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Cyclocondensation of Oxalyl Chloride with 1,2-Glycols

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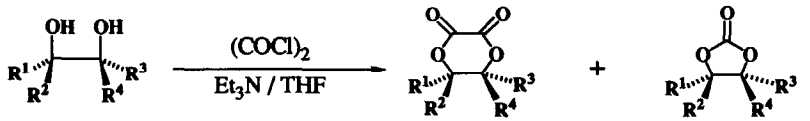
Abstract Oxalyl chloride reacts with a wide range of acyclic 1,2-glycols **1** in the presence of triethylamine to produce 1,3-dioxolan-2-ones **3** together with 1,4-dioxane-2,3-diones **2** Ethylene glycol (**1d**), monosubstituted ethylene glycols **1e, j**—**l**, and *erythro*-1,2-disubstituted ethylene glycols **1f, m,o** provide the cyclic carbonates **3** as the minor products, while the *threo*-compounds **1g, i, n,p,q** and pinacol (**1h**) afford **3** as the main products The formation of **3** may be rationalized in terms of stereoelectronically controlled cleavage of the conjugate base **17**⁻ of the tetrahedral intermediates The rate for the conformational change of **17**⁻ into **18**⁻ and the equilibrium constant between these conformers are proposed to be the major factors affecting the reaction pattern

Oxalyl chloride normally reacted with alcohols,[1] amines,[2] mercaptans,[2] amino acids,[2] hydrazines,[2] ureas,[2,3] thioureas,[3a] biurets,[3b] carbamates,[4] carboxamides,[5] dithiocarboxamides,[6] sulfonamides,[7] phenyl methylphosphonamidate,[8] carboximides,[9] carbodiimides,[10] isopropylcyanamide,[11] 2,3-diaminobutanedinitrile,[12] imino ethers,[13] amidines,[13] guanidines,[14] hydrazones,[15] nitrosamines,[16] *N*-arylnitrones,[17] isocyanates,[18] isothiocyanates,[18] isonitriles,[19] benzophenone oxime,[20] 2,5-dihydroperoxy-2,5-dimethylhexane,[21] phenols,[22] enols,[23] enol ethers,[24] enol thioethers,[25] enamines,[26] 1,1-diarylethylenes,[27] arylpropiolic acids,[28] diazomethane,[29] phosphoranes,[30] carbanions,[31] organometals,[32] and other nucleophiles[33] to afford the corresponding oxalic acid derivatives In certain cases, products the same as those which would form from phosgene were obtained [1,2,3*b*,4,27,32*d*,*i*,34] The reaction of one mole of oxalyl chloride with two moles of *N,N*-dimethylaniline at 0 °C afforded 4-(dimethylamino)phenylglyoxalyl chloride in quantitative yield, while 4-(dimethylamino)benzoyl chloride was formed at higher temperature, 4,4'-bis(dimethylamino)benzil and 4,4'-bis(dimethylamino)benzophenone were also formed depending on the reaction conditions [35] Similar decarbonylative reactions were reported for *m*-dimethoxybenzene,[36] triphenylamine,[37] polynuclear aromatic hydrocarbons,[38] thiophenes,[39] and pyrazoles,[40] whereas more reactive pyrroles[41] and condensed pyrroles[42] provided the corresponding 1,2-diketones in good yields In the presence of aluminum chloride, alkylbenzenes produced the benzoic acid derivatives,[43] while alkoxybenzenes provided the corresponding benzils [44] Despite many reports on the decarbonylative reactions of oxalyl chloride, the mechanisms have not been thoroughly explored

In 1986, we found that the reactions of oxalyl chloride with 1,2-glycols **1a**—**c** in the presence of triethylamine afforded the cyclic carbonates **3a**—**c** instead of the cyclic oxalates **2a**—**c** (entries 1—3 in Table 1) [45] There is only one precedent for the reaction of oxalyl chloride with **1** leading to **3** Adams and Weeks reported the formation of **3h** from pinacol (**1h**) in the absence of base, while ethylene glycol (**1d**) afforded

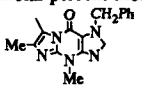
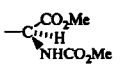


1 2 3

Table 1 Reactions of Oxalyl Chloride and 1,2-Glycols 1 in THF in the Presence of Triethylamine

Entry	Glycol	R^1	R^2	R^3	R^4	Reaction conditions [a]				Estimated yield (%) [b]			Isolated yield (%)	
						Et_3N [c]	Solvent [d]	Temp (°C)	Time (min)	2	3	Polymers	2	3
1	**1a**	Ar [e]	H	H	Me_2CH	—[f]	—[f]	0	10	—[g]	—[g]	—[g]	—[h]	63
2	**1b**	Ar [e]	H	H	Am [i]	—[f]	—[f]	0	25	—[g]	—[g]	—[g]	—[h]	66
3	**1c**	H	Ar [e]	Am [i]	H	—[f]	—[f]	rt	20	—[g]	—[g]	—[g]	—[h]	45
4	**1d**	H	H	H	H	3	5	0	15	—[g]	—[g]	—[g]	72	19
5	(±)-**1e**	Me	H	H	H	22	23	0	30	—[g]	—[g]	—[g]	66	59
6	**1f**	Me	H	Me	H	54	110	0	45	54	4	20	63	37
7	(±)-**1g**	Me	H	H	Me	50	110	0	45	25	42	8	—[h]	35
8	**1h**	Me	Me	Me	Me	22	6	rt	3240	—[g]	—[g]	—[g]	08	24
9	(±)-**1i**	$BrCH_2$	H	H	$BrCH_2$	23	53 [j]	rt	10	5	70	25	—[h]	58
10	(±)-**1j**	Ph	H	H	H	3	6	0	10	40	20	40	37	14
11	(±)-**1j**	Ph	H	H	H	3	85	0	10	75	19	6	58	19
12	(±)-**1k**	4-Me_2N-C_6H_4	H	H	H	55	30	0	15	53	16	32	—[h]	—[h]
13	(±)-**1l**	4-O_2N-C_6H_4	H	H	H	56	88	0	10	61	26	13	—[h]	17
14	**1m**	Ph	H	Ph	H	22	12	0	15	67	33	—[k]	—[h]	29
15	(±)-**1n**	Ph	H	H	Ph	22	12	0	15	36	64	—[k]	—[h]	58
16	(±)-**1o**	Ph	H	Me_2CH	H	45	24	0	10	77	23	—[k]	—[h]	20
17	(±)-**1p**	Ph	H	H	Me_2CH	4.5	24	0	10	13	87	—[k]	—[h]	84
18	(±)-**1q**	4-Me_2N-C_6H_4	H	H	Me_2CH	32	24	0	15	11	89	—[k]	—[h]	88

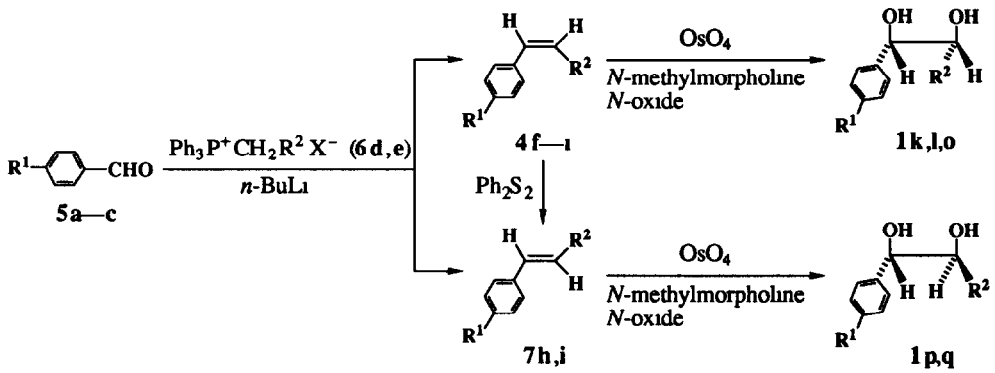
[a] Ten molar percent excess of oxalyl chloride was used [b] Determined by ^{1}H-NMR spectroscopy [c] Molar ratio to 1 [d] Volume (ml) per mmol of 1

[e] Ar =  [f] Experimental details will be reported elsewhere [g] Not determined [h] Could not be isolated [i] Am = 

[j] The reaction was carried out using five molar percent excess of oxalyl chloride in dichloromethane according to the reported procedure [46i] [k] A trace if any

ethylene oxalate (**2d**) under similar conditions [1] We confirmed the formation of **3h** (28%) from **1h** under these conditions Apart from the formation of the carbonate **3**, few 1,4-dioxane-2,3-diones (type **2**)[46] derived from 1,2-glycols are in the literature notwithstanding that they are expected to be normal products of the reactions between oxalyl chloride and **1** Furthermore, it was surprising that there were only two precedents on the reaction of **1** and oxalyl chloride in the presence of triethylamine,[46b,c] we concluded that the supposed products **2i,m,n** were in fact **3i,m,n**, as will be described below We accordingly felt that it was necessary to perform systematic experiments on the reaction of oxalyl chloride with **1** We now report results of the reactions of **1** with oxalyl chloride in tetrahydrofuran (THF) in the presence of triethylamine [47]

Scheme 1 represents the synthesis of the commercially unavailable 1,2-glycols **1** by the Wittig reactions between appropriate aldehydes **5** and phosphonium salts **6**, followed by osmylation [48] Some of authentic cyclic carbonates **3** were prepared from **1** by the action of phosgene



a $R^1 = H$ **d.** $R^2 = H$ **f** $R^1 = NMe_2$, $R^2 = H$
b $R^1 = NMe_2$ **e** $R^2 = CHMe_2$ **g** $R^1 = NO_2$, $R^2 = H$
c $R^1 = NO_2$ **h** $R^1 = H$, $R^2 = CHMe_2$
i $R^1 = NMe_2$, $R^2 = CHMe_2$

