

Synthesis and Silica Gel-catalysed Decomposition of 3-(1-Arylcycloalkyl)-substituted 1,2,4-Trioxolanes and 1,2,4-Dioxazolidines

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Decomposition of 3-(1-phenylcyclopentyl)- and 3-(1-phenylcyclohexyl)-4-benzyl-5-phenyl-1,2,4-dioxazolidines, derived from [3 + 2] cycloadditions of benzaldehyde *O*-oxide and imines, by silica gel gave mixtures of the corresponding phenylcycloalkene, benzaldehyde, and *N*-benzylformamide. In the case of 3-(1-arylcyclopentyl)- and 3-(1-phenylcyclohexyl)-substituted 1,2,4-trioxolanes also, a similar mode of decomposition was observed. A mechanism involving heterolytic fission of the C–C bond between the peroxide ring and the cycloalkyl substituent, is proposed.

Recent renewed interest in the chemistry of cyclic peroxides has been stimulated by the potent pharmacological activities exhibited by a variety of naturally occurring cyclic peroxides.^{1–4} Because of our continuing interest in the synthesis of cyclic peroxides by cycloaddition of carbonyl oxides, generated from the ozonolysis of vinyl ether, with the 1,3-dipolarophiles^{5–8} and the acid-catalysed decomposition of the derived peroxides,⁹ we subjected 1-(1-arylcycloalkyl)-2-methoxyethenes to ozonolysis in the presence of trifluoroacetophenone, benzaldehyde, α -phenylbenzylideneamine, and α -phenyl-*N*-benzylnitron yielding the corresponding cycloadducts. Interestingly, 3-(1-arylcyclopentyl)- and 3-(1-phenylcyclohexyl)-substituted 1,2,4-trioxolanes and 1,2,4-dioxazolidines prepared as above were smoothly decomposed on silica gel by the novel pathways involving heterolytic fission of the C–C bond between the peroxide ring and the cycloalkyl substituent. In this connection, Griesbaum and his co-workers¹⁰ have found that the thermal decomposition of the diozonide from 2,3,4,5-tetramethylhexa-2,4-diene proceeds by a similar pathway involving heterolytic cleavage of the C–C bond that connects the two ozonide rings.

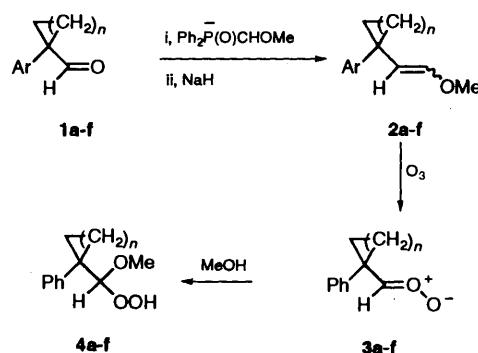
Results and Discussion

Ozonolysis of the Vinyl Ethers 2a–f.—Ozonolyses of the vinyl ethers 2a–f in methanol–methylene dichloride gave, in each case, the corresponding methanol-derived products 4a–f in good yields of 81, 73, 65, 81, 93 and 65%, respectively, suggesting that the expected carbonyl oxides 3a–f were efficiently generated from the vinyl ethers (Scheme 1). From ozonolyses of the relevant vinyl ethers 2g–i, the corresponding α -methoxyalkyl hydroperoxides 4g–i were obtained in yields of 47, 69 and 97%, respectively (Scheme 5).

Ozonolysis of the vinyl ethers 2a–f was then conducted in CH₂Cl₂ in the presence of benzaldehyde 5 or trifluoroacetophenone 7. As expected, the carbonyl oxides 3a–f underwent cycloadditions with the aldehyde 5 and the ketone 7 yielding the corresponding 1,2,4-trioxolanes, 6 and 8, in excellent yields (Scheme 2 and Table 1). The exception was the ozonolysis of 1-[1-(*p*-methoxyphenyl)cyclopentyl]-2-methoxyethene 2d in the presence of the aldehyde 5. Although the ¹H NMR spectrum of the mixture of the crude products showed the formation of the corresponding ozonide 6d in ca. 80% yield, substantial decomposition occurred during the isolation by column chromatography on silica gel. Thus, the ozonide 6d was isolated in low yield (36%), together with 1-(*p*-methoxyphenyl)cyclopentene 13d (41%).

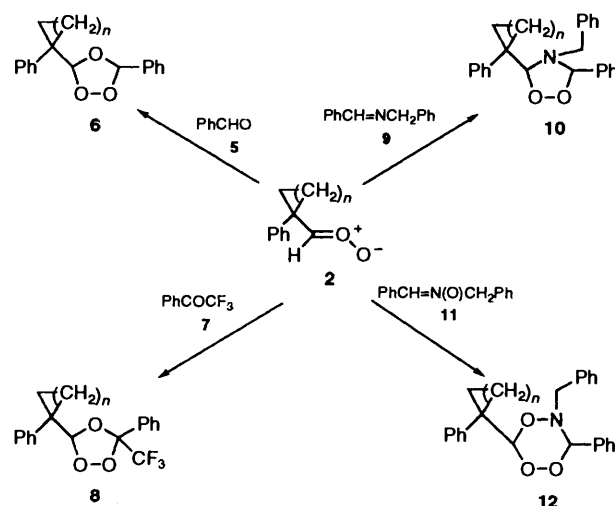
The ¹H NMR spectra of the crude product mixtures obtained from the ozonolyses of the vinyl ethers 2b, c, f in the presence of α -phenylbenzylideneamine 9 indicated the formation of the

corresponding 3-(1-phenylcycloalkyl)-substituted 5-phenyl-1,2,4-dioxazolidines 10b, c, f in high yield (Scheme 2). However, since these cycloadducts 10 were labile toward silica gel they were isolated, albeit in low yields (24–35%), by trituration with



| | Ar | n |
|---|---|---|
| a | Ph | 1 |
| b | Ph | 2 |
| c | Ph | 3 |
| d | <i>p</i> -MeC ₆ H ₄ | 3 |
| e | <i>o</i> -FC ₆ H ₄ | 3 |
| f | Ph | 4 |

