

## Synthetic Studies with Carbonates. Part 10.<sup>1</sup> Reactions of Ethylene Carbonate with Some Active Methylene Compounds catalysed by Quaternary Ammonium or Alkali Metal Halides

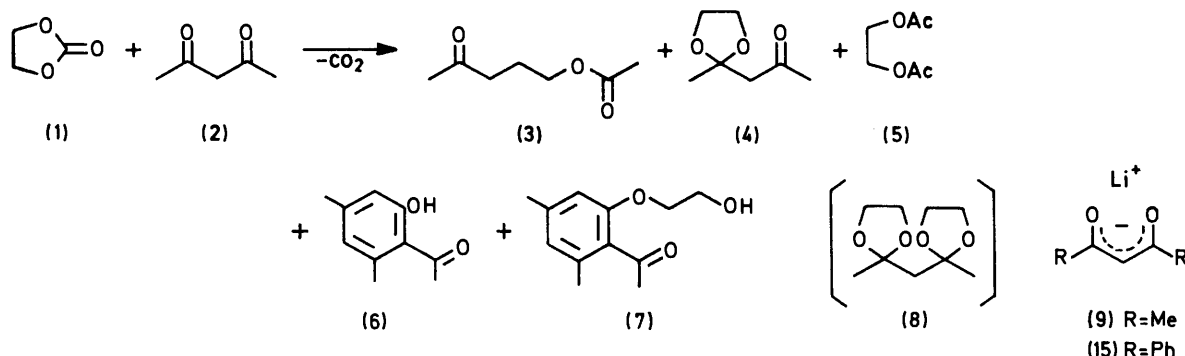
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The reaction of ethylene carbonate (1) with pentane-2,4-dione (2) was carried out in the presence of a series of halides as catalysts. As examples, the reaction catalysed by sodium iodide gave 4-oxopentyl acetate (3), and that catalysed by tetraethylammonium chloride gave 2-methyl-2-(2-oxopropyl)-1,3-dioxolan (4), as the predominant product in high yield. Reactions with 1,3-diphenylpropane-1,3-dione (11) in place of (2) showed the same trend. However, reactions with 2-alkyl-1,3-diphenylpropane-1,3-diones (20) and (25), gave no oxoalkyl esters corresponding to (3), but other types of product [(21), (22), and (26)]. In reactions with 3,3-dibenzylpentane-2,4-dione (30), which has no proton dissociable under the conditions used, were obtained 3-benzyl-4-phenylbutan-2-one (31), 2-(2-acetoxyethoxy)-3-benzyl-4-phenylbut-2-ene (32), and 2-hydroxyethyl acetate (33). Reaction mechanisms are discussed.

Moreover, ethyl acetoacetate (34) and diethyl malonate (35) gave lactone derivatives, (37) and (39), respectively, but diethyl 2-acetamidomalonate (36) gave ethyl 2-acetamidobutyrate (40), in reactions with (1). Furthermore, the reactions of (1) with the diones (2) and (11) in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) gave the corresponding ethylene acetals (4) and (16), respectively.

AUTOCATALYTIC reactions of ethylene carbonate (1) with alcohols, carboxylic acids, thiols, and aromatic amines have been shown to give the corresponding 2-hydroxyethyl derivatives,<sup>2</sup> and reactions of (1) with nucleophiles such as alkali metal halides in aqueous ethylene glycol to give 2-substituted ethanols.<sup>3</sup> We have recently demonstrated<sup>4</sup> that in the presence of quaternary ammonium

dioxolan (4), and ethylene diacetate (5), along with small amounts of 2-acetyl-3,5-dimethylphenol (6) and 2-acetyl-3,5-dimethylphenyl 2-hydroxyethyl ether (7) (Scheme 1; Table 1). The bis-ethylene acetal (8) was not detected in any of the resulting mixtures. In the reactions catalysed by the lithium halides (experiments 13–15), unexpected precipitation of pentane-2,4-dionatolithium



SCHEME 1

halides the 2-hydroxyethylation can be carried out at lower temperatures; the reactions were considered to proceed *via* an intermediate 2-halogenoethoxide ion, converted into a 2-halogenoethanol by abstraction of the dissociable proton of the nucleophile used. We now describe the reactions of ethylene carbonate (1) with active methylene compounds catalysed by quaternary ammonium or alkali metal halides. The reactions were of additional interest in view of the generalization<sup>5</sup> that ambident anions are more susceptible to *O*-alkylation by alkyl chlorides than by alkyl iodides.

The reactions of ethylene carbonate (1) with pentane-2,4-dione (2) with halides as catalysts, gave mixtures of 4-oxopentyl acetate (3), 2-methyl-2-(2-oxopropyl)-1,3-

(9) (70–80% yield) was observed within several minutes from the beginning of the reaction,<sup>†</sup> and the rate of gas evolution was then markedly reduced. The <sup>1</sup>H n.m.r. spectrum of the mixture from the reaction catalysed by potassium iodide (experiment 23), after removal of the halide, showed no signals due to (1), although the signals of (2) were still apparent. The total yield of (3) and (4) in this case might have been reduced owing to loss of ethylene oxide by evaporation (*cf.* ref. 3). The yield was improved to 65% by performing the reaction with an excess of (1). The phenol (6) was also produced in the

<sup>1</sup> Part 9, Y. Ishido, H. Komura, and T. Yoshino, *Carbohydrate Res.*, in the press.

<sup>2</sup> W. W. Carlson and L. H. Cretchen, *J. Amer. Chem. Soc.*, 1947, **69**, 1952.

<sup>3</sup> E. D. Bergmann and I. Shahak, *J. Chem. Soc. (C)*, 1966, 899.

<sup>4</sup> T. Yoshino, S. Inaba, and Y. Ishido, *Bull. Chem. Soc. Japan*, 1973, **46**, 553.

<sup>5</sup> C. L. Liotta, H. P. Harris, M. McDermott, T. Gonzalez, and K. Smith, *Tetrahedron Letters*, 1974, 2417; A. Knochel and G. Rudolph, *ibid.*, p. 3739.

<sup>†</sup> No precipitation was induced in the other reactions. The salts recovered in the reactions catalysed by sodium or potassium halides were too hygroscopic for their structures to be elucidated. Those recovered in the reactions catalysed by the ammonium halides were identical in i.r. spectra with the original ammonium halides.

reaction of propylene carbonate (10) with (2) catalysed by sodium iodide, in 16% yield, and has been shown to be formed by treatment of (2) in aqueous 0.7M-sodium

TABLE I

Reactions of ethylene carbonate (1) with pentane-2,4-dione (2) in the presence of a variety of quaternary ammonium and alkali metal halides <sup>a</sup>

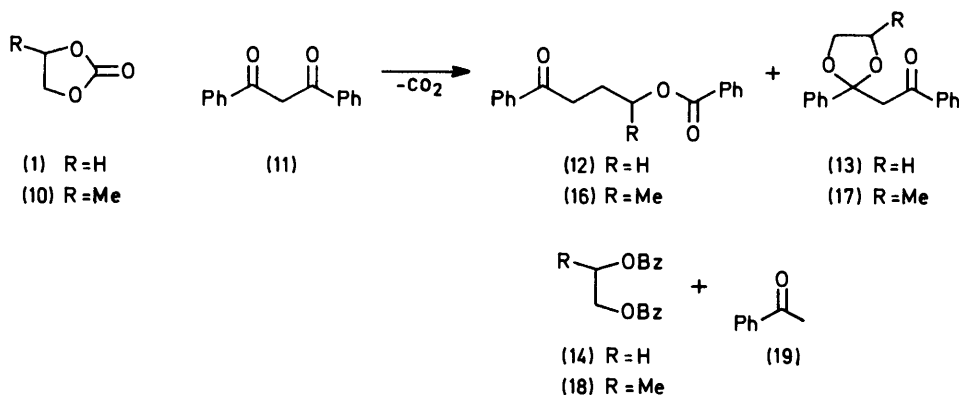
Halide	Reaction conditions		Products (3) and (4), total yield (%) <sup>c</sup>	Product (5), yield (%) <sup>d</sup>
	Temp. <sup>b</sup> (°C)	Period (h)		
1 Me <sub>4</sub> N <sup>+</sup> Cl <sup>-</sup>	155—160	0.75	80 (15 : 85)	<1
2 Me <sub>4</sub> N <sup>+</sup> Br <sup>-</sup>	155—160	4.5	67 (35 : 65)	<1
3 Me <sub>4</sub> N <sup>+</sup> I <sup>-</sup>	155—160	4.5	56 (50 : 50)	<1
4 Et <sub>4</sub> N <sup>+</sup> Cl <sup>-</sup>	155—160	0.75	80 (15 : 85)	<1
5 Et <sub>4</sub> N <sup>+</sup> Br <sup>-</sup>	155—160	3	78 (40 : 60)	<1
6 Et <sub>4</sub> N <sup>+</sup> I <sup>-</sup>	130—135	9	49 (70 : 30)	<1
7 Et <sub>4</sub> N <sup>+</sup> I <sup>-</sup>	155—160	2	74 (65 : 35)	<1
8 Et <sub>4</sub> N <sup>+</sup> I <sup>-</sup>	185—195	0.5	59 (65 : 35)	<1
9 Bu <sub>4</sub> N <sup>+</sup> Br <sup>-</sup>	155—160	4.5	42 (40 : 60)	<1
10 Bu <sub>4</sub> N <sup>+</sup> I <sup>-</sup>	155—160	4.5	69 (60 : 40)	<1
11 C <sub>16</sub> H <sub>33</sub> N <sup>+</sup> Me <sub>3</sub> Cl <sup>-</sup>	155—160	2	77 (15 : 85)	<1
12 C <sub>16</sub> H <sub>33</sub> N <sup>+</sup> Me <sub>3</sub> Br <sup>-</sup>	155—160	2	65 (30 : 70)	<1
13 LiCl	175—180	8	ca. 6 (20 : 80)	ca. 1
14 LiBr, H <sub>2</sub> O	175—180	5	ca. 70 (65 : 35)	ca. 3
15 LiI, 3H <sub>2</sub> O	175—180	1.5	81 (75 : 25)	<1
16 NaF	175—180	9	27 (10 : 90)	<1
17 NaCl	175—180	4.5	ca. 40 (20 : 80)	ca. 15
18 NaBr	175—180	2	ca. 45 (55 : 45)	ca. 5
19 NaI	130—135	9	67 (85 : 15)	4
20 NaI	175—180	0.25	73 (80 : 20)	1
21 KCl	175—180	2	ca. 65 (10 : 90)	ca. 4
22 KBr	175—180	2	ca. 35 (40 : 60)	ca. 5
23 KI	175—180	2.5	50 (35 : 65)	1

