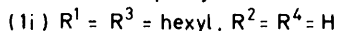
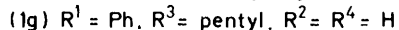
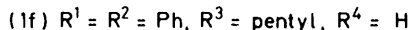
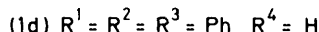
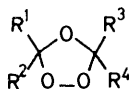
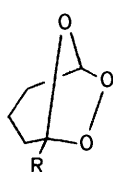
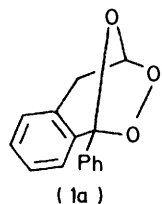


Reaction of Ozonides with Methanol in the Presence of Chlorosulphonic Acid: Selective Cleavage of the C–O Bond of the Peroxide Bridge

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The reaction of the 1,2,4-trioxolans (ozonides) (1) with methanol in the presence of chlorosulphonic acid gives good yields of products formed *via* the corresponding α -methoxy hydroperoxides. The order of reactivity of the ozonides, as estimated by periodic measurement of the n.m.r. spectra of a mixture of the ozonide and chlorosulphonic acid in CD₃OD, is as follows: (1a), (1b) > (1c), (1d), (1e), (1f), (1g) > (1h).

RECENTLY we reported that the reaction of the 1,2,4-trioxolans (ozonides) (1) with catalytic amounts of antimony pentachloride or chlorosulphonic acid gives 3,6-dialkyl-1,2,4,5-tetroxans and/or 1,4-dialkyl-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecanes.^{1,2} To obtain insight into the mechanism of the reaction, we have examined

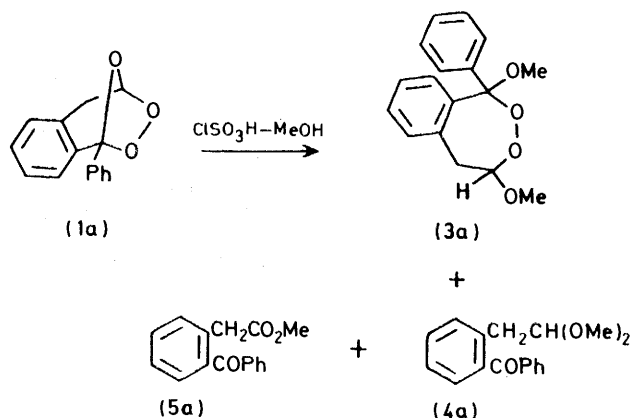


the reactions of the ozonide (1a–i) with methanol in the presence of chlorosulphonic acid; product analysis should clarify which bond is broken in the first step.

RESULTS AND DISCUSSION

The reaction of 1,4-epoxy-4,5-dihydro-1*H*-2,3-benzodioxepin (1a) with methanol in the presence of 10⁻³ mol equiv. of chlorosulphonic acid was followed by measuring the n.m.r. spectra periodically (Table 1). The signals due to (1a) were not observed after 45 min, and the yield of methyl *o*-benzoylphenylacetate (5a) increased as that of the benzodioxepin (3a) decreased with longer reaction times, with a very slow decrease in the yield of *o*-(2,2-dimethoxyethyl)benzophenone (4a). The reaction of (1a) on a preparative scale was performed in the presence of 1 mol equiv. of chlorosulphonic acid (Table 2). Consistent with the n.m.r. data, a mixture of (3a), (4a), and (5a) was isolated after reaction for 1 h. However, the ester (5a) was the major product after 80 h, and treatment of (3a) with 3 mol equiv. of chlorosulphonic