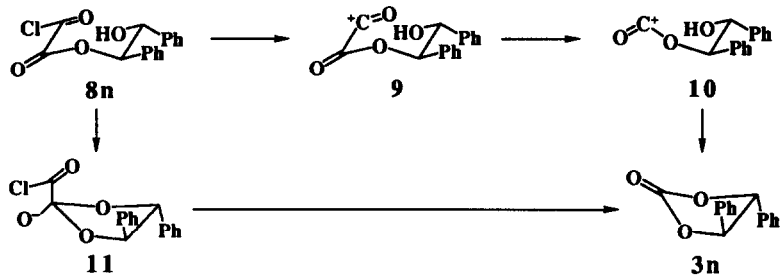
Scheme 1

Carothers *et al* obtained monomeric ethylene oxalate (**2d**) by pyrolysis of its polymers, which were prepared by heating ethylene glycol (**1d**) with diethyl oxalate [49] When we treated a solution of **1d** in THF with a slight excess of oxalyl chloride in the presence of an excess of triethylamine at 0 °C, the major products were also suggested to be polymeric ethylene oxalates by NMR spectroscopy, **2d** (72%) was obtained after pyrolysis of the crude products, as shown in Table 1 (entry 4) A small amount of the carbonate **3d** was also produced Propylene oxalate [(±)-**2e**][32a,49] (66%) was similarly obtained by pyrolysis of the corresponding polymers (entry 5) *meso*-2,3-Butanediol (**1f**) afforded the cyclic oxalate **2f** more than the polymers (entry 6) Compounds **2d**—**f** thus obtained were all susceptible to hydrolysis even in plain water, as already reported for **2f** and (–)-**2g**,[50] and rapidly decomposed on silica gel Progressive methylation of the carbon atoms of **1d** tended to cause increasing production of the carbonate **3** A similar trend was reported for the reactions of oxalyl chloride with 2,2-dibutyl-1,3,2-dioxastannolane series [32a] Thus pinacol (**1h**) afforded the carbonate **3h** in 24% yield and the oxalate **2h** in 0 8% yield (entry 8) Interestingly, **2h** was stable enough for purification by chromatography on silica gel The yield of the carbonate **3** was more efficiently increased by substitution with a phenyl group than with a methyl group (entry 10 vs entry 5), and was not largely affected by the electronic

property of the *p*-substituent of the phenyl group (entries 10, 12, and 13), suggesting that the formation of **3** was mainly controlled by the steric bulk of the substituent of ethylene glycol Substitution with phenyl groups at both the 1- and 2-positions of **1d** further favored the formation of **3**. Thus *meso*-hydrobenzoin (**1m**) produced the *cis*-carbonate **3m** in 29% yield (entry 14), and (±)-hydrobenzoin [(±)-**1n**] gave the *trans*-carbonate (±)-**3n** in 58% yield (entry 15) Replacement of the phenyl group of **1n** with a bulkier isopropyl group further favored the formation of the carbonate (±)-**1p** afforded (±)-**3p** in 84% yield (entry 17) Comparison of the results, obtained with three pairs of diastereomers [entry 6 vs. 7, 14 vs 15, and 16 vs 17], permits us to conclude that the *threo*-compound more preferentially produces the cyclic carbonate **3** than the corresponding *erythro*-isomer does, the highly selective formation of **3** was also realized in the reactions with other *threo*-compounds (entries 1—3[45] and 18) These results suggested that the structure (±)-*trans*-5,6-bis(bromomethyl)-1,4-dioxane-2,3-dione [(±)-**2i**] had been wrongly assigned to the product from *threo*-1,4-dibromo-2,3-butanediol [(±)-**1i**] [46i] The main product was in fact the carbonate (±)-**3i** (entry 9)

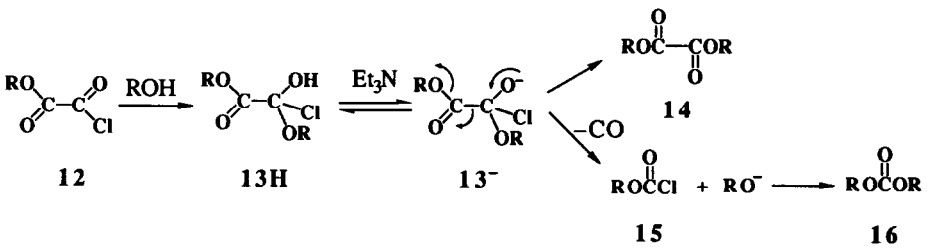
Examination of the reaction mixtures, obtained from **1g,i—q**, by NMR spectroscopy furnished evidence for the formation of what we presumed to be the corresponding **2**, we failed to isolate these compounds by means of chromatography because of their instability on silica gel We consequently concluded that the products from hydrobenzoins, reported by White[46b] as **2m,n** without characterization, were probably **3m,n** Of these unstable cyclic oxalates, **2j** was successfully obtained without using chromatography; **2j** polymerized on storage even in the solid state, as reported for **2d** [49] In the presence of **1j** and triethylamine, **2j** polymerized rapidly in THF Dilution with the solvent increased the yield of **2j** with unchanged yield of the carbonate **3j** (entry 10 vs entry 11) These results suggest that the polymers were mainly formed through **2j** Compound **2j** is the first example of cyclic oxalates having an aromatic substituent(s) at the skeletal framework

We next devoted our attention to the mechanism for the formation of the carbonate **3**. Although Adams and Weeks supposed that **3h** was formed by the action of phosgene, which might be generated *in situ*,[1] it is unlikely that oxalyl chloride so rapidly decomposes to phosgene under such mild conditions as we employed, furthermore, phosgene afforded (±)-**3q** in only poor yield in the reaction with (±)-**1q**, while oxalyl chloride provided the same compound in high yield under similar conditions (entry 18) Another possibility that **3** is formed through the oxalate **2**, is also unlikely, because the prolonged reaction with **1j** did not change the product ratio We also confirmed that **2h, j** did not produce **3h, j** under conditions similar to those employed for the reactions, from which **2h, j** were obtained Davies *et al* proposed for the reactions with 2,2-dibutyl-1,3,2-dioxastannolanes that the carbonates **3** were produced by cyclization of the alkoxyacylium intermediates (type **10**), which might be formed from the half esters of oxalyl chloride by dechlorination followed by decarbonylation [32i] Scheme 2 exemplifies the analogous mechanism (**8n** → **9** → **10** → **3n**) for the formation of the carbonate **3n** The fragmentation of **8n** to **10** may be important only when the transformation of **8n** to the cyclic oxalate **2n** is retarded, the fact is that **1n** was transformed into **2n** at a rate faster than that for the oxalate diester formation from a monohydroxy compound [51] In addition, if such a mechanism were operative, the carbonate ester **16** 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 the carbonate ester from such a compound, no matter whether it is primary, secondary, or tertiary [51] We thus concluded that **10** could not be a true intermediate for the formation of **3n** By the same reasoning, an alternative pathway (**8n** → **11** → **3n**) was also ruled out Anyhow, none of these mechanisms give a satisfactory explanation to the difference in the reaction pattern observed between the diastereomers

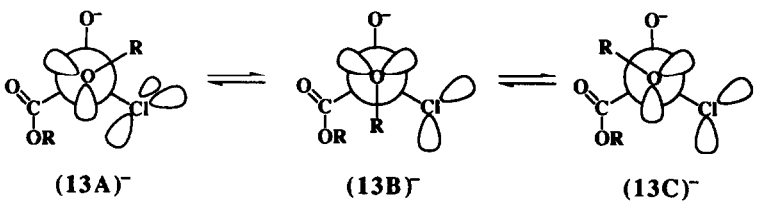


Scheme 2

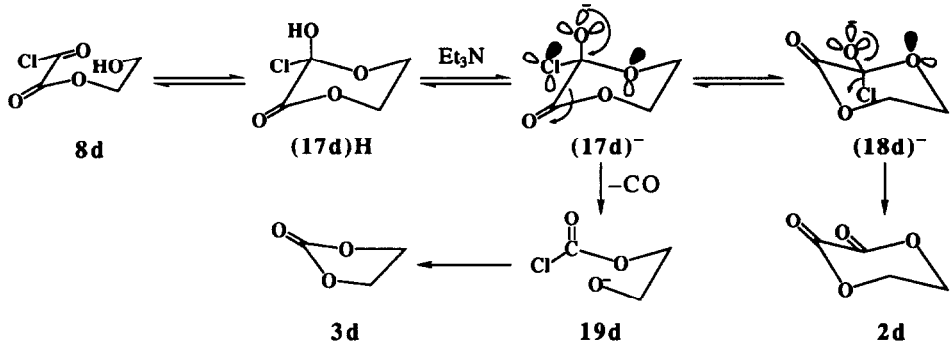
Scheme 3 represents our mechanism proposed for the reaction of one mole of oxalyl chloride with two moles of an alcohol The primary intermediate **12** will produce the tetrahedral intermediate **13H** It is most likely that **13H** dissociates into the more reactive $\mathbf{13}^-$ in the presence of triethylamine (pK_a 10 75[52]) because its pK_a may be estimated to be 6 3—6 8 according to the method of pK_a prediction [52] The intermediate $\mathbf{13}^-$ exists as a very rapidly equilibrated mixture of the conformers $(\mathbf{13A})^-$, $(\mathbf{13B})^-$, and $(\mathbf{13C})^-$ According to the theory of stereoelectronic control,[53] the C–Cl bond in $(\mathbf{13A})^-$ or $(\mathbf{13B})^-$ is cleaved because there is a nonbonding electron pair oriented antiperiplanar to this bond other than that of the oxygen anion, resulting in the production of the oxalate ester **14** On the other hand, the C–C bond in $(\mathbf{13B})^-$ or $(\mathbf{13C})^-$ may be cleaved by the assistance of such electron pairs of the chlorine and the oxygen atoms The C–C bond cleavage of $(\mathbf{13B})^-$ or $(\mathbf{13C})^-$ followed by decarbonylation would give rise to the chlorocarbonate ester **15** and the alkoxide, recombination of these species produces the carbonate ester **16** The fact that monohydroxy compounds afford neither **15** nor **16** reveals that the energy barrier for the C–C bond cleavage of $(\mathbf{13B})^-$ or $(\mathbf{13C})^-$ is much higher than that for the C–Cl bond cleavage of $(\mathbf{13A})^-$ or $(\mathbf{13B})^-$ If $\mathbf{13}^-$ were restricted to the conformer $(\mathbf{13C})^-$, in which the C–Cl bond is not cleaved because there is no extra nonbonding electron pair oriented antiperiplanar to this bond, the carbonate ester **16** would be formed Such a restricted conformer may be possible for the cyclic intermediate in the reaction with an appropriately substituted diol



