

## Synthesis and Reaction of 1,2,4-Trioxanes

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The peroxides (**1a—e**) and epoxides (**2a—g**) in methylene dichloride were treated with tungsten(vi) oxide and then with catalytic amounts of chlorosulphonic acid to give the corresponding 1,2,4-trioxanes (**3a—r**) in 10—63% yield. The mode of decomposition of the 1,2,4-trioxanes was studied by treating a number with the following reagents: triethylamine, sodium ethoxide, lithium di-isopropylamide, Grignard and lithium reagents, lithium aluminium hydride, anthrylsodium, triphenylphosphine, and titanium tetrachloride.

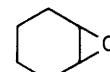
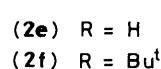
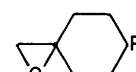
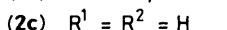
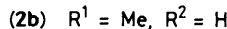
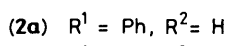
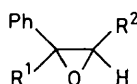
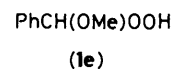
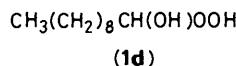
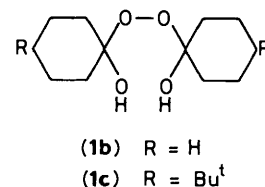
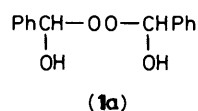
Because of its relevance to Qinghaosu chemistry,<sup>1</sup> the synthesis and reactions of 1,2,4-trioxane have attracted great attention.<sup>2</sup> While developing a new, general synthetic method for cyclic peroxides from  $\alpha$ -hydroxy hydroperoxides,<sup>3</sup> we discovered that the reaction of the peroxides (**1a—e**) and the epoxides (**2a—g**) in the presence of tungsten(vi) oxide and catalytic amounts of chlorosulphonic acid gave the corresponding 1,2,4-trioxanes (**3a—r**).<sup>4</sup> In this paper we report details of the synthesis and the mode of decomposition of some 1,2,4-trioxanes under a variety of conditions.

### Results and Discussion

**Synthesis of 1,2,4-Trioxanes.**—A mixture of each of the peroxide (**1a—e**) and the epoxide (**2a—g**) was treated with tungsten(vi) oxide and then with a catalytic amount of chlorosulphonic acid to give the corresponding 1,2,4-trioxanes (**3a—r**) in 10—63% yield (Table 1). Although a number of stereoisomers are possible for many of the trioxanes synthesized, *e.g.* (**3c**) and (**3f**) each have two chiral centres, and (**3d**) and (**3g**) each have three chiral centres, the <sup>1</sup>H n.m.r. spectra of the crude products showed in each case the existence of only one isomer: the latter is probably that most stable under the reaction conditions employed. By-products such as the ketols (**7d, e**) and the 1,2,4,5-tetroxanes (**8a, b**) were, however, formed in the reactions and since these and the 1,2,4-trioxane (**3**) have similar polarities, elaborate column chromatography was required to isolate the latter.

The following results demonstrate that the reaction has two steps. Treatment of a mixture of styrene oxide (**2c**) and a peroxide (**1a**) with tungsten(vi) oxide at 25 °C for 3 h, followed by column chromatography of the reaction mixture on silica gel, gave the dihydroxy peroxide (**4**) (31%). The reaction of this intermediate (**4**) with chlorosulphonic acid (0.1 equiv.) yielded the 1,2,4-trioxane (**3c**) quantitatively [equation (1)].

To obtain further insight into the mechanism of this reaction, the peroxide (**1a**) was treated with (*E*)-2-deuteriostyrene oxide [ $\beta$ -<sup>2</sup>H]-*E*-(**2c**). The product was a mixture of *cis*- and *trans*-[<sup>5-2</sup>H]-(**3c**), in a ratio of 63:37. The mechanism outlined in Scheme 1 seems to rationalize the results in the most satisfactory manner. The first step of the reaction involves WO<sub>3</sub>-mediated ring opening of the epoxide [ $\beta$ -<sup>2</sup>H]-*E*-(**2c**) to afford a zwitterionic intermediate (**6**), followed by attack of the peroxide (**1a**) from the less hindered direction and subsequent ClSO<sub>3</sub>H-catalysed ring closure to give [<sup>5-2</sup>H]-*cis*-(**3c**), in which the 5-<sup>2</sup>H and 6-Ph are *cis*-related. In the intermediate (**6**), however, C—C bond rotation is likely to compete with nucleophilic attack by the peroxide (**1a**) and, consequently, the *trans* isomer is also produced in a small but significant amount.



**Reaction with Triethylamine, Sodium Ethoxide, or Lithium Diisopropylamide.**—Treatment of each 1,2,4-trioxane (**3a—b**) with triethylamine gave the corresponding esters (**9a—b**) [equation (2), and Table 2]. In the case of 1,2,4-trioxane (**3c**), benzaldehyde (**5c**) and 2-phenylethane-1,2-diol (**10c**) were also produced together with the ester (**9c**). Since the reaction of the ester (**9c**) with triethylamine gave the diol (**10c**) in good yield, then the primary product from (**3c**) is the ester (**9c**). Thus, the first step of the reaction of (**3a—c**) with triethylamine must involve abstraction of the hydrogen at the 3-position, followed by electron migration and subsequent proton transfer to yield ester (**9**). A similar transformation has been discovered by Jefford *et al.* for bicyclic 1,2,4-trioxanes.<sup>2*n,p*</sup>

Treatment of 1,2,4-trioxanes (**3a—c**) with an excess of sodium ethoxide in ethanol afforded the corresponding diols (**10a—c**) together with ethyl benzoate (**11**), as did the reaction of the corresponding ester (**9a**) under the same conditions [equation (3) and Table 2]. This implies that the reaction of a 1,2,4-trioxane (**3a—c**) with sodium ethoxide yields first the corresponding hydroxy ester (**9a—c**), which in turn reacts with an excess of sodium ethoxide to give (**10a—c**) and (**11**).