<sup>a</sup> All reactions performed by use of 20 mmol each of (1) and (2), and 2 mmol of halide. <sup>b</sup> Bath temperatures. <sup>c</sup> Ratios of (3) and (4) in each product, calculated on the basis of n.m.r. integration. <sup>d</sup> Calculated on the assumption that (5) is formed from an equimolar amount of (2).

hydroxide under reflux.<sup>6</sup> Experiments 6—8 and 19 and 20 demonstrated that the ratio of compounds (3) and (4) was almost independent of temperature in the presence of

cations result in preferential formation of (3) rather than (4). Sodium iodide was most advantageous for the preparation of (3), and quaternary ammonium chlorides for that of (4); experiment 4 afforded (4) in 42% yield by fractional distillation of the resulting mixture after treatment with sodium methoxide in methanol, which is more advantageous than the reaction of (2) with ethylene glycol catalysed by toluene-*p*-sulphonic acid (27% yield).<sup>7</sup>

The reactions of ethylene carbonate (1) with 1,3-diphenylpropane-1,3-dione (11) were performed similarly and the products were separated chromatographically after removal of the catalyst. They were 3-benzoylpropyl benzoate (12) and 2-benzoylmethyl-2-phenyl-1,3-dioxolan (13), together with ethylene dibenzoate (14) (Scheme 2; Table 2). As in the previous reactions, those catalysed by sodium iodide gave (12), and those catalysed by the ammonium chlorides gave (13) as the main product. Sodium chloride was inadequate as catalyst, giving the dibenzoate (14) as the main product, and lithium iodide was also ineffective [the rate of gas evolution was markedly reduced with precipitation of crystalline 1,3-diphenylpropane-1,3-dionatolithium (15)]. The addition of dibenzo-18-crown-6 ether in the reactions catalysed by sodium iodide (experiments 6—8) resulted in a small decrease in the ratio of (12) to (13) from 8 : 2 to 7 : 3 (independent of the amount of ether added) although addition in reactions catalysed by the ammonium chlorides (2 and 4) brought about almost no difference in ratio. The reaction performed in a highly polar system, *i.e.* with an excess of (1) (experiment 9) gave (12) and (13) in the ratio 1 : 1. The reactions of propylene carbonate (10) and (11) (experiments 11 and 12) showed a similar trend, giving 3-benzoyl-1-methylpropyl benzoate (16) and 2-benzoylmethyl-4-methyl-2-phenyl-1,3-dioxolan (17), together with a small amount of propylene dibenzoate (18). Compound (10) was less reactive than (1).



SCHEME 2

the same catalyst, and 185—195 °C was too high a reaction temperature (experiment 8); the reduced yield is likely to arise from decomposition of 2-iodoethanol to ethylene oxide. On the basis of experiments 1—23, less electronegative and/or 'softer' halide ions and 'harder'

<sup>6</sup> A. Heikel, *Suomen Kem.*, 1935, **8B**, 33 (*Chem. Abs.*, 1936, **30**, 4379).

Reactions of both (1) and (10) always afforded acetophenone (19) as a by-product, identified as its 2,4-dinitrophenylhydrazone and by <sup>1</sup>H n.m.r. spectroscopy. The results show that (12) and (16) are most advantageously prepared by use of sodium iodide, and (13) and (17)

<sup>7</sup> P. C. Dutta, P. K. Dutta, and K. N. Sastry, *J. Indian Chem. Soc.*, 1954, **31**, 881.

by use of an ammonium chloride as catalyst. In the absence of catalyst, none of these reactions took place even on heating the mixture to 230 °C.

To elucidate the reaction mechanism, we studied the reactions of ethylene carbonate (1) with 2-methyl- (20) and 2-benzyl-1,3-diphenylpropane-1,3-dione (25), and 3,3-dibenzylpentane-2,4-dione (30), with only one or no

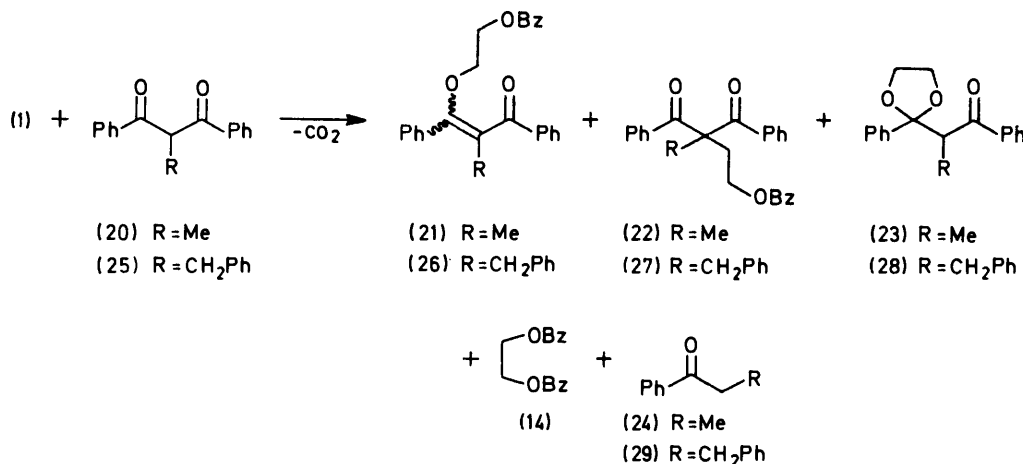
give 3-benzoyl-3-benzyl-4-oxo-4-phenylbutyl benzoate (27) analogous to (22). These results suggest that the formation of compounds (22) and (27), a C-C bond formation reaction, is depressed by the steric effects of the methyl and benzyl groups, in contrast with the reactions involving (2) and (11). Ratios of the conformational isomers of compounds (21) and (26) were confirmed as

TABLE 2

Reactions of ethylene carbonate (1) and propylene carbonate (10) with 1,3-diphenylpropane-1,3-dione (11) in the presence of quaternary ammonium or alkali metal halides <sup>a</sup>

	Reaction conditions		Products, yield (%)					Recovery (%) (11)			
	R	Halide	Temp. (°C)	Period (h)	(12)	(15)	(13)		(16)	(14)	(17)
1.	H	Et <sub>4</sub> N <sup>+</sup> Cl <sup>-</sup>	155—160	1.5	10		80		<1		
2.	H	Me <sub>4</sub> N <sup>+</sup> Cl <sup>-</sup> <sup>b</sup>	150—155	3	69 (13 : 87) <sup>c</sup>						19
3.	H	Me <sub>4</sub> N <sup>+</sup> Cl <sup>-</sup> <sup>d</sup>	160—165	1	9		68		<1		
4.	H	NaCl	200—205	11	6		10		25		
5.	H	NaI	155—160	3	80		17		1		
6.	H	NaI <sup>b</sup>	130—135	10	77 (69 : 31) <sup>c</sup>						23
7.	H	NaI <sup>b</sup>	150—155	2	77 (67 : 33) <sup>c</sup>						20
8.	H	NaI <sup>e</sup>	150—155	2	84 (67 : 33) <sup>c</sup>						15
9.	H	NaI <sup>d</sup>	160—165	10	32		34			2	
10.	H	LiI, 3H <sub>2</sub> O	175—180	0.5	10		1				80
11.	Me	Me <sub>4</sub> N <sup>+</sup> Cl <sup>-</sup>	170—175	4				40			3
12.	Me	NaI	160—170	4		49		10			2

<sup>a</sup> All reactions performed by use of 4.0 mmol of (1) or (9), 3.0 mmol of (11), and 0.3 mmol of halide. <sup>b</sup> Dibenzo-18-crown-6 (0.3 mmol) added in this case. <sup>c</sup> Concentration of the chromatographic eluate from elution with 0.5 : 99.5 acetone-cyclohexane from a silica gel column gave a syrupy mixture of (12) and (13), whose yields were calculated on the basis of n.m.r. integration. <sup>d</sup> This reaction was conducted by use of 100 mmol of (1), and discontinued after evolution of 100 ml of carbon dioxide. <sup>e</sup> This reaction was conducted by use of 2 equiv. of the crown ether with respect to the halide.



