A Convenient Synthesis of Aldehydes by Rearrangement of Cyclic Epoxides with Lithium Bromide on Alumina

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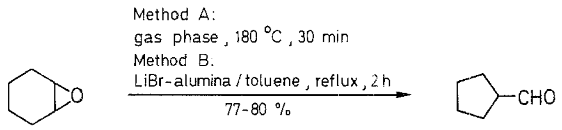
Epoxides can be converted effectively to aldehydes by rearrangement with lithium bromide supported on alumina. In the case of the alicyclic epoxides, ring contracted cycloalkanecarbaldehydes can be formed. The conversion is achieved by gas-phase reaction or in toluene as solvent.

The conversion of epoxides to aldehydes has been very important in synthetic chemistry. Synthesis of aldehydes by rearrangement of epoxides has been extensively investigated, e.g., (1) with lithium bromide/hexamethylphosphoric triamide (HMPA) or lithium bromide/tributylphosphine oxide in benzene;[1] (2) with a molten salt of lithium bromide rubidium bromide at 280°C in a gas chromatography column,[2] and (3) with magnesium bromide etherate in ether.[3] However, these methods are inappropriate for a large scale production of aldehydes because of the following reasons: (1) HMPA is highly carcinogenic;[4] (2) tributylphosphine oxide is expensive; (3) rubidium bromide is expensive and the apparatus required is inconvenient; and (4) the yields are relatively low.



1a 2a

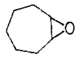
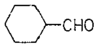
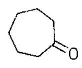
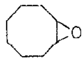
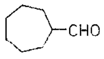
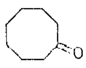
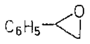
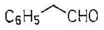
Epoxide	Products	
 1b	 2b	 3
 1c	 2c	 4
 1d	 2d	

Table. Rearrangement of Epoxides **1**

Reagent-Support	Epoxide	Conversion[a] (%)	Products (ratio)[a]	Yield (%)
LiBr-alumina	**1a**	95[c]	**2a**	77[e], 80[f]
	1b[b]	95[c]	**2b** + **3** (7 : 3)	60[e]
	1c[b]	95[c]	**2c** + **4** (1 : 1)	60[e]
	1d[b]	95[c]	**2d**	64[e]
LiBr-silica gel	**1a**	95[c]	**2a**	52[f]
LiCl-alumina	**1a**	65[d]	**2a**	75[e]
$MgBr_2$-alumina	**1a**	85[d]	**2a**	64[e]
LiBr-alumina[g]	**1a**	20[d]	**2a**	16[f]

[a] Determined by ^{1}H-NMR analysis.

[b] The gas-phase reaction was carried out under reduced pressure.

[c] No epoxide was detected.

[d] Epoxide was recovered.

[e] Isolated yield in the gas-phase reaction.

[f] The reaction was carried out in toluene and the product was isolated as the crystalline adduct of sodium bisulfite.

[g] LiBr and alumina were mixed in the reaction without first forming the support.

We have now found that cyclopentanecarbaldehyde **2a** can be obtained easily and inexpensively from cyclohexene oxide **1a** by rearrangement using lithium bromide supported on alumina. Other epoxides could also be converted effectively to aldehydes by this method. We examined other systems, i.e., lithium chloride or magnesium bromide instead of lithium bromide, silica gel instead of alumina, benzene, chloroform and hexane as the reaction solvents. However, lithium bromide-alumina in toluene or in the gas-phase reaction were the most effective among them. The results are summarized in the Table.

In conclusion, the present procedure provides a simple and convenient method for the preparation of aldehydes from epoxides. The gas-phase reaction is especially convenient for the preparation of neat aldehydes with lower molecular weights.

The ^{1}H-NMR spectra were recorded on a JEOL FX-90Q spectrometer. The IR spectra were recorded on a HITACHI 260-30 infrared spectrophotometer.

Preparation of Lithium Bromide on Alumina:

Lithium bromide hydrate (50 g) is dissolved in water (150 mL) and the solution is added to activated aluminum oxide (150 g; ca. 200 mesh). After evaporation of water, the powder is dried for 2 d at 150 °C at atmospheric pressure.

Rearrangement of Epoxides; Typical Procedure:

Method A (the gas-phase reaction): A column (50 mm × 15 mm) packed with 25% (w/w) LiBr-alumina (15 g) is heated at 180 °C using the ribbon heater. Vapor of cyclohexene oxide (**1a**; 15.0 g, 153 mmol) is passed through the column over a period of 30 min. The product is collected in a trap at 0 °C. *Cyclopentanecarbaldehyde* (**2a**) is obtained; yield: 11.6 g (77%); oil.

IR (neat): $\nu = 2950, 2860, 2810, 2700\ \mathrm{cm}^{-1}$.

^{1}H-NMR ($CDCl_3$): $\delta = 1.3-2.3$ (m, 8H, $4CH_2$); 2.5–3.0 (m, 1H, CHCHO); 9.6 (d, 1H, $J = 2.6$ Hz, CHO).

Method B (the liquid-phase reaction): A mixture of 25% (w/w) LiBr-alumina (12 g) and **1a** (2.5 g, 25 mmol) is suspended in toluene (25 mL) and this suspension is refluxed with stirring for 2 h. The alumina is removed by filtration, and the product is added to a solution of $NaHSO_3$ (5.2 g, 50 mmol) in water (25 mL). The solution is stirred at 0 °C for 30 min. The precipitated product is isolated by suction and washed with Et_2O (50 mL). *α-Hydroxycyclopentylmethanesulfonic acid sodium salt* is obtained as a white powder; yield: 4.1 g (80%).

IR (KBr): $\nu = 3470, 2940, 2860, 1180\ \mathrm{cm}^{-1}$.

^{1}H-NMR (D_2O): $\delta = 1.2-2.0$ (m, 8H, $4CH_2$); 2.0–2.5 (m, 1H, $CHCHSO_3$); 4.25 (d, 1H, $J = 7.2$ Hz, $CHSO_3$).

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