The reaction of 1,2,4-trioxane (**3a—c**) with lithium diisopropylamide (LDA) gave benzoic acid (**12**), benzamide (**13**), and the diol (**10a—c**), together with the hydroxy ester (**9a**,

**Table 1.** Synthesis of 1,2,4-trioxanes

Peroxide (1a)	Epoxide (2a)	1,2,4-Trioxane yield (%) (3a)	Others yield (%) (5c) 12, (8a) 10, (10a) 28
(1a)	(2b)	(3b) 10	(5c) 20, (8a) 30
(1a)	(2c)	(3c) 37	(5c) 20, (8a) 10
(1a)	(2d)	(3d) 22	(5c) 20, (8a) 25
(1d)	(2a)	(3e) 28 <sup>a</sup>	
(1d)	(2c)	(3f) 23 <sup>a</sup>	
(1d)	(2d)	(3g) 10 <sup>a</sup>	
(1b)	(2a)	(3h) 11	(7d) 11, (8b) 10 <sup>b</sup>
(1b)	(2c)	(3i) 30	(7e) 18, (8b) 7 <sup>b</sup>
(1c)	(2c)	(3j) 22 <sup>c</sup>	
(1a)	(2e)	(3k) 42	(8a) 10
(1a)	(2f)	(3l) 22	(8a) 22
(1b)	(2e)	(3m) 35	(8b) 5 <sup>b</sup>
(1b)	(2f)	(3n) 38	(8b) 3 <sup>b</sup>
(1c)	(2f)	(3o) 17 <sup>c</sup>	
(1a)	(2g)	(3p) 63	(5c) 10, (8a) 3
(1d)	(2g)	(3q) 46 <sup>a</sup>	
(1b)	(2g)	(3r) 47	(8b) 3 <sup>b</sup>
(1e)	(2c)	(3c) 10	(5c) 20, (8a) 35

<sup>a</sup> The by-products were not determined. <sup>b</sup> Cyclohexanone was also isolated in *ca.* 40% yield. <sup>c</sup> 4-t-Butylcyclohexanone was also obtained in *ca.* 30% yield.

**Table 2.** Reaction with triethylamine,<sup>a</sup> sodium ethoxide<sup>b</sup> or lithium di-isopropylamide<sup>c</sup>

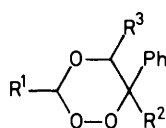
Substrate	Reagent [mol equiv.]	Reaction time, h	Products, yield (mol %)
(3a)	NEt <sub>3</sub> [10]	2 <sup>d</sup>	(9a) 75
(3b)	NEt <sub>3</sub> [10]	4	(9b) 75
(3c)	NEt <sub>3</sub> [10]	6	(5c) 22, (9c) 31, (10c) 45
(9c)	NEt <sub>3</sub> [10]	6	(10c) 84
(3a)	NaOEt [14]	0.2	(10a) 63, (11) 63
(3b)	NaOEt [19]	0.2	(10b) 70, (11) 73
(3c)	NaOEt [11]	1	(10c) 64, (11) 65
(9a)	NaOEt [14]	0.2	(10a) 73, (11) 60
(3a)	LiNPr <sub>2</sub> [3]	2	(9a) 21, (10a) 47, (12) 29
(3b)	LiNPr <sub>2</sub> [5]	8	(9b) 43, (10b) 21, (12) 27
(3c)	LiNPr <sub>2</sub> [10]	24	(10c) 21, (12) 18, (13) 26, (14d) 27
(9a)	LiNPr <sub>2</sub> [3]	2	(10a) 66, (12) 30
(9b)	LiNPr <sub>2</sub> [5]	6	(10b) 71, (12) 26, (13) 8
(9c)	LiNPr <sub>2</sub> [10]	24	(12) 33, (13) 11

<sup>a</sup> The reaction in methylene chloride at 38 °C unless otherwise noted. <sup>b</sup> The reaction in ethanol at 20 °C. <sup>c</sup> The reaction in tetrahydrofuran at 20 °C. <sup>d</sup> The reaction at 20 °C.

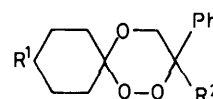
**b**) [equation (4) and Table 2]. Treatment of the ester (9) with LDA under the same conditions resulted in the formation of a mixture of (12), (13), and (10), suggesting that in the reaction of 1,2,4-trioxane (3) with this reagent, the hydroxy ester (9) was the primary product.

Judged by the percentage of recovered 1,2,4-trioxane in the reaction with 3 equiv. of LDA for 2 h, the relative reactivity of the trioxanes (3a–c) towards LDA was found to follow the sequence: (3a) [0%] > (3b) [70%] > (3c) [90%]. The same sequence was observed in the reaction of (3a–c) with 10 mol equiv. of triethylamine at 20 °C for 2 h: (3a) [0%] > (3b) [60%] > (3c) [0%] (the figure in brackets shows the percentage of recovered 1,2,4-trioxane).

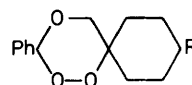
Thus, the first step of the reaction of a 1,2,4-trioxane (3a–c) with triethylamine, sodium ethoxide or LDA seems to involve proton abstraction and, as a result, a hydroxy ester (9a–c) is



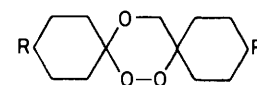
- (3a) R<sup>1</sup> = R<sup>2</sup> = Ph, R<sup>3</sup> = H  
 (3b) R<sup>1</sup> = Ph, R<sup>2</sup> = Me, R<sup>3</sup> = H  
 (3c) R<sup>1</sup> = Ph, R<sup>2</sup> = R<sup>3</sup> = H  
 (3d) R<sup>1</sup> = R<sup>3</sup> = Ph, R<sup>2</sup> = H  
 (3e) R<sup>1</sup> = CH<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>, R<sup>2</sup> = Ph, R<sup>3</sup> = H  
 (3f) R<sup>1</sup> = CH<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>, R<sup>2</sup> = R<sup>3</sup> = H  
 (3g) R<sup>1</sup> = CH<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>, R<sup>2</sup> = H, R<sup>3</sup> = Ph



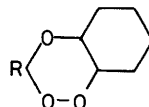
- (3h) R<sup>1</sup> = H, R<sup>2</sup> = Ph  
 (3i) R<sup>1</sup> = R<sup>2</sup> = H  
 (3j) R<sup>1</sup> = Bu<sup>t</sup>, R<sup>2</sup> = H



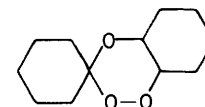
- (3k) R = H  
 (3l) R = Bu<sup>t</sup>



- (3m) R<sup>1</sup> = R<sup>2</sup> = H  
 (3n) R<sup>1</sup> = H, R<sup>2</sup> = Bu<sup>t</sup>  
 (3o) R<sup>1</sup> = R<sup>2</sup> = Bu<sup>t</sup>



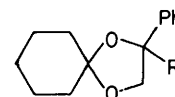
- (3p) R = Ph  
 (3q) R = CH<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>



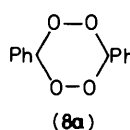
- (3r)

PhCOR

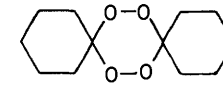
- (5a) R = Ph  
 (5b) R = Me  
 (5c) R = H



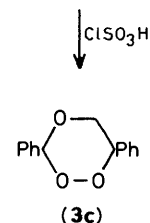
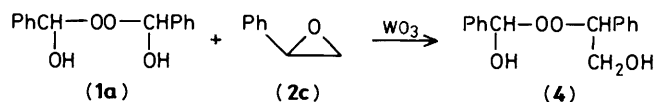
- (7d) R = Ph  
 (7e) R = H



- (8a)



- (8b)



Equation (1)

obtained as the primary product. In accordance with this, 1,2,4-trioxane (3h), having no hydrogen at C-3, is inert towards these reagents.