SCHEME 3

dissociable protons, respectively. Reactions with (20) and (25) did not give 4-oxoalkyl benzoates corresponding to (3), (12), and (16), but afforded 3-(2-benzoyloxyethoxy)-2-methyl-1,3-diphenylprop-2-en-1-one (21) and 3-benzoyl-3-methyl-4-oxo-4-phenylbutyl benzoate (22) or 3-(2-benzoyloxyethoxy)-2-benzyl-1,3-diphenylprop-2-en-1-one (26) together with the monoethylene acetal (23) or (28), ethylene dibenzoate (14), and 1-phenylpropan-1-one (24) or 1,3-diphenylpropan-1-one (29), respectively (Scheme 3; Table 3). Moreover, compound (25) did not

1 : 2 (<sup>1</sup>H n.m.r.) and 1 : 3 (<sup>13</sup>C n.m.r.), respectively.† The transformation of (26) into the acetal (28) by treatment with methanolic 20% ammonia in 78% yield suggested the possibility that this reaction involves an intermediate such as 2-benzyl-3-(2-hydroxyethoxy)-1,3-diphenylprop-2-en-1-one for the formation of (28).‡

The reactions of (1) with the dione (30) in the presence of tetramethylammonium chloride or sodium iodide were similarly performed (Scheme 4); the former gave 3-benzyl-4-phenylbutan-2-one (31), 2-(2-acetoxyethoxy)-3-benzyl-4-phenylbut-2-ene (32), and 2-hydroxyethyl acetate (33), and the latter compounds (31) and (33),

<sup>8</sup> M. W. Crown and J. E. Goodrich, *J. Amer. Chem. Soc.*, 1952, **74**, 3331.

† The n.m.r. data could not be assigned to the specific isomers.

‡ This assumption was supported by the successful conversion of a 2-hydroxyethyl enol ether into the corresponding 1,3-dioxolan derivative (*cf.* ref. 8).

with a considerable amount of unchanged dione (30) and without (32) (Table 4). In this case, no C-C bond formation reaction is involved, in contrast with the foregoing reactions.

From Tables 1-4 we concluded that the order of nucleophilicity of the halide ions in this system is  $\text{Cl}^- > \text{Br}^-, \text{I}^-$ , probably arising from strong solvation of the cationic species and/or lack of solvation of the anions by the carbonate (1) or (10).

(B) induced solely by attack of the halide ion, giving 2-halogenoethoxide ion which with (a) constitutes system II. The two systems are assumed to exist in equilibrium.

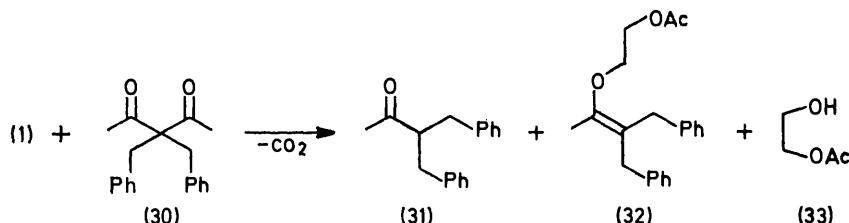
Reactions *via* system I involve pathways (C) and (D). Pathway (C) affords the intermediate (c) (C-alkylated product), which is then transformed into the 4-oxoalkyl ester (f) *via* a hemiacetal intermediate. Pathway (D) affords the vinyl ether (d) (O-alkylated product), which is then transformed into the 1,3-dioxolan (g) through a

TABLE 3

Reactions of ethylene carbonate (1) with 2-substituted 1,3-diphenylpropane-1,3-diones (20) and (25) in the presence of tetramethylammonium or sodium halides <sup>a</sup>

	R	Halide	Reaction conditions		Products, yield (%)							Recovery (%)			
			Temp. (°C)	Period (h)	(21)	(26)	(22)	(27)	(23)	(28)	(14)	(24)	(29)	(20)	(25)
1.	Me	$\text{Me}_4\text{N}^+\text{Cl}^-$	155-160	1.5	18					41		2	27		
2.	Me	$\text{Me}_4\text{N}^+\text{I}^-$	160-165	11	10					13		4	12	59	
3.	Me	$\text{Me}_4\text{N}^+\text{I}^-$	185-190	3	9					19		3	14	48	
4.	Me	NaCl	200-205	7	26			1		21		13	19		
5.	Me	NaI	155-160	3	24			6				15	42		
6.	$\text{PhCH}_2$	$\text{Me}_4\text{N}^+\text{Cl}^-$	155-160	1		26					40	4		34	
7.	$\text{PhCH}_2$	$\text{Me}_4\text{N}^+\text{I}^-$	160-170	20		22					9	5		43	22
8.	$\text{PhCH}_2$	NaCl	200-205	9		41					2	8		59	
9.	$\text{PhCH}_2$	NaI	150-155	3		36						7		61	
10.	$\text{PhCH}_2$ <sup>b</sup>	NaI	150-155	3		26					7	5		45	18
11.	$\text{PhCH}_2$ <sup>b</sup>	NaI	175-180	5		23					6	6		54	

<sup>a</sup> All reactions performed by use of 4.0 mmol of (1), 3.0 mmol of (20) or (25), and 0.3 mmol of halide. <sup>b</sup> Dibenzo-18-crown-6 equiv. to sodium iodide added in this case.



SCHEME 4

We suggest that the reactions of the carbonates (1) and (10) with the active methylene compounds in the presence of the halides take place as shown in Scheme 5. The first step is considered to involve two pathways:

TABLE 4

Reactions of ethylene carbonate (1) with 3,3-dibenzylpentane-2,4-dione (30) in the presence of tetramethylammonium chloride or sodium iodide <sup>a</sup>

Halide	Reaction conditions		Products, yield (%)			Recovery (%) (30)
	Temp. (°C)	Period (h)	(31)	(32)	(33)	
1 $\text{Me}_4\text{N}^+\text{Cl}^-$	170-175	6	73	5	30	5
2 NaI	155-160	5	26		10	73
3 NaI	170-175	6	37		19	60

<sup>a</sup> All reactions performed by use of 4.0 mmol of (1), 3.0 mmol of (30), and 0.3 mmol of halide.

(A) induced by nucleophilic attack of the halide ion on the methylene carbon of (1), assisted by hydrogen bonding by the enol and/or keto tautomer of the active methylene compound (a), giving 2-halogenoethanol and the corresponding ambident anion (b) (system I), and

<sup>9</sup> R. G. Pearson and A. C. Sandy, *J. Amer. Chem. Soc.*, 1951, **73**, 931.

Michael-type addition. Reactions of ethylene carbonate (1) with both the diones (2) and (11) are likely to conform to this mechanism. The following evidence supports the above explanation. (i) The effect of the halide ions and the cations on the reactions (Tables 1 and 2) is compatible with the trend observed in the alkylation of a series of ambident anions.<sup>5</sup> (ii) The reactions of (2) with alkoxide ions have been shown to involve predominant proton-exchange rather than nucleophilic attack of alkoxide ion on the carbonyl group of (1).<sup>9</sup> (iii) The reactions catalysed by lithium halides gave the lithio-complex of the original active methylene compound. (iv) The reaction of the carbonate (1) with the dione (11) catalysed by sodium iodide, provided that a large excess of (1) was used, furnished compounds (13) and (12) in a ratio larger than that obtained in the corresponding equimolar reaction, consistent with the predominant O-alkylation of ambident anions in solvents with larger dielectric constants;<sup>10</sup> the dielectric constant of (1) is 89.1 at 40 °C.<sup>11</sup> (v) The small increase in the ratio of (13)