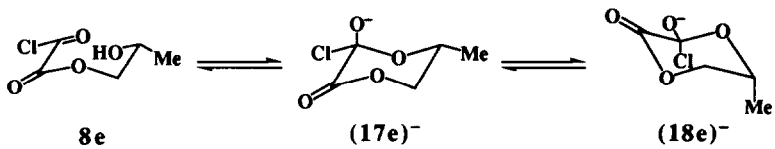
Scheme 3



For the formation of the cyclic oxalate **2d** and the cyclic carbonate **3d** from ethylene glycol (**1d**), the reaction of **8d** in the next step will be intramolecular nucleophilic addition When perpendicular attack (107° according to the literature[54]) of the hydroxy group on the acyl chloride moiety proceeds from the side of the plane of the conjugated carbonyl system so as to form the chair-like transition state, the tetrahedral intermediate **(17d)**$^-$, where the chlorine atom must be equatorially oriented because **8d** mainly exists as the *s*-trans conformer,[55] is produced The C–Cl bond in **(17d)**$^-$ is not cleaved because there is no extra nonbonding electron pair oriented antiperiplanar to this bond, whereas the C–C bond may be cleaved by the stereoelectronic assistance of the electron pairs (shown as shaded) The formation of **3d** may be interpreted as the result of the C–C bond cleavage in **(17d)**$^-$ followed by decarbonylation leading to the formation of **19d** Once **(17d)**$^-$ conformationally changes into **(18d)**$^-$, the C–Cl bond is cleaved to form **2d**, having the assistance of the electron pair of the oxygen (shown as shaded) The energy barrier for the breakdown of **(17d)**$^-$ is thought to be much higher than that of **(18d)**$^-$ as in the case of the decay of **13**$^-$ It follows that the formation of **3d** does not compete with the formation of **2d**, unless the rate of interconversion between **(17d)**$^-$ and **(18d)**$^-$ is retarded near the rate of breakdown of **(17d)**$^-$, or unless the equilibrium between these conformers is overwhelmingly favorable for **(17d)**$^-$ The tetrahedral intermediate **(18d)**$^-$, in which the electronegative chlorine atom is axially oriented, is probably more stable than **(17d)**$^-$ owing to the anomeric effect[56] Furthermore, **(17d)**$^-$ and **(18d)**$^-$ exist in a rapidly established equilibrium As a consequence, **2d** is produced predominantly, this compound would undergo polymerization under the reaction conditions



Scheme 4

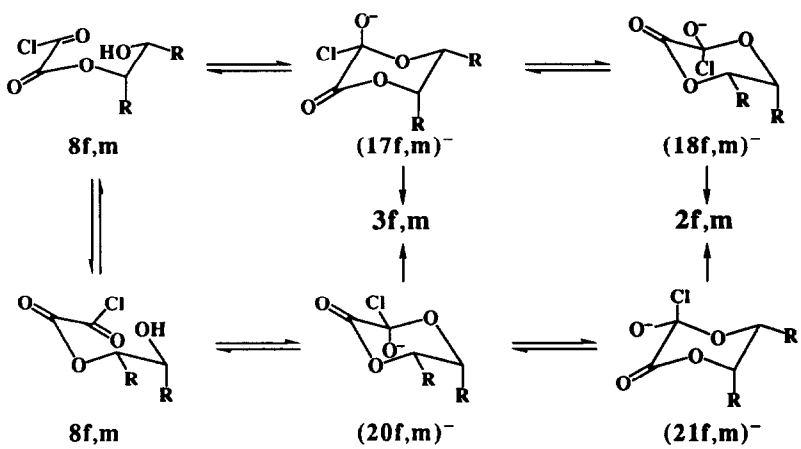


Scheme 5

In the reaction of the monosubstituted ethylene glycol **1e**, the first acylation will be dominant at the primary hydroxy group[57] to yield the intermediate **8e**, which provides the secondary intermediates **(17e)**$^-$ and **(18e)**$^-$ existing in a more slowly established equilibrium than that between **(17d)**$^-$ and **(18d)**$^-$ owing to steric hindrance of the methyl group Furthermore, there is a 1,3-diaxial interaction between the chlorine atom and the methyl group in **(18e)**$^-$ Probably, both factors are responsible for the higher yield of **3e** than that of **3d** The

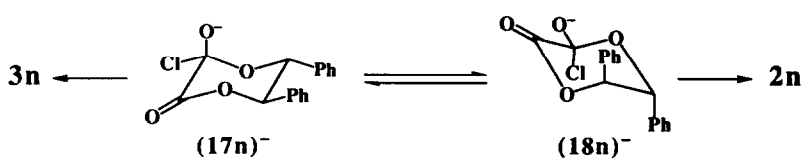
higher yields of other monosubstituted 1,3-dioxolan-2-ones **3j**—**l** than that of **3e** may be a reflection of these steric effects enhanced by the bulkier substituent

The tetrahedral intermediate from *erythro*-hydrobenzoin (**1m**) will prefer the structure $(\mathbf{17m})^-$ to the alternative $(\mathbf{20m})^-$ to avoid the 1,3-diaxial interaction The equilibrium constant for the conversion of $(\mathbf{17m})^-$ to $(\mathbf{18m})^-$ is greater than that of $(\mathbf{17j})^-$ to $(\mathbf{18j})^-$, because the additional phenyl group axially oriented in $(\mathbf{17m})^-$ becomes equatorial in $(\mathbf{18m})^-$ This is a factor increasing the yield of **2m** The equilibrium between $(\mathbf{17m})^-$ and $(\mathbf{18m})^-$ is, however, established more slowly, though fast enough to allow the preferential formation of **2m**, because two phenyl groups are *syn*-periplanar to each other in the transition state Consequently, the observed higher yield of **2j** (entry 11) than that of **2m** (entry 14) indicates that the latter factor overcomes the former. It should be noted that the formation of **3f** from *erythro*-1,2-butanediol (**1f**) was suppressed to an appreciable extent, as compared with those from two other *erythro*-compounds **1m,o** This may be due to the more rapidly established equilibrium between $(\mathbf{17f})^-$ and $(\mathbf{18f})^-$ owing to the smaller substituents The smaller substituents may also contribute to the formation of the less favorable intermediate $(\mathbf{20f})^-$ Once $(\mathbf{20f})^-$ is formed, even though to a slight extent, it will be smoothly converted into $(\mathbf{21f})^-$, the intermediate for the formation of **2f**, because there is the favorable anomeric effect and no 1,3-diaxial interaction in $(\mathbf{21f})^-$



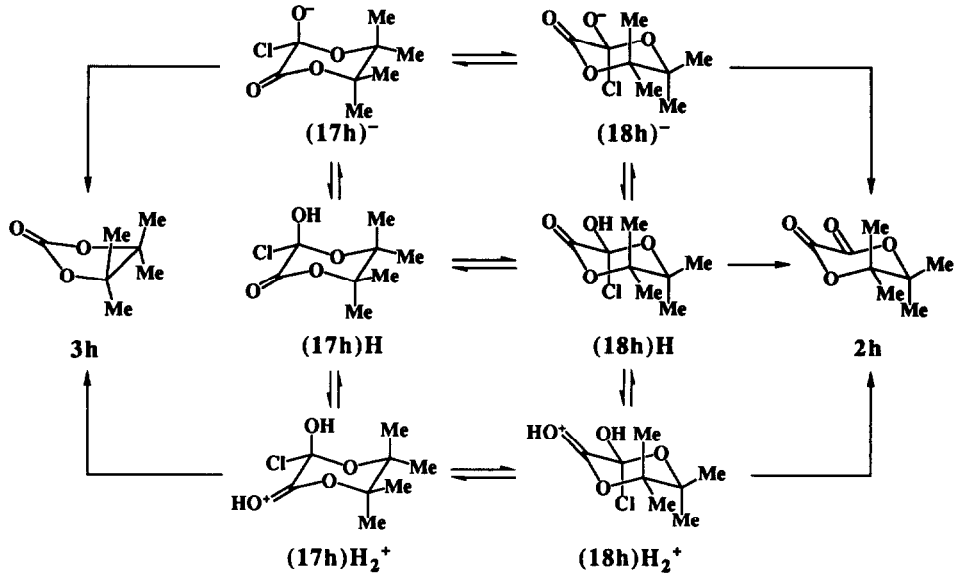
Scheme 6

The interconversion of $(\mathbf{17n})^-$ and $(\mathbf{18n})^-$, the intermediates from *threo*-hydrobenzoin (**1n**), takes place more rapidly than that of the *erythro*-isomers, because the two phenyl groups do not pass each other during the conversion It follows that the preferential formation of **3n** is a result of the equilibrium very unfavorable for $(\mathbf{18n})^-$ the two equatorial phenyl groups in $(\mathbf{17n})^-$ become axial in $(\mathbf{18n})^-$ The same explanation is valid for the order of the observed yield of **3** paralleling the order of size of the substituents of the *threo*-compounds **1g,i,n,p,q**



Scheme 7

An explanation for the preferential formation of **3h** from pinacol (**1h**) must be sought in an entirely different direction the result is ascribed to slow interconversion between $(17h)^-$ and $(18h)^-$ owing to their fully substituted structures, because there is little difference in free energy between them



Scheme 8

In the absence of base, the formation of **3h** may be interpreted by assuming acid-catalyzed cleavage of the tetrahedral intermediate [$(17h)H \rightarrow (17h)H_2^+ \rightarrow 3h$] Probably, the C–Cl bond of the tetrahedral intermediate **(18h)H** is cleaved even in the neutral form, whereas the energy barrier for the breakdown of the neutral conformer **(17h)H** is higher than that for the conformational change to **(18h)H** If this is the case, the reaction pattern may be changed to produce **2h** as the major product by using an appropriate base, which prevents the formation of either $(17h)^-$ or $(17h)H_2^+$ Results of the investigation along this line will be reported in a separate paper.

