ISSN 0012-5008, Doklady Chemistry, 2009, Vol. 428, Part 2, pp. 250–251. © Pleiades Publishing, Ltd., 2009.
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CHEMISTRY

Catalytic Reduction of 2-Dichloromethyl-1,3-dioxolanes with $(iso\text{-}Bu)_2AlH$

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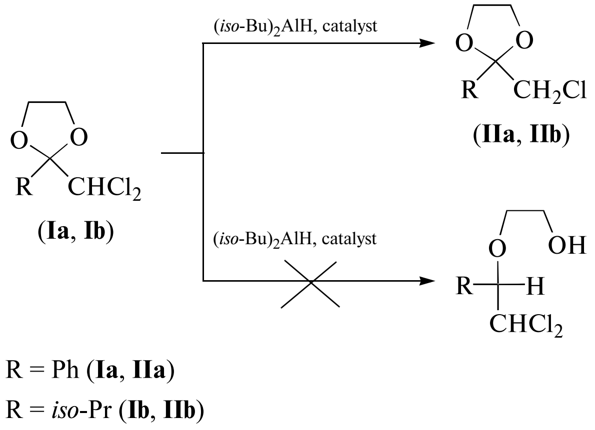
Presented by Academician N.S. Zefirov April 9, 2009

Received April 22, 2009

DOI: 10.1134/S001250080910005X

It was previously shown that cyclic acetals and ketals readily undergo reduction and ring opening when reacted with dialkylaluminum hydrides to form corresponding glycol monoethers [1–3]. It is also known that $(iso\text{-}Bu)_2AlH$ in the presence of Ti and Zr complexes reduces a *gem*-dichloromethylene group to chloromethylene one [4]. It was interesting to reveal the direction and results of catalytic reduction of 2-dichloromethyl-1,3-dioxolanes (**Ia**, **Ib**) with $(iso\text{-}Bu)_2AlH$ (Scheme 1). Compounds **Ia**, and **Ib** form in practically quantitative yields when dichlorocarbene combines with corresponding cyclic acetals [5, 6].

We have found that $(iso\text{-}Bu)_2AlH$ in 1,4-dioxane medium in the presence of catalytic amounts of Ti and Zr complexes converts compounds **Ia** and **Ib** into corresponding 2-chloromethyl derivatives (**Ia**, **Ib**), whereas in the absence of the noted catalysts the initial dioxolanes (**Ia**, **Ib**) were recovered intact from reaction mixture.



Scheme 1.

Reaction mixture contains no products resulting from the opening of dioxolane ring (compounds comprising a hydroxy group).

The catalysts used were alkoxides and complexes of Ti and Zr: $(n\text{-}BuO)_4Ti$, $ZrCl_4$, Cp_2TiCl_2, Cp_2ZrCl_2 (table).

The yield of compound **IIa** varied in a wide range (from 15 to 99%) depending on experimental conditions. Quantitative yield was obtained at 75°C when two- to fourfold excess of $(iso\text{-}Bu)_2AlH$ was used in the presence of $(n\text{-}BuO)_4Ti$ or Cp_2ZrCl_2. Compound **IIa** partially decomposes to give phenyl chloromethyl ketone (not more than 5%) when the reaction was carried at 90°C for 8 h.

The reduction of ketal **Ib** proceeds much more difficult and the yield of monochloro derivative (**IIb**) does not exceed 22%. In this case, only Cp_2TiCl_2 shows catalytic activity. No reaction is observed in the presence of other catalysts (the table).

It should be noted that we failed to convert **Ib** into **IIb** using such reagents as $LiAlH_4$ [7] and zinc dust [8].

The relative reactivity of compounds **Ia** and **Ib** was assessed by competitive reactions with $(iso\text{-}Bu)_2AlH$ in the presence of Cp_2TiCl_2. Benzaldehyde acetal **Ia** proved to be four times more reactive than isobutyraldehyde derivative **Ib**, which agree well with above results (table).

Let us note that the products of complete reduction of compounds (**Ia**, **Ib**) were not found, whereas the reaction of $(iso\text{-}Bu)_2AlH$ with *gem*-dichlorocyclopropanes leads to a partial formation of carbocycles containing no chlorine atoms [4].