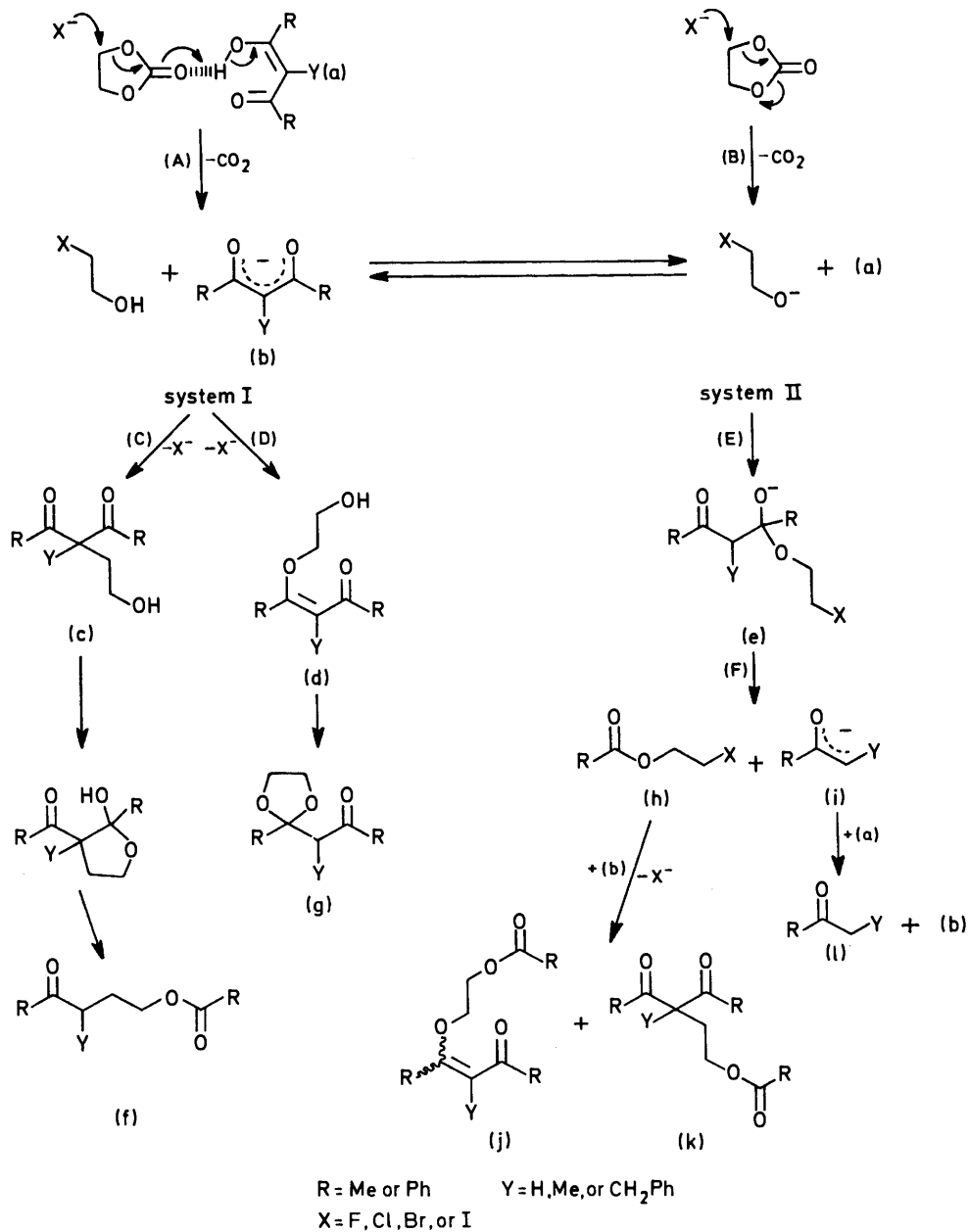
<sup>10</sup> N. Kornblum, R. Seltzer, and P. Haberfeld, *J. Amer. Chem. Soc.*, 1963, **85**, 1148.

<sup>11</sup> R. Kempa and W. H. Lee, *J. Chem. Soc.*, 1958, 1936.

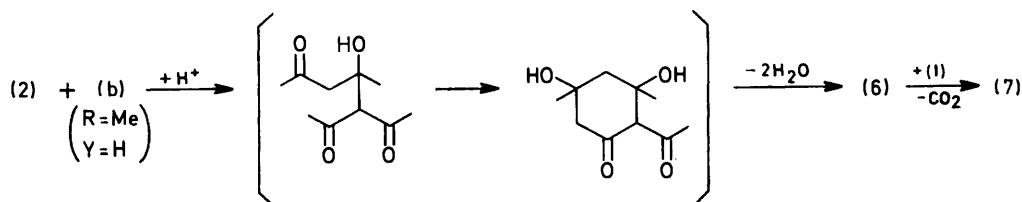
to (12) on addition of dibenzo-18-crown-6 ether (Table 2) is likely to arise from abstraction of sodium cation from the medium. (vi) The intermediate (b) ( $R = \text{Me}$ ,  $Y = \text{H}$ ) may be assumed to give the phenol (6) by an aldol-type condensation with (2). Thus, 2-hydroxyethyl

ether (7) can be formed by nucleophilic attack of (6) on the carbonate (1) (Scheme 6). This mechanism may also apply in the reaction of (10) with (11).

In marked contrast with these reactions, the reaction of the carbonate (1) with the dione (30) (Table 4) is

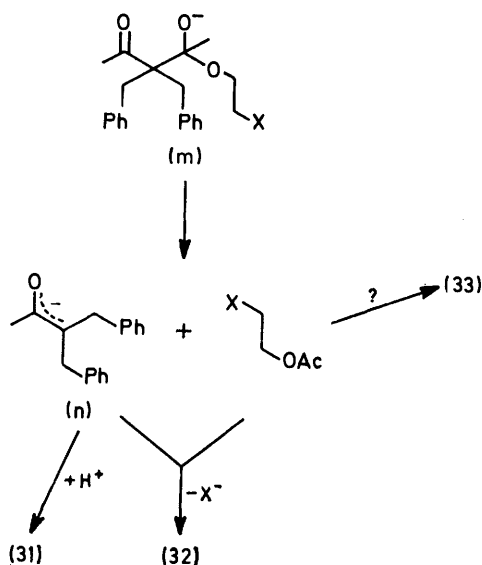


SCHEME 5



SCHEME 6

concluded to proceed *via* pathways (B) and (E), *via* system II, as specifically depicted in Scheme 7; *i.e.* the



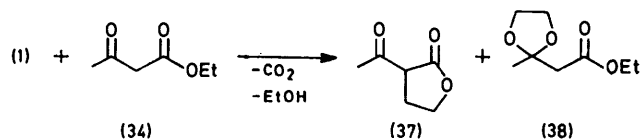
SCHEME 7

intermediate (m) produced from (30) and 2-halogenoethoxide ion affords the ambident anion (n) and 2-halogenoethyl acetate, which react with each other to give (32). On abstraction of a proton from a proton donor, (n) may also give (31). The lack of formation of a 1,3-dioxolan in this case can be explained by the absence of a dissociable proton in (30) under the conditions used.

On the other hand, the reactions of (1) with the 2-alkyl-1,3-diphenylpropane-1,3-diones (20) and (25) are likely to proceed *via* pathway (D) as well as (E) since (i) the  $pK_a$  values of (20) and (25) are larger than those of (2) and (11), (ii) even the reaction catalysed by sodium iodide

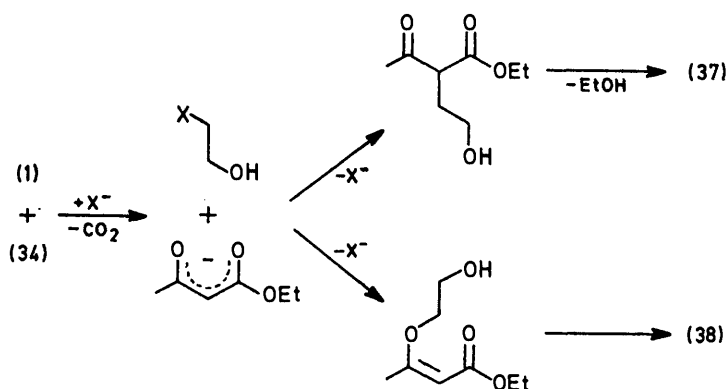
the corresponding ketonic species (l) by proton-exchange with (a). The lack of formation of (f) *via* pathway (C) is likely to be due to steric effects of the bulky alkyl groups at the 2-position of (a), and *O*-alkylation [pathway (D)] is thus preferred. The addition of the crown ether to the reaction catalysed by sodium iodide (experiments 10 and 11 in Table 3) might be expected to increase the nucleophilicity of the more electronegative oxygen part of (b), giving the 1,3-dioxolan derivative (g), although its yield was only 6–7%. We offer no explanation for the formation of ethylene diesters and 2-hydroxyethyl acetate (33) in these owing to lack of evidence.

In the light of the above results, the reaction of ethylene carbonate (1) with ethyl acetoacetate (34), diethyl malonate (35), and diethyl 2-acetamidomalonate (36) were performed. The products from the reaction with (34) were separated by chromatography; on catalysis with sodium iodide 3-acetyloxacyclopentan-2-one (37) (*C*-alkylated product) was obtained in greater amount than 2-ethoxycarbonylmethyl-2-methyl-1,3-dioxolan (38) (*O*-alkylated product), and on catalysis with tetramethylammonium chloride only (38) was isolated (Table 5) [although the formation of (37) was indicated by  $^1\text{H}$  n.m.r. spectroscopy]. The mechanism for the formation



SCHEME 8

of these products shown in Scheme 9 is suggested by analogy with those for the previous reactions. The sodium-iodide-catalysed reaction of (1) with (35) gave a



SCHEME 9

gave no 4-oxoalkyl ester, and (iii) considerable amounts of 1,3-dioxolan derivatives (23) and (28) were formed in these reactions (Table 3). Products (j) and (k) are likely to arise from the reaction of (b) with (h), which is produced from (e) *via* pathway (F). The ambident anion (i) formed concomitantly may be readily transformed into

mixture of many products (g.l.c.) which we were unable to separate by chromatography; however, crystallization from diethyl ether gave 2,7-dioxaspiro[4.4]nonane-1,6-dione (39) (Scheme 10). Both the above reactions proceeded with formation of coloured products suggesting the occurrence of side reactions, *e.g.* decarboxylation of

oxo-esters induced by halide ions.<sup>12</sup> A decarboxylation product (40) was in fact obtained in the reaction with (36) catalysed by tetraethylammonium iodide. No other product was isolated.