*Reaction with Phenyl-lithium or Alkylmagnesium Halides.*—The reaction of 1,2,4-trioxane (3a) with phenyl-lithium gave a





**Table 4.** Reaction with lithium aluminium hydride,<sup>a</sup> anthrylsodium<sup>b</sup> or triphenylphosphine<sup>c</sup>

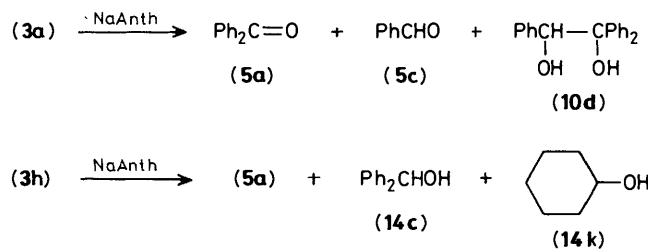
Substrate	Reagent (mol equiv.)	Reaction time (h)	Products, yield (mol %)
(3a)	LiAlH <sub>4</sub> (2)	2	(10a) 45, (14c) 54, (14d) 60
(3b)	LiAlH <sub>4</sub> (5)	4	(10b) 26, (14d) 84, (14f) 11
(3c)	LiAlH <sub>4</sub> (5)	6	(14d) 144
(3h)	LiAlH <sub>4</sub> (2)	2	(14c) 66, (14k) 31
(9a)	LiAlH <sub>4</sub> (2)	2	(10a) 85, (14d) 74
(3a)	NaAnth <sup>d</sup> (2)	0.2	(5a) 56, (5c) 16, (10d) 27
(3h)	NaAnth <sup>d</sup> (2)	0.2	(5a) 10, (14c) 44, (14k) 30
(3a)	PPh <sub>3</sub> (1)	24	(5c) 16, (7a) 62, (9a) 3 <sup>e</sup>
(3b)	PPh <sub>3</sub> (1)	24	(5c) 33, (7b) 42, (9b) 13 <sup>e</sup>
(3c)	PPh <sub>3</sub> (1)	24	(2c) 28, (5c) 53, (7c) 14, (10c) 6 <sup>e</sup>

<sup>a</sup> The reaction in ether at 38 °C. <sup>b</sup> The reaction in tetrahydrofuran at 20 °C. <sup>c</sup> The reaction in benzene at 80 °C. <sup>d</sup> Sodium anthracene. <sup>e</sup> The yield of triphenylphosphine oxide was not determined.

**Table 5.** Thermolysis<sup>a</sup> and titanium tetrachloride-mediated decomposition<sup>b</sup> of 1,2,4-trioxanes

Substrate	Reagent	Products, yield (mol %)
(3a)	Heat	(5a) 70, (5c) 72, (12) 20, (17) 16
(3b)	Heat	(5b) 91, (5c) 52, (9b) 6
(3c)	Heat	(5c) 113
(3a)	TiCl <sub>4</sub>	(5c) 47, (18) 79, (19a) 53
(3b)	TiCl <sub>4</sub>	(5b) 17, (5c) 74, (18) 41
(3c)	TiCl <sub>4</sub>	(5c) 65, (18) 102

<sup>a</sup> The reaction in benzene at 200 °C for 3 h. <sup>b</sup> The reaction with an equiv. mol of titanium tetrachloride in methylene dichloride at -30 °C for 15 min.



Equations (11) and (12)

benzaldehyde (5c), and 1,1,2-triphenylethanol (10d) [equation (11) and Table 4]. 1,2,4-Trioxane (3h), yielded a mixture of cyclohexanol (14k), benzophenone (5a), and diphenylmethanol (14c) [equation (12)].

**Reaction with Triphenylphosphine.**—Deoxygenation of 1,2,4-trioxanes (3a–c) with triphenylphosphine proceeded smoothly. In the case of trioxane (3a, b), the corresponding acetal (7a, b) was the major product. A small amount of the ester (9a, b) was also produced. From (3c), however, styrene oxide (2c) and 2-phenylethane-1,2-diol (10c) were obtained, together with benzaldehyde (5c) and acetal (7c) (Table 4). The first step would involve insertion of triphenylphosphine into the O–O bond of (3).<sup>9</sup> There would be two alternative modes (paths a and b in Scheme 3) for subsequent bond reorganization to yield acetal (7) and epoxide (2), respectively. Alternatively, triphenylphosphine could act as a base to yield the ester (9) (path c in Scheme 3).

**Thermal and TiCl<sub>4</sub>-Mediated Decomposition of 1,2,4-Trioxane.**—Thermolysis of 1,2,4-trioxane (3a) gave a mixture of benzophenone (5a), benzaldehyde (5c), benzoic acid (12), and deoxybenzoin (17) in yields of 70, 72, 20, and 16%, respectively