Scheme 1



Scheme 2

Table 1 Ozonolysis of vinyl ether in the presence of a 1,3-dipolarophile^a

| Vinyl ether | Dipolarophile (equiv.) | Products | |
|-------------|------------------------|----------------------|-------|
| | | (% yield) | Ratio |
| 2a | 5 (1.3) | 6a (73) | 2:1 |
| 2a | 7 (1) | 8a (94) | 7:6 |
| 2b | 5 (2) | 6b (55) | 3:2 |
| 2b | 7 (1) | 8b (66) | 5:4 |
| 2c | 5 (5) | 6c (67) | 5:4 |
| 2c | 7 (1) | 8c (95) | 6:5 |
| 2d | 5 (2) | 6d (36) ^b | 1:1 |
| 2d | 7 (1) | 8d (75) | 6:5 |
| 2e | 5 (1.5) | 6e (96) | 3:1 |
| 2e | 7 (1) | 8e (94) | 1:1 |
| 2f | 5 (1.5) | 6f (82) | 4:3 |
| 2f | 7 (1) | 8f (90) | 4:3 |
| 2g | 5 (2) | 6g (75) | 3:2 |
| 2g | 7 (1) | 8g (86) | 4:3 |
| 2h | 7 (1) | 8h (74) | 3:1 |
| 2i | 5 (1.5) | 6i (42) ^c | |
| 2i | 7 (1) | 8i (72) | 7:3 |
| 2b | 9 (1) | 10b (33) | |
| 2c | 9 (1) | 10c (34) | |
| 2f | 9 (1) | 10f (25) | |
| 2b | 11 (1) | 12b (95) | 5:1 |
| 2c | 11 (1) | 12c (79) | 3:1 |
| 2f | 11 (1) | 12f (87) | 4:1 |

^a Treatment of a solution of vinyl ether and a 1,3-dipolarophile in methylene dichloride with ozone (1 equiv.) at -70°C . ^b 1-*p*-Methoxyphenylcyclopentene was isolated in 41% yield. ^c The ratio of two isomeric ozonides could not be determined.

methanol (Table 1). Treatment of the vinyl ethers **2b**, **c**, **f** with ozone in the presence of α -phenyl-*N*-benzylnitron **11** gave the corresponding 5-benzyl-5,6-dihydro-6-phenyl-3-(1-phenylcycloalkyl)-1,2,4,5-trioxazines **12b**, **c**, **f**, which could be conveniently isolated by column chromatography on silica gel (Scheme 2 and Table 1). Consistent with this, treatment of the adducts **12b**, **c**, **f** with silica gel in methylene dichloride for 3 days resulted in quantitative recovery of starting material.

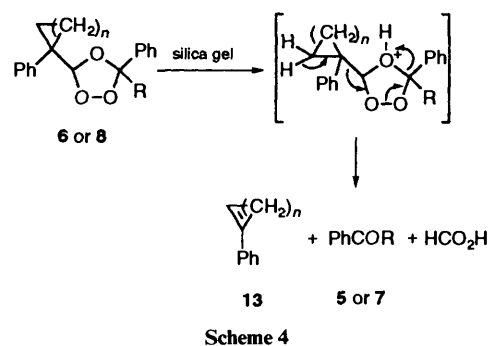
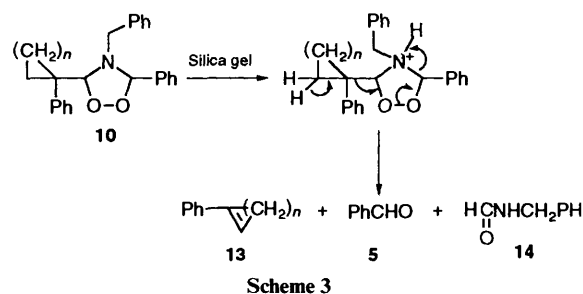
Silica Gel-catalysed Decomposition of 1,2,4-Trioxolanes and 1,2,4-Dioxazolidines.—During the isolation of the prepared cyclic peroxides, 1,2,4-trioxolane **6d** and dioxazolidines **10b**, **c**, **f** were noticed to be particularly labile toward silica gel. Therefore, we then investigated systematically the silica gel-catalysed decomposition of the isolated cycloadducts, **6**, **8** and **10**. Treatment of the dioxazolidine **10c** with silica gel in methylene dichloride for 1 day afforded a mixture of the ring-cleavage products, phenylcyclopentene **13c** (61%), benzaldehyde **5** (47%), and *N*-benzylformamide **14** (64%). From the dioxazolidine **10f**, phenylcyclohexene **13f** was obtained, together with the aldehyde **5** and the amide **14** (Table 2). This decomposition could be rationalized in terms of the mechanism illustrated in Scheme 3. Since silica gel is a very weak acid, protonation (or co-ordination of silica gel) to the dioxazolidine **10c** is likely to occur at the most basic nitrogen.* The subsequent electron migration, followed by deprotonation from the cyclopentane ring, leads to the formation of three products **13c**, **5** and **14**.

3-(1-Arylcyclopentyl)- **6c–e** and 3-(1-phenylcyclohexyl)- **6f** 5-phenyl-1,2,4-trioxolanes decomposed in a similar fashion (Scheme 4). A mixture of the corresponding 1-arylcycloalkenes

Table 2 Silica gel-catalysed decomposition of 1,2,4-trioxolanes and 1,2,4-dioxazolidines

| Substr. | Products (% yield) | Recovered substr. (%) |
|------------|--|-----------------------|
| 10c | 13c (61), 5 (47), 14 (64) | |
| 10f | 13f (70), 5 (67), 14 (71) | |
| 6c | 13c (42), 5 (35) | (38) |
| 8c | 13c (50), 7 (48) | (40) |
| 6d | 13d (69), 5 (40) | |
| 8d | 13d (64), 7 (61) | (15) |
| 6e | 13e (15), 5 (13) | (70) |
| 8e | 13e (12), 7 (11) | (75) |
| 6f | 13f (56), 5 (50) | (34) |
| 8f | 13f (41), 7 (10) | (47) |
| 6g | 13g (40), 5 (35) | (9) |
| 8g | 13g (22), 7 (21) | (54) |

^a Treatment of a solution of a substrate (1 mmol) and silica gel (3 g) in methylene dichloride (10 cm³) at 20°C for 1 day.