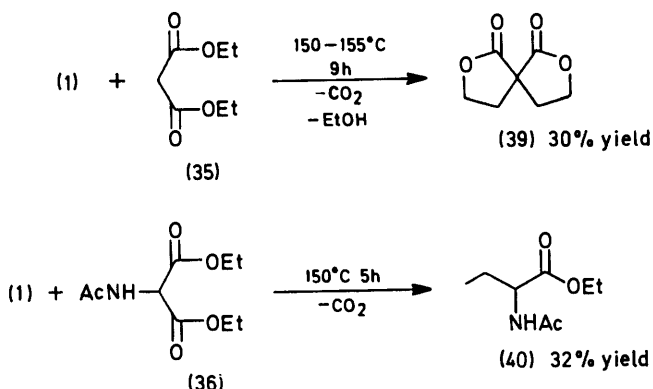
TABLE 5

Reactions of ethylene carbonate (1) with ethyl acetoacetate (34) catalysed by tetramethylammonium chloride or sodium iodide<sup>a</sup>

Halide	Reaction conditions		Products, yield (%)	
	Temp. (°C)	Period (h)	(37)	(38)
Me <sub>4</sub> N <sup>+</sup> Cl <sup>-</sup>	150—155	4	17	<sup>b</sup>
NaI	150—155	9	12	41

<sup>a</sup> Both reactions performed by use of 5.0 mmol of (1) and (34), and 0.5 mmol of halide. <sup>b</sup> This product was not isolated, but its formation was confirmed by n.m.r. spectroscopy.

Finally we performed the reactions of ethylene carbonate (1) with the diones (2) and (11) catalysed by 1,4-diazabicyclo[2.2.2]octane (DABCO) on the basis of



SCHEME 10

the hypothesis that all the above reactions involve the ambident anion of an active methylene compound or a 2-halogenoethoxide ion, *i.e.* a basic species, as intermediate. Moreover, the carbonate (1) has been shown to give

TABLE 6

Reactions of ethylene carbonate (1) with pentane-2,4-dione (2) and 1,3-diphenylpropane-1,3-dione (11) in the presence of 1,4-diazabicyclo[2.2.2]octane<sup>a</sup>

Dione	Reaction conditions		Products, yield (%)					
	Temp. (°C)	Period (h)	(3)	(12)	(4)	(13)	(5)	(14)
1. <sup>b</sup> (2)	165—170	0.34	4		33		5	
2. (11)	125—130	6		7		56		18

<sup>a</sup> Expt. 1 was performed by use of (1) (20 mmol), (2) (20 mmol), and 1,4-diazabicyclo[2.2.2]octane (2.0 mmol), and Run 2 by use of (1) (4.0 mmol), (11) (3.0 mmol), and the base (0.3 mmol). <sup>b</sup> In this case 2-acetyl-3,5-dimethylphenyl 2-hydroxyethyl ether (7) was obtained in 7% yield.

the corresponding 2-hydroxyethyl carbamate in reactions with mono- or di-alkylamines.<sup>13</sup> The reactions gave O-alkylated products, *i.e.* the monoethylene acetals, (4)

<sup>12</sup> F. Elsinger, J. Schreiber, and A. Eschenmoser, *Helv. Chim. Acta*, 1960, **43**, 113; M. Asaoka, K. Miyake, and H. Takei, *Chem. Letters*, 1975, 1149.

<sup>13</sup> F. Strain, W. E. Bissinger, W. R. Dial, H. Rudoff, B. J. Dewitt, H. C. Stevens, and J. H. Landston, *J. Amer. Chem. Soc.*, 1950, **72**, 1254.

and (13), as the predominant products, together with C-alkylated products, *i.e.* the 4-oxoalkyl acylates (3) and (12), and the ethylene diesters (5) and (14) (Table 6). This base-catalysed acetal formation reaction is an alternative to the reaction of 1,3-diphenylprop-2-yn-1-one with sodium 2-hydroxyethoxide reported by Vereschagin *et al.*<sup>14</sup>

## EXPERIMENTAL

The following instruments were used: i.r., Hitachi 215 and 218; <sup>1</sup>H n.m.r., Varian T-60 and XL-100; <sup>13</sup>C n.m.r., Varian CFT-20 (solutions in CDCl<sub>3</sub> containing 5% of tetramethylsilane); mass spectra, Hitachi RMU-6E and RMU-2; g.l.c., Hitachi K-53 (10% SE-30 on Chromosorb W).

Column chromatographic separations were performed by use of Wakogel C-300 (Wako Pure Chemicals, Japan), and t.l.c. by use of Merck silica gel 60-F254 precoated plates (thickness 0.25 mm); spots were detected with a u.v. lamp (S. L. Light, Tokyo Machinery Co., Ltd.; 253.7 and 365.0 nm).

Determinations of <sup>1</sup>H n.m.r. spectra with Varian T-60 and XL-100 instruments and <sup>13</sup>C n.m.r. spectra with the Varian CFT-20 spectrometer were performed by Mr. K. Kushida and his staff, Nippon Electric Varian Inc. Mass spectral determinations were carried out by Mr. A. Murai, Central Research Laboratories, Ajinomoto Co., Inc. Microanalyses were performed by the Laboratory of Organic Analysis (Perkin-Elmer 240-0002 instrument).

We purchased commercially ethylene carbonate (1), pentane-2,4-dione (2), propylene carbonate (10), dibenzo-18-crown-6, and 1,4-diazabicyclo[2.2.2]octane.

1,3-Diphenylpropane-1,3-dione (11).—This was prepared from 1,3-diphenylprop-2-en-1-one according to the method of Allen *et al.*; <sup>15</sup> m.p. 77—78° (from MeOH) (lit., <sup>15</sup> 77—78°).

2-Methyl-1,3-diphenylpropane-1,3-dione (20).—This was prepared in 70% yield by methylation of (11) according to the method of Sprange *et al.*; <sup>16</sup> m.p. 83—84° (from MeOH) (lit., <sup>16</sup> 82—83°).

2-Benzyl-1,3-diphenylpropane-1,3-dione (25).—This dione was prepared similarly to (20) in 75% yield; m.p. 106—107° (from MeOH),  $\nu_{\max}$  (KBr) 1 698 and 1 670 cm<sup>-1</sup>,  $\delta$  3.46 (2 H, d, *J* 6.5 Hz, CH<sub>2</sub>-Ph), 5.53 (1 H, t, *J* 6.5 Hz, =CH-), 7.23 (5 H, s, CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>), and 7.3—8.1 (10 H, m, aromatic) (Found: C, 84.05; H, 5.85. C<sub>22</sub>H<sub>18</sub>O<sub>2</sub> requires C, 84.05; H, 5.75%).

3,3-Dibenzylpentane-2,4-dione (30).—This was prepared by benzylation of (2) according to the method of Cocker *et al.*; <sup>17</sup> m.p. 111—112° (from MeOH) (lit., <sup>17</sup> 111—112°).

Reaction of Ethylene Carbonate (1) with the Dione (2).—A mixture of compounds (1) (1.8 g, 20 mmol), (2) (2.0 g, 20 mmol), and one of the series of the halides (2 mmol) was heated at 155—160 °C (ammonium halides) or 175—180 °C (alkali metal halides) until evolution of carbon dioxide ceased. To the resulting mixture was added benzene (10 ml), and the solution was allowed to cool (ice-bath). The precipitated halide was filtered off. When it did not precipitate out, we added chloroform or diethyl ether in place of

<sup>14</sup> L. I. Vereschagin, V. N. Sushkova, S. R. Buzilova, L. P. Krillova, and S. I. Demie, *Zhur. org. Khim.*, 1975, **11**, 286 (*Chem. Abs.*, 1975, **82**, 155,211m).

<sup>15</sup> C. F. H. Allen, R. D. Abel, and J. B. Normington, *Org. Synth.*, Coll. Vol. I, 1944, p. 205.

<sup>16</sup> J. M. Sprange and H. Adkins, *J. Amer. Chem. Soc.*, 1934, **56**, 2665.

<sup>17</sup> W. Cocker and D. H. Grayson, *J.C.S. Perkin I*, 1975, 1347.

benzene. The filtrate was evaporated *in vacuo* to give an oil, which was fractionally distilled at 20 mmHg, yielding, in the following order, the dione (2), ethylene diacetate (5), 2-methyl-2-(2-oxopropyl)-1,3-dioxolan (4), and 4-oxopentyl acetate (3). The  $^1\text{H}$  n.m.r. spectrum of the distillation residue showed it to contain 2-acetyl-3,5-dimethylphenol (6) and 2-acetyl-3,5-dimethylphenyl 2-hydroxyethyl ether (7).

**4-Oxopentyl acetate (3).** A pure sample was isolated from the reaction catalysed by NaI, conducted for 0.25 h. The ester was redistilled; b.p.  $91^\circ$  at 11 mmHg (lit.,<sup>18</sup> 213–214 $^\circ$  at 728 mmHg),  $\nu_{\text{max}}$  (NaCl) 1 730, 1 705, and 1 240  $\text{cm}^{-1}$ ,  $\delta$  1.95 (2 H, m, C-CH<sub>2</sub>-C), 2.01 (3 H, s, OAc), 2.14 (3 H, s, CAc), 2.53 (2 H, t, *J* 6.7 Hz, C-CH<sub>2</sub>-CO), and 4.08 (2 H, t, *J*, 6.0 Hz, C-CH<sub>2</sub>-O), *m/e* 144 ( $M^+$ ), 129 ( $M^+ - \text{COCH}_3$ ), 89, 61, and 48 (Found: C, 58.3; H, 8.4. Calc. for C<sub>7</sub>H<sub>12</sub>O<sub>3</sub>: C, 58.3; H, 8.4%). A considerable amount of (3) was lost on distillation.