acid for 3 h afforded (5a) quantitatively. In the reaction of 1-phenyl-6,7,8-trioxabicyclo[3.2.1]octane (1b) in the presence of 10⁻³ mol equiv. of chlorosulphonic acid (Scheme) evidence was obtained for the formation of 1-methoxy-4-benzoylbutyl hydroperoxide (2b). The n.m.r. spectra of the solution showed an absorption at δ 4.76 (t, *J* 6.0 Hz), along with signals assignable to (3b), (4b), and (5b) (Table 1). Although we failed to isolate (2b) in a pure state, the following facts support its formation. After 1 h, the mixture of (1b) and chlorosulphonic acid (1 mol equiv.) was poured into ice-water, and extracted with ether. The i.r. spectrum of the crude products showed an absorption due to the hydroperoxy group (ν_{max} 3335 cm⁻¹), and no absorption attributable to 4-benzoylbutylaldehyde. When the products were treated with aqueous potassium hydroxide, however, 4-benzoylbutylaldehyde was isolated from the aqueous layer in 30% yield. Consistent with this result, the organic layer did not contain a compound with a hydroperoxy group, and column chromatography on silica gel afforded (3b), (4b), and (5b) (Table 2). These results may be explained by considering the fact that the α -methoxy hydroperoxide (2b) is reduced by aqueous potassium hydroxide.³ The reaction of (3b) in the



presence of 1 mol equiv. of chlorosulphonic acid in methanol gave a mixture of (2b), (4b), and (5b) (Table 2). When a solution of (4b), 30% aqueous hydrogen peroxide (1 mol equiv.), and chlorosulphonic acid (1 mol equiv.) in methanol was kept at 20 °C for 4 days, (5b) was obtained quantitatively. In the absence of hydrogen peroxide (4b) was stable (Table 2).

TABLE I

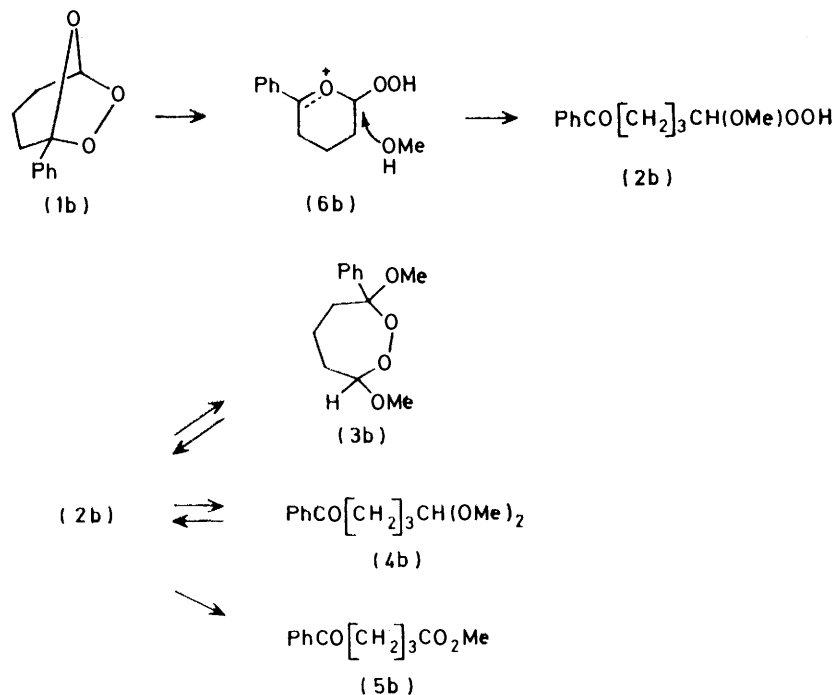
N.m.r. investigation of the reaction of ozonides with CD₃OD in the presence of chlorosulphonic acid ^a