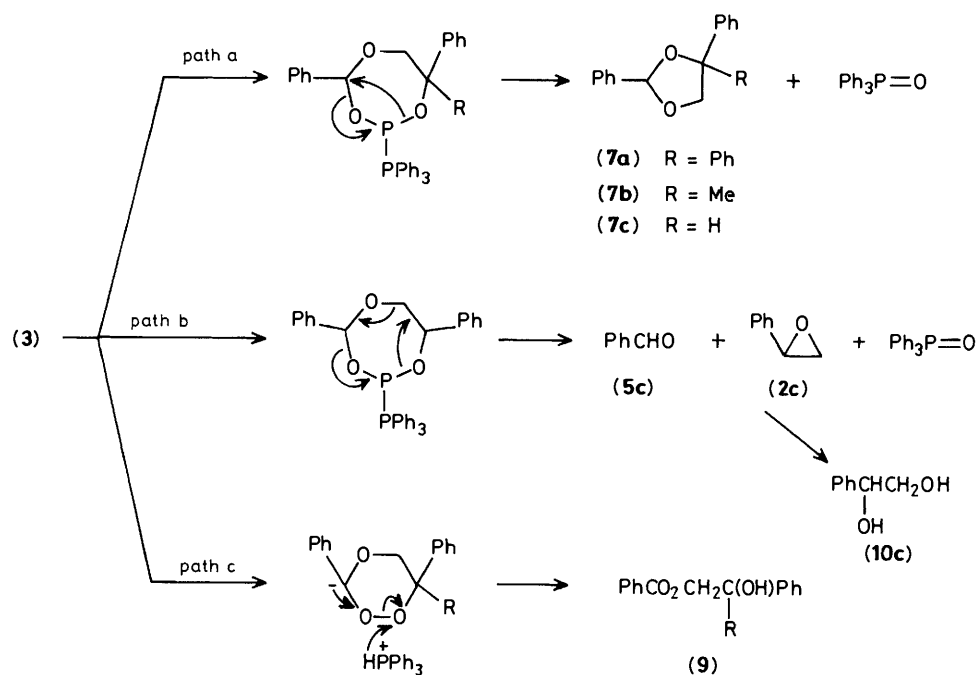
(Table 5). Formation of benzophenone (5a) and benzaldehyde (5c) would be a result of cleavage of the O–O, C–O, and C–C bonds (path a in Scheme 4). The distribution of products demonstrates that in the thermal decomposition of 1,2,4-trioxanes (3b, c) this process was also the most important. For the formation of benzoic acid (12) and deoxybenzoin (17) from (3a), however, path b in Scheme 4 seems to be most plausible. The first step involves O–O bond fission, followed by cleavage of the C–O bond. Subsequent migration of a phenyl group affords (12) and (17). Formation of the hydroxy ester (9b) from (3b) would imply that the oxy radical produced by O–O bond fission can intramolecularly abstract hydrogen (path c in Scheme 4). Similar modes of decay have been discovered for other 1,2,4-trioxanes.<sup>2k,m</sup>

TiCl<sub>4</sub>-Mediated decomposition of 1,2,4-trioxane (3a) led to the formation of benzaldehyde (5c), phenol (18), and hydroxyacetophenone (19a) in yields of 47, 79, and 53%, respectively (Table 5). This result can be rationalized in terms of the mechanism illustrated in path a in Scheme 5. The first step would involve co-ordination of titanium tetrachloride to the sterically less-hindered peroxidic oxygen of the 1,2,4-trioxane (3a). The subsequent cleavage of the O–O bond and migration of the phenyl group at C-6 would afford finally a mixture of benzaldehyde (5c), phenol (18), and hydroxyacetophenone (19a). From 1,2,4-trioxanes (3b, c), the major products were benzaldehyde (5c) and phenol (18) suggesting that in this case also path a in Scheme 5 is important. We failed, however, to isolate hydroxyacetone (19b) or formylmethanol (19c), also expected to be formed by this process although it should be noted that these compounds are very soluble in water. The formation of acetophenone (5b) from (3b) may demonstrate the participation of an alternative pathway, path b in Scheme 5 being a reasonable one, where a mixture of the carbonyl compounds (5b–d) would be produced. A similar mechanism has been proposed by Jefford *et al.*<sup>2o</sup> for trimethylsilyl trifluoromethanesulphonate-mediated rearrangement of some 1,2,4-trioxanes.

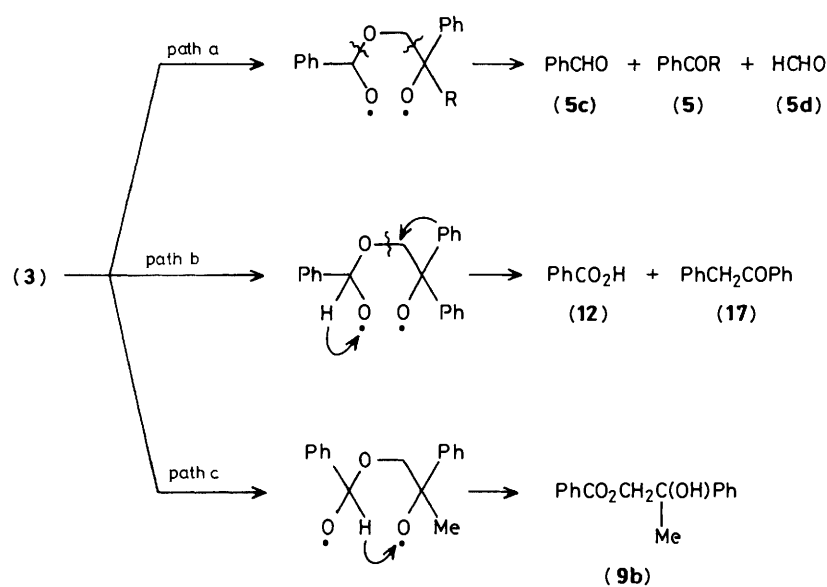
## Experimental

<sup>1</sup>H N.m.r. spectra were recorded on a JNM-PS-100 spectrometer for CDCl<sub>3</sub> solutions (standard Me<sub>4</sub>Si). Mass spectra were obtained on a Hitachi RMU-6H spectrometer and i.r. spectra on a Hitachi 215 spectrometer. G.l.c. analysis was carried out on a Hitachi 164 gas chromatograph.

**Material.**— $\alpha,\alpha'$ -Dioxydibenzyl alcohol (1a),<sup>10</sup> 1,1'-dioxydicyclohexan-1-ol (1b),<sup>10</sup> 1,1'-dioxydi(4-*t*-butylcyclohexan-1-ol) (1c),<sup>10</sup> 1-hydroperoxydodecan-1-ol (1d),<sup>11</sup> 1-hydroperoxy-



Scheme 3.