13c–f and benzaldehyde **5** were isolated in moderate yields. In the case of the ozonides **8c–f**, trifluoroacetophenone **7** was obtained together with the corresponding 1-arylcycloalkene **13**.† In contrast, 3-(1-arylcyclopropyl)- **6a** and 3-(1-phenylcyclobutyl)- **6b** 1,2,4-trioxolanes were stable toward silica gel. Even after reaction for 3 days, these ozonides remained unchanged. Apparently, the ring size of the cycloalkyl group in the ozonides **6** and **8** plays an important role in determining the rate of decomposition of the ozonides. As a reasonable explanation, formation of the highly strained cycloalkenes, 1-arylcyclopropene and 1-phenylcyclobutene, from the ozonides **6a**, **b** must be quite difficult.

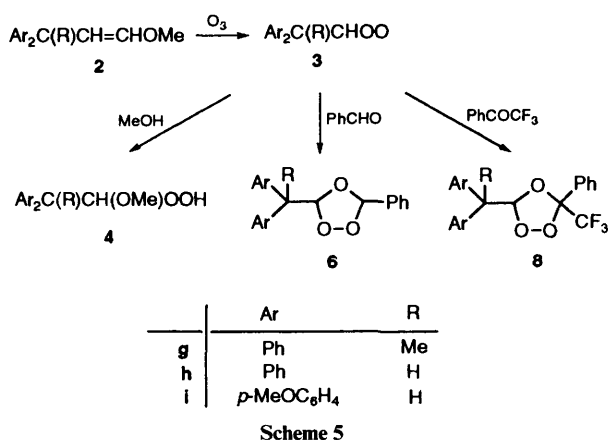
A further factor, which may affect the rate of decomposition of the ozonide **6**, is the electron-donating ability of the aryl-substituent attached to the cyclopentane ring at the 1-position. The reaction of the *p*-methoxyphenyl-substituted ozonide **6d**

* Semiempirical molecular orbital calculations (PM3¹¹) suggests that the protonated dioxazolidine **10c** at the nitrogen is *ca.* 160 KJ mol⁻¹ more stable than that protonated at the peroxide oxygen.

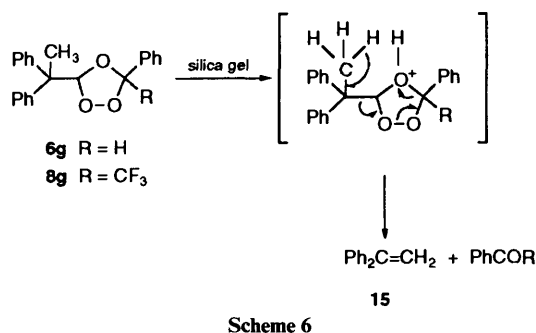
† In connection with the formation of 1-arylcycloalkenes from the ozonides **6** and **8**, Griesbaum and his co-workers¹² have found that thermal decomposition of 2,3-dimethylnorbornene ozonide yields 3-acetylcyclopentene.

for 1 day resulted in complete decomposition. Under the same conditions, however, both the phenyl-substituted **6c** and the *o*-fluorophenyl-substituted ozonide **6e** were recovered (40 and 70%, respectively), together with the corresponding decomposition products **13c, e** and **5** (Table 2).

These results imply that the ozonide may be easily decomposed by silica gel if two conditions are satisfied, *i.e.* (i) the carbenium ion, produced by heterolytic cleavage of the bond between the trioxolane ring and the attached alkyl group, is stable and (ii) deprotonation from the carbenium ion leads to the formation of a stable alkene. To test whether this hypothesis is correct or not, we prepared some 3-benzhydryl-substituted 1,2,4-trioxolanes **6g, i** and **8g-i** (Scheme 5), and undertook the



silica gel-catalysed decomposition. 3-(α,α -Diphenylethyl)-substituted 1,2,4-trioxolanes **6g** and **8g** were certainly decomposed by silica gel affording diphenylethylene **15** in moderate yields (Scheme 6 and Table 1). In contrast, diarylmethyl-substituted



1,2,4-trioxolanes **6i** and **8h, i** were stable on silica gel. If the relative stability of the carbenium ion produced by the heterolytic C–C bond fission were the controlling factor in determining the decomposition rate, the ozonide **8h** might have decomposed much faster than the ozonide **8g** (the stability of the di-*p*-methoxyphenylcarbenium ion is significantly higher than that of the α -methylbenzhydryl cation¹³). Experimental results are clearly inconsistent with this hypothesis and may suggest that silica gel-catalysed decomposition of the ozonide, **6** or **8**, does not proceed by a stepwise mechanism involving the participation of a discrete carbenium ion. Perhaps in accordance with this, treatment of the ozonide **6c** with silica gel in methanol for 1 day did yield phenylcyclopentene (51%) and benzaldehyde (33%); no evidence was obtained for the formation of methyl 1-phenylcyclopentyl ether, a possible product from nucleophilic attack on the 1-phenylcyclopentyl cation by the solvent. Also, silica gel-catalysed decomposition of the ozonide **6g** in methanol for 3 days yielded diphenylethylene

15 (40%) and benzaldehyde **5** (35%); the ozonide **6h** was recovered (15%).*

Experimental

General.—¹H NMR and ¹³C NMR spectra were obtained in CDCl₃ (unless otherwise noticed) with SiMe₄ as a standard, on JNM-PS-100 and JNM-GSX-400 spectrometers, respectively. *J* Values are given in Hz. IR spectra were obtained with a Hitachi 215 spectrometer.