**2-Methyl-2-(2-oxopropyl)-1,3-dioxolan (4).** A pure sample was prepared by the reaction of (1) (2.8 g, 32 mmol) with (2) (3.0 g, 30 mmol) catalysed by Me<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup> (460 mg, 3 mmol) conducted for 1 h. After removal of the chloride by addition of benzene followed by filtration, the solution was dissolved in absolute methanol (50 ml), to which methanolic *m*-sodium methoxide (3 ml) was added. The resulting solution was stirred for 5 h at room temperature, after which the methoxide was quenched by bubbling carbon dioxide gas, and the solution was evaporated *in vacuo*. The residue was triturated with CHCl<sub>3</sub> (30 ml), and the extract was washed with water (20 ml  $\times$  2). The organic layer was dried (MgSO<sub>4</sub>) and evaporated *in vacuo*, and the oily residue was distilled to give the acetal (4) (1.82 g, 42%), b.p.  $90\text{--}91^\circ$  at 20 mmHg (lit.,<sup>7</sup> 185–195 $^\circ$ ),  $\nu_{\text{max}}$  (NaCl) 1 705 and 1 050  $\text{cm}^{-1}$ ,  $\delta$  1.40 (3 H, s, C-CH<sub>3</sub>), 2.20 (3 H, s, CO-CH<sub>3</sub>), 2.76 (2 H, s, C-CH<sub>2</sub>-C), and 3.95 (4 H, s, O-CH<sub>2</sub>-CH<sub>2</sub>-O), *m/e* 144 ( $M^+$ ), 129 ( $M^+ - \text{CH}_3$ ), 101 ( $M^+ - \text{COCH}_3$ ), 87, 57, and 43 (Found: C, 58.15; H, 8.4. Calc. for C<sub>7</sub>H<sub>12</sub>O<sub>3</sub>: C, 58.3; H, 8.4%).

The ratios of (3) and (4) shown in Table 1 were calculated from integration of the  $^1\text{H}$  n.m.r. signals at  $\delta$  1.4 (3 H) and 3.95 (4 H), and 4.08 (2 H), respectively.

**Ethylene diacetate (5).** In one of the reactions catalysed by NaCl (experiment 17 in Table 1), the diester (5) was isolated; however, it was impossible to purify it enough for elemental analysis. The product was identical with an authentic specimen ( $^1\text{H}$  n.m.r. and g.l.c.).

**2-Acetyl-3,5-dimethylphenol (6) and 2-acetyl-3,5-dimethylphenyl 2-hydroxyethyl ether (7).** One of the mixtures from the reaction catalysed by NaI (experiment 20) was chromatographed on a column of silica gel; elution with benzene afforded (6) as the first fraction, and elution with 5 : 95 acetone–benzene subsequently afforded (7) (final fraction) together with other, intermediary fractions [(3), (4), and (5)]. The phenol (6) (*ca.* 1%) had m.p.  $55\text{--}56^\circ$  (from petroleum) (lit.,<sup>6</sup> 58 $^\circ$ ),  $\nu_{\text{max}}$  (KBr) 3 500–3 200 (H-bonded OH), 1 620, and 1 600  $\text{cm}^{-1}$ ,  $\delta$  2.37, 2.56, 2.63 (each 3 H, s, CH<sub>3</sub>), 6.54 and 6.64 (each 1 H, broad s, aromatic), and 12.53 (1 H, s, H-bonded OH), *m/e* 164 ( $M^+$ ), 149 ( $M^+ - \text{COCH}_3$ ), 93, 91, and 77 (Found: C, 73.3; H, 7.35. Calc. for C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>: C, 73.15; H, 7.35%). The ether (7) (*ca.* 1%) had m.p.  $38\text{--}40^\circ$  (from petroleum),  $\nu_{\text{max}}$  (KBr) 3 650–3 250 (OH), 1 690, and 1 310  $\text{cm}^{-1}$ ,  $\delta$  2.21, 2.30, and 2.48 (each 3 H, s, CH<sub>3</sub>), 3.7–4.2 (4 H, O-CH<sub>2</sub>-CH<sub>2</sub>-O), and 6.58 and 6.62 (each 1 H, broad s, aromatic), *m/e* 208 ( $M^+$ ), 193 ( $M^+ - \text{CH}_3$ ), 190 ( $M^+ - \text{H}_2\text{O}$ ), 163 ( $M^+ - \text{CH}_2\text{CH}_2\text{OH}$ ),

149, 119, and 77. The sample obtained was not pure enough for elemental analysis.

**Peniane-2,4-dionatolithium (9).** In experiments 13–15 in Table 1, this compound was isolated; m.p.  $265^\circ$  (decomp.). It was identical with a sample prepared from the dione (2) and lithium hydride (i.r. spectroscopy).

**Reaction of Ethylene Carbonate (1) with 1,3-Diphenylpropane-1,3-dione (11).**—The reaction of the carbonate (1) (362 mg, 4.1 mmol) with the dione (11) (676 mg, 3.0 mmol) was conducted in the presence of NaI (45 mg, 0.3 mmol) at  $155\text{--}160^\circ\text{C}$  for 3 h. After removal of the iodide, the mixture was chromatographed (elution with cyclohexane, 1 : 1 cyclohexane–benzene, and benzene in turn), affording 3-benzoylpropyl benzoate (12) (534 mg, 63%) and a mixture of (12) and 2-benzoylmethyl-2-phenyl-1,3-dioxolan (13) (242 mg) (1 : 1 by  $^1\text{H}$  n.m.r.). Other reactions in Table 2 were performed similarly. The order of elution of the products was the dione (11), acetophenone (19), ethylene dibenzoate (14), (12), and (13).

**Reaction with excess of the carbonate (1).** Experiments 3 and 9 in Table 2 were conducted with an excess of (1): a mixture of (1) (8.80 g, 100 mmol), (11) (675 mg, 3.0 mmol), and a halide (0.3 mmol) was heated with stirring until the volume of evolved CO<sub>2</sub> reached 100 ml (at room temperature). The mixture was then treated as above.

**Reactions in the presence of dibenzo-18-crown-6.** Experiments 2 and 6–8 in Table 2 were conducted in the presence of dibenzo-18-crown-6: a mixture of (1) (180 mg, 2.0 mmol), (11) (337 mg, 1.5 mmol), and a halide (0.15 mmol) was heated together with the ether (amount shown in footnotes to the Table) with stirring until evolution of CO<sub>2</sub> ceased. The mixture was then poured into acetone (10 ml), and the precipitated ether was filtered off. The filtrate was evaporated and the residue chromatographed on a column of silica gel; elution with 0.2 : 99.8 acetone–cyclohexane gave (11), and subsequent elution with 0.5 : 99.5 acetone–cyclohexane gave a mixture of (12) and (13), whose ratio was calculated from integration of  $^1\text{H}$  n.m.r. signals at  $\delta$  3.13 (2 H) [for (12)] and 3.5–4.1 (6 H) [for (13)].

**3-Benzoylpropyl benzoate (12)** had m.p.  $87\text{--}88^\circ$  (from EtOH),  $\nu_{\text{max}}$  (KBr) 1 700, 1 665, and 1 285  $\text{cm}^{-1}$ ,  $\delta$  2.23 (2 H, m, C-CH<sub>2</sub>-C), 3.13 (2 H, t, *J* 7.0 Hz, CO-CH<sub>2</sub>-C), 4.40 (2 H, t, *J* 6.6 Hz, C-CH<sub>2</sub>-O), and 7.2–8.2 (10 H, m, aromatic) (Found: C, 75.85; H, 6.15. C<sub>17</sub>H<sub>16</sub>O<sub>3</sub> requires C, 76.1; H, 6.0%).

**2-Benzoylmethyl-2-phenyl-1,3-dioxolan (13)** had b.p.  $154\text{--}156^\circ$  at 0.26 mmHg (lit.,<sup>14</sup> 200–203 $^\circ$  at 3 mmHg),  $\nu_{\text{max}}$  (NaCl) 1 680, 1 330, 1 115, and 1 025  $\text{cm}^{-1}$ ,  $\delta$  3.58 (2 H, s, C-CH<sub>2</sub>-CO), 3.70–4.03 (4 H, m, O-CH<sub>2</sub>-CH<sub>2</sub>-O), and 7.2–8.1 (10 H, m, aromatic) (Found: C, 75.85; H, 6.15. Calc. for C<sub>17</sub>H<sub>16</sub>O<sub>3</sub>: C, 76.1; H, 6.0%).

**Ethylene dibenzoate (14)** had m.p.  $71.5\text{--}73^\circ$  (from EtOH) (lit.,<sup>19</sup> 73–74 $^\circ$ ).

**1,3-Diphenylpropane-1,3-dionatolithium (15)** had m.p.  $>260^\circ$ , and was identical with a sample prepared from (11) and lithium hydride (i.r. spectroscopy).

**Acetophenone (19)** was identical with a commercial sample (Wako Pure Chemicals, Japan) ( $^1\text{H}$  n.m.r., i.r., and g.l.c.). Its 2,4-dinitrophenylhydrazone had m.p.  $249\text{--}250^\circ$  (lit.,<sup>20</sup> 248–250 $^\circ$ ).