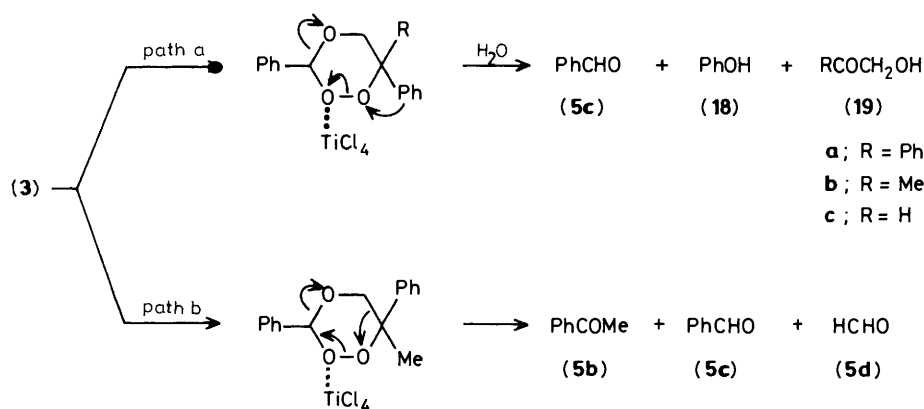
Scheme 4.

benzyl methyl ether (**1e**),<sup>12</sup> and epoxides (**2a**),<sup>13</sup> (**2b**),<sup>14</sup> (**2e**),<sup>15</sup> and (**2f**)<sup>15</sup> were prepared by the reported methods. [ $\beta$ -<sup>2</sup>H]-(*E*)-Styrene oxide, [ $\beta$ -<sup>2</sup>H]-*E*-(**3c**), was prepared by treating [ $\beta$ -<sup>2</sup>H]-*trans*-styrene<sup>16</sup> with *m*-chloroperbenzoic acid.<sup>17</sup> [ $\beta$ -<sup>2</sup>H]-*E*-(**3c**) had b.p. 101 °C (40 mmHg);  $\delta_{\text{H}}$  2.58 (1 H, d, *J* 5.0 Hz), 3.67 (1 H, d, *J* 5.0 Hz), and 7.15 (5 H, s).

**Synthesis of 1,2,4-Trioxanes.**—To a solution of peroxide (**1a**) (493 mg, 2 mmol) and 1,1-diphenylethylene oxide (**2a**) (393 mg, 2 mmol) in methylene dichloride (20 ml), was added tungsten(vi) oxide (464 mg, 2 mmol) and the resulting mixture kept at 25 °C with stirring for 3 h. To this mixture, a solution of chlorosulphonic acid (20 mg, 0.2 mmol) in methylene dichloride (10 ml) was syringed during 5 min and the mixture was stirred at 25 °C for a further 2 h. Ether (50 ml) was then added and the mixture poured into aqueous NaHCO<sub>3</sub> and extracted with

ether (3 × 20 ml). After evaporation of the solvent, the neutral products were chromatographed on silica gel. The first fraction (benzene–hexane, 3:7) contained 3,6-diphenyl-1,2,4,5-tetroxane (**8a**) (24 mg, 10%); m.p. 202–203 °C.<sup>10</sup> From the second fraction (benzene–hexane, 3:7), 3,6,6-triphenyl-1,2,4-trioxane (**3a**) was isolated (254 mg, 40%); m.p. 169–170 °C (from methanol) (Found: C, 78.9; H, 5.9. C<sub>21</sub>H<sub>18</sub>O<sub>3</sub> requires C, 79.2; H, 5.7);  $\delta_{\text{H}}$  4.32 (1 H, d, *J* 12.0 Hz), 4.96 (1 H, d, *J* 12.0 Hz), 6.34 (1 H, s), and 7.1–7.7 (15 H, m). The third fraction (benzene–hexane, 1:1) contained benzaldehyde (**5c**) (50 mg, 12%). From the final fraction (ether–benzene, 1:10), 1,1-diphenylethane-1,2-diol (**10a**) was isolated (120 mg, 28%). Benzoic acid (**12**) (12 mg, 5%) was isolated from the acid layer.

The 1,2,4-trioxanes (**3b–o**) prepared as above, were isolated by column chromatography. The solid materials were purified



Scheme 5.