In conclusion, we have systematically explored the reactions of oxalyl chloride with 1,2-glycols **1** for the first time, disclosing that formation of a cyclic carbonate **3** in the presence of triethylamine appears to be a general reaction, and that 1,4-dioxane-2,3-diones **2** are common products despite a so far so limited number of known compounds with this ring system We have also proposed the reaction mechanism, which is consistent with the different reaction patterns observed with various types of acyclic 1,2-glycols **1** Recently, the formation of the cyclic carbonate from a cyclic 1,2-glycol by the action of oxalyl chloride was reported without a comment on the reaction mechanism [58] Work is now in progress to test further the present mechanism

EXPERIMENTAL

General Notes

All melting points were taken on a Yamato MP-1 or a Buchi 530 capillary melting point apparatus and are corrected. IR spectra and mass spectra were recorded on a JASCO A-202 or a Shimadzu FTIR-8100 IR spectrophotometer and a Hitachi M-80 mass spectrometer NMR spectra were measured with JEOL JNM-EX-270 and

JEOL JNM-GSX-500 NMR spectrometers with tetramethylsilane as an internal standard; unless otherwise stated, ^{1}H-NMR spectra were recorded at 270 MHz and ^{13}C-NMR spectra at 67.8 MHz. Microanalyses were conducted by Mr. Y Itatani and his associates at Kanazawa University Flash chromatography was performed on silica gel according to the reported procedure [59] The following abbreviations are used. br = broad, d = doublet, dd = doublet-of-doublets, ddd = doublet-of-doublets-of-doublets, ddq = doublet-of-doublets-of-quartets, dqq = doublet-of-quartets-of-quartets, ds = doublet-of-septets, m = multiplet, s = singlet, t = triplet. Magnesium sulfate was used for drying organic solutions, and they were concentrated under reduced pressure

4-(Dimethylamino)styrene (4f)

Compound **4f** (1 50 g, 68%) was prepared from methyltriphenylphosphonium iodide (**6d** X = I) (6 67 g, 16 5 mmol) and 4-(dimethylamino)benzaldehyde (**5b**) (2 24 g, 15 mmol), according to a procedure similar to that described below for the preparation of **7h**, followed by vacuum distillation, as a slightly yellow oil, $bp_{0\,2}$ 73—75 °C (lit [60] mp 15—16 °C), MS *m/z* 147 (M^+), ^{1}H-NMR ($CDCl_3$) δ 2.96 (6H, s, NMe_2), 5 02 (1H, dd, *J* = 1 and 10 9 Hz) and 5 57 (1H, dd, *J* = 1 and 17 5 Hz) (CH_2), 6 63 (1H, dd, *J* = 10 9 and 17.5 Hz, CH), 6 68 (2H, m, aromatic protons ortho to NMe_2), 7 31 (2H, m, aromatic protons meta to NMe_2)

4-Nitrostyrene (4g)

The Wittig reaction between **6d** (X = Br) (10 7 g, 30 mmol) and 4-nitrobenzaldehyde (**5c**) (4 53 g, 30 mmol) was carried out in a manner similar to that described below for the preparation of **7h** The reaction mixture was concentrated to a small volume, and the residue was partitioned between water and dichloromethane The aqueous layer was extracted with dichloromethane (2 × 50 ml) The organic layers were combined, dried, and concentrated The residual semisolid was extracted with a mixture of hexane–ethyl acetate (1 1, v/v) (80 ml) The extracts were concentrated, and the residue was purified by flash chromatography [hexane–ethyl acetate (7 1, v/v)] to afford **4g**[61] (4 23 g, 95%) as a brown oil, ^{1}H-NMR ($CDCl_3$) δ 5 50 (1H, d, *J* = 10 9 Hz) and 5 93 (1H, d, *J* = 17 5 Hz) (CH_2), 6 79 (1H, dd, *J* = 10 9 and 17 5 Hz, CH), 7.54 (2H, m, aromatic protons meta to NO_2), 8 19 (2H, m, aromatic protons ortho to NO_2)

(E)-3-Methyl-1-phenyl-1-butene (7h)

A 0 91 M solution of *n*-butyllithium in hexane (16 5 ml, 15 mmol) was added dropwise to a suspension of (2-methylpropyl)triphenylphosphonium iodide (**6e** X = I)[62] (6 69 g, 15 mmol) in dry THF (150 ml) under nitrogen at –78 °C over a period of 10 min After being allowed to warm to 0 °C with stirring, the mixture was again cooled to –78 °C, and then benzaldehyde (1 53 ml, 15 mmol) was added. The temperature of the mixture was allowed to rise to 0 °C, and stirring was continued for a further 1 h Water (100 ml) was added, and the mixture was extracted with benzene (150 ml and 2 × 75 ml) The organic layers were combined, dried, and concentrated The residue was extracted with hexane (20 ml) The solution was concentrated, and the residue was distilled to afford a 5 5 1 mixture of the (*Z*)-isomer **4h**[63] and **7h** as a colorless oil (1 92g, 88%), bp_{20} 80—86 °C A solution of the mixture (1 45 g) and phenyl disulfide[64] (433 mg) in THF (50 ml) was refluxed for 15 h under nitrogen and then for a further 22 h after addition of azobisisobutyronitrile (325 mg) The resulting mixture was concentrated *in vacuo*, and the residue was extracted with hexane (5 ml) Flash chromatography (hexane) of this solution afforded **7h**[63] (1 14 g, 69%) as a colorless oil, ^{1}H-NMR ($CDCl_3$) δ 1 09 (6H, d, *J* = 6 6 Hz, Me_2), 2 47 (1H, m, C*H*Me_2), 6 19 (1H, dd, *J* = 6 6 and 16 2 Hz, =C*H*CHMe_2), 6 34 (1H, d, *J* = 16 2 Hz, =C*H*Ph), 7 18—7 37 (5H, m, Ph)

(E)-1-[4-(Dimethylamino)phenyl]-3-methyl-1-butene (7i)

The Wittig reaction between **6e** (X = I)[62] (1 34 g, 3 mmol) and **5b** (448 mg, 3 mmol) was conducted in a manner similar to that described for the preparation of **7h** The resulting crude products were purified by flash chromatography [hexane–ethyl acetate (5 1, v/v)] instead of distillation to afford a 2 6 1 mixture of the (*Z*)-

isomer **4i** [^{1}H-NMR ($CDCl_3$) δ 1 05 (6H, d, J = 6 6 Hz, CMe_2), 2.95 (6H, s, overlapped with a 1H multiplet due to C*H*Me_2, NMe_2), 5.31 (1H, dd, J = 9 9 and 11 7 Hz, =C*H*CHMe_2), 6.20 (1H, d, J = 11 7 Hz, =C*H*Ar), 6 71 (2H, m, aromatic protons ortho to NMe_2), 7 19 (2H, m, aromatic protons meta to NMe_2)] and **7i** as a yellow oil (494 mg, 87%)

The whole of the mixture of **4i** and **7i**, and phenyl disulfide[64] (114 mg, 0 52 mmol) were dissolved in dry THF (20 ml) The solution was refluxed under nitrogen for 3 h. The resulting mixture was concentrated *in vacuo*, and the residue was purified by flash chromatography [hexane–chloroform (4:1, v/v) to afford **7i**[65] (441 mg, 78%) as a yellow oil, MS *m/z* 189 (M^+), ^{1}H-NMR ($CDCl_3$) δ. 1 07 (6H, d, J = 6.6 Hz, CMe_2), 2 43 (1H, m, C*H*Me_2), 2 93 (6H, s, NMe_2), 5 99 (1H, dd, J = 6 9 and 16 2 Hz, =C*H*CHMe_2), 6.25 (1H, d, J = 16 2 Hz, =C*H*Ar), 6 82 (2H, m, aromatic protons ortho to NMe_2), 7 24 (2H, m, aromatic protons meta to NMe_2)

(±)-1-[4-(Dimethylamino)phenyl]-1,2-ethanediol [(±)-1k]

This compound was prepared by treating **4f** (1 01 g, 6 86 mmol) with osmium tetroxide as described below for the preparation of (±)-**1p**, followed by flash chromatography [hexane–ethyl acetate (1 5, v/v)] yield 1 04 g (84%), mp 81—83 °C Recrystallization of crude (±)-**1k** from benzene afforded an analytical sample of (±)-**1k** as colorless pillars, mp 82 5—83 5 °C, MS *m/z* 181 (M^+), 500 MHz ^{1}H-NMR ($CDCl_3$) δ. 2 09 (1H, t, J = 5 5 Hz, CH_2OH), 2 35 (1H, br, CHO*H*), 2 94 (6H, s, NMe_2), 3 65—3 74 (2H, m, CH_2), 4 72 (1H, dd, J = 4 5 and 7 3 Hz, CH), 6 72 (2H, m, aromatic protons ortho to NMe_2), 7 23 (2H, m, aromatic protons meta to NMe_2) *Anal* Calcd for $C_{10}H_{15}NO_2$ C, 66 27, H, 8 34, N, 7 73 Found C, 66 20, H, 8.48, N, 7 68

(±)-1-(4-Nitrophenyl)-1,2-ethanediol [(±)-1l]

Compound **4g** (616 mg, 4 13 mmol) was treated with osmium tetroxide in a manner similar to that described below for the preparation of (±)-**1p** Crude products were washed successively with benzene and benzene–ethanol (10 1, v/v) to give (±)-**1l** (345 mg), mp 76 5—77 5 °C The mother liquor was concentrated to a small volume, and the residue was purified by flash chromatography [hexane–ethyl acetate (1 5, v/v)] to afford a second crop of (±)-**1l** (237 mg, the total yield was 77%), mp 73 5—78 °C Recrystallization of crude (±)-**1l** from benzene–ethanol (20 1, v/v) afforded slightly yellow needles, mp 77 5—79 °C (lit[66] mp 79—81 °C), ^{1}H-NMR ($CDCl_3$) δ 2 06 and 2 79 (1H each, br , two OH's), 3 64 (1H, dd, J = 7 9 and 11 2 Hz) and 3 85 (1H, dd, J = 3 3 and 11 2 Hz) (CH_2), 4 95 (1H, dd, J = 3 3 and 7 9 Hz, CH), 7 57 (2H, m, aromatic protons meta to NO_2), 8 23 (2H, m, aromatic protons ortho to NO_2)

