

Table. 2-Oxo-1,3-dioxolanes (3) prepared

Prod- uct	X in 1	Reaction Time at 20°C [min]	Yield ^a [%]	r.t.p. ^b [°C] (solvent) or t.p. [°C]/torr	
				found	reported
3a	Cl	45	94	b.p. 67–68°/1	b.p. 65–67°/1 ⁷
	Br	10	95	m.p. 36–37° (ether)	m.p. 36.2° ¹⁴
3b ^c	Cl	75 ^d	95	b.p. 62–64°/0.5	b.p. 75°/1.8 ⁸
	J	10	95		
3c (trans)	Br	20	93	b.p. 49–51°/0.2 m.p. 37–38° (PE, b.p. 40–70°C)	m.p. 37° ⁶
3c' (cis)	Br	45	88	b.p. 70–72°/0.1	b.p. 70–75°/0.1 ⁵
3d	Br	15	92	b.p. 110°/0.05 m.p. 54–56° (ethanol)	b.p. 150°/2 ⁸ m.p. 55.7–56.7° ⁴
3e ^e	Cl	75 ^d	96	b.p. 67–69°/0.5	b.p. 75–80°/0.8 ¹⁵
	Br	15	95		
3f (trans)	Br	15	84 ^e	m.p. 111–112° (ethanol/H ₂ O)	m.p. 110–111.5° ¹⁶

^a Yield (based on the starting halohydrin **1**) of product isolated by distillation, unless otherwise stated. Purities (>98%) were checked by G.L.C. [glass column (1.5 m × 2 mm ID); 5% Carbowax 20 M on 60/80 Chromosorb W; T 75°C then 10°C/min to 220°C]. All products gave satisfactory microanalyses: C ± 0.20; H ± 0.10.

^b Melting points were determined by the Kofler method and are uncorrected.

^c The starting *vic*-halohydrin used was an isomer mixture [75/25 ("normal"/"abnormal") for **1b** (X = Cl) and **1e** (X = Cl), 80/20 for **1e** (X = Br), and 88/12 for **1b** (X = J)].

^d Reaction at 50°C.

^e Yield after washing of the crude product **3f** with cold ether (20 ml) and recrystallization from aqueous ethanol. The crude product contains 8–10% of *trans*-1,2-diphenyloxirane.

nate in acetonitrile in the presence of quaternary ammonium halides Q⁺X⁻ (e.g., Aliquat 336) as phase-transfer catalysts were also successful. However, prolonged (4–5 h) heating at 80°C (molar ratio 1/Q⁺X⁻ = 10 and 1/KHCO₃ = 1.6) was required to achieve satisfactory conversions. Moreover, this approach was found to have a narrower scope, among the substrates examined its application being practically limited to chlorohydrins and to a few bromohydrins (**1a**, **1e**), while in the other cases only modest or poor results were obtained. Under the above conditions, the reactions (4h) of chlorohydrin **1b** and bromohydrin **1e** gave the cyclic carbonates **3b** and **3e** in 90 and 60% yield of distilled product, respectively. Crown ethers could also be used as catalysts.

The synthesis reported here, by virtue of its simplicity, rapidity, and effectiveness, may represent a convenient procedure for large-scale laboratory preparations of 1,2-alkanediyl carbonates.

All 1,2-alkanediyl carbonates prepared are known. Their identity was confirmed by microanalyses, spectral data, and comparison with authentic samples.

Ethylene chlorohydrin and bromohydrin were obtained commercially. Halohydrins **1b**¹⁷, **1c** (*erythro*)¹⁸, **1c'** (*threo*)¹⁸, and **1e**¹⁹ were prepared from the corresponding epoxide and the appropriate hydrohalic acid. 1-Chloro(iodo)-2-propanol and 1-chloro(bromo)-2-butanol were obtained together with the positional isomer (minor component) 2-chloro(iodo)-1-propanol and 2-chloro(bromo)-1-

butanol, respectively; they were used as such without any separation. Bromohydrins **1d** and **1f** (*erythro*) were prepared by reaction of *N*-bromosuccinimide with styrene and *trans*-stilbene, respectively²⁰.

2-Oxo-1,3-dioxolanes (3, 1,2-Alkanediyl Carbonates); General Procedure:

A 25% w/w solution of tetramethylammonium hydroxide in methanol (47 g, ~0.13 mol), diluted with methanol (50 ml), is saturated with carbon dioxide at room temperature for 40 min. Then, methanol is distilled off under reduced pressure. Acetonitrile (250 ml) is added to the solid residue thus obtained, and the resultant suspension is stirred in a carbon dioxide atmosphere for an additional 10 min until gas absorption is no longer noticed. To tetramethylammonium hydrogen carbonate (**2**) in acetonitrile thus prepared is added the appropriate halohydrin (**1**; 0.10 mol) (dissolved in acetonitrile, if solid) and the whole is stirred in a carbon dioxide atmosphere at 20°C for the time given in the Table. The solid material (most of tetramethylammonium halide formed and of the excess of **2**) is filtered off and washed well with acetonitrile (2 × 40 ml). The combined acetonitrile solution is distilled under reduced pressure. Acetone (70 ml) is then added to the residue, whereby a further portion of salts separates. The solid material is filtered off and washed with acetone (2 × 15 ml). The acetone solutions are combined and passed through a short silica gel column (70–230 mesh; 20 g) to remove residual traces of salts. Evaporation of the solvent gives an oil (**3b**, **c**, **e**) or a syrup which solidifies at room temperature (**3a**, **c**, **d**, **f**). The oily or the solid product thus obtained is purified by vacuum distillation through a short Vigreux column (**3a–e**) or by recrystallization (**3f**).

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