by recrystallization from methanol. (3b) had m.p. 113–114 °C (Found: C, 74.7; H, 6.2.  $\text{C}_{16}\text{H}_{16}\text{O}_3$  requires C, 75.0; H, 6.3%);  $\delta_{\text{H}}$  1.98 (3 H, s), 4.12 (2 H, s), 6.17 (1 H, s), and 7.1–7.6 (10 H, m). (3c) had m.p. 149 °C (Found: C, 74.4; H, 5.8.  $\text{C}_{15}\text{H}_{14}\text{O}_3$  requires C, 74.4; H, 5.8%);  $\delta_{\text{H}}$  4.23 (1 H, dd,  $J$  10 and 11 Hz), 4.31 (1 H, dd,  $J$  3 and 11 Hz), 5.52 (1 H, dd,  $J$  10 and 3 Hz), 6.28 (1 H, s), and 7.1–8.0 (10 H, m).<sup>18</sup> (3d) had m.p. 123–124 °C (Found: C, 79.2; H, 5.6.  $\text{C}_{21}\text{H}_{18}\text{O}_3$  requires C, 79.2; H, 5.7%);  $\delta_{\text{H}}$  5.07 (1 H, d,  $J$  10 Hz), 5.32 (1 H, d,  $J$  10 Hz), 6.59 (1 H, s), and 7.1–7.8 (15 H, m). (3e) had m.p. 53–54 °C (Found: C, 78.3; H, 8.8.  $\text{C}_{24}\text{H}_{32}\text{O}_3$  requires C, 78.2; H, 8.8%);  $\delta_{\text{H}}$  0.8–1.6 (19 H, m), 4.10 (1 H, d,  $J$  12 Hz), 4.79 (1 H, d,  $J$  12 Hz), 5.41 (1 H, t,  $J$  5 Hz), and 7.1–7.7 (10 H, m). (3f) had m.p. 34–35 °C (Found: C, 73.7; H, 9.9.  $\text{C}_{18}\text{H}_{28}\text{O}_3$  requires C, 73.9; H, 9.7%);  $\delta_{\text{H}}$  1.7–1.8 (19 H, m), 3.86 (1 H, dd,  $J$  10 and 11.5 Hz), 4.07 (1 H, dd,  $J$  11.5 and 3.5 Hz), 5.32 (1 H, t,  $J$  4 Hz), 5.34 (1 H, dd,  $J$  10.0 and 3.5 Hz), and 7.3–7.4 (5 H, m). (3g) was an oil (Found: C, 74.1; H, 9.7.  $\text{C}_{18}\text{H}_{28}\text{O}_3$  requires C, 74.0; H, 9.8%);  $\delta_{\text{H}}$  0.8–2.0 (19 H, m), 4.66 (1 H, d,  $J$  10 Hz), 4.97 (1 H, d,  $J$  10 Hz), 5.49 (1 H, t,  $J$  4 Hz), and 6.8–7.3 (10 H, m). (3h) had m.p. 120–122 °C (Found: C, 77.1; H, 7.1.  $\text{C}_{20}\text{H}_{22}\text{O}_3$  requires C, 77.4; H, 7.1%);  $\delta_{\text{H}}$  1.2–2.0 (10 H, m), 4.40 (2 H, s), and 7.2–7.5 (10 H, m). (3i) had m.p. 62–63 °C (Found: C, 71.4; H, 7.8.  $\text{C}_{14}\text{H}_{18}\text{O}_3$  requires C, 71.8; H, 7.7%);  $\delta_{\text{H}}$  1.3–2.5 (10 H, m), 3.7–3.9 (1 H, m), 4.0–4.3 (1 H, m), 5.30 (1 H, dd,  $J$  10 and 4 Hz), and 7.2–7.4 (5 H, m);  $\nu_{\text{max}}$  2 925, 2 850, 1 500, 1 450, 1 370, 1 340, 1 280, 1 260, 1 160, 1 100, 930, 760, and 700  $\text{cm}^{-1}$ . (3j) had m.p. 143–146 °C (Found: C, 73.8; H, 9.2.  $\text{C}_{18}\text{H}_{26}\text{O}_3$  requires C, 74.5; H, 9.0%);  $\delta_{\text{H}}$  0.88 (9 H, s), 1.0–1.9 (9 H, m), 3.7–4.2 (2 H, m), 5.27 (1 H, dd,  $J$  4 and 11 Hz), and 7.3–7.4 (5 H, m). (3k) had m.p. 68 °C (Found: C, 71.7; H, 7.7.  $\text{C}_{14}\text{H}_{18}\text{O}_3$  requires C, 71.8; H, 7.7%);  $\delta_{\text{H}}$  1.1–1.9 (8 H, m), 2.3–2.6 (2 H, m), 3.60 (1 H, d,  $J$  10 Hz), 3.88 (1 H, d,  $J$  10 Hz), 5.94 (1 H, s), and 7.2–7.6 (5 H, m). (3l) had m.p. 81–82 °C (Found: C, 74.4; H, 9.0.  $\text{C}_{18}\text{H}_{26}\text{O}_3$  requires C, 74.5; H, 9.0%);  $\delta_{\text{H}}$  0.88 (9 H, s), 0.9–1.9 (8 H, m), 3.7 (1 H, d,  $J$  12 Hz), 4.33 (1 H, d,  $J$  12 Hz), 6.05 (1 H, s), and 7.2–7.6 (5 H, m). (3m) had m.p. 34–35 °C (Found: C, 69.0; H, 9.7.  $\text{C}_{13}\text{H}_{22}\text{O}_3$  requires C, 69.0; H, 9.7%);  $\delta_{\text{H}}$  1.1–1.6 (20 H, m) and 3.44 (2 H, br s). (3n) had m.p. 91–92 °C (Found: C, 72.7; H, 10.9.  $\text{C}_{17}\text{H}_{30}\text{O}_3$  requires C, 72.3; H, 10.7%);  $\delta_{\text{H}}$  0.86 (9 H, s), 1.0–2.1 (18 H, m), and 3.78 (2 H, s). (3o) had m.p. 215–216 °C;  $m/z$  338 ( $M^+$ ); (Found: C, 73.8; H, 11.2.  $\text{C}_{21}\text{H}_{38}\text{O}_3$  requires C, 74.5; H, 11.3%);  $\delta_{\text{H}}$  0.86 (18 H, s), 0.9–2.0 (18 H, m), and 3.79 (2 H, s). (3p) had m.p. 65–66 °C (Found: C, 70.6; H, 7.4.  $\text{C}_{13}\text{H}_{16}\text{O}_3$  requires C, 70.9; H, 7.3%);  $\delta_{\text{H}}$  1.0–2.2 (8 H, m), 3.5–3.9 (1 H, m), 4.1–4.4 (1 H, m), 6.27 (1 H, s), and 7.1–7.6 (5 H, m). (3q) was an oil;  $m/z$  270 ( $M^+$ ) (Found: C, 71.2; H, 11.2.  $\text{C}_{16}\text{H}_{30}\text{O}_3$  requires C, 71.1; H, 11.1%);  $\delta_{\text{H}}$  0.8–2.1 (27 H, m), 3.2–3.5 (1 H, m), 3.8–4.0 (1 H, m), and 5.18 (1 H, t,  $J$  4 Hz). (3r) had m.p. 33–34 °C;  $m/z$  212 ( $M^+$ ) (Found: C, 68.0; H, 9.2.  $\text{C}_{12}\text{H}_{20}\text{O}_3$  requires C, 67.9; H,

9.4%);  $\delta_{\text{H}}$  0.8–2.3 (18 H, m) and 3.5–4.0 (2 H, m);  $\nu_{\text{max}}$  2 930, 2 850, 1 450, 1 380, 1 280, 1 160, 1 090, 960, and 920  $\text{cm}^{-1}$ .

From the reactions of epoxides (2a) and (2c) with peroxide (1b), the corresponding ketals (7d) and (7e) were also produced in 11% and 18% yields, respectively. (7d) had m.p. 99–100 °C (from methanol) (Found: C, 81.3; H, 7.5.  $\text{C}_{20}\text{H}_{22}\text{O}_2$  requires C, 81.6; H, 7.5%);  $\delta_{\text{H}}$  1.4–1.8 (10 H, m), 4.50 (2 H, s), and 7.2–7.5 (10 H, m). (7e) was an oil;  $\delta_{\text{H}}$  1.4–1.8 (10 H, m), 3.47 (1 H, t,  $J$  13 Hz), 4.08 (1 H, dd,  $J$  13 and 10 Hz), 4.85 (1 H, dd,  $J$  13 and 10 Hz), and 7.1–7.4 (5 H, m).<sup>19</sup>

**The Isolation and Cyclization of the Dihydroxy Peroxide (4).**—A mixture of the peroxide (1a) (2 mmol), the epoxide (2c) (2 mmol), and tungsten(vi) oxide (2 mmol) in methylene dichloride (20 ml) was stirred at 25 °C for 3 h and then diluted with ether. The organic layer was separated, washed with saturated brine, dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated. Column chromatography of the residue on silica gel (elution with ether) afforded the peroxide (4) (163 mg, 31% yield) as an oil;  $\delta_{\text{H}}$  3.75 (1 H, d,  $J$  7 Hz), 3.77 (1 H, d,  $J$  5 Hz), 3.4–3.9 (2 H, br s), 5.05 (1 H, dd,  $J$  7 and 5 Hz), and 6.6–7.5 (11 H, m). Compound (4) being labile, was not further purified. On treatment with chlorosulphonic acid (0.1 mol equiv.) in methylene dichloride (20 ml) it gave 1,2,4-trioxane (3c) in quantitative yield.

