{|}{\overset{R^1}{\overset{|}{C}}}}\text{——}\underset{OR^2}{\underset{|}{\overset{R^1}{\overset{|}{C}}}}\text{-}Ar \qquad (7)$$



$$Ar\text{-}\underset{OR^2}{\underset{|}{\overset{R^1}{\overset{|}{C}}}}\text{——}\underset{OR^2}{\underset{|}{\overset{R^1}{\overset{|}{C}}}}\text{-}Ar + 2Ti^{II} \rightarrow Ar\text{-}\overset{R^1}{\overset{|}{C}}=\overset{R^1}{\overset{|}{C}}\text{-}Ar + 2Ti^{III}\text{-}OR^2 \qquad (8)$$

Reductin of acetals derived from aromatic aldehydes and ketones by the Ti(II) reagent may give a radical intermediate (Eq. 6), which dimerizes into pinacol ethers. Further reaction of the pinacol ether with Ti(II) reagent may give olefins.

In order to certify the hypothesis embodied in Scheme 1, we examined the reductive coupling using well-defined Ti(II) species. We have found Ti(II) complexes of known structure which are capable of effecting the reduvtive coupling of acetal derived from aromatic aldehyde. The complex [**A**],[16] prepared by the reaction of Al–$AlCl_3$, $TiCl_4$, and hexamethylbenzene is especially effective: 1,2-diethoxy-1,2-bis(*p*-methoxyphenyl)ethane (**7**) was obtained in 52% yield by the reaction of [**A**] with *p*-methoxybenzaldehyde diethyl acetal (6).[17]



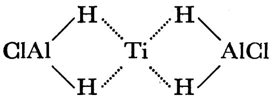
[**A**]

The observed solvent effects may reflect the different coordination ability of Ti(II) species with THF from that with diethyl ether.

On the other hand, the mechanism of the reduction of acetals derived from aliphatic aldehydes and ketones by $TiCl_4$–$2LiAlH_4$ could not be made clear. However, when $TiCl_4$ is treated with two molar amounts of $LiAlH_4$, titanium metal is supposed to be formed (Eq. 9). In fact, the formation of titanium metal was observed in this reaction.

$$TiCl_4 + 2LiAlH_4 \rightarrow Ti(0) + 2LiCl + H_2AlCl + H_2 \quad (9)$$

It is well known that the low valent titanium compound form complexes with organic or inorganic aluminum compounds[16,18] and with alkyl halides.[19]



[**B**]

Accordingly, we assume that the reactive intermediate is complex [**B**] in the reduction of acetals derived from aliphatic aldehydes and ketones by using $TiCl_4$–$2LiAlH_4$.

We are continuing the mechanistic study on the intermediates of the titanium complex [**B**] in this reductive dealkoxylation.

In conclusion, it has been made clear that the combination of $TiCl_4$ and $LiAlH_4$ is effectively applied to the reduction of acetal like $AlCl_3$–$LiAlH_4$. It is characteristic that when the acetals derived from aromatic aldehydes and ketones are treated with $TiCl_4$–$LiAlH_4$ in THF, pinacol ethers are obtained in high yields.

Experimental

Materials. Commercially available $TiCl_4$ was distilled under argon atmosphere before use. Various acetals were prepared according to the procedures described in the literature[20] and purified by distillation. All boiling points and melting points were uncorrected. The IR spectra were recorded with a Hitachi 215 grating infrared spectrophotometer. The proton NMR spectra were recorded using Varian EM360 spectrometer and Hitachi R-20B high resolution spectrometer with TMS as an internal standard. The physical properties and analytical data of the products are shown in Table 4.

*Reductive Coupling of Benzaldehyde Diethyl Acetal (**1**).* To a stirred suspension of $TiCl_4$ (0.95 g, 5 mmol) in 15 ml of THF was added a suspension of $LiAlH_4$ (0.19 g, 5 mmol) in 10 ml of THF at room temperature under argon atmosphere. During the addition of $LiAlH_4$ hydrogen evolved vigorously and the reaction mixture turned to black, which indicated the formation of a low valent titanium compound. After stirring the mixture for 30 min at room temperature, benzaldehyde diethyl acetal (0.90 g, 5 mmol) in 10 ml of THF was added dropwise to the reaction mixture during 10 min at room temperature, and the reaction mixture was stirred for 3 h. The reaction was quenched by the addition of 10 ml of 10% aqueous potassium carbonate, and a dark brown precipitate appeared was filtered off. The filtrate was extracted with ether. The ether extract was washed with saturated sodium chloride solution and dried over sodium sulfate. After removal of the solvent under reduced pressure, 1,2-diethoxy-1,2-diphenylethane (**2**) and stilbene (**3**) were isolated by column chromatography (silica gel) using hexane-dichloromethane (1:1) as an eluent in 85% (0.75 g) and 10% (0.045 g) yields, respectively.

*Reduction of 1,2-Diethoxy-1,2-bis(*p*-methoxyphenyl)ethane (**7**) with $TiCl_4$–$LiAlH_4$.* To a sirred suspension of $TiCl_4$ (0.38 g, 2 mmol) in 5 ml of diethyl ether was added a suspension of $LiAlH_4$ (0.08 g, 2 mmol) in 8 ml of diethyl ether at room temperature under argon atmosphere. After stirring the mixture for 20 min at room temperature, pinacol ether (**7**) (0.33 g, 1 mmol) in 5 ml of diethyl ether was added at room temperature during the period of 5 min. The mixture was stirred at room temperature for 2 h. The reaction mixture was worked up as mentioned in the previous case. After removal of the solvent and purification by preparative TLC (silica gel) using dichloromethane to give 0.13 g (57%) of 4,4′-dimethoxystilbene (**8**).

*Reduction of 3-Phenylpropanal Dimethyl Acetal (**13**).* To a stirred suspension of $TiCl_4$ (0.95 g, 5 mmol) in 15 ml of diethyl ether was added a suspension of $LiAlH_4$ (0.38 g, 10 mmol) in 10 ml of diethyl ether at room temperature under argon atmosphere. After stirring the mixture for 30 min at room temperature, 3-phenylpropanal dimethyl acetal (0.90 g, 5 mmol) in 15 ml of diethyl ether was added at room temperature. The mixture was stirred at room temperature for 2 h, then refluxed for an additional 1 h, and worked up as mentioned in the previous procedure. After removal of the solvent and purification by column chromatography (silica gel), 1-methoxy-3-phenylpropane (**14**) was isolated in 87% (0.65 g) yield. The NMR and IR spectra of the product (**14**) are shown in Table 4.

*Reduction of Cyclohexanone Ethylene Acetal (**23**).* To a stirred suspension of $TiCl_4$ (9.5 g, 50 mmol) in 150 ml of diethyl ether was added a suspension of $LiAlH_4$ (3.8 g, 100 mmol) in 100 ml of diethyl ether at room temperature under argon atmosphere. After stirring the mixture for 1 h at room temperature, cyclohexanone ethylene acetal (7.1 g, 50 mmol) in 100 ml of diethyl ether was added during the period of 40 min. The mixture was stirred at room temperature for 2 h. After the usual work-up, 2-(cyclohexyloxy)ethanol (**24**) (5.4 g, 75%) was collected by distillation.

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