(R*,S*)-3-Methyl-1-phenyl-1,2-butanediol [(±)-1o]

An experimental procedure similar to that described below for the preparation of (±)-**1p** was employed to oxidize a 5 5 1 mixture of **4h** and **7h** (1 92 g, 13 1 mmol) The crude products was recrystallized from hexane–benzene (2 1, v/v) to afford colorless pillars (1 50 g), mp 95—97 °C Fractional recrystallizations of this material from ethanol–water (1 2, v/v) afforded pure (±)-**1o** (the yield was 1 19 g, 44% based on **6e**) as colorless pillars, mp 102 5—104 °C (lit[67] mp 103 2—103 9 °C), 500 MHz ^{1}H-NMR ($CDCl_3$) δ 0 97 and 0 98 (3H each, d, J = 6 4 Hz, Me_2), 1 71 (1H, ds, J = 6 4 and 5 9 Hz, C*H*Me_2), 1 74 (1H, d, J = 3 7 Hz, OH), 2 33 (1H, J = 2 3 Hz, OH), 3 57 (1H, ddd, J = 3 7, 5 9, and 6 6 Hz, C*H*CHMe_2), 4 68 (1H, br, C*H*Ph), 7 30—7 41 (5H, m, Ph)

(R*,R*)-3-Methyl-1-phenyl-1,2-butanediol [(±)-1p]

A 2 3% (w/v) solution of osmium tetroxide in *tert*-butanol (1 ml, 0 09 mmol) was added to a solution of **7h** (1 04 g, 7 11 mmol) and *N*-methylmorpholine *N*-oxide monohydrate (1 15 g, 8 51 mmol) in a mixture of acetone (35 ml) and water (3 5 ml) After the resulting solution was stirred at room temperature for 3 5 h, sodium metabisulfite[68] (1 79 g, 9 4 mmol) was added, and the whole was stirred for a further 20 min The mixture was extracted with dichloromethane (3 × 50 ml) after water (50 ml) was added The extracts were dried

and concentrated The residue was washed with hexane (25 ml) to afford (±)-**1p** (1 03 g) as a colorless solid, mp 75 5—76 5 °C The washings were concentrated, and the residue was recrystallized from hexane to afford a second crop of (±)-**1p** (61 mg, the total yield was 85%), mp 72 5—75 5 °C. Recrystallization of crude (±)-**1p** from hexane afforded an analytical sample of (±)-**1p** as colorless needles, mp 75 5—77 °C (lit [67] mp 73 6—74 2 °C), MS *m/z* 180 (M^+), 500 MHz ^{1}H-NMR ($CDCl_3$) δ 0 95 and 0 96 (3H each, d, *J* = 6 8 Hz, CMe_2), 1 61 (1H, ds, *J* = 4 5 and 6 8 Hz, C*H*Me_2), 2 26 and 2 67 (1H each, br, two OH's), 3 49 (1H, dd, *J* = 4 5 and 6 4 Hz, C*H*CHMe_2), 4 64 (1H, d, *J* = 6 4 Hz, C*H*Ph), 7 35 (5H, m, Ph) *Anal* Calcd for $C_{11}H_{16}O_2$ C, 73 30, H, 8 95 Found C, 73 00, H, 9 09

(R*,R*)-3-Methyl-1-[4-(dimethylamino)phenyl]-1,2-butanediol [(±)-1q]

Compound (±)-**1q** (361 mg, 64%), mp 76—80 °C, was prepared from **7i** (480 mg, 2 54 mmol) according to a procedure similar to that described for the oxidation of **7h**, followed by flash chromatography [hexane–ethyl acetate (1 1, v/v)] Recrystallization of crude (±)-**1q** from hexane–ethanol (10 1, v/v) afforded an analytical sample of (±)-**1q** as colorless needles, mp 79—81 °C, MS *m/z* 223 (M^+), 500 MHz ^{1}H-NMR ($CDCl_3$) δ 0 92 and 0 95 (3H each, d, *J* = 6 9 Hz, CMe_2), 1 58 (1H, dqq, *J* = 6 9, 6 9, and 3 7 Hz, C*H*Me_2), 2 32 and 2 35 (1H each, br s, two OH's), 2 95 (6H, s, NMe_2), 3 52 (1H, br dd, *J* = 3 7 and 7 3 Hz, C*H*CHMe_2), 4 53 (1H, d, *J* = 7 3 Hz, C*H*Ar), 6 72 (2H, m, aromatic protons ortho to NMe_2), 7 22 (2H, m, aromatic protons meta to NMe_2) *Anal* Calcd for $C_{13}H_{21}NO_2$ C, 69 92, H, 9 48, N, 6 27 Found C, 69 86, H, 9 51, N, 6 28

Preparation of the Cyclic Carbonates 3 of 1,2-Glycols 1 by the Reaction with Phosgene

The procedure for the preparation of (±)-**3p** using a phosgene solution in toluene was described in detail as a typical example Unless otherwise stated, the other compounds were obtained in a similar manner

cis-4,5-Dimethyl-1,3-dioxolan-2-one (3f)

A 2 M solution of phosgene (1 5 ml, 3 mmol) was added to a cold solution of **1f** (180 mg, 2 mmol) and pyridine (1 ml, 12 mmol) in toluene (20 ml), and the mixture was stirred at 0 °C for 15 min The whole was washed successively with water (10 ml), 5% aqueous citric acid (10 ml), and saturated aqueous sodium bicarbonate (10 ml), dried, and concentrated to leave **3f**[69] (71 mg) as a colorless oil The washings were combined, brought to pH 4 by addition of 10% hydrochloric acid, saturated with sodium chloride, and then extracted with ether (3 × 20 ml) The extracts were dried and concentrated The resulting residue was purified by flash chromatography (dichloromethane) to afford a second crop of **3f** (105 mg, the total yield was 76%), MS *m/z* 116 (M^+), 117 (M^+ + 1), IR $\nu_{max}^{liquid\ film}$ cm^{-1} 1799 (C=O), ^{1}H-NMR ($CDCl_3$) δ 1 37 (6H, m, two Me's), 4 85 (2H, m, two CH's), ^{13}C-NMR ($CDCl_3$) δ 14 6 (Me), 76 3 (CH), 154 9 (C=O)

(±)-trans-4,5-Dimethyl-1,3-dioxolan-2-one [(±)-3g]

This compound was obtained from (±)-**1g** (180 mg, 2 mmol) in 79% yield in a manner similar to that described for the preparation of **3f** Recrystallization of the crude product from hexane–ether (3 1, v/v) afforded (±)-**3g** as colorless prisms, mp 36 5—38 °C (lit [70] mp 37 °C), MS *m/z* 116 (M^+), 117 (M^+ + 1), IR ν_{max}^{Nujol} cm^{-1} 1779 (C=O), 500 MHz ^{1}H-NMR ($CDCl_3$) δ 1 46 (6H, m, two Me's), 4 34 (2H, m, two CH's), ^{13}C-NMR ($CDCl_3$) δ 18 3 (Me), 79 8 (CH), 154 4 (C=O)

(±)-4-Phenyl-1,3-dioxolan-2-one [(±)-3j]

Compound (±)-**3j** (47 mg, 57%) was prepared from (±)-**1j** (69 mg, 0 5 mmol) by the reaction in THF (12 ml) at 0 °C for 1 h under nitrogen, followed by flash chromatography [hexane–ethyl acetate (3 2, v/v)]· a colorless oil, which crystallized on storage, mp 54—55 °C [recrystallized from ether–pentane (1 1, v/v)] (lit [71] mp 55 7—56 7 °C), MS *m/z* 164 (M^+), IR ν_{max}^{Nujol} cm^{-1} 1771 and 1778 (C=O), ^{1}H-NMR ($CDCl_3$) δ 4 35 (1H, dd, *J* = 7 9 and 8 6 Hz) and 4 80 (1H, dd, *J* = 8 2 and 8 6 Hz) (CH_2), 5 68 (1H, dd, *J* = 7 9 and 8 2 Hz,

C*H*Ph), 7 31—7 51 (5H, m, Ph), ^{13}C-NMR ($CDCl_3$) δ 71 1 (CH_2), 78 0 (*C*Ph), 125 8, 129 2, 129 7, and 135 8 (Ph), 154 8 (C=O)

(±)-4-[(Dimethylamino)phenyl]-1,3-dioxolan-2-one [(±)-3k]

The reaction of (±)-**1k** (363 mg, 2 mmol) using a 2 M solution of phosgene (1 1 ml, 2 2 mmol) was carried out in toluene (40 ml) in the presence of triethylamine (1.4 ml, 10 mmol) at 0 °C for 1 h The resulting suspension was washed with water, dried, and concentrated The residue was purified by flash chromatography [hexane–ethyl acetate (3 2, v/v)] to afford (±)-**3k** (288 mg, 69%) as a yellow solid, mp 116—118 °C Recrystallization of crude (±)-**3k** from ether–dichloromethane (10 1, v/v) afforded an analytical sample of (±)-**3k** as colorless pillars, mp 120—121 °C, MS *m/z*: 207 (M^+), IR ν_{max}^{Nujol} cm^{-1} 1779 (C=O), 500 MHz ^{1}H-NMR ($CDCl_3$) δ 2 98 (6H, s, NMe_2), 4 37 and 4 70 (1H each, dd, J = 8 3 Hz each, CH_2), 5 57 (1H, dd, J = 8 3 Hz each, CH), 6.72 (2H, m, aromatic protons ortho to NMe_2), 7 23 (2H, m, aromatic protons meta to NMe_2), ^{13}C-NMR ($CDCl_3$) δ 40 3 (Me), 70 9 (CH_2), 79 0 (CH), 112 2, 121 8, 127 9, and 151 4 (Ar), 155 1 (C=O) *Anal* Calcd for $C_{11}H_{13}NO_3$ C, 63 76, H, 6 32, N, 6 76 Found C, 63 73, H, 6 32, N, 6 99