Synthesis of Vinyl Ethers.—The vinyl ethers **2a-i** were prepared from the corresponding aldehydes **1a-f**,¹⁵ **1g**,¹⁶ **1h**¹⁷ and **1i** following the method developed by Earnshaw *et al.*¹⁸ The synthesis of the vinyl ether **2a** is representative. Methoxymethyldiphenylphosphine oxide (7.4 g, 30 mmol) in dry THF (100 cm³) was stirred with lithium diisopropylamide [from diisopropylamine (5.3 cm³) and butyllithium (1.6 mol dm⁻³ solution in hexane; 17 cm³)] in THF (100 cm³) at 0 °C for 10 min. The mixture was cooled at -70 °C and 1-phenylcyclopropanecarbaldehyde **1a** (3.65 g, 25 mmol) in dry THF (50 cm³) was added dropwise to it. The solution was allowed to warm to room temperature when it was diluted with saturated aqueous ammonium chloride (100 cm³) and ether. The separated organic layer was washed with saturated brine, dried (MgSO₄) and concentrated. Column chromatography on silica gel of the residue gave 2-diphenylphosphinoyl-2-methoxy-1-(1-phenylcyclopropyl)ethanol [oil; δ_{H} 0.5–2.3 (4 H, m), 2.83 (s) + 2.99 (s) (3 H, OMe), 3.3–4.0 (3 H, m), 7.2–8.2 (15 H, m)] (4.0 g, 10 mmol), which was used for the subsequent reaction without further purification. The alcohol was dissolved in dry THF (150 cm³) and stirred with sodium hydride (60% dispersion in oil; washed with dry hexane, 1.4 g, 35 mmol) for 24 h. The mixture was filtered and the residue was washed with ether. The combined organic filtrate and washings were washed with saturated brine, dried (MgSO₄), and concentrated. The crude products were separated by column chromatography on silica gel. Elution with benzene–hexane (1:5) gave the vinyl ether **2a** (1.2 g, 28% yield from aldehyde **1a**). The vinyl ethers **2a, c-i** were obtained as mixture of two stereoisomers.

1-Methoxy-2-(1-phenylcyclopropyl)ethene 2a: oil (a 9:5 mixture) (Found: C, 82.55; H, 8.1. C₁₂H₁₄O requires C, 82.8; H, 8.1%); δ_{H} (CCl₄) 0.8–1.1 (4 H, m), 3.33 (s, major) + 3.43 (s, minor) (3 H, OMe), 4.56 (d, *J* 6.5, minor) + 4.83 (d, *J* 10.5, major) (1 H, 2-H), 5.74 (d, *J* 6.5, minor) + 6.07 (d, *J* 10.5, major) (1 H, 1-H), 6.8–7.5 (5 H, m).

1-Methoxy-2-(1-phenylcyclobutyl)ethene 2b: oil (Found: C, 83.1; H, 8.3. C₁₃H₁₆O requires C, 83.0; H, 8.5%); δ_{H} (CCl₄) 1.6–2.6 (6 H, m), 3.44 (3 H, s), 5.11 (1 H, d, *J* 12.5), 6.05 (1 H, d, *J* 12.5), 7.1–7.4 (5 H, m).

1-Methoxy-2-(1-phenylcyclopentyl)ethene 2c: oil (a 6:5 mixture) (Found: C, 83.0; H, 9.0. C₁₄H₁₈O requires C, 83.2; H, 8.9%); δ_{H} (CCl₄) 1.5–2.3 (8 H, m), 3.40 (s, major) + 3.44 (s, minor) (3 H, OMe), 4.35 (d, *J* 7, minor) + 4.80 (d, *J* 13, major) (1 H, 2-H), 5.63 (d, *J* 7, minor) + 6.03 (d, *J* 13, major) (1 H, 1-H) and 6.9–7.7 (5 H, m).

2-[1-Methoxy-1-(*p*-methoxyphenyl)-cyclopentyl]ethene 2d: oil (a 4:3 mixture); δ_{H} (CCl₄) 1.4–2.4 (8 H, m), 3.41 (s, major) + 3.48 (s, minor) (3 H, OMe), 3.75 (3 H, s), 4.34 (d, *J* 6, major) + 4.70 (d, *J* 14, minor) (1 H, 2-H), 5.65 (d, *J* 6, major) + 6.01 (d, *J* 14, minor) (1 H, 1-H) and 6.6–7.5 (4 H, m).

1-[1-(*o*-Fluorophenyl)cyclopentyl]-2-methoxyethene 2e: oil (a

* In contrast, Griesbaum and his co-workers^{14a} have found that solvolysis of 3-acetoxy-1,2,4-trioxolanes, which proceeds by heterolytic cleavage of the C–O bond between the ozonide ring and the attached acetoxy group, yields the corresponding 3-alkoxy-substituted 1,2,4-trioxolanes.

7:6 mixture); $\delta_{\text{H}}(\text{CCl}_4)$ 1.5–2.5 (8 H, m), 3.32 (s, minor) + 3.36 (s, major) (3 H, OMe), 4.50 (dd, J 6.5 and 2, minor) + 4.85 (d, J 13.5, major) (1 H, 2-H), 5.60 (d, J 6.5, minor) + 6.10 (d, J 13.5, major) (1 H, 1-H) and 6.6–7.5 (4 H, m).

1-Methoxy-1-(2-phenylcyclohexyl)ethene 2f: oil (a 4:3 mixture) (Found: C, 83.2; H, 9.35. $\text{C}_{15}\text{H}_{20}\text{O}$ requires C, 83.3; H, 9.3%; $\delta_{\text{H}}(\text{CCl}_4)$ 0.7–2.3 (10 H, m), 3.41 (3 H, s), 4.23 (d, J 7, minor) + 4.73 (d, J 13, major), (1 H, 2-H), 5.77 (d, J 7, minor) + 5.95 (d, J 13, major) (1 H, 1-H) and 7.0–7.6 (5 H, m).