Ozonide	Conditions	Reaction time/min	% Unchanged ozonide	Product [yield, %] ^b
(1a)	A ^c	45	0	(3a) [59], (4a) [35], (5a) [6]
(1a)	A	72	0	(3a) [47], (4a) [35], (5a) [18]
(1a)	A	99	0	(3a) [44], (4a) [31], (5a) [25]
(1b)	A	45	0	(2b) [44], (3b) [15], (4b) [34], (5b) [12]
(1b)	A	72	0	(2b) [45], (3b) [18], (4b) [20], (5b) [17]
(1b)	A	97	0	(2b) [42], (3b) [20], (4b) [18], (5b) [20]
(1c)	A	43	75	(3c) [7], (4c) [18]
(1c)	A	70	69	(3c) [14], (4c) [17]
(1c)	A	100	57	(3c) [22], (4c) [21]
(1c)	B ^d	31	26	(3c) [52], (4c) [22]
(1c)	B	69	2	(3c) [67], (4c) [31]
(1c)	B	173	0	(3c) [70], (4c) [30]
(1d)	B	35	94	(2e) [2], (4e) [4], (7) [6]
(1d)	B	70	76	(2e) [7], (4e) [17], (7) [24]
(1d)	B	177	49	(2e) [13], (4e) [24], (5c) [14], (7) [51]
(1e)	B	32	67	(2e) [8], (4e) [58]
(1e)	B	67	56	(2e) [16], (4e) [64], (5e) [18]
(1e)	B	175	36	(2e) [25], (4e) [74], (5e) [29]
(1f)	B	27	76	(2h) [10], (4h) [14], (7) [24]
(1f)	B	67	51	(2h) [27], (4h) [24], (7) [49]
(1f)	B	176	22	(2h) [32], (4h) [26], (5h) [20], (7) [78]
(1g)	C ^e	48	29	(4e) [50], (5e) [21]
(1g)	C	222	0	(2h) [7], (4h) [43], (5h) [21]
(1g)	C	1 470	0	(4e) [50], (5e) [50]
(1h)	C	54	100	(4h) [57], (5h) [43]
(1h)	C	228	88	(4e) [55], (5e) [45]
(1h)	C	1 490	81	(4h) [43], (5h) [57]

^a Reactions were performed at 20 °C. ^b Yields shown are mol % yields. ^c A: solution of the ozonide (0.5 mmol/ml) and 10⁻³ mol equiv. of chlorosulphonic acid in CD₃OD-CDCl₃ (2/1, v/v). ^d B: solution of the ozonide (0.3 mmol/ml) and 0.1 mol equiv. of chlorosulphonic acid in CD₃OD-CDCl₃ (2/1 v/v). ^e C: solution of the ozonide (0.25 mmol/l) and 1 mol equiv. of chlorosulphonic acid in CD₃OD.

1-Methyl-6,7,8-trioxabicyclo[3.2.1]octane (1c) was less reactive than (1a) or (1b) (Table I), and the products were the cyclic peracetal (3c) (mixture of *cis*- and *trans*-isomers) and the acetal (4c). However, (1c) is more

reactive than the monocyclic ozonides 3,3,5-triphenyl- (1d), 3,5-diphenyl- (1e), 5-pentyl-3,3-diphenyl- (1f), 5-pentyl-3-phenyl- (1g), and 3,5-dipentyl-1,2,4-trioxolan (1h) (Table I). The reaction of (1h) is quite slow; when the



SCHEME

reaction was performed in the presence of 1 mol equiv. of chlorosulphonic acid for 4 h, 88% of (1h) remained unchanged. Under these conditions the other ozonides were consumed completely (Table 1). In summary, the order of reactivity of the ozonides is roughly as follows: (1a), (1b) > (1c) > (1d), (1e), (1f), (1g) > (1h). The higher reactivity of the bicyclic ozonides compared with the monocyclic ozonides may be explained as follows. The considerable amount of strain in the bicyclic ozonides is released by ring opening, and, in addition, the intermediate (6) with a carboxonium ion structure (Scheme) formed from bicyclic ozonides by heterolytic C-O bond

TABLE 2

Reaction of ozonides and the related compounds with methanol in the presence of chlorosulphonic acid ^a

