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A NEW METHOD OF SYNTHESIS OF β-HALOETHYLBENZYL ETHERS

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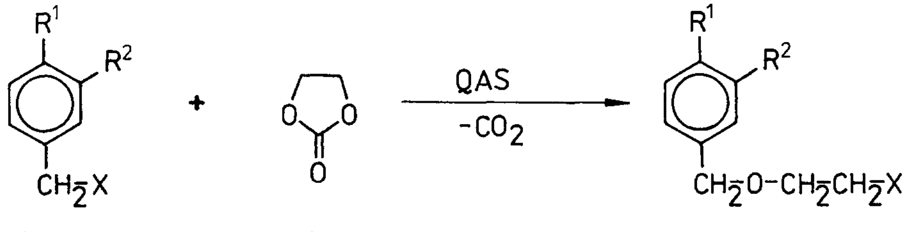
Several β-haloethylbenzyl ethers were prepared with satisfactory yields by the reaction of ethylene carbonate with benzyl halides in the presence of quaternary ammonium salts as catalysts

Among the few methods of synthesis of β-haloethylbenzyl ethers, the insertion of ethylene oxide into the carbon-halogen bond in benzyl halides has been reported.[1)] However, given the specific conditions and preparative route of this reaction, it cannot be recommended as a convenient preparative procedure

We have found that the compounds in question may be easily obtained with satisfactory yields by the reaction of benzyl halides (**1**) with ethylene carbonate (**2**) in the presence of the quaternary ammonium salt (QAS) as a catalyst:



1a-e **2** **3a-e**

a: $R^1, R^2 = H$; $X = Cl$

b: $R^1, R^2 = H$; $X = Br$

c: $R^1, R^2 = H$; $X = I$

d: $R^1 = Cl$; $R^2 = H$; $X = Cl$

e: $R^1 = OH$; $R^2 = CHO$; $X = Cl$

The general procedure for this reaction is as follows: a mixture of **1** (10 mmol) and tetraethylammonium iodide (TEAI) (0.2 - 1.5 mmol) was heated with stirring to 145 - 155 ^{o}C. Next, **2** was added in small portions until 95% of **1** had reacted (ca. 2 - 3 hrs.). The progress of reaction was checked by GLC$^{2)}$. However, in view of the partial decomposition of **2** into CO_2 and ethylene oxide, monitoring the course of this reaction by evolved gas volume measurements is not feasible. The catalyst may be recovered from the reaction mixture by extraction with water.

The structure of the ethers **3** was confirmed by the satisfactory elemental analysis$^{3)}$ and their IR$^{3)}$, C^{13}-NMR$^{4)}$, H^{1}-NMR as well as mass spectra$^{5)}$. We have obtained analytically pure samples of **3** by preparative GLC and TLC$^{2)}$ as well.

We have also carried out this reaction in the presence of tetraethylammonium chloride (TEAC), but in this case the yields of **3** were lower.

Table I

Preparation of Ethers **3** Catalyzed by Tetraethylammonium Iodide

Compound	Mole Ratio TEAI/1	Mole Ratio **2/1**	%Conversion of 1	Yield of **3*** %	H^{1}-NMR data, δ ppm** **Ar-CH$_2$-O-CH$_2$-CH$_2$-X** **a b c**
3a:	0.15	1.6	98	77	**a:** 7.68, s, 5H; **b:** 4.92, s, 2H **c:** 4.05, s***, 4H;
3b:	0.02	1.6	98	90	**a:** 7.40, s, 5H; **b:** 4.50, s. 2H **c:** 3.55, m, 4H; no solvent
3c:	0.07	1.7	95	73	**a:** 7.60, s, 5H; **b:** 4.82, s, 2H; **c:** 3.76, m, 4H;
3d:	0.06	1.6	95	76	**a:** 7.30, s, 4H; **b:** 4.47, s, 2H; **c:** 3.72, s***, 4H; no solvent
3e:	0.15	1.2	96	89	**a:** 7.00 - 7.92, m, 3H; **b:** 4.75, s,2H; **c:** 3.92,s***,4H;H_{OH}:11.15, s, 1H; H_{CHO}:10.08, s, 1H