1-Methoxy-3,3-diphenylbut-1-ene 2g: oil (a 4:1 mixture) (Found: C, 85.55; H, 7.7. $\text{C}_{17}\text{H}_{18}\text{O}$ requires C, 85.7; H, 7.6%; $\delta_{\text{H}}(\text{CCl}_4)$ 1.76 (s, major) + 1.87 (s, minor) (3 H, Me), 3.42 (s, minor) + 3.50 (s, major) (3 H, OMe), 4.75 (d, J 7, minor) + 5.27 (d, J 13, major) (1 H, 2-H), 5.80 (d, J 7, minor) + 5.90 (d, J 13, major) (1 H, 2-H) and 7.0–7.5 (10 H, m).

1-Methoxy-3,3-di(p-methoxyphenyl)propene 2h: oil (a 5:1 mixture) (Found: C, 77.8; H, 7.1. $\text{C}_{18}\text{H}_{20}\text{O}_3$ requires C, 78.1; H 7.0%; $\delta_{\text{H}}(\text{CCl}_4)$ 3.49 (s, major) + 3.57 (s, minor) (3 H, OMe), 3.71 (6 H, s), 4.3–5.4 (2 H, m), 5.8–6.3 (1 H, m), 6.68 (4 H, d, J 8.5) and 7.09 (4 H, d, J 8.5).

1-Methoxy-3,3-diphenylpropene 2i: oil (a 8:7 mixture) (Found: C, 80.2; H, 6.5. $\text{C}_{16}\text{H}_{16}\text{O}$ requires C, 80.0; H, 6.7%; $\delta_{\text{H}}(\text{CCl}_4)$ 3.48 (s, minor) + 3.58 (s, major) (3 H, OMe), 4.5–5.4 (2 H, m), 5.95 (d, J 6, minor) + 6.17 (d, J 12, major) (1 H) and 7.2 (10 H, br s).

Ozonolysis of Vinyl Ethers in MeOH–CH₂Cl₂.—Ozonolysis of the vinyl ether **2a** is representative. To a solution of methanol–methylene dichloride (1:2; 15 cm³) was passed a slow stream of ozone (1 mmol; Nippon Ozone Model ON-1-2 ozonator) at –70 °C. The mixture was poured into water and extracted with ether and the extract was washed with saturated brine and dried (MgSO₄). After evaporation of the solvent, the crude products were separated by column chromatography on silica gel. Elution with ether–benzene (1:10) gave the methoxyalkyl hydroperoxide **4a**.

Methoxy(1-phenylcyclopropyl)methyl hydroperoxide 4a: oil (Found: C, 67.9, H, 7.3. $\text{C}_{11}\text{H}_{14}\text{O}_3$ requires C, 68.0; H, 7.2%; δ_{H} 0.74 (2 H, d, J 4), 0.97 (2 H, d, J 4), 3.40 (3 H, s), 4.67 (1 H, s), 7.2–7.5 (5 H, m) and 8.96 (1 H, s).

Methoxy(1-phenylcyclobutyl)methyl hydroperoxide 4b: m.p. 96–99 °C (Found: C, 69.2; H, 7.8. $\text{C}_{12}\text{H}_{16}\text{O}_3$ requires C, 69.2; H, 7.8%; δ_{H} 1.6–2.8 (6 H, m), 3.42 (3 H, s), 4.90 (1 H, s), 7.0–7.5 (5 H, m) and 9.02 (1 H, s).

Methoxy(1-phenylcyclopentyl)methyl hydroperoxide 4c: m.p. 107–110 °C (Found: C, 70.4; H, 8.3. $\text{C}_{13}\text{H}_{18}\text{O}_3$ requires C, 70.2; H, 8.2%; δ_{H} 1.3–2.2 (8 H, m), 3.42 (3 H, s), 4.76 (1 H, s), 7.31 (5 H, s) and 8.75 (1 H, s); δ_{C} 23.60, 23.70, 34.29, 34.65, 55.18, 60.86, 113.22, 126.16, 127.56, 128.15 and 143.21.

Methoxy[1-(p-methoxyphenyl)cyclopentyl]methyl hydroperoxide 4d: m.p. 106–110 °C (Found: C, 66.3; H, 8.0. $\text{C}_{14}\text{H}_{20}\text{O}_4$ requires C, 66.6; H, 8.0%; δ_{H} 1.2–2.3 (8 H, m), 3.47 (3 H, s), 3.75 (3 H, s), 4.73 (1 H, s) and 6.5–7.5 (4 H, m); δ_{C} 23.58, 23.67, 34.57, 34.77, 54.54, 55.10, 60.67, 112.96, 113.53, 129.10, 135.25 and 157.81.

[1-(o-Fluorophenyl)cyclopentyl]methoxymethyl hydroperoxide 4e: m.p. 83–85 °C (Found: C, 64.8; H, 7.3. $\text{C}_{13}\text{H}_{17}\text{FO}_3$ requires C, 65.0; H, 7.15%; δ_{H} 1.4–2.5 (8 H, m), 3.50 (3 H, s), 5.13 (1 H, s), 6.8–7.6 (4 H, m) and 8.87 (1 H, s).

Methoxy(1-phenylcyclohexyl)methyl hydroperoxide 4f: m.p. 136–138 °C (Found: C, 71.3; H, 8.7. $\text{C}_{14}\text{H}_{20}\text{O}_3$ requires C, 71.1; H, 8.6%; δ_{H} 1.1–2.6 (10 H, m), 3.49 (3 H, s), 4.61 (1 H, s) and 7.2–7.6 (5 H, m).

1-Methoxy-2,2-diphenylpropyl hydroperoxide 4g: m.p. 84–88 °C (Found: C, 74.3; H, 7.0. $\text{C}_{16}\text{H}_{18}\text{O}_3$ requires C, 74.4; H, 7.0%; δ_{H} 1.66 (3 H, s), 3.32 (3 H, s), 5.19 (1 H, s), 7.2–7.5 (10 H, m) and 8.73 (1 H, s).

