

FORMATION OF CYCLIC CARBONATES IN THE REACTIONS OF 1,2-GLYCOLS WITH OXALYL CHLORIDE

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Oxalyl chloride reacts with a wide range of 1,2-glycols in the presence of triethylamine to produce 1,3-dioxolan-2-ones together with 1,4-dioxane-2,3-diones; the ratio of the products largely depends on the structure of the 1,2-glycol. The formation of the cyclic carbonates may be rationalized in terms of stereoelectronically controlled cleavage of the tetrahedral intermediates.

KEYWORDS oxalyl chloride decarbonylation; 1,2-glycol; 1,3-dioxolan-2-one; 1,4-dioxane-2,3-dione; stereoelectronic effect; tetrahedral intermediate cleavage

We have already reported that the reactions of oxalyl chloride with 1,2-glycols **1a—c** in the presence of triethylamine afford the cyclic carbonates **3a—c** instead of the cyclic oxalates **2a—c**.¹⁾ There is only one precedent for the reaction of oxalyl chloride with **1** leading to **3**: Adams and Weeks reported the formation of **3g** from pinacol (**1g**) in the absence of base.^{2,3)} On the other hand surprisingly few examples have been known for the formation of the cyclic oxalates **2** notwithstanding that they are expected to be normal products of the reactions between oxalyl chloride and **1**.^{2,4)} From aralkyl 1,2-glycols, the cyclic oxalates **2m, n** of hydrobenzoin (**1m, n**) have been recorded as the only two examples.^{4b)} As **2m, n** had not been characterized,^{4b,c)} we performed the reaction with (±)-hydrobenzoin (**1m**), obtaining the *trans*-carbonate **3m**⁵⁾ in 58% yield. Similar reaction with *meso*-hydrobenzoin (**1n**) also proceeded stereospecifically to produce the *cis*-carbonate **3n**.⁵⁾ Examination of the reaction mixtures by NMR spectroscopy furnished evidence for the formation of what we presumed to be the oxalates **2m, n**; ⁶⁾ we failed to isolate these compounds because of their instability on silica gel. It was accordingly necessary for us to perform systematic experiments on the reaction of oxalyl chloride with **1**.

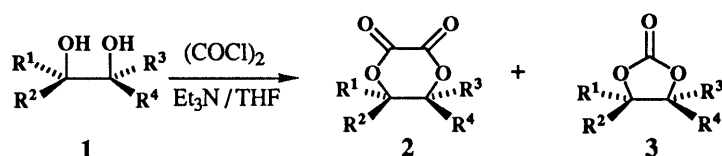
The results of the reactions of some selected 1,2-glycols **1** with oxalyl chloride in tetrahydrofuran (THF) in the presence of triethylamine are shown in Table I. Ethylene glycol (**1d**) afforded ethylene oxalate (**2d**)^{2,4a)} in 72% yield, while progressive methylation of the carbon atoms of **1d** caused increasing production of the carbonate **3**; pinacol (**1g**) afforded the carbonate **3g**²⁾ more than the oxalate **2g**. A similar trend was reported for the reactions of oxalyl chloride with 2,2-dibutyl-1,3,2-dioxastannolane series.^{4a)} The yield of the carbonate **3** was more efficiently increased by substitution with a phenyl group than with a methyl group (**1h, j, l** versus **1e**) and was almost independent of the nature of the *p*-substituent of the phenyl group. Substitution with phenyl groups at both the 1- and 2-positions (**1m, n**) further increased the yield of **3**. More important information derived from the experiments with **1m, n** is that the three-dimensional structure of **1** is closely related to the ratio of the products. Thus the (*R**, *R**)-compounds **1a—c, i, k, m** all afforded the corresponding **3** in high yields.