EXPERIMENTAL

Initial 2-dichloromethyl-1,3-dioxolanes (**Ia**, **Ib**) were obtained by the known procedure [6], distilled in an argon flow, and stored in an inert atmosphere. The reactions were carried out using a commercial solution of $(iso\text{-}Bu)_2AlH$. All experiments with the use of orga-

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Effect of catalyst nature, temperature, and reaction time on the yields of 2-chloromethyl-1,3-dioxolanes (**IIa**, **IIb**)

Initial compound	Catalyst	T, °C	Time, h	Yield of reaction products, %
Ia	$ZrCl_4$	75	6	72
Ib	$ZrCl_4$	90	8	–
Ia	Cp_2ZrCl_2	75	6	≥99
Ib	Cp_2ZrCl_2	90	8	–
Ia	$Ti(n\text{-}BuO)_4$	75	2	15
Ia	$Ti(n\text{-}BuO)_4$	75	4	48
Ia	$Ti(n\text{-}BuO)_4$	75	6	≥99
Ia	$Ti(n\text{-}BuO)_4$	75	2	≥99*
Ia	$Ti(n\text{-}BuO)_4$	90	8	65*
Ib	$Ti(n\text{-}BuO)_4$	75	6	–
Ib	$Ti(n\text{-}BuO)_4$	90	8	–
Ib	Cp_2TiCl_2	90	8	4
Ib	Cp_2TiCl_2	90	12	11
Ib	Cp_2TiCl_2	90	16	20
Ib	Cp_2TiCl_2	90	20	22
Ib	Cp_2TiCl_2	90	8	4*
Ia	Cp_2TiCl_2	75	6	20*

Note: Molar ratio (**Ia**, **Ib**) : $(iso\text{-}Bu)_2AlH$: catalyst = 5 : 10 : 0.08, the chemicals were dissolved in 10 mL of 1,4-dioxane.
* Molar ratio (**Ia**, **Ib**) : $(iso\text{-}Bu)_2AlH$: catalyst = 5 : 20 : 0.08.

noaluminum compounds were accomplished in a dry argon atmosphere. The qualitative and quantitative analysis of initial mixtures and reaction products was performed on a Chrom-5 chromatograph equipped with a flame-ionization detector (column 1200 × 5 mm with 5% of SE-30, helium carrier gas). ^1H and ^{13}C NMR spectra of solution in $CDCl_3$ were recorded on a Bruker AM-300 spectrometer operating at 300.13 and 75.47 MHz, respectively. Chemical shifts are given in the δ scale relative to $SiMe_4$ as an internal reference.

2-Chloromethyl-2-phenyl-1,3-dioxolane (IIa). Two milliliters (10 mmol) of $(iso\text{-}Bu)_2AlH$ was added dropwise to a solution of 1.16 g (5 mmol) of the substrate (**Ia**) and 0.027 g (0.08 mmol) of $(n\text{-}BuO)_4Ti$ in 10 mL of 1,4-dioxane at 0°C with vigorous stirring in an argon flow, heated to 75°C, and stirred for 6 h at 75°C. The mixture was diluted with an equal volume of anhydrous benzene, cooled to 0°C, 1.3 g (30 mmol) of NaF was added, and the mixture was stirred vigorously for 0.5 h to form a complex of $(iso\text{-}Bu)_2AlH$ with NaF. The reaction mixture was quenched by dropwise addition of 0.5 mL (30 mmol) of water, stirred until gas evolution ceased, the precipitate was filtered off and washed on the filter with 1,4-dioxane, the combined filtrates were concentrated, and the residue was distilled in vacuum.

^1H NMR ($CDCl_3$, δ, ppm): 3.35–3.75 (m, 4H, $2CH_2$), 3.61 (s, 2H, CH_2Cl), 7.12–7.57 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$, δ, ppm): 49.4 (CH_2Cl), 65.6 ($2CH_2$), 107.9 (C arom.), 126.4 (2CH arom.), 128 (CH arom.), 128.5 (2CH arom.).

2-Chloromethyl-2-isopropyl-1,3-dioxolane (IIb). The cleavage of **Ib** was carried out as described above. 2-Chloromethyl-2-isopropyl-1,3-dioxolane (**IIb**) was isolated by column chromatography with hexane–ethyl acetate (7 : 3) as eluent. ^1H NMR ($CDCl_3$, δ, ppm, J, Hz): 1.16 (d, 6H, $2CH_3$, $(CH_3)_2CH$, $J = 6.9$), 2.25 (m, 1H, CH, $(CH_3)_2CH$, $J = 6.9$), 3.57 (s, 2H, CH_2Cl), 4.05–4.15 (m, 4H, $2CH_2$). ^{13}C NMR ($CDCl_3$, δ, ppm): 16.4 ($2CH_3$), 32.7 (CH), 45.6 (CH_2Cl), 65.9 ($2CH_2$), 110.5 (C).

Thus, we have established that organoaluminum compounds reduce the halogen in 2-dichloromethyl-1,3-dioxolanes without affecting the cycloacetal fragment.

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