1-Methoxy-2,2-bis(p-methoxyphenyl)ethyl hydroperoxide 4h:

oil (Found: C, 67.25; H, 6.4. $\text{C}_{17}\text{H}_{20}\text{O}_5$ requires C, 67.1; H, 6.6%; δ_{H} 3.30 (3 H, s), 3.61 (6 H, s), 4.12 (1 H, d, J 7), 5.09 (1 H, d, J 7), 6.5–7.3 (8 H, m) and 8.88 (1 H, s); δ_{C} 51.61, 55.09, 57.11, 110.16, 113.74, 113.80, 129.49, 129.51, 132.71, 132.83, 158.05 and 158.09.

1-Methoxy-2,2-diphenylethyl hydroperoxide 4i: oil (Found: C, 74.1; H, 6.7. $\text{C}_{15}\text{H}_{16}\text{O}_3$ requires C, 73.7; H, 6.6%; δ_{H} 3.32 (3 H, s) 4.27 (1 H, d, J 7), 5.22 (1 H, d, J 7), 7.21 (10 H, br s) and 8.66 (1 H, s).

Ozonolysis of Vinyl Ethers in the Presence of Benzaldehyde or Trifluoroacetophenone.—Reaction of a mixture of the vinyl ether **2a** and benzaldehyde **5** is representative. A solution of **2a** (1 mmol) and **5** (1.3 mmol) in methylene dichloride (15 cm³) was treated with 1 mmol of ozone at –70 °C. After evaporation of the solvent, the products were separated by column chromatography on silica gel. Elution with benzene–hexane (3:7) gave the trioxolane **6a** as a mixture of two stereoisomers (for the ratio, see Table 1).

3-Phenyl-5-(1-phenylcyclopropyl)-1,2,4-trioxolane 6a: oil (Found: C, 76.1; H, 6.2. $\text{C}_{17}\text{H}_{16}\text{O}_3$ requires C, 76.1; H, 6.0%; δ_{H} 0.7–1.2 (4 H, m), 5.14 (s, major) + 5.21 (s, minor) (1 H, 5-H), 5.58 (s, major) + 5.92 (s, minor) (1 H, 3-H) and 7.0–7.6 (10 H, m).

3-Phenyl-5-(1-phenylcyclobutyl)-1,2,4-trioxolane 6b: oil (Found: C, 76.6; H, 6.5. $\text{C}_{18}\text{H}_{18}\text{O}_3$ requires C, 76.6; H, 6.4%; δ_{H} 1.6–2.8 (6 H, m), 5.37 (s, minor) + 5.55 (s, major) (1 H, 5-H), 5.72 (s, major) + 6.00 (s, minor) (1 H, 3-H) and 7.0–7.6 (10 H, m).

5-Phenyl-3-(1-phenylcyclopentyl)-1,2,4-trioxolane 6c: oil (Found: C, 77.2; H, 6.7. $\text{C}_{19}\text{H}_{20}\text{O}_3$ requires C, 77.0; H, 6.8%; δ_{H} 1.4–2.5 (8 H, m), 5.34 (s, major) + 5.46 (s, minor) (1 H, 5-H), 5.54 (s, minor) + 5.94 (s, major) (1 H, 3-H) and 7.1–7.7 (10 H, m); δ_{C} 23.33, 24.10, 24.16, 33.15, 33.33, 34.22, 34.54, 53.15, 104.33, 109.28, 125.53, 126.07, 126.57, 126.79, 127.84, 127.92, 128.23, 128.41, 128.53, 130.56, 131.97, 136.79, 142.41 and 142.60.

3-[1-(p-Methoxyphenyl)cyclopentyl]-5-phenyl-1,2,4-trioxolane 6d: oil; δ_{H} 1.4–2.4 (8 H, m), 3.76 (3 H, s), 5.32 (s) + 5.43 (s) (1 H), 5.58 (s) + 6.00 (s) (1 H) and 6.7–8.1 (9 H, m).

3-[1-(o-Fluorophenyl)cyclopentyl]-5-phenyl-1,2,4-trioxolane 6e: oil (Found: C, 73.7; H, 6.3. $\text{C}_{19}\text{H}_{19}\text{FO}_3$ requires C, 72.6; H, 6.1%; δ_{H} 1.5–2.6 (8 H, m), 5.60 (s, minor) + 5.68 (s, major), 5.68 (s, major) + 5.93 (s, minor) (1 H) and 6.6–7.5 (9 H, m).

3-Phenyl-5-(1-phenylcyclohexyl)-1,2,4-trioxolane 6f: oil (Found: C, 77.1; H, 7.1. $\text{C}_{20}\text{H}_{22}\text{O}_3$ requires C, 77.4; H, 7.2%; δ_{H} 1.0–2.7 (10 H, m), 5.09 (s, minor) + 5.19 (s, major) (1 H, 5-H), 5.44 (s, major) + 5.88 (s, minor) (1 H, 5-H) and 7.0–7.6 (10 H, m); δ_{C} 21.29, 21.36, 26.32, 30.26, 30.31, 30.61, 30.80, 36.46, 45.03, 45.27, 103.53, 104.06, 109.83, 110.16, 124.91, 126.44, 127.39, 127.89, 128.12, 128.20, 128.27, 128.29, 128.46, 128.72, 128.79, 129.97, 130.49, 131.90, 133.14, 139.00 and 139.31.

3-(1,1-Diphenylethyl)-5-phenyl-1,2,4-trioxolane 6g: oil (Found: C, 79.2; H, 6.2. $\text{C}_{22}\text{H}_{20}\text{O}_3$ requires C, 79.5; H, 6.1%; δ_{H} 1.73 (s, minor) + 1.81 (s, major) (3 H, Me), 5.57 (s, major) + 5.93 (s, minor) (1 H, 3-H), 6.02 (1 H, s) and 7.0–7.5 (15 H, m).

3-Diphenylmethyl-5-phenyl-1,2,4-trioxolane 6i: oil (Found: C, 78.9; H, 5.7. $\text{C}_{21}\text{H}_{18}\text{O}_3$ requires C, 79.2; H, 5.7%; δ_{H} 4.3–4.5 (1 H, m), 5.60 (s) + 5.8–6.1 (m) (2 H) and 7.0–7.6 (15 H, m); δ_{C} 52.93, 54.33, 104.00, 104.26, 105.90, 106.06, 127.03, 127.08, 127.11, 127.15, 127.55, 127.91, 128.43, 128.51, 128.54, 128.56, 129.08, 129.14, 129.22, 129.34, 130.22, 130.63, 131.90 and 138.67.