**Reaction of the Peroxide (1a) with the [ $\beta$ - $^2\text{H}$ ]-Epoxide E-(3c).**—The reaction of (1a) (2 mmol) and [ $\beta$ - $^2\text{H}$ ]-E-(3c) (2 mmol) with tungsten(vi) oxide (2 mmol) in methylene dichloride (20 ml), followed by treatment with a solution of chlorosulphonic acid in methylene dichloride (10 ml), gave the mono-deuteriated 1,2,4-trioxane [ $5$ - $^2\text{H}$ ]-E-(3c) (30%). The *cis/trans* ratio of the trioxane [ $5$ - $^2\text{H}$ ]-E-(3c) was determined by  $^1\text{H}$  n.m.r. spectroscopy. Irradiation of the 6-H signal [ $\delta_{\text{H}}$  5.52 (1 H, 2d,  $J$  10 and 3 Hz)] resulted in the appearance of two singlets at  $\delta$  4.23 and 4.31 (5- $\text{H}_2$ ), the ratio of the peak areas being 37:63. Because of the field effect, the equatorial proton signal was expected at a relatively lower field. Its observed resonance was consistent with this and showed a smaller coupling constant with 6-H. Thus, the 1,2,4-trioxane [ $5$ - $^2\text{H}$ ]-E-(3c) was shown to be a mixture of *cis-trans* isomers (63:37).

**Reaction of 1,2,4-Trioxane with Triethylamine.**—A solution of (3a) (100 mg, 0.31 mmol) and triethylamine (318 mg, 3.1 mmol) in methylene dichloride (20 ml) was stirred at 20 °C for 2 h. After evaporation of the solvent and triethylamine, the crude products were chromatographed on silica gel (elution with ether–benzene, 1:4). The sole isolated product was the hydroxy ester (9a) (75 mg, 75%), m.p. 155–156 °C (from benzene–

hexane) (Found: C, 79.2; H, 5.7.  $C_{21}H_{18}O_3$  requires C, 79.2; H, 5.7%);  $\delta_H$  3.04 (1 H, s), 4.89 (2 H, s), and 7.2–7.9 (15 H, m).

From the 1,2,4-trioxanes (**3b**, **c**), the corresponding hydroxy esters (**9b**, **c**) were isolated. (**9b**) was an oil;  $m/z$  256 ( $M^+$ ) (Found: C, 74.8; H, 6.4.  $C_{16}H_{16}O_3$  requires C, 75.0; H, 6.3%);  $\delta_H$  1.56 (3 H, s), 4.40 (2 H, s), and 7.1–7.9 (10 H, m);  $\nu_{max}$ , 3 500 and 1 720  $cm^{-1}$ . (**9c**) was an oil;  $m/z$  242 ( $M^+$ ) (Found: C, 74.6; H, 5.8.  $C_{15}H_{14}O_3$  requires C, 74.4; H, 5.8%);  $\delta_H$  2.2–2.3 (1 H, m), 3.8–3.9 (2 H, m), 5.99 (1 H, t,  $J$  6 Hz), 7.3–7.5 (8 H, m), and 8.0–8.2 (2 H, m);  $\nu_{max}$ , 3 400 and 1 720  $cm^{-1}$ .

*Reaction of 1,2,4-Trioxane with Sodium Ethoxide.*—To a solution of (**3a**) (100 mg, 0.31 mmol) in ethanol (10 ml), a solution of sodium ethoxide (4.4 mmol) in ethanol (10 ml) was added and the mixture was stirred at 20 °C for 10 min. After conventional work-up, the products were chromatographed on silica gel. The first fraction (elution with benzene–hexane, 3:2) afforded ethyl benzoate (**11**) (30 mg, 63%). From the second fraction (elution with ether–benzene, 2:3), the diol (**10a**) was isolated (43 mg, 63%), m.p. 121–121.5 °C (from benzene) (Found: C, 78.7; H, 6.5.  $C_{14}H_{14}O_2$  requires C, 78.5; H, 6.6%).<sup>20</sup>

From (**3b**), the diol (**10b**) was obtained together with (**11**). The diol (**10b**) had m.p. 44–45 °C;  $m/z$  152 ( $M^+$ );  $\delta_H$  1.32 (3 H, s), 3.39 (2 H, s), 3.88 (2 H, s), and 6.9–7.3 (5 H, m).<sup>21</sup>

*Reaction of 1,2,4-Trioxane (3a) with Lithium Di-isopropylamide.*—A solution of LDA (1.9 mmol) in tetrahydrofuran (20 ml) was prepared by the reported method.<sup>22</sup> A solution of (**3a**) (100 mg, 0.31 mmol) in tetrahydrofuran (10 ml) was added to this at 0 °C and the mixture was stirred at 20 °C for 2 h under  $N_2$ . It was then diluted with ether and the organic layer was washed with aqueous HCl, and then aqueous  $NaHCO_3$ . After evaporation of the solvent, the neutral products were chromatographed on silica gel. The first fraction (elution with ether–benzene, 1:4) contained the hydroxy ester (**9a**) (21 mg, 21%). From the second fraction diol (**10a**) was isolated (40 mg, 47%). The acid layer contained benzoic acid (**12**) (17 mg, 29%).

*Reaction of 1,2,4-Trioxane (3a) with Phenyl-lithium.*—The reaction of (**3a**) (100 mg, 0.31 mmol) and phenyl-lithium (1.6 mmol) in ether (30 ml) was undertaken at 20 °C for 5 h under  $N_2$ . Column chromatography on silica gel yielded triphenylmethanol (**14a**) (58 mg, 71%) and the diol (**10a**) (46 mg, 69%).

*Reaction of 1,2,4-Trioxane (3a) with MeMgI.*—To a solution of MeMgI (3.1 mmol) in ether (20 ml), a solution of (**3a**) (100 mg, 0.31 mmol) in ether (10 ml) was added under  $N_2$ , and the mixture stirred at 20 °C for 3 h. After work-up column chromatography of the product on silica gel yielded 1,1-diphenylethanol (**14i**) (27 mg, 43%),  $\alpha$ -methylbenzyl alcohol (**14f**) (27 mg, 70%), and the diol (**10a**) (6 mg, 9%).