Substrate	Reaction time/h	Product [yield, %] ^b
(1a)	4 ^c	(3a) [37], (4a) [39]
(1a)	80 ^c	(3a) [21], (4a) [25], (5a) [45]
(1a)	4	(3a) [16], (4a) [18], (5a) [32]
(1a)	80	(4a) [13], (5a) [70]
(1b)	1	(3b) [14], (4b) [20], (5b) [21] ^d
(1b)	80 ^d	(3b) [3], (4b) [9], (5b) [66]
(1c)	1 ^d	(3c) [7], (4c) [5] ^{f,g}
(1d)	80	(4e) [25], (5e) [75], (7) [95]
(1e)	50	(5e) [90], (8) [77]
(1g)	80	(4e) [49], (5e) [37], (4h) [39], (5h) [31]
(1i)	100	(11) [33], (12) [27] ^h
(3a)	3 ⁱ	(5a) [95]
(3b)	3	(2b) [5], (4b) [6], (5b) [89] ^j
(3b)	120	(5b) [94]
(4b)	100 ^{k,t}	(5b) [98]
(4b)	100 ^m	(4b) [100] ^j
(4c)	100 ^k	(5e) [93]

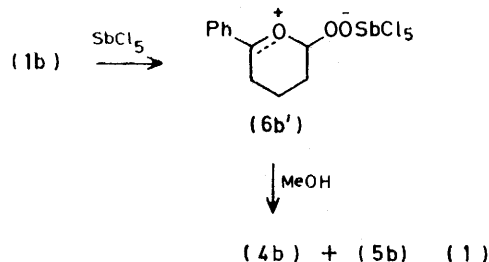
^a Reactions were performed in the presence of 1 mol equiv. of chlorosulphonic acid unless otherwise noticed. ^b Yields shown are mol % yields. ^c 0.03 mol equiv. of chlorosulphonic acid was used. ^d 0.1 mol equiv. of chlorosulphonic acid was used. ^e 4-Benzoylbutyaldehyde was isolated in 27% yield. ^f The ozonide (1c) was recovered (27%). ^g The low yields of the products are due to the volatility of (1c) and (3c). ^h The ozonide (1i) was recovered (34%). ⁱ In the presence of 3 mol equiv. of chlorosulphonic acid. ^j The product ratio was determined by n.m.r. spectroscopy. ^k A solution of the acetal, 30% aqueous hydrogen peroxide (1 mol equiv.), and chlorosulphonic acid (1 mol equiv.) in methanol was kept at 20 °C. ^l The n.m.r. spectrum of a solution of (4b), chlorosulphonic acid (0.1 mol equiv.), and 30% aqueous hydrogen peroxide (1 mol equiv.) in methanol kept at 20 °C for 3 h showed the presence of (2b) along with (4b). ^m Reaction in the absence of hydrogen peroxide.

fission of the peroxide bridge would be expected to be more stable than that formed from monocyclic ozonides.⁴ Zwitterionic intermediates (6a') or (6b') with a carboxonium ion structure were isolated from the reaction of (1a) or (1b) with 1 mol equiv. of antimony pentachloride in carbon tetrachloride [reaction (1)]. The reaction of (6b') with methanol yielded a mixture of (4b) (45%) and (5b) (8%).⁵ In contrast, the other ozonides did not give similar intermediates in a stable form.

From previous results, we suggest the mechanism in

* Ozonides bearing at least one H atom on the trioxolan ring are known to react slowly with methanol to afford 1 mol equiv. of acid and 1 mol equiv. of aldehyde (ketone). A mechanism has been proposed which involves the abstraction of a hydrogen atom from the trioxolan ring in the rate-determining step.⁶ However, this process does not seem to participate in our reactions.

the Scheme to explain the reaction of (1b).^{*} The first step involves heterolytic fission of one of the C-O bonds of the peroxide bridge (that leading to the more stable carbonium ion) to afford the intermediate (6b). Attack by methanol on C-6 of (6b) would yield (2b), and acid-catalysed hydroperoxy-methoxy exchange would give (4b). The peracetalization of α -methoxy hydroperoxides is well known.⁷ However, compounds (2b), (3b), and (4b) are not stable under the acidic conditions, and longer reaction times lead to the formation of (5b) as the final product. The acid-catalysed formation of an ester from the corresponding α -methoxy hydroperoxide is well established.⁸ The Scheme involves the participation of the carboxonium ion intermediate (6b), but it may be



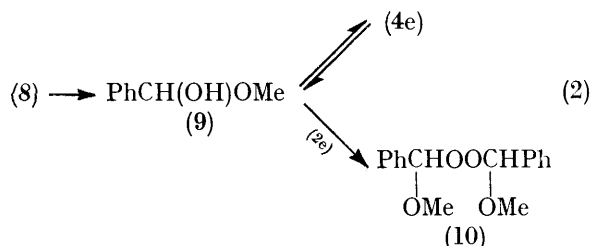
better to consider that heterolytic C-O bond fission and attack of methanol occur in a concerted manner in the presence of a large excess of methanol.