(±)-4-(4-Nitrophenyl)-1,3-dioxolan-2-one [(±)-3l]

A 1 M solution of phosgene (0 88 ml, 0 88 mmol) was added dropwise to an ice-cooled solution of (±)-**1l** (147 mg, 0 803 mmol) and triethylamine (0 25 ml, 1 8 mmol) in THF (15 ml) over a period of 5 min under nitrogen Then the mixture was stirred at room temperature for 2 h The resulting precipitate was removed by filtration and washed with THF (10 ml) The filtrate and the washings were combined and concentrated. The residue was dissolved in dichloromethane (15 ml), and the solution was washed successively with 5% hydrochloric acid (5 ml) and saturated aqueous sodium bicarbonate (5 ml), dried, and concentrated to leave a yellow solid, mp 89—90 5 °C This was purified by flash chromatography [hexane–ethyl acetate (2 3, v/v)] to afford (±)-**3l** (103 mg, 61%), mp 98 5—101 °C Recrystallization of crude (±)-**3l** from ethanol afforded colorless prisms, mp 101—101 5 °C (melted at *ca* 90 °C and resolidified), MS *m/z* 209 (M^+), IR ν_{max}^{Nujol} cm^{-1} 1798 and 1823 (C=O), 500 MHz ^{1}H-NMR ($CDCl_3$) δ 4 32 (1H, dd, J = 7 3 and 8 8 Hz) and 4 90 (1H, dd, J = 8 3 and 8 8 Hz) (CH_2), 5 80 (1H, dd, J = 7 3 and 8 3 Hz, CH), 7 57 (2H, m, aromatic protons meta to NO_2), 8.33 (2H, m, aromatic protons ortho to NO_2), ^{13}C-NMR ($CDCl_3$) δ 70 6 (CH_2), 76 4 (CH), 124 5, 126 5, 142 7, and 148 6 (Ar), 154 0 (C =O) *Anal* Calcd for $C_9H_7NO_5$ C, 51 68, H, 3 37, N, 6 70 Found C, 51 74, H, 3 43, N, 6 69

(±)-cis-4-Isopropyl-5-phenyl-1,3-dioxolan-2-one [(±)-3o]

This compound (135 mg, 66%) was obtained from (±)-**1o** (180 mg, 1 mmol) as colorless prisms, mp 65 5—66 5 °C [recrystallized from hexane–ether (1 1, v/v)], MS *m/z* 206 (M^+), IR ν_{max}^{Nujol} cm^{-1} 1797 (C=O), 500 MHz ^{1}H-NMR ($CDCl_3$) δ 0 68 (3H, d, J = 6 9 Hz) and 0 98 (3H, d, J = 6 4 Hz) (Me_2), 1 63 (1H, dqq, J = 6 4, 6 9, and 9 2 Hz, C*H*Me_2), 4 54 (1H, dd, J = 9 2 and 7 3 Hz, C*H*CHMe_2), 5 63 (1H, d, J = 7 3 Hz, C*H*Ph), 7 30—7 42 (5H, m, Ph), ^{13}C-NMR ($CDCl_3$) δ 17 8 and 18 6 (Me_2), 28 2 (*C*HMe_2), 81 2 (*C*HPh), 86 1 (*C*HCHMe_2), 127 1, 128 7, 129 5, and 133 5 (Ph), 154 9 (C=O) *Anal* Calcd for $C_{12}H_{14}O_3$ C, 69 89, H, 6 84 Found C, 69 98, H, 6 87

(±)-trans-4-Isopropyl-5-phenyl-1,3-dioxolan-2-one [(±)-3p]

A 2 M solution of phosgene (0 55 ml, 1 1 mmol) was diluted with THF (4 ml), and added dropwise to an ice-cooled solution of (±)-**1p** (180 mg, 1 mmol) and triethylamine (0 63 ml, 4 5 mmol) in THF (20 ml) over a period of 5 min Then the mixture was stirred at 0 °C for 15 min The resulting precipitate was removed by filtration and washed with THF (20 ml) The filtrate and the washings were combined and concentrated The residue was dissolved in dichloromethane (15 ml), and the solution was washed successively with 5% aqueous citric acid (5 ml) and saturated aqueous sodium bicarbonate (5 ml), dried, and concentrated to leave a yellow oil

This was purified by flash chromatography [hexane–ethyl acetate (4.1, v/v)] to afford (±)-**3p** (164 mg, 80%) as a colorless oil, MS *m/z*: 206 (M^+), IR $\nu_{max}^{liquid\ film}$ cm^{-1}. 1803 (C=O), ^{1}H-NMR ($CDCl_3$) δ. 1.00 (3H, d, *J* = 6 6 Hz) and 1 08 (3H, d, *J* = 6 9 Hz) (Me_2), 2 06 (1H, dqq, *J* = 6.6, 6 9, and 6 3 Hz, C*H*Me_2), 4.34 (1H, dd, *J* = 6 3 Hz each, C*H*CHMe_2), 5 28 (1H, d, *J* = 6 3 Hz, C*H*Ph), 7.33—7 44 (5H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ 17 0 and 17 5 (two Me's), 31 6 (*C*HMe_2), 81 0 (*C*HPh), 88 3 (*C*HCHMe_2), 126 2, 129 2, 129.6, and 136 8 (Ph), 154 5 (C=O)

(±)-trans-4-[(Dimethylamino)phenyl]-5-isopropyl-1,3-dioxolan-2-one [(±)-3q]

Compound (±)-**1q** (56 mg, 0 25 mmol) was treated with a 1 M solution of phosgene (1 38 ml, 1 38 mmol) in THF (6 ml) in the presence of triethylamine (0 6 ml, 4 3 mmol) at room temperature for 22 5 h The resulting precipitate was removed by filtration and washed with THF (40 ml) The filtrate and the washings were combined and concentrated The residue was dissolved in dichloromethane (15 ml), and the solution was washed with water (2 × 10 ml), dried, and concentrated to leave a yellow oil This was purified by flash chromatography [hexane–ethyl acetate (3 1, v/v)] The faster moving substance was collected, and further purified by layer chromatography on silica gel [hexane–ethyl acetate (5 1, v/v)] to afford 1-[4-(dimethylamino)-phenyl]-3-methyl-2-butanone (16 mg, 31%) as a slightly yellow oil, MS *m/z* 205 (M^+), IR $\nu_{max}^{liquid\ film}$ cm^{-1} 1709 (C=O), ^{1}H-NMR ($CDCl_3$) δ 1 07 (6H, d, *J* = 6 9 Hz, CMe_2), 2 73 (1H, septet, *J* = 6 9 Hz, C*H*Me_2), 2 93 (6H, s, NMe_2), 3 63 (2H, s, CH_2), 6 70 (2H, m, aromatic protons ortho to NMe_2), 7 06 (2H, m, aromatic protons meta to NMe_2)

Further elution of the column afforded a yellow oil (6 mg) Although the ^{1}H-NMR spectrum of the main component of this material was identical with that of (±)-**3q**, which was obtained by the reaction of (±)-**1q** and oxalyl chloride, purification of this compound was unsuccessful

Reactions of 1,2-Glycols 1 with Oxalyl Chloride in the Presence of Triethylamine

Every reaction was carried out using 0.1 molar excess of oxalyl chloride and results were summarized in Table 1 Some representative reactions are described below in detail, the others were performed similarly under the conditions specified in Table 1

Reaction of 1d

A solution of oxalyl chloride (1 41 ml, 16 5 mmol) in THF (15 ml) was added dropwise to an ice-cooled solution of **1d** (931 mg, 15 mmol) and triethylamine (6 3 ml, 45 mmol) in dry THF (60 ml) over a period of 10 min The resulting mixture was stirred at 0 °C for 5 min The precipitate that separated was collected by filtration, washed with water (200 ml), and dried to give the oxalate polymers (805 mg) as a yellow solid, mp 180—185 °C (dec) (softened at 150 °C) The filtrate and the washings were combined and concentrated *in vacuo* The residue was washed with chloroform (15 ml) to afford a second crop of the polymers (617 mg), mp 184—190 °C (dec) (softened at 150 °C) A further crop of the polymers (136 mg), mp 165 °C (dec) (softened at 135 °C), was obtained from the mother liquor by concentration and washing with chloroform (3 ml) The mother liquor was concentrated, and the residue was purified by flash chromatography [hexane–ethyl acetate (1 2, v/v)] to afford crude **3d** (25 mg, 1 9%) as a yellowish oil Recrystallization of crude **3d** from ether afforded colorless prisms (12 mg, 0 9%), mp 34 5—35 5 °C, whose chromatographic behavior and IR, ^{1}H-NMR, and ^{13}C-NMR spectra were identical with those of an authentic sample[72] prepared from **1d** and phosgene

Crude oxalate polymers were combined, and pyrolysis of these compounds was performed by Kugelrohr distillation at 0 5—0 9 mmHg and 200—300 °C for 10 5 h 1,4-Dioxane-2,3-dione (**2d**) (1.26 g, 72%) was obtained as a distillate, mp 134—135 5 °C (softened below this temperature) (lit[32i] mp 138—140 °C); ν_{max}^{Nujol} cm^{-1} 1760 (C=O), ^{1}H-NMR ($CDCl_3$) δ 4 67 (s, CH_2)