**Reaction of Propylene Carbonate (10) with 1,3-Diphenylpropane-1,3-dione (11).**—A mixture of propylene carbonate

<sup>18</sup> A. Lipp, *Ber.*, 1889, **22**, 1196.

<sup>19</sup> S. Gabriel and T. H. Heymann, *Ber.*, 1890, **23**, 2498.

<sup>20</sup> B. Witkop, *J. Amer. Chem. Soc.*, 1956, **78**, 2873.



(10) (412 mg, 4.0 mmol), the dione (11) (674 mg, 3.0 mmol), and a halide (0.3 mmol) was heated under the conditions shown for experiments 11 and 12 in Table 2 until evolution of CO<sub>2</sub> ceased. The resulting mixture was, after the removal of the halide, chromatographed on a silica gel column with cyclohexane, 0.2 : 99.8 acetone-cyclohexane, and 0.5 : 99.5 acetone-cyclohexane in turn as eluants. The order of elution of the products was the dione (11), propylene dibenzoate (18), 3-benzoyl-1-methylpropyl benzoate (16), and 2-benzoylmethyl-4-methyl-2-phenyl-1,3-dioxolan (17).

3-Benzoyl-1-methylpropyl benzoate (16) was a syrup,  $\nu_{\max}$  (NaCl) 1 720, 1 690, and 1 280 cm<sup>-1</sup>,  $\delta$  1.39 (3 H, d,  $J$  6.3 Hz, C-CH<sub>3</sub>), 2.16 (2 H, m, C-CH<sub>2</sub>-C), 3.10 (2 H, t,  $J$  7.5 Hz, C-CH<sub>2</sub>-CO), 5.27 (1 H, sextet,  $J$  6.3 Hz, C-CH-O), and 7.2—8.2 (10 H, m, aromatic) (Found: C, 76.8; H, 6.4. C<sub>18</sub>H<sub>18</sub>O<sub>3</sub> requires C, 76.55; H, 6.45%).

2-Benzoylmethyl-4-methyl-2-phenyl-1,3-dioxolan (17) was a syrup,  $\nu_{\max}$  (NaCl) 1 680, 1 595, 1 442, and 1 318 cm<sup>-1</sup>,  $\delta$  1.10 (3 H, d,  $J$  6.0 Hz, C-CH<sub>3</sub>), 3.53 (2 H, s, C-CH<sub>2</sub>-C), 3.2—4.4 (3 H, m, O-CH-CH<sub>2</sub>-O), and 7.2—8.2 (10 H, m, aromatic) (Found: C, 76.65; H, 6.5. C<sub>18</sub>H<sub>18</sub>O<sub>3</sub> requires C, 76.55; H, 6.45%). A shoulder at  $\delta$  3.50 was observed on the n.m.r. signal at  $\delta$  3.53, probably due to a geometrical isomer.

Propylene dibenzoate (18) was identical with an authentic sample (lit.,<sup>21</sup> b.p. 202—203° at 4 mmHg) (n.m.r., i.r., and g.l.c.).

*Reactions of Ethylene Carbonate (1) with 2-Alkyl-1,3-diphenylpropane-1,3-diones (20) and (25).*—A mixture of the carbonate (1) (357 mg, 4.0 mmol), 2-methyl-1,3-diphenylpropane-1,3-dione (20) (715 mg, 3.0 mmol), and NaI (47 mg, 0.3 mmol) was heated with stirring at 155—160 °C for 3 h. The resultant mixture was, after removal of the iodide, chromatographed on a column of silica gel with 0.2 : 99.8 acetone-cyclohexane and then 0.5 : 99.5 acetone-cyclohexane as eluant. The order of elution of the products was 1-phenylpropan-1-one (24), ethylene dibenzoate (14), 3-benzoyl-3-methyl-4-oxo-4-phenylbutyl benzoate (22), and 3-(2-benzoyloxyethoxy)-2-methyl-1,3-diphenylprop-2-en-1-one (21). In the case of the reaction catalysed by Me<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup>, 2-(1-benzoyl-2-phenyl-1,3-dioxolan (23) was obtained [eluted after (14) in place of (22)].

The reaction with 2-benzyl-1,3-diphenylpropane-1,3-dione (25) (945 mg, 3.0 mmol) was performed in the same way. The results are summarized in Table 3.

3-(2-Benzoyloxyethoxy)-2-methyl-1,3-diphenylprop-2-en-1-one (21), confirmed by <sup>1</sup>H n.m.r. as consisting of two geometrical isomers was obtained as a syrup,  $\nu_{\max}$  (NaCl) 1 720, 1 660—1 640, and 1 315—1 025 cm<sup>-1</sup>,  $\delta$  (isomer A) 1.93 (3 H, s, C-CH<sub>3</sub>), 3.4—3.7 and 3.8—4.0 (4 H, m, O-CH<sub>2</sub>-CH<sub>2</sub>-O), and 7.0—8.5 (15 H, m, aromatic),  $\delta$  (isomer B) 2.20 (3 H, s, C-CH<sub>3</sub>), 3.8—4.0 and 4.3—4.5 (4 H, m, O-CH<sub>2</sub>-CH<sub>2</sub>-O), and 7.0—8.5 (15 H, m, aromatic) (Found: C, 77.45; H, 5.8. C<sub>25</sub>H<sub>22</sub>O<sub>4</sub> requires C, 77.7; H, 5.75%). The C-methyl signals at  $\delta$  1.93 (A) and 2.20 (B) had a ratio of 1 : 2.

3-Benzoyl-3-methyl-4-oxo-4-phenylbutyl benzoate (22) was obtained as a syrup,  $\delta$  1.80 (3 H, s, C-CH<sub>3</sub>), 2.80 (2 H, t,  $J$  6.0 Hz, C-CH<sub>2</sub>-C), 4.42 (2 H, t,  $J$  6.0 Hz, C-CH<sub>2</sub>-O), and 7.1—8.0 (15 H, m, aromatic),  $m/e$  264.1140 ( $M^+$  - PhCO<sub>2</sub>H), 238, 160, 149, 122 (PhCO<sub>2</sub>H<sup>+</sup>), and 105 (PhCO<sup>+</sup>), not pure enough for elemental analysis.

2-(1-Benzoyl-2-phenyl-1,3-dioxolan (23) was obtained

<sup>21</sup> R. J. P. Allen, E. Jones, and R. D. Richie, *J. Chem. Soc.*, 1957, 524.

<sup>22</sup> T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 1932, 2607.

as a syrup,  $\nu_{\max}$  (NaCl) 1 680 and 1 230—1 040 cm<sup>-1</sup>,  $\delta$  1.77 (3 H, d,  $J$  7.2 Hz, C-CH<sub>3</sub>), 3.4—4.1 (4 H, m, O-CH<sub>2</sub>-CH<sub>2</sub>-O), 4.13 (1 H, q,  $J$  7.2 Hz, CH), and 7.1—8.1 (10 H, m, aromatic) (Found: C, 76.35; H, 6.65. C<sub>18</sub>H<sub>18</sub>O<sub>3</sub> requires C, 76.55; H, 6.45%).

1-Phenylpropan-1-one (24) was obtained as an oil; the 2,4-dinitrophenylhydrazone had m.p. 189—190° (from MeOH) (lit.,<sup>22</sup> 187—189°).

3-(2-Benzoyloxyethoxy)-2-benzyl-1,3-diphenylprop-2-en-1-one (26) was obtained as a syrup composed from two geometrical isomers,  $\nu_{\max}$  (NaCl) 1 725, 1 640, 1 275, 1 150, 1 100, and 1 070 cm<sup>-1</sup>,  $\delta_{\text{H}}$  (isomer A) 3.4—3.7 and 3.8—4.0 (4 H, m, O-CH<sub>2</sub>-CH<sub>2</sub>-O), 3.71 (2 H, s, CH<sub>2</sub>Ph), and 7.0—8.5 (20 H, m, aromatic),  $\delta_{\text{H}}$  (isomer B) 3.8—4.0 and 4.3—4.6 (4 H, m, O-CH<sub>2</sub>-CH<sub>2</sub>-O), 4.12 (2 H, s, CH<sub>2</sub>Ph), and 7.0—8.5 (20 H, m, aromatic),  $\delta_{\text{C}}$  (isomer A) 36.02 (CH<sub>2</sub>Ph) and 63.04 and 67.10 (O-CH<sub>2</sub>-CH<sub>2</sub>-O),  $\delta_{\text{C}}$  (isomer B) 35.41 (CH<sub>2</sub>Ph) and 63.70 and 67.84 (O-CH<sub>2</sub>-CH<sub>2</sub>-O) (Found: C, 80.25; H, 5.85. C<sub>31</sub>H<sub>26</sub>O<sub>4</sub> requires C, 80.5; H, 5.75%). The <sup>13</sup>C n.m.r. signals at 36.02 (A) and 35.41 (B) had a ratio of 1 : 3.