Periodic measurement of the n.m.r. spectra of a solution of (1d) and 0.1 mol equiv. of chlorosulphonic acid (Figure 1) indicated the following. (a) The reaction affords a mixture of α -methoxybenzyl hydroperoxide (2e), α -dimethoxytoluene (4e), methyl benzoate (5e), and benzophenone (7) the yields of which increase with consumption of (1d) as the reaction proceeds. (b) The amount of the ozonide (1d) consumed corresponds to the amount of benzophenone formed throughout the reaction. The reaction of (1d) in the presence of 1 mol equiv. of chlorosulphonic acid for 80 h, gave a mixture of (7) and (5e) in yields of 96 and 89%, respectively. The n.m.r. spectra of a solution of (1e) in the presence of 0.1 mol equiv. of chlorosulphonic acid indicated that (4e) was the major product, along with small amounts of (2e) and (5e) in the first stage of the reaction, suggesting that benzaldehyde (8), the expected product, reacts under these conditions to give the acetal (4e) (Table 1 and Figure 2). In the preparative scale reaction of (1e) in the presence of 1 mol equiv. of chlorosulphonic acid, a mixture of (8) and (5e) was obtained in a molar ratio of 1 : 1, suggesting that almost 1 mol equiv. of the acetal (4e) can be converted into (5e) *via* (2e).[†]

Of relevance to our results is the fact that the ozonolysis of stilbene in methanol-methylene chloride⁹ gave bis-(α -methoxybenzyl) peroxide (10) as the major product, the formation of which was explained in terms of the reaction of the hemiacetal (9) as the pivotal intermediate with (2e) in the presence of adventitious acid

[†] The reaction of a mixture of (4e), 30% aqueous hydrogen peroxide (1 mol equiv.), and chlorosulphonic acid (1 mol equiv.) in methanol gave (5e) quantitatively (Table 2).

catalyst [reaction (2)]. However, (10) was not observed in our system, probably because it affords (4e) or (5e) rather than reacting with the hemiacetal (9). It should



be noted that the ozonolysis of alkenylbenzenes does not give the corresponding $\alpha\alpha'$ -dimethoxy peroxide, but instead affords the α -methoxy hydroperoxide.⁹ These facts, however, do not exclude the possibility of the participation of the peroxide in question as the transient intermediate in our system, in view of the behaviour of the cyclic peracetals (3a) and (3b) in the presence of chlorosulphonic acid in methanol. When (1f) was