We next devoted our attention to the mechanism for the formation of the carbonate **3**. The possibility that **3** is formed by the action of phosgen, which may be formed from oxalyl chloride,²⁾ can be ruled out because phosgen afforded **3k** in only poor yield under similar conditions. Another possibility that **3** is formed through the oxalate **2** is unlikely because **2h** did not change into **3h** under conditions similar to those employed for the reaction from which **2h** was obtained. If the mechanism (type **5** → type **4** → type **7** → **3**⁷⁾ or (type **5** → type **8** → **3**) were operative, a carbonate ester from a monohydroxy compound would be formed by the action of oxalyl chloride: we have found no evidence for the formation of even a trace of a carbonate ester from a monohydroxy compound, no matter whether it is primary or secondary. Furthermore, the former mechanism seems hardly to explain the difference in the product distribution observed between the reaction with **1m** and that with **1n**. Because the 1,2-dicarbonyl group of the intermediate (type **5**) must exist mainly as the *s-trans* conformer,⁸⁾ perpendicular attack (107° according to the literature⁹⁾) of the intramolecular hydroxy group on the acid chloride moiety should give rise to the tetrahedral intermediate (type **6A**), in which the chlorine is equatorially oriented. According to the theory of stereoelectronic control,¹⁰⁾ the C—Cl bond in the conformer **6A** is not allowed to be cleaved because only one oxygen has an orbital oriented antiperiplanar to this bond, whereas the cleavage of the C—C bond is favored because the two oxygens and the chlorine have each one electronic effect, leading to **3m** through **9**. On the other hand the C—Cl bond in the conformer **6B** should be smoothly cleaved because the two oxygens have each one electron pair antiperiplanar to this bond. This means that the more difficult the conformational change from type

6A into type **6B** is, the more preferentially the carbonate **3** is formed. We can thus rationalize the results shown in Table I; for instance, (*R**,*R**)-hydrobenzoin (**1m**) should preferentially afford **3m** because the transition from **6A** to **6B** requires changing the two equatorial phenyl groups to axial ones, whereas the transition between the two corresponding conformers from the (*R**,*S**)-isomer **1n** is much easier because they each have one equatorial phenyl group and one axial phenyl group, allowing the preferential formation of **2n**.

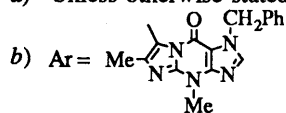
In conclusion, we have disclosed that formation of a cyclic carbonate **3** appears to be a general reaction of oxalyl chloride with a 1,2-glycol **1** in the presence of triethylamine. We have also demonstrated that 1,4-dioxane-2,3-diones **2** are common products although the number of known compounds with this ring system was so far so limited and have presented, for the first time, evidence for the formation of this type of compound from benzylic diols. Work is now in progress to test further the present mechanism.

TABLE I. Reactions of Oxalyl Chloride and 1,2-Glycols in THF in the Presence of Triethylamine

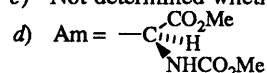


1,2-Glycol	Substituent				Reaction conditions		Product (yield, %) ^{a)}	
	R ¹	R ²	R ³	R ⁴	Temperature (°C)	Time (min)	Oxalate	Carbonate
(±)- 1a	Ar ^{b)}	H	H	CHMe ₂	0	10	(±)- 2a (—) ^{c)}	(±)- 3a (63)
1b	Ar ^{b)}	H	H	Am ^{d)}	0	25	2b (—) ^{c)}	3b (66)
1c	H	Ar ^{b)}	Am ^{d)}	H	rt	20	2c (—) ^{c)}	3c (45)
1d	H	H	H	H	0	20	2d (72) ^{e)}	3d (1)
(±)- 1e	Me	H	H	H	0	30	(±)- 2e (57) ^{e, f)}	(±)- 3e (6)
1f g)	Me	H	H (Me)	Me (H)	0	20	(±)- 2f (20) ^{e, f, h)}	(±)- 3f (13) ^{h)}
1g	Me	Me	Me	Me	rt	3240	2g (1) ^{i, j)}	3g (24)
(±)- 1h	Ph	H	H	H	0	10	(±)- 2h (37) ^{i, k)}	(±)- 3h (14)
(±)- 1i l)	Ph	H	H	CHMe ₂	0	10	(±)- 2i (13) ^{l)}	(±)- 3i (84) ⁱ⁾
(±)- 1j i, m)	4-Me ₂ N-Ph	H	H	H	0	15	(±)- 2j (53) ^{l)}	(±)- 3j (16) ^{l)}
(±)- 1k i, l)	4-Me ₂ N-Ph	H	H	CHMe ₂	0	15	(±)- 2k (11) ^{l)}	(±)- 3k (88) ⁱ⁾
(±)- 1l i, m)	4-NO ₂ -Ph	H	H	H	0	30	(±)- 2l (36) ^{l)}	(±)- 3l (15) ⁱ⁾
(±)- 1m	Ph	H	H	Ph	0	15	(±)- 2m (32) ^{l)}	(±)- 3m (58)
1n	Ph	H	Ph	H	0	15	2n (58) ^{l)}	3n (29)

a) Unless otherwise stated, the product was obtained by flash chromatography.



c) Not determined whether this compound was formed or not.



e) Obtained by Kugelrohr distillation of a mixture of the products.

f) The yield was estimated by means of NMR spectroscopy.

g) A 1:1 mixture of the (±)- and the *meso*-compounds.

h) A mixture of the (±)- and the *meso*-compounds.