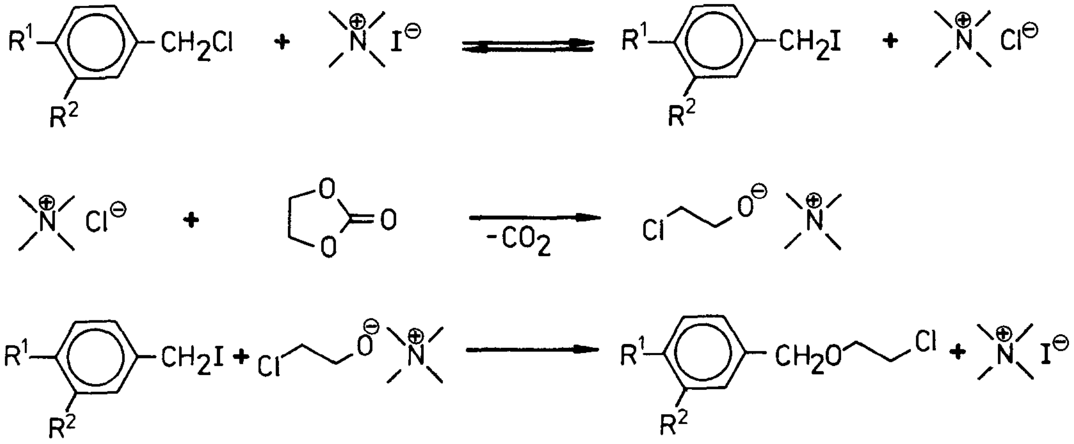
*By GLC$^{2)}$, all yields not maximized.

**80 MHz, $CDCl_3$, HMDS ext.

***At sweep width of 250 Hz - multiplet.

The presence of QAS is essential in this reaction. One may expect, however, that this catalyst might be replaced by some other known catalysts of ethylene carbonate decomposition.[6)]

During the synthesis of **3a**, **3b**, **3d**, and **3e** in the presence of TEAI we have identified, other than the major products, small amounts (ca. 3 - 4%) of the corresponding 2-iodoethylbenzyl ethers as well as trace amounts of the corresponding benzyl iodides. These observations seem to suggest the following mechanism of the reaction:



An additional argument supporting the proposed mechanism is that during the synthesis of **3c** in the presence of TEAC we have identified an amount of **3a** present in the reaction mixture almost corresponding to the amount of catalyst used.

We have also observed that when the temperature of the reaction exceeds 155 °C, high-molecular weight tar products are formed, decreasing the yield of the main product. It is recommended that the synthesis of **3c** be carried out at 115-120 °C.

It is noteworthy that during the synthesis of **3e**, the side-reaction of hydroxyethylation of the hydroxy group in **1e** and **3e** was not observed, although the reaction conditions were quite similar to those of hydroxyethylation of phenols with ethylene carbonate.[7)]

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References and Notes

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2. **GLC:** FID, 2 m glass column of 3 mm i.d., 10% DC-200 + 15% OF-1 on Gas Chrom Q (1:1), N_2 : 40 ml/min; compounds **3a - 3d** were chromatographed at $160^{\circ}C$, and **3e** at 190 $^{\circ}C$; calibration was performed for both substrate and product;

   Preparative GLC: FID, 4 m glass column of 8 mm i.d., 10% XE-60 on GasChrom Q, $140^{\circ}C$, N_2 : 110 ml/min;

   Preparative TLC; Silica Gel-60, F_{256}, Merck; hexane : acetone (20:1).

3. All compounds gave satisfactory elemental analysis data and showed a characteristic IR band at 1105 - 1115 cm^{-1} in $CHCl_3$ solution.

4. **C^{13}-NMR** (δppm, in $CDCl_3$, HMDS ext,);

   3a: 136.96, 127.61, 126.96, 72.25, 69.26, 42.10;

   3e: 238.32, 195.70, 135.67, 131.90, 128.65, 119.42, 116.68, 71.08, 69.26,42.10.

5. **Mass spectrum:** m/e (%):

   3a: 170(10.2)M^+, 92(2.8), 91(100), 79(11.2), 77(8.4), 65(13.8), 63(8.9), 51(10.0), 39(5.5), 27(9.6);

   3c: 262(5.6)M^+, 155(6.7), 105(7.9), 92(43.4), 91(100), 79(12.8), 77(11.6), 65(13.7), 51(10.9), 27(8.8);

   3e: 214(15.7)M^+, 151(12.4), 136(12.0), 135(100), 133(19.3), 77(21.4), 63(14.0), 51(10.6), 39(9.9), 27(15.3).

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