Reaction of (±)-1e

The reaction mixture obtained from (±)-**1e** (1 52 g, 20 mmol) was filtered, and the filter cake was washed with THF (100 ml). The filtrate and the washings were combined and concentrated *in vacuo* to leave an orange oil (3 30 g) A portion (2 1 g) of this material was submitted to pyrolysis in a manner similar to that described for the preparation of **2d** The distillate obtained below 135 °C at 1 mmHg was an equimolar mixture (109 mg) of (±)-**2e** and (±)-**3e** (±)-5-Methyl-1,4-dioxane-2,3-dione [(±)-**2e**] (1 09 g, 66%) was obtained at 170—300 °C as a slightly yellow oil (lit.[49] mp 142 °C), MS *m/z* 131 ($M^+ + 1$), IR $\nu_{max}^{liquid\ film}$ cm^{-1} 1780 (C=O), ^{1}H-NMR ($CDCl_3$) δ 1 51 (3H, d, J = 6 6 Hz, Me), 4 46 (1H, dd, J = 8 6 and 12 9 Hz) and 4 55 (1H, dd, J = 3 0 and 12 9 Hz) (CH_2), 4 98 (1H, ddq, J = 6 6, 8 6, and 3 0 Hz, CH), ^{13}C-NMR ($CDCl_3$) δ 15 9 (Me), 70 7 (CH_2), 74 1 (CH), 152 9 (C=O)

The rest (1 2 g) of the raw material was purified by flash chromatography [hexane–ethyl acetate (1.1, v/v) to afford (±)-**3e** (44 mg, 5 9%) as a colorless oil, whose IR, ^{1}H-NMR, and ^{13}C-NMR spectra were identical with those of an authentic sample[72] obtained by the reaction of **1e** and phosgene

Reaction of 1f

The reaction mixture obtained from **1f** (318 mg, 3 53 mmol) was filtered, and the solid was washed with THF (40 ml) The filtrate and the washings were combined and concentrated *in vacuo* to leave a partially crystallized oily residue The ^{1}H-NMR spectrum of this sample showed about 20% of **1f** remained unreacted Kugelrohr distillation of this residue at 0 2—0 8 mmHg and 100—150 °C afforded an oily distillate (56 mg) and a sublimate (336 mg), mp 67—71 °C The sublimate was extracted with boiling ether (40 ml). The extracts were concentrated to afford *cis*-5,6-dimethyl-1,4-dioxane-2,3-dione (**2f**) (319 mg, 63%), mp 77—79 5 °C Recrystallization of crude **2f** from carbon tetrachloride afforded an analytical sample of **2f** as colorless scales, mp 79 5—80 5 °C (lit[50] mp 78 4—80 4 °C), MS *m/z* 145 ($M^+ + 1$), IR ν_{max}^{Nujol} cm^{-1}. 1779, 1771, and 1759 (C=O), 500 MHz ^{1}H-NMR ($CDCl_3$) δ 1 48 (6H, d, J = 6 8 Hz, two Me's), 4 87 (2H, m, two CH's), ^{13}C-NMR ($CDCl_3$) δ 15 0 (Me), 76 9 (CH), 153 2 (C=O) *Anal* Calcd for $C_6H_8O_4$: C, 50 00, H, 5 59 Found C, 49 84, H, 5 51

Repeated flash chromatography [hexane–ethyl acetate (1 1, v/v) and then with hexane–ether (2 5, v/v)] of the oily distillate afforded **3f** (15 mg, 3 7%) as a colorless oil, identical (IR and NMR) with an authentic sample

Reaction of (±)-1g

The reaction mixture obtained from (±)-**1g** (180 mg, 2 mmol) was filtered, and the solid residue was washed with THF (40 ml) The filtrate and the washings were combined and concentrated to afford a mixture of (±)-**1g** (ca 25%), (±)-**2g**,[73] (±)-**3g**, and the polymers. This was submitted to flash chromatography (dichloromethane) to afford (±)-**3g** (81 mg, 35%), mp 34—36 °C This sample was identical with an authentic sample

Reaction of 1h

The reaction mixture obtained from **1h** (1 18 g, 10 mmol) was filtered off, and the solid was washed with THF (100 ml) The filtrate and the washings were combined and concentrated *in vacuo* The residue was dissolved in dichloromethane (120 ml), and the solution was washed successively with water (40 ml) and saturated aqueous sodium bicarbonate (30 ml), dried, and concentrated The residue was then purified by flash chromatography [hexane–ethyl acetate (2 1, v/v)] 4,4,5,5-Tetramethyl-1,3-dioxolan-2-one (**3h**) (346 mg, 24%), mp 173—179 °C, was obtained as the faster moving component From the fractions containing the slower moving component, 5,5,6,6-tetramethyl-1,4-dioxane-2,3-dione (**2h**) (14 mg, 0 8%), mp 108—110 5 °C, was obtained after recrystallization from ether Further elution of the column afforded **1h** (119 mg, 10%)

Recrystallization of crude **3h** from ethanol followed by sublimation at 0 5 mmHg and 80 °C afforded an analytical sample of **3h** as colorless prisms, mp 178—179 °C (lit[1] mp 176—177 °C), MS *m/z* 145 ($M^+ + 1$),

IR ν_{max}^{Nujol} cm^{-1} 1779 (C=O), ^{1}H-NMR ($CDCl_3$) δ 1 41 (s, Me), ^{13}C-NMR ($CDCl_3$) δ· 22 3 (Me), 85.9(*C*Me$_2$), 153 9 (C=O) *Anal* Calcd for $C_7H_{12}O_3$ C, 58 32, H, 8 39 Found C, 58 05; H, 8 59.

An analytical sample of **2h** was obtained by recrystallization of crude **2h** from ether as colorless prisms, mp 110 5—111 5 °C, MS *m/z* 173 (M^+ + 1), IR ν_{max}^{Nujol} cm^{-1} 1774, 1763, and 1751 (C=O), ^{1}H-NMR ($CDCl_3$) δ 1 54 (s, Me), ^{13}C-NMR ($CDCl_3$) δ 23 7 (Me), 85 6 (*C*Me$_2$), 153 3 (C=O) *Anal* Calcd for $C_8H_{12}O_4$· C, 55 81, H, 7 02 Found C, 55 81, H, 7 05

The carbonate **3h** was not formed when the oxalate **2h** was treated with oxalyl chloride in the presence of triethylamine and its hydrochloride in THF at room temperature for 5 d.

Reaction of (±)-1i

According to the reported procedure,[46i] the reaction of (±)-**1i** (496 mg, 2 mmol) and oxalyl chloride (0 18 ml, 2 1 mmol) was conducted in dry dichloromethane The resulting solution was concentrated to a small volume, and the residue was washed with ethyl acetate (50 ml) The washings were concentrated *in vacuo* to afford a mixture of (±)-*trans*-4,5-bis(bromomethyl)-1,3-dioxolan-2-one [(±)-**3i**], (±)-*trans*-5,6-bis(bromomethyl)-1,4-dioxane-2,3-dione [(±)-**2i**] [^{1}H-NMR ($CDCl_3$) δ, 5 07 (m, CH)], and the polymers [^{1}H-NMR ($CDCl_3$) δ, 5 30—5 70 (m, CH's)] Flash chromatography (dichloromethane) of the residue afforded (±)-**3i** (316 mg, 58%) as a slightly yellow solid, mp 74—75 °C Recrystallization of crude (±)-**3i** from ether afforded an analytical sample of (±)-**3i** as colorless prisms, mp 74 5—75 °C [lit [46i] mp 76—77 °C for the product thought to be (±)-**2i**], MS *m/z* 272, 274, and 276 (M^+), IR ν_{max}^{Nujol} cm^{-1}· 1787 and 1799 (C=O), 500 MHz ^{1}H-NMR ($CDCl_3$) δ 3 63 (4H, m, two CH_2's), 4 77 (2H, m, two CH's), 500 MHz ^{1}H-NMR (CD_2Cl_2) δ 3 58—3 73 (4H, m, two CH_2's), 4 77 (2H, m, two CH's), ^{13}C-NMR ($CDCl_3$) δ 31 3 (CH_2), 77 6 (CH), 152 9 (C=O) *Anal* Calcd for $C_5H_6Br_2O_3$ C, 21 93, H, 2 21 Found C, 22 01, H, 2 17

Reaction of (±)-1j

From the reaction mixture obtained from (±)-**1j** (1 11 g, 8 03 mmol), the precipitate was removed by filtration and washed with THF (50 ml) The filtrate and the washings were combined and concentrated to a small volume The oily residue was crystallized by treating it with a small volume of benzene The solid was collected by filtration and washed with benzene to afford (±)-5-phenyl-1,4-dioxane-2,3-dione [(±)-**2j**] (569 mg, 37%), mp 120—124 °C The filtrate and the washings were combined and concentrated The residue was dissolved in dichloromethane (20 ml), and the solution was washed successively with water (5 ml) and saturated aqueous sodium bicarbonate (5 ml), dried, and concentrated The oily residue was purified by flash chromatography [hexane–ethyl acetate (3 2, v/v)] to afford (±)-**3j** (182 mg, 14%) as a colorless oil, identical (IR) with an authentic sample

Recrystallization of crude (±)-**2j** from benzene afforded an analytical sample of (±)-**2j** as colorless prisms, mp 124—125 °C, MS *m/z* 192 (M^+), IR ν_{max}^{Nujol} cm^{-1} 1758 and 1780 (C=O), ^{1}H-NMR ($CDCl_3$) δ 4 64 (1H, dd, *J* = 3 3 and 12 9 Hz) and 4 71 (1H, dd, *J* = 9 2 and 12 9 Hz) (CH_2), 5 86 (1H, dd, *J* = 3 3 and 9 2 Hz, C*H*Ph), 7 46 (5H, m, Ph), ^{13}C-NMR ($CDCl_3$) δ 70 8 (CH_2), 78 8 (*C*HPh), 126 3, 129 3, 130 2, and 131 3 (Ph), 152 7 and 152 8 (two C=O's) *Anal* Calcd for $C_{10}H_8O_4$ C, 62 50, H, 4 20 Found C, 62 52, H, 4 20

The oxalate (±)-**2j** did not change into the carbonate (±)-**3j** on treatment in THF at room temperature in the presence of triethylamine for 18 h, or in the presence of triethylamine and its hydrochloride for 30 h After storage at room temperature for one year, (±)-**2j** polymerized to a considerable extent

Reaction of (±)-1k

The precipitate, that separated from the reaction mixture obtained from (±)-**1k** (37 mg, 0 2 mmol), was removed by filtration and washed with THF (20 ml) The filtrate and the washings were combined and concentrated *in vacuo* to afford a tarry residue, which contained (±)-5-[4-(dimethylamino)phenyl]-1,4-dioxane-2,3-dione [(±)-**2k**] [^{1}H-NMR ($CDCl_3$) δ 4 56 (dd, *J* = 3 and 12 9 Hz) and 4 71 (dd, *J* = 9 9 and 12 9 Hz)