3-Phenyl-5-(1-phenylcyclopropyl)-3-trifluoromethyl-1,2,4-trioxolane 8a: oil (Found: C, 64.55; H, 4.5. $\text{C}_{18}\text{H}_{15}\text{F}_3\text{O}_3$ requires C, 64.3; H, 4.5%; δ_{H} 0.7–1.3 (4 H, m), 5.20 (s, minor) + 5.43 (s, major) (1 H) and 7.0–7.6 (10 H, m).

3-Phenyl-5-(1-phenylcyclobutyl)-3-trifluoromethyl-1,2,4-trioxolane 8b: oil (Found: C, 65.5; H, 4.9. $\text{C}_{19}\text{H}_{17}\text{F}_3\text{O}_3$ requires C,

65.1; H, 4.9%); δ_{H} 1.6–2.9 (6 H, m), 5.21 (s, major) + 5.59 (s, minor) (1 H) and 6.9–7.7 (10 H, m).

3-Phenyl-5-(1-phenylcyclopentyl)-3-trifluoromethyl-1,2,4-trioxolane **8c**: oil (Found: C, 65.9; H, 5.3. $\text{C}_{20}\text{H}_{19}\text{F}_3\text{O}_3$ requires C, 65.9; H, 5.2%); δ_{H} 1.4–2.5 (8 H, m), 5.20 (s, minor) + 5.56 (s, major) (1 H) and 7.0–7.7 (10 H, m); δ_{C} 24.13, 24.24, 24.28, 24.30, 33.44, 33.60, 34.74, 34.89, 51.84, 52.57, 103.38 (q, *J* 26), 104.18 (q, *J* 26), 109.49, 111.15, 121.42 (q, *J* 289), 121.54 (q, *J* 289), 126.62, 126.74, 126.82, 126.93, 127.91, 127.95, 128.00, 128.09, 128.35, 128.39, 130.00, 130.41, 131.37, 132.30, 142.33 and 142.45.

3-[1-(*p*-Methoxyphenyl)cyclopentyl]-5-phenyl-5-trifluoromethyl-1,2,4-trioxolane **8d**: oil (Found: C, 66.7; H, 5.5. $\text{C}_{21}\text{H}_{21}\text{F}_3\text{O}_3$ requires C, 66.7; H, 5.6%); δ_{H} 1.4–2.5 (8 H, m), 3.67 (s, minor) + 3.70 (s, major) (3 H), 5.19 (s, minor) + 5.51 (s, major) (1 H) and 6.6–7.7 (9 H, m).

3-[1-(2-Fluorophenyl)cyclopentyl]-5-phenyl-5-trifluoromethyl-1,2,4-trioxolane **8e**: oil (Found: C, 62.8; H, 4.9. $\text{C}_{20}\text{H}_{18}\text{F}_4\text{O}_3$ requires C, 62.8; H, 4.75%); δ_{H} 1.4–2.8 (8 H, m), 5.46 (s, minor) + 5.81 (s, major) (1 H) and 6.6–7.6 (9 H, m).

3-Phenyl-5-(1-phenylcyclohexyl)-3-trifluoromethyl-1,2,4-trioxolane **8f**: oil (Found: C, 66.8; H, 5.7. $\text{C}_{21}\text{H}_{21}\text{F}_3\text{O}_3$ requires C, 66.6; H, 5.6%); δ_{H} 0.9–2.7 (10 H, m), 4.94 (s, minor) + 5.30 (s, major) (1 H) and 7.2–7.6 (10 H, m).

3-(2,2-Diphenylethyl)-5-phenyl-5-trifluoromethyl-1,2,4-trioxolane **8g**: oil (Found: C, 69.5; H, 4.95. $\text{C}_{23}\text{H}_{19}\text{F}_3\text{O}_3$ requires C, 69.0; H, 4.8%); δ_{H} (CCl₄) 1.59 (s, major) + 1.87 (s, minor) (3 H), 5.79 (s, minor) + 6.14 (s, major) (1 H) and 7.0–7.6 (15 H, m).

3-[Bis(*p*-methoxyphenyl)methyl]-5-phenyl-5-trifluoromethyl-1,2,4-trioxolane **8h**: oil (Found: C, 69.55; H, 5.1. $\text{C}_{24}\text{H}_{21}\text{F}_3\text{O}_3$ requires C, 69.6; H, 5.1%); δ_{H} 3.66 (6 H, s), 4.08 (1 H, d, *J* 6), 6.01 (1 H, d, *J* 6) and 6.4–7.6 (13 H, m).

3-Diphenylmethyl-5-phenyl-5-trifluoromethyl-1,2,4-trioxolane **8i**: oil (Found: C, 68.5; H, 4.5. $\text{C}_{22}\text{H}_{17}\text{F}_3\text{O}_3$ requires C, 68.4; H, 4.4%); δ_{H} 4.19 (d, *J* 7, major) + 4.45 (d, *J* 7, minor) (1 H), 5.82 (d, *J* 7, minor) + 6.15 (d, *J* 7, major) (1 H) and 7.1–7.6 (15 H, m).

Ozonolysis of Vinyl Ethers in the Presence of Imines.—A solution of the vinyl ether **2** (1.5 mmol) and the imine **9** (1.5 mmol) in methylene dichloride (15 cm³) was treated with ozone (1 equiv.) at –70 °C. After evaporation of the solvent, the products were triturated with ether–hexane (1:5; 10 cm³) to give the dioxazolidine **10**.

4-Benzyl-5-phenyl-3-(1-phenylcyclobutyl)-1,2,4-dioxazolidine **10b**: m.p. 98–102 °C (from methanol) (Found: C, 80.7; H, 6.8; N, 3.8. $\text{C}_{25}\text{H}_{25}\text{NO}_2$ requires C, 80.8; H, 6.7; N, 3.8%); δ_{H} 1.4–2.7 (6 H, m), 3.62 (2 H, s), 4.56 (1 H, s), 5.32 (1 H, s) and 7.0–8.6 (15 H, m).