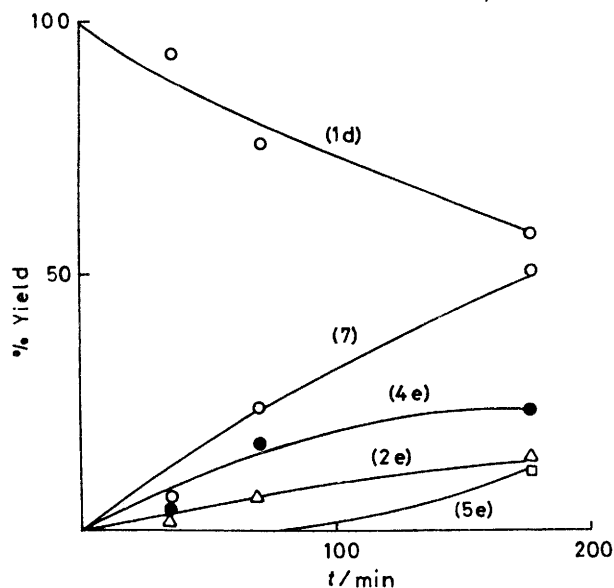


FIGURE 1 Reaction of (1d) with ClSO_3H in CD_3OD

treated with 1 mol equiv. of chlorosulphonic acid, n.m.r. spectroscopy indicated the formation of 1-methoxyhexyl hydroperoxide (2h),⁹ 1,1-dimethoxyhexane (4h), methyl hexanoate (5h), and (7). This behaviour of (1f) is consistent with that of (1d). In contrast, the n.m.r. spectra of a solution of (1g) under the same conditions showed the presence of (4e) and (5e) along with (2h), (4h), and (5h). More surprisingly, the ratio of (5e) to (5h) was *ca.* 1 : 1. If (5e) is formed from (2e), both the C-O bonds of the peroxide bridge of (1g) must be cleaved to an almost equal extent, in spite of the expectation that the C-O bond attached to the phenyl ring would be cleaved more easily. These results, however, are consistent with that in the reaction of (1g) with catalytic amounts of antimony pentachloride in methylene chloride; a mixture of 3,6-diphenyl- (4%), 3,6-

dipentyl- (13%), and 3-pentyl-6-phenyl-1,2,4,5-tetroxan (27%) was obtained.² The reaction of 3,5-dialkyl-1,2,4-trioxolans is quite slow. However, a mixture of 1,1-diethoxyheptane (11) and ethyl heptanoate (12) was

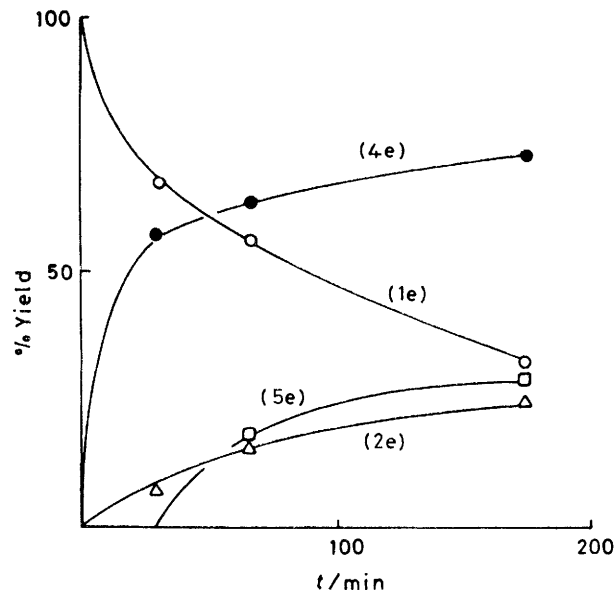
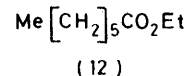
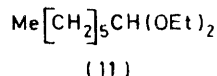
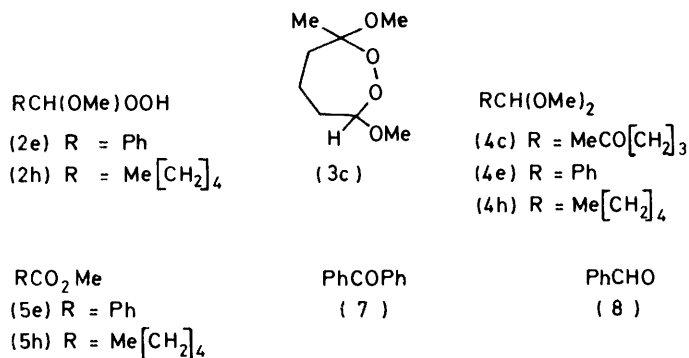


FIGURE 2 Reaction of (1e) with ClSO_3H in CD_3OD

obtained in a molar ratio of 1 : 1 from the reaction of 3,5-hexyl-1,2,4-trioxolan (1i) in the presence of 1 mol equiv. of chlorosulphonic acid in ethanol for 4 days.



EXPERIMENTAL

¹H N.m.r. spectra were obtained with a JEOL LNM 4P100 instrument, mass spectra with a Hitachi RMU-6H spectrometer, and i.r. spectra with a Hitachi 215 spectrometer.