2-(1-Benzoyl-2-phenylethyl)-2-phenyl-1,3-dioxolan (28) had m.p. 135—136° (from MeOH),  $\nu_{\max}$  (KBr) 1 680, 1 270, 1 235, 1 160, and 1 040 cm<sup>-1</sup>,  $\delta$  2.95 (1 H, dd,  $J$  13.8 and 3.0 Hz, PhCHH), 3.20 (1 H, dd,  $J$  13.8 and 10.6 Hz, PhCHH), 3.6—4.2 (4 H, m, O-CH<sub>2</sub>-CH<sub>2</sub>-O), 4.41 (1 H, dd,  $J$  10.6 and 3.0 Hz, CH), and 7.1—7.8 (10 H, m, aromatic) (Found: C, 80.7; H, 6.2. C<sub>24</sub>H<sub>22</sub>O<sub>3</sub> requires C, 80.4; H, 6.2%). On irradiation at  $\delta$  4.41, both the quartets at  $\delta$  2.95 and 3.20 were changed into doublets.

1,3-Diphenylpropan-1-one (29) had m.p. 67—68° (from MeOH) (lit.,<sup>23</sup> 72—73°).

*Transformation of the Ester (26) into the Acetal (28).*—To a methanolic 20% ammonia (50 ml), was added the ester (26) (290 mg, 0.63 mmol), and the solution was set aside at room temperature for 13 h in a tightly stoppered round-bottomed flask. Evaporation, after cooling in an ice-bath, gave a crystalline residue which was chromatographed on a column of silica gel (eluant 1 : 99 acetone-cyclohexane). The product (28) (176 mg, 78%) was identical (mixed m.p.) with the foregoing sample.

*Reaction of Ethylene Carbonate (1) with 3,3-Dibenzylpentane-2,4-dione (30).*—A mixture of the carbonate (1) (360 mg, 4.0 mmol), the dione (30) (845 mg, 3.0 mmol), and a halide (0.3 mmol) was heated under the conditions shown in Table 4 with stirring until CO<sub>2</sub> evolution ceased. The resulting mixture was, after removal of the halide, chromatographed on a column of silica gel with 0.1 : 99.9 acetone-cyclohexane and subsequently 0.3 : 99.7 acetone-cyclohexane for elution. The order of elution of the products was 3-benzyl-4-phenylbutan-2-one (31), the dione (30), 2-(2-acetoxyethoxy)-3-benzyl-4-phenylbut-2-ene (32), and 2-hydroxyethyl acetate (33).

3-Benzyl-4-phenylbutan-2-one (31) was obtained as an oil,  $\nu_{\max}$  (NaCl) 1 718 cm<sup>-1</sup>,  $\delta$  1.75 (3 H, s, CH<sub>3</sub>), 2.5—3.5 (5 H, m, CH<sub>2</sub>-CH-CH<sub>2</sub>), and 7.16 (10 H, s, aromatic) (Found: C, 85.7; H, 7.55. Calc. for C<sub>17</sub>H<sub>18</sub>O: C, 85.65; H, 7.6%); 2,4-dinitrophenylhydrazone, m.p. 126—127° (from MeOH) [lit.,<sup>24</sup> 126—127° (from MeOH)].

2-(2-Acetoxyethoxy)-3-benzyl-4-phenylbut-2-ene (32) was obtained as a syrup,  $\delta_{\text{H}}$  2.00 and 2.13 (each 3 H, s, C-CH<sub>3</sub>), 3.05 (4 H, s, 2 CH<sub>2</sub>Ph), 3.6—4.0 and 4.1—4.4 (4 H, m,

<sup>23</sup> R. Adams, J. W. Kern, and R. L. Shriner, *Org. Synth.*, Coll. Vol. I, 1944, p. 101.

<sup>24</sup> R. A. Barns and B. D. Beitchman, *J. Amer. Chem. Soc.*, 1954, 76, 5430.

O-CH<sub>2</sub>-CH<sub>2</sub>-O), and 7.17 (10 H, broad s, aromatic),  $\delta_C$  20.77 (CH<sub>3</sub>-CO), 26.78 (CH<sub>2</sub>-C=), 37.86 (CH<sub>2</sub>Ph), 62.18 and 62.34 (O-CH<sub>2</sub>-CH<sub>2</sub>-O), 125—130 (C<sub>6</sub>H<sub>5</sub>), 137.29 (O-C=), and 162.43 (CH<sub>3</sub>-CO<sub>2</sub>). The quantity of the isolated product was not enough for elemental analysis or an i.r. spectrum.

2-Hydroxyethyl acetate (33) was identical with an authentic specimen<sup>25</sup> (n.m.r., i.r., and g.l.c.).

*Reaction of Ethylene Carbonate (1) with Ethyl Acetoacetate (34).*—A mixture of the carbonate (1) (442 mg, 5.0 mmol), the oxo-ester (34) (660 mg, 5 mmol), and NaI (75 mg, 0.5 mmol) was heated at 150—155 °C for 4 h while ethanol was distilled out. The resulting mixture was, after removal of NaI, chromatographed on a silica gel column; elution with cyclohexane gave 2-ethoxycarbonylmethyl-2-methyl-1,3-dioxolan (38), and elution with chloroform subsequently gave 3-acetyloxacyclopentan-2-one (37). The reaction catalysed by Me<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup> was similarly performed. The results are summarized in Table 5.

3-Acetyloxacyclopentan-2-one (37), obtained as an oil, was identical with an authentic specimen<sup>26</sup> (n.m.r., i.r., and g.l.c.).

2-Ethoxycarbonylmethyl-2-methyl-1,3-dioxolan (38) was obtained as an oil,  $\nu_{\max}$  (NaCl) 1 730, 1 220, 1 180, 1 110, 1 090, and 1 040 cm<sup>-1</sup>,  $\delta$  1.27 (3 H, t, *J* 7.5 Hz, CH<sub>2</sub>-CH<sub>3</sub>), 1.51 (3 H, s, C-CH<sub>3</sub>), 2.76 (2 H, s, C-CH<sub>2</sub>-C), 3.98 (4 H, s, O-CH<sub>2</sub>-CH<sub>2</sub>-O), and 4.08 (2 H, q, *J* 7.5 Hz, O-CH<sub>2</sub>-CH<sub>3</sub>) (Found: C, 55.25; H, 8.15. C<sub>8</sub>H<sub>14</sub>O<sub>4</sub> requires C, 55.15; H, 8.1%).

*Reaction of Ethylene Carbonate (1) with Diethyl Malonate (35).*—A mixture of the carbonate (1) (1.77 g, 20 mmol), the diester (35) (1.60 g, 10 mmol), and NaI (0.15 g, 2.0 mmol) was heated at 150—155 °C for 9 h, while ethanol was distilled out. The resulting mixture was, after removal of the iodide, poured into ether (40 ml), and set aside in a refrigerator; crystals of 2,7-dioxaspiro[4.4]nonane-1,6-dione

(39) (0.45 g, 30%), m.p. 108—109° (from Et<sub>2</sub>O) (lit.,<sup>27</sup> 109—110°), were deposited.

*Reaction of Ethylene Carbonate (1) with Diethyl 2-Acetamidomalonnate (36).*—A mixture of the carbonate (1) (1.76 g, 20 mmol), the diester (36) (4.30 g, 20 mmol), and Et<sub>4</sub>N<sup>+</sup>I<sup>-</sup> (1.28 g, 5.0 mmol) was heated at 150 °C for 5 h, until CO<sub>2</sub> evolution ceased. The resulting mixture was, after removal of the iodide, evaporated *in vacuo* to give an oil, which was distilled under reduced pressure to afford ethyl 2-acetamidobutyrate (40) (1.12 g, 32%), b.p. 75—77° at 0.08 mmHg,  $\nu_{\max}$  (NaCl) 1 740, 1 656, and 1 200 cm<sup>-1</sup>,  $\delta$  0.90 (3 H, t, *J* 8.0 Hz, C-CH<sub>2</sub>-CH<sub>3</sub>), 1.29 (3 H, t, *J* 7.4 Hz, O-CH<sub>2</sub>-CH<sub>3</sub>), 1.5—2.1 (2 H, m, C-CH<sub>2</sub>-CH<sub>3</sub>), 2.07 (3 H, s, CO-CH<sub>3</sub>), 4.19 (2 H, q, *J* 7.4 Hz, O-CH<sub>2</sub>-CH<sub>3</sub>), 4.3—4.7 (1 H, m, N-CH), and 6.3 (1 H, broad, NH) (Found: C, 55.25; H, 8.45; N, 8.2. C<sub>8</sub>H<sub>15</sub>NO<sub>3</sub> requires C, 54.5; H, 8.75; N, 8.1%).

*Reactions of Ethylene Carbonate (1) with the Diones (2) and (11) in the Presence of DABCO.*—A mixture of the carbonate (1) (1.79 g, 20 mmol), the dione (2) (2.01 g, 20 mmol), and DABCO (0.22 g, 2.0 mmol) was heated at 150—155 °C for 1 h. The mixture was then chromatographed. The reaction of the dione (11) (673 mg, 3.0 mmol) was performed similarly with the carbonate (1) (350 mg, 4.0 mmol) and the base (33 mg, 0.3 mmol), heated at 150—155 °C for 1 h. The results are summarized in Table 6.

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<sup>26</sup> I. L. Knunyantz, G. V. Chelintev, and E. D. Osetrova, *Compt. rend. acad. sci. U.R.S.S.[N.S.]*, 1934, **1**, 312 (*Chem. Abs.*, 1934, **28**, 4382).

<sup>27</sup> L. Herman and G. Frich, *Ber.*, 1912, **45**, 189.