Cycloadditions between Carbonyl Oxides and Dicarbonyl Compounds: Isolation and Characterisation of Novel Polycyclic 1,2,4,6-Tetroxepane Derivatives

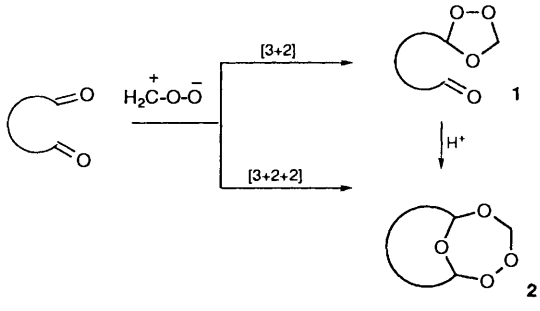
Kevin J. McCullough,*[,a] Toshiya Sugimoto,[b] Shogo Tanaka,[b] Shigekazu Kusabayashi[b] and Masatomo Nojima*[,b]

[a] *Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, UK*

[b] *Department of Chemical Process Engineering, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan*

Formaldehyde *O*-oxide reacts with dicarbonyl compounds to produce mono-ozonides formed by conventional [3 + 2] cycloadditions to an aldehydic carbonyl group of the substrate, and/or polycyclic 1,2,4,6-tetroxepane derivatives arising from formal [3 + 2 + 2] cycloadditions involving both carbonyl groups. Similar reactions between the more highly substituted carbonyl oxides, benzaldehyde and octanal *O*-oxides, and dicarbonyl compounds yielded the corresponding mono-ozonides as the sole isolable cycloaddition products. In certain favourable cases, mono-ozonides could undergo acid-catalysed intramolecular rearrangement to the corresponding 1,2,4,6-tetroxepanes. X-Ray crystallographic analyses of two 1,2,4,6-tetroxepanes, **6a** and **13b**, are recorded.

Mono- and poly-cyclic peroxides have attracted considerable attention as models or analogues of an increasing number of peroxidic natural products, some of