4-Benzyl-5-phenyl-3-(1-phenylcyclopentyl)-1,2,4-dioxazolidine **10c**: m.p. 109–111 °C (Found: C, 81.0; H, 7.4; N, 3.5. $\text{C}_{26}\text{H}_{27}\text{NO}_2$ requires C, 80.6; H, 7.6; N, 3.6%); δ_{H} 0.8–2.3 (8 H, m), 3.52 (1 H, d, *J* 14), 3.70 (1 H, d, *J* 14), 4.39 (1 H, s), 5.00 (1 H, s) and 6.9–7.7 (15 H, m); ν_{max} /cm^{–1} (KBr) 2950, 1500, 1455, 1390, 1120, 1100, 720 and 700.

4-Benzyl-5-phenyl-3-(1-phenylcyclohexyl)-1,2,4-dioxazolidine **10f**: m.p. 102–106 °C (Found: C, 81.5; H, 7.4; N, 3.3. $\text{C}_{27}\text{H}_{29}\text{NO}_2$ requires C, 81.2; H, 7.3; N, 3.5%); δ_{H} 0.6–2.7 (10 H, m), 3.50 (1 H, d, *J* 14), 3.70 (1 H, d, *J* 14), 4.46 (1 H, s), 4.84 (1 H, s) and 6.9–8.0 (15 H, m).

Ozonolysis of Vinyl Ethers in the Presence of Nitrones.—A mixture of the vinyl ether **2** (1.5 mmol) and the nitron **11** (1.5 mmol) in methylene dichloride (15 cm³) was treated with ozone (1 equiv.) at –70 °C. After evaporation of the solvent, the crude products were separated by column chromatography on silica gel. Elution with benzene–hexane (1:5) gave the corresponding dihydro-1,2,4,5-trioxazine **12** as a mixture of two isomers (for the ratio, see Table 1).

5-Benzyl-6-phenyl-3-(1-phenylcyclobutyl)-5,6-dihydro-1,2,4,5-trioxazine **12b**: m.p. 108–109 °C (Found: C, 77.2; H, 6.5; N, 3.6. $\text{C}_{25}\text{H}_{25}\text{NO}_3$ requires C, 77.5; H, 6.5; N, 3.6%); δ_{H} 1.6–2.8 (6 H, m), 3.64 (s, major) + 4.25 (s, minor) (2 H), 5.32 (s, minor) + 5.42 (s, major) (1 H), 5.83 (s, major) + 6.02 (s, minor) (1 H) and 6.9–7.7 (15 H, m).

5-Benzyl-6-phenyl-3-(1-phenylcyclopentyl)-5,6-dihydro-1,2,4,5-trioxazine **12c**: m.p. 91–94 °C (Found: C, 77.9; H, 6.8; N, 3.45. $\text{C}_{26}\text{H}_{27}\text{NO}_3$ requires C, 77.8; H, 6.8; N, 3.5%); δ_{H} 1.3–2.8 (8 H, m), 3.60 (s, major) + 4.21 (s, minor) (2 H), 5.30 (s, minor) + 5.39 (s, major) (1 H), 5.72 (s, major) + 5.95 (s, minor) (1 H) and 7.1–7.8 (15 H, m).

5-Benzyl-6-phenyl-3-(1-phenylcyclohexyl)-5,6-dihydro-1,2,4,5-trioxazine **12f**: m.p. 139–141 °C (Found: C, 78.0; H, 7.0; N, 3.3. $\text{C}_{27}\text{H}_{29}\text{NO}_3$ requires C, 78.0; H, 7.05; N, 3.4%); δ_{H} 1.0–2.6 (10 H, m), 3.64 (s, major) + 4.21 (s, minor) (2 H), 5.34 (s, minor) + 5.45 (s, major) (1 H), 5.70 (s, major) + 5.90 (s, minor) (1 H) and 7.0–7.5 (15 H, m).

Silica Gel-catalysed Decomposition of 1,2,4-Dioxazolidines 10c, f.—The reaction of **10c** is representative. A solution containing the dioxazolidine **10c** (136 mg, 0.36 mmol) and silica gel (YMC-Gel; 60–200 mesh, 3 g) in methylene dichloride (15 cm³) was stirred at room temperature for 1 day. The silica gel was washed with ether (20 cm³ × 3) and the combined filtrate and washings were concentrated. The crude products were separated by column chromatography on silica gel. The first fraction (benzene–hexane, 1:9) contained 1-phenylcyclopentene (31 mg, 61%) [oil; δ_{H} 1.8–3.0 (6 H, m), 6.20 (1 H, t, *J* 2) and 7.1–7.6 (5 H, m)]. From the second fraction (elution with benzene) was obtained benzaldehyde (37 mg, 47%). The third fraction (elution with ether–benzene, 1:20) contained *N*-benzylformamide (31 mg, 64%) [m.p. 66–61 °C; δ_{H} 6.40 (1 H, s), 6.66 (1 H, s), 7.33 (5 H, s) and 8.27 (1 H, s)].

Silica Gel-catalysed Decomposition of 1,2,4-Dioxazolidine 6 and 8.—The reaction of **6c** is representative. To a solution of the ozonide **6c** (394 mg, 1.33 mmol) in methylene dichloride (15 cm³) was added silica gel (3 g) and the mixture was stirred at room temperature for 1 day. After the silica gel had been washed with ether (20 cm³ × 3), the combined filtrate and washings were concentrated. The crude products were separated by column chromatography on silica gel. First fraction (elution with benzene–hexane, 1:9) contained 1-phenylcyclopentene **13c** (80 mg, 42%). From the second fraction (elution with benzene–hexane, 3:17), was obtained the unchanged ozonide **6c** (150 mg, 38%). The third fraction (elution with benzene) contained benzaldehyde **5** (49 mg, 35%).

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