Ozonolysis.—The procedure has been described previously.² 3,5-Dihexyl-1,2,4-trioxolan (1i) (mixture of *cis*- and *trans*-isomers) was obtained in the ozonolysis of oct-1-ene in the presence of octanal as an oil, δ 0.88 (6 H, t, *J* 4.5 Hz), 1.04—1.88 (20 H, m), and 4.92—5.28 (2 H, m); ν_{max} . 1460, 1380, 1100, and 1050 cm^{-1} . The ozonides (1a),¹⁰ (1b),¹¹ (1c),¹² (1d),¹¹ (1e),¹¹ (1f),² (1g),² and (1h)² were prepared according to the reported methods.

Investigation of the Reactions of Ozonides with Methanol in the Presence of Chlorosulphonic Acid by N.m.r. Spectroscopy.

—A solution of the ozonide and an appropriate amount of chlorosulphonic acid in $\text{CD}_3\text{OD}-\text{CDCl}_3$ (Table 1) was sealed in an n.m.r. tube and the n.m.r. spectra were recorded periodically at 20 °C. The decrease in the amount of ozonide and increase in the amount of products was estimated by comparing the intensities of the following characteristic peaks: (1a), δ 6.20br (1 H, s); (1b), 5.96br (1 H, s); (1c), 5.76 (1 H, s); (1d), 6.36 (1 H, s); (1e), 6.34 (2 H, s); (1f), 5.46 (1 H, t, J 3.8 Hz); (1g) 5.96 (1 H, s); (1h), 5.12 (2 H, t, J 3.8 Hz); (2b), 4.76 (1 H, t, J 6.0 Hz); (2e), 5.64 (1 H, s); (2h), 4.68 (1 H, t, J 5.8 Hz); (3a), 5.02 (1 H, 2 \times d, J 9.0 and 4.5 Hz); (3b), 4.88 (1 H, t, J 4.8 Hz); (3c), 4.78 (1 H, t, J 5.4 Hz) and 4.86 (1 H, t, J 5.4 Hz); (4a), 4.48 (1 H, t, J 6.0 Hz); (4b), 4.32 (1 H, t, J 5.4 Hz); (4c), 4.35 (1 H, t, J 5.2 Hz); (4e), 5.35 (1 H, s); (4h), 5.35 (1 H, t, J 5.2 Hz); (5a), 3.86 (2 H, s); (5b), 3.02 (2 H, t, J 7.5 Hz); (5e), 7.96—8.5 (2 H, m); (5h), 2.30 (2 H, t, J 7.5 Hz); (7), 7.70—7.92 (4 H, m).

Reaction of the Ozonide (1a) with Methanol in the Presence of 1 Mol Equiv. of Chlorosulphonic Acid.

—To a stirred solution of (1a) (10 mmol) in methanol (20 ml) was added chlorosulphonic acid (10 mmol) in methanol (20 ml) in one portion. The mixture was stirred for a further 30 min, and then poured into ice-cold aqueous potassium hydroxide, and the products were extracted with ether. Column chromatography on silica gel (elution with benzene) afforded first 4,5-dihydro-1,4-dimethoxy-1-phenyl-1H-2,3-benzodioxepin (3a); an oil (Found: C, 71.1; H, 6.4. $\text{C}_{17}\text{H}_{18}\text{O}_4$ requires C, 71.3; H, 6.3%); δ 2.88 (1 H, 2 \times d, J 15.0 and 4.5 Hz), 3.48 (3 H, s), 3.54 (3 H, s), 3.78 (1 H, 2 \times d, J 15.0 and 9.0 Hz), 5.02 (1 H, 2 \times d, J 9.0 and 4.5 Hz), and 7.00—7.72 (9 H, m); ν_{max} 1 450, 1 360, 1 180, 1 100, 1 070, 970, and 750 cm^{-1} . From the second fraction *o*-(2,2-dimethoxyethyl)-benzophenone (4a) was isolated; an oil, m/e 270 (M^+); δ 3.02 (2 H, d, J 6.0 Hz), 3.18 (6 H, s), 4.48 (1 H, t, J 6.0 Hz), and 7.20—7.88 (14 H, m); ν_{max} 1 660, 1 445, 1 270, 1 120, 1 065, 920, and 760 cm^{-1} , the physical properties of which were identical with those of the product of the reaction of *o*-benzoylphenylacetaldehyde and methanol in the presence of chlorosulphonic acid. Elution with ether gave methyl *o*-benzoylphenylacetate (5a); m.p. 70—70.5 °C (from ethanol) (lit.,¹³ 70—70.5 °C); δ 3.52 (3 H, s), 3.86 (2 H, s), and 7.16—7.88 (9 H, m); ν_{max} 1 740, 1 660, 1 600, 1 445, 1 270, 1 170, 760, and 700 cm^{-1} .