*Reaction of 1,2,4-Trioxane (3c) with Hex-5-enylmagnesium Bromide.*—Compound (**3c**) (0.4 mmol) was allowed to react with hex-5-enylmagnesium bromide<sup>7b</sup> (4 mmol) in ether (30 ml) at 20 °C for 3 h under  $N_2$ . After work-up column chromatography of the residue on silica gel (elution with ether–benzene, 1:10) yielded  $\alpha$ -(cyclopentylmethyl)benzyl alcohol (**16**) and then  $\alpha$ -hex-5-enylbenzyl alcohol (**15**). The alcohol (**16**) was an oil (Found: C, 81.9; H, 9.5.  $C_{13}H_{18}O$  requires C, 82.1; H, 9.6%);  $\delta_H$  0.9–2.5 (12 H, m), 4.45 (1 H, t,  $J$  6 Hz), and 7.1–7.3 (5 H, m);  $m/z$  190 ( $M^+$ ). The alcohol (**15**) was converted into the corresponding acetate: this was an oil;  $m/z$  232 ( $M^+$ );  $\delta_H$  1.1–2.2 (8 H, m), 1.98 (3 H, s), 3.44 (1 H, t,  $J$  6 Hz), 4.9–5.1 (1 H,

m), 5.3–5.4 (1 H, m), 5.64 (1 H, t,  $J$  7 Hz), and 7.2–7.4 (5 H, m).<sup>23</sup>

*Competition Reaction between Two Grignard Reagents.*—The reaction of 1,2,4-trioxane (**3c**) (100 mg, 0.41 mmol) was undertaken in the presence of MeMgI (10 mol equiv.) and  $Pr^iMgBr$  (10 mol equiv.) in ether (30 ml) at 20 °C for 3 h. The product was a mixture of  $\alpha$ -methylbenzyl alcohol (**14f**) (41 mg, 81%) and 1-phenyl-2-methylpropanol (**14g**) (15 mg, 24%). From the reaction of (**3c**) (100 mg) with a mixture of  $Pr^iMgBr$  (10 mol equiv.) and  $Bu^iMgCl$  (10 mol equiv.), 1-phenyl-2-methylpropanol (**14g**) (66 mg, 106%) was obtained exclusively.

*Reaction of the 1,2,4-Trioxane (3a) with Lithium Aluminium Hydride.*—A solution of (**3a**) (150 mg, 0.47 mmol) and lithium aluminium hydride (36 mg, 0.63 mmol) in ether (30 ml) was stirred for 2 h under reflux. After conventional work-up, the products were chromatographed on silica gel. The first fraction contained diphenylmethanol (**14c**) (49 mg, 54%), the second fraction benzyl alcohol (**14d**) (32 mg, 60%), and the third fraction contained the diol (**10a**) (48 mg, 45%).

*Reaction of the 1,2,4-Trioxane (3a) with Anthrylsodium.*—A solution of anthrylsodium (3.1 mmol) in tetrahydrofuran (30 ml) was prepared from anthracene (560 mg) and sodium (69 mg). Anthrylsodium (0.62 mmol) was syringed into a solution of 1,2,4-trioxane (**3a**) (100 mg, 0.31 mmol) in tetrahydrofuran (20 ml) at 20 °C. After 5 min, the mixture was poured into aqueous HCl. The organic layer was separated, washed with aqueous  $NaHCO_3$ , dried ( $Na_2SO_4$ ), and evaporated. Column chromatography of the residue on silica gel afforded benzophenone (**5a**) (32 mg, 56%), benzaldehyde (**5c**) (3 mg, 10%), and 1,1,2-triphenylethane-1,2-diol (**10d**) (25 mg, 27%). The diol (**10d**) had m.p. 170–171 °C (from benzene–hexane) (lit.,<sup>24</sup> 167–167.5 °C) (Found: C, 82.5; H, 6.3. Calc. for  $C_{20}H_{18}O_2$ : C, 82.8; H, 6.2%);  $\delta_H$  2.46 (1 H, d,  $J$  3 Hz), 3.14 (1 H, s), 5.60 (1 H, d,  $J$  3 Hz), and 6.9–7.7 (15 H, m);  $\nu_{max}$ , 3 560 and 3 450  $cm^{-1}$ .

*Reaction of 1,2,4-Trioxane with Triphenylphosphine.*—A solution of (**3a**) (150 mg, 0.47 mmol) and triphenylphosphine (124 mg, 0.47 mmol) in benzene (20 ml) was stirred for 24 h under reflux. After evaporation of the solvent, the crude products were chromatographed on silica gel. The first fraction contained 2,4,4-triphenyl-1,3-dioxolane (**7a**) (88 mg, 62%); the second fraction benzaldehyde (**5c**) (8 mg, 16%); the third fraction contained 2-hydroxy-2,2-diphenylethyl benzoate (**9a**) (5 mg, 3%).

The dioxolane (**7a**) had m.p. 104–105 °C (from methanol) (Found: C, 83.4; H, 6.0.  $C_{21}H_{18}O_2$  requires C, 83.4; H, 6.0%);  $\delta_H$  4.50 (1 H, d,  $J$  9 Hz), 4.65 (1 H, d,  $J$  9 Hz), 5.97 (1 H, s), and 7.1–7.7 (15 H, m). (**7b**) was an oil (Found: C, 79.9; H, 6.7.  $C_{16}H_{16}O_2$  requires C, 80.0; H, 6.7%);  $\delta_H$  1.61 (3 H, s), 4.05 (2 H, s), 5.82 (1 H, s), and 7.0–7.6 (10 H, m). (**7c**) had b.p. 138 °C (2 mmHg);  $\delta_H$  3.8–4.0 (1 H, m), 4.47 (1 H, t,  $J$  6 Hz), 5.18 (1 H, t,  $J$  6 Hz), 6.17 (1 H, s), and 7.1–7.6 (10 H, m).<sup>25</sup>

*Thermolysis of the 1,2,4-Trioxane (3a).*—A solution of (**3a**) (100 mg, 0.31 mmol) in benzene (10 ml) in a sealed tube was kept at 200 °C for 3 h. Column chromatography of the neutral products on silica gel yielded deoxybenzoin (**17**) (10 mg, 16%), benzophenone (**5a**) (40 mg, 70%), and benzaldehyde (**5c**) (24 mg, 72%). Benzoic acid (**12**) (8 mg, 20%) was isolated from the acid layer.

*TiCl<sub>4</sub>-Mediated Decomposition of the 1,2,4-Trioxane (3a).*—To a solution of (**3a**) (100 mg, 0.31 mmol) in methylene dichloride (20 ml), a solution of  $TiCl_4$  (59 mg, 0.31 mmol) in methylene dichloride (10 ml) was added at –30 °C and the mixture was stirred at –30 °C for 15 min. Ether (50 ml) was added and the mixture was poured into aqueous  $NaHCO_3$ .



The organic layer was washed with saturated brine, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated. After work-up column chromatography of the residue on silica gel afforded benzaldehyde (**5c**) (23 mg, 47%), phenol (32 mg, 79%), and  $\alpha$ -hydroxyacetophenone (**19**) (32 mg, 53%).

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