(CH_2), 5.72 (dd, J = 3 and 9.9 Hz, CH)], (±)-**3k**, and the polymers [^{1}H-NMR ($CDCl_3$) δ· 4.5—4 7 (m, CH_2's), 6 17 (m, CH's)]. Purification of these compounds was unsuccessful

Reaction of (±)-1l

The precipitate, that separated from the reaction mixture obtained from (±)-**1l** (46 mg, 0.25 mmol), was removed by filtration and washed with THF (15 ml) The filtrate and the washings were combined and concentrated *in vacuo*. The residue contained 5-(4-nitrophenyl)-1,4-dioxane-2,3-dione [(±)-**2l**], [^{1}H-NMR ($CDCl_3$) δ 4.70 (dd, J = 8 3 and 13 0) and 4.72 (dd, J = 4.4 and 13 0 Hz) (CH_2), 6 00 (dd, J = 4 4 and 8 3 Hz, CH), 7 67 (m) and 8.35 (m) (Ar)], (±)-**3l**, and the polymers [^{1}H-NMR ($CDCl_3$) δ· 4.5—4 9 (br, CH_2's), 6 32 (br, CH's)]. It was dissolved in dichloromethane (10 ml), and the solution was washed successively with 5% aqueous citric acid (3 ml) and saturated aqueous sodium bicarbonate (3 ml), dried, and concentrated. The mixture was purified by layer chromatography on silica gel [hexane–ethyl acetate (3 2, v/v)] to afford (±)-**3l** (9 mg, 17%) as a colorless solid, mp 99—101 °C, identical (IR) with an authentic sample

Reaction of 1m

Compound **1m** (107 mg, 0 5 mmol) was treated in the same way as described below for the reaction of (±)-**1n** to give a mixture of *cis*-5,6-diphenyl-1,4-dioxane-2,3-dione (**2m**) [^{1}H-NMR ($CDCl_3$) δ 6 00 (2H, s, two CH's), 6 95 (4H) and 7 2—7 4 (6H) (m each, two Ph's); ^{13}C-NMR ($CDCl_3$) δ 81 9 (CH), 126 7, 128 5, 129 5, and 130 7 (Ph), 153 2 (C=O)] and **3m** The mixture was submitted to flash chromatography [hexane–ethyl acetate (3.2, v/v)] to afford **3m** (35 mg, 29%) as a colorless solid, 123—125 5 °C Recrystallization of this product from ethanol afforded an analytical sample of *cis*-4,5-diphenyl-1,3-dioxolan-2-one (**3m**) as colorless prisms, mp 125 5—126 5 °C, (lit [74] mp 126—127 °C), MS *m/z* 240 (M^+), IR ν_{max}^{Nujol} cm^{-1} 1788 (C=O), ^{1}H-NMR ($CDCl_3$) δ 5 98 (2H, s, two CH's), 6 88—6 98 (4H) and 7 08—7 20 (6H), (m each, two Ph's), ^{13}C-NMR ($CDCl_3$) δ 82 1 (CH), 126 1, 128 2, 128 8, and 132 8 (Ph), 154 9 (C=O) *Anal* Calcd for $C_{15}H_{12}O_3$ C, 74 99, H, 5 03 Found C, 74.71, H, 5 06

Prolonged reaction (at 0 °C for 15 h) did not increase the yield of **3m**

Reaction of (±)-1n

Triethylamine hydrochloride was removed by filtration from the reaction mixture, obtained from (±)-**1n** (107 mg, 0 5 mmol), and washed with THF (20 ml) The filtrate and the washings were combined and concentrated *in vacuo*. The residue was dissolved in dichloromethane (10 ml), and the solution was washed successively with water (3 ml) and saturated aqueous sodium bicarbonate (3 ml), dried, and concentrated. The resulting mixture of (±)-**2n**[73] and (±)-**3n** was purified by flash chromatography [hexane–ethyl acetate (3 1, v/v)] to afford (±)-**3n** (70 mg, 58%) as a colorless solid, mp 109.5—110 °C (softened below this temperature) Recrystallization of this product from ethanol afforded an analytical sample of (±)-*trans*-4,5-diphenyl-1,3-dioxolan-2-one [(±)-**3n**] as colorless prisms with unchanged melting point, (lit [74] mp 110—111 °C), MS *m/z* 240 (M^+), IR ν_{max}^{Nujol} cm^{-1} 1817 (C=O), ^{1}H-NMR ($CDCl_3$) δ 5 43 (2H, s, two CH's), 7.33 (4H) and 7 44 (6H), (m each, two Ph's), ^{13}C-NMR ($CDCl_3$) δ 85 4 (CH), 126 1, 129 2, 129 8, and 134 8 (Ph), 154 1 (C=O) *Anal*. Calcd for $C_{15}H_{12}O_3$ C, 74 99, H, 5 03 Found C, 75 07, H, 5 13

Reaction of (±)-1o

Compound (±)-**1o** (180 mg, 1 mmol) was treated with oxalyl chloride in the same way as described for the reaction with (±)-**1p** to give a mixture of (±)-*cis*-5-isopropyl-6-phenyl-1,4-dioxane-2,3-dione [(±)-**2o**], [^{1}H-NMR ($CDCl_3$) δ 0 98 and 1 06 (d each, J = 6 6 Hz, Me_2), 1 86 (m, C*H*Me_2), 4 67 (dd, J = 3 0 and 7 9 Hz, C*H*CHMe_2), 5 80 (d, J = 3 0 Hz, C*H*Ph)] and (±)-**3o** A solution of the mixture in dichloromethane was treated in the same way as described below for the preparation of (±)-**3p**, followed by flash chromatography [hexane–ethyl acetate (3 1, v/v)] to afford (±)-**3o** (41 mg, 20%) as a colorless solid, mp 58—60 5 °C

Recrystallization of crude (±)-**3o** from hexane–ether (1 1, v/v) provided colorless pillars, mp 65 5—66.5 °C, identical (IR) with an authentic sample

Reaction of (±)-1p

A solution of oxalyl chloride (0 097 ml, 1 1 mmol) in THF (4 ml) was added to an ice-cooled solution of (±)-**1p** (180 mg, 1 mmol) and triethylamine (0 63 ml, 4 5 mmol) in THF (20 ml) over a period of 5 min, and the mixture was stirred at 0 °C for a further 5 min The resulting precipitate was removed by filtration and washed with THF (30 ml) The filtrate and the washings were combined and concentrated *in vacuo* to give a mixture of (±)-**3p** and (±)-**2p** [73] The residue was dissolved in dichloromethane (15 ml), and the solution was washed successively with 5% aqueous citric acid (5 ml) and saturated aqueous sodium bicarbonate (5 ml), dried, and concentrated The oily residue was purified by flash chromatography [hexane–ethyl acetate (4 1, v/v)] to afford (±)-**3p** (173 mg, 84%) as an colorless oil, identical (IR) with an authentic sample

Reaction of (±)-1q

Compound (±)-**1q** (56 mg, 0 25 mmol) was treated in a manner similar to that described for the reaction with (±)-**1n** to afford a mixture of (±)-**3q** and (±)-*trans*-5-[(4-dimethylamino)phenyl]-6-isopropyl-1,4-dioxane-2,3-dione [(±)-**2q**] [^{1}H-NMR ($CDCl_3$) δ 4 66 (dd, J = 2 3 and 9 3 Hz, C*H*CHMe$_2$), 5 44 (d, J = 9 3 Hz, C*H*Ph)] Purification of the mixture by flash chromatography [hexane–ethyl acetate (2 1, v/v)] to afford (±)-**3q** (55 mg, 88%) as a slightly yellow viscous oil, MS *m/z* 249 (M^+), IR $\nu_{max}^{liquid\ film}$ cm^{-1} 1797 (C=O), ^{1}H-NMR ($CDCl_3$) δ 0 95 (d, J = 6 9 Hz) and 1 06 (d, J = 6 6 Hz) (3H each, CMe$_2$), 2 01 (1H, dqq, J = 6 9, 6 6, and 6 6 Hz, C*H*Me$_2$), 2 98 (6H, s, NMe$_2$), 4 35 (1H, dd, J = 6 6 and 7 3 Hz, C*H*CHMe$_2$), 5 18 (1H, d, J = 7 3 Hz, C*H*Ar), 6 71 (2H, m, aromatic protons ortho to NMe$_2$), 7 21 (2H, m, aromatic protons meta to NMe$_2$), ^{13}C-NMR ($CDCl_3$) δ 17 3 and 17 6 (C*Me*$_2$), 31 6 (*C*Me$_2$), 40 3 (NMe$_2$), 82 2 (*C*HAr), 88 1 (*C*HCHMe$_2$), 112 3, 123 1, 128 1, and 151 3 (Ar), 154 8 (C=O)

Reaction of 1h with Oxalyl Chloride in the Absence of Base

According to the reported procedure,[1] oxalyl chloride (8 9 ml, 0 104 mol) was added dropwise to **1h** (11 84 g, 0 1 mol) over a period of 20 min with occasional cooling with ice The mixture was stirred at room temperature for a further 1 5 h The resulting precipitate was collected by filtration, washed with ether and recrystallized from ethanol to afford **3h** (3 07 g), mp 178—180 °C From the ethanolic mother liquor, were obtained additional crops of **3h** (725 mg) by repeated recrystallization from ethanol The ethereal washings of the crude product was concentrated to dryness, and the solid residue was combined with the residue, which was obtained by removal of ethanol from the mother liquor of the final recrystallization This crude material was purified by repeated flash chromatography [hexane–ethyl acetate (2 1, v/v)] to afford **3h** (277 mg, the total yield was 28%), **2h** (126 mg, 0 7%), and pinacol (427 mg, 3 6%) The main component of the distillate of the ethereal washings was suggested to be pinacolone by the ^{1}H-NMR spectrum, and was identified by the formation of the oxime [75]

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