Products.—3-Phenyl-3,7-dimethoxy-1,2-dioxepan (3b) was an oil (Found: C, 65.7; H, 7.7. $\text{C}_{13}\text{H}_{18}\text{O}_4$ requires C, 65.6; H, 7.6%); δ 1.44—2.48 (6 H, m), 3.20 (3 H, s), 3.56 (3 H, s), 4.88 (1 H, t, J 4.8 Hz), and 7.20—7.52 (5 H, m); ν_{max} 1 445, 1 205, 1 160, 1 720, 1 005, 940, and 760 cm^{-1} . 5,5-Dimethoxyvalerophenone (4b) was obtained as an oil; δ

1.52—1.92 (4 H, m), 2.92 (2 H, t, J 7.5 Hz), 3.24 (6 H, s), 4.32 (1 H, t, J 5.4 Hz), 7.20—7.52 (3 H, m), and 7.80—7.92 (2 H, m); ν_{max} 1 685, 1 450, 1 205, 1 065, and 755 cm^{-1} , the physical properties of which were identical with those of authentic sample prepared by the reaction of 4-benzoylbutyraldehyde and methanol in the presence of chlorosulphonic acid. Methyl 4-benzoylbutyrate (5b) was an oil; b.p. 130—132 °C at 1 mmHg (lit.,¹⁴ b.p. 127—128 °C at 0.7 mmHg), m/e 206 (M^+); δ 1.80—2.28 (2 H, m), 2.42 (2 H, t, J 7.5 Hz), 3.02 (2 H, t, J 7.5 Hz), 3.64 (3 H, s), 7.20—7.64 (3 H, m), and 7.82—8.40 (2 H, m); ν_{max} 1 730, 1 680, 1 440, 1 205, and 745 cm^{-1} . 3-Methyl-3,7-dimethoxy-1,2-dioxepan (3c) was obtained as an oil (mixture of *cis*- and *trans*-isomers in a ratio of 1 : 1) (Found: C, 54.2; H, 9.3. $\text{C}_8\text{H}_{16}\text{O}_4$ requires C, 54.5; H, 9.2%); δ 1.26 (6 H, s), 1.40—2.16 (12 H, m), 3.35 (3 H, s), 3.37 (3 H, s), 3.46 (3 H, s), 3.52 (3 H, s), 4.78 (1 H, t, J 5.4 Hz), and 4.86 (1 H, t, J 5.4 Hz); ν_{max} 1 710, 1 440, 1 360, 1 125, 1 020, 980, 940, 900, and 850 cm^{-1} . 6,6-Dimethoxyhexan-2-one (4c) was an oil; δ 1.32—1.96 (4 H, m), 2.12 (3 H, s), 2.46 (2 H, t, J 5.8 Hz), 3.32 (6 H, s), and 4.35 (1 H, t, J 5.4 Hz); ν_{max} 1 710, 1 440, 1 360, 1 115, and 1 080 cm^{-1} . The acetal (4e) had b.p. 205 °C (lit.,¹⁵ 207 °C), (4h) had b.p. 59—60 °C at 15 mmHg (lit.,¹⁶ 52—53 °C at 12 mmHg), and (11) had b.p. 209 °C (lit.,¹⁵ 209 °C).

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