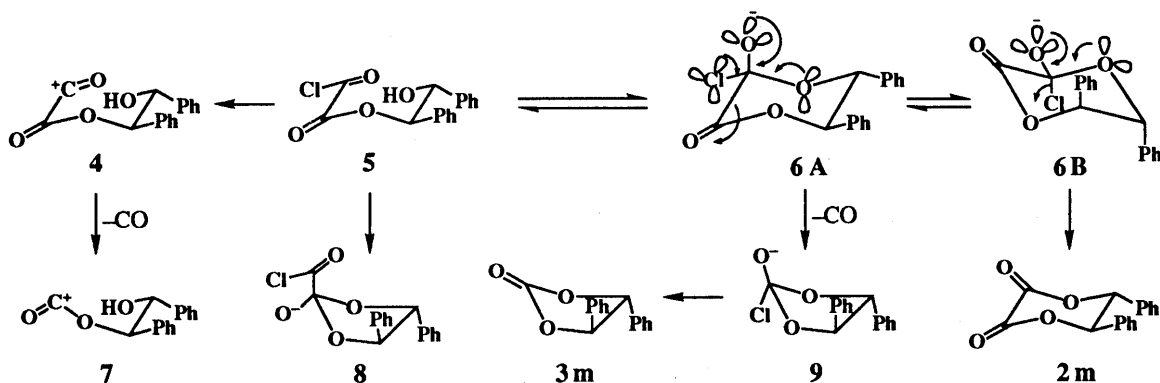
i) Satisfactory analytical and/or spectral data were obtained for all new compounds.

j) Unlike **2h—n**, this compound was inert on silica gel.

k) Obtained by recrystallization from benzene.

l) Prepared by the Wittig reaction between the appropriate aldehyde and (2-methylpropyl)triphenylphosphonium iodide¹¹⁾ followed successively by geometrical isomerization¹²⁾ and osmylation.¹³⁾

m) Prepared from the appropriate aldehyde by the Wittig reaction with methyltriphenylphosphonium bromide followed by osmylation.¹³⁾



A Representative Experimental Procedure A solution of oxalyl chloride (0.75 ml, 8.8 mmol) in dry THF (10 ml) was added dropwise to a solution of ($\pm$)-1h (1.11 g, 8.03 mmol) and triethylamine (3.4 ml, 24 mmol) in dry THF (40 ml) with cooling in an ice-bath over a period of 5 min. The mixture was stirred at 0 °C for a further 5 min. The resulting precipitate was filtered off and washed with THF (50 ml). The filtrate and the washings were combined and concentrated *in vacuo*. The residue was washed with benzene to give ($\pm$)-2h (569 mg, 37%), mp 124–125 °C (recrystallized from benzene). The benzene washings were concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel [hexane–ethyl acetate (3:2, v/v)] to afford ($\pm$)-3h (182 mg, 14%) as a colorless oil.

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- 5) Compound 3m: mp 109.5–110 °C (lit.¹⁴) mp 110–111 °C; ¹H-NMR (CDCl₃) δ : 5.43 (2H, s, two CH's), 7.33 (4H, m) and 7.44 (6H, m) (two Ph's); ¹³C-NMR (CDCl₃) δ : 85.4 (CH), 126.1, 129.2, 129.8, and 134.8 (Ph), 154.1 (C=O). Compound 3n: mp 125.5–126.5 °C (lit.¹⁴) mp 126–127 °C; ¹H-NMR (CDCl₃) δ : 5.98 (2H, s, two CH's), 6.88–6.98 (4H, m) and 7.08–7.20 (6H, m) (two Ph's); ¹³C-NMR (CDCl₃) δ : 82.1 (CH), 126.1, 128.2, 128.8, and 132.8 (Ph), 154.9 (C=O).
- 6) Compound 2m: ¹H-NMR (CDCl₃) δ : 5.69 (2H, s, two CH's), 7.07 (4H, m) and 7.3 (6H, m) (two Ph's); ¹³C-NMR (CDCl₃) δ : 84.3 (CH), 127.3, 128.7, 129.9, and 131.6 (Ph), 153.0 (C=O). Compound 2n: ¹H-NMR (CDCl₃) δ : 6.04 (2H, s, two CH's), 6.95 (4H, m) and 7.2–7.4 (6H, m) (two Ph's); ¹³C-NMR (CDCl₃) δ : 81.9 (CH), 126.7, 128.5, 129.5, and 130.7 (Ph), 153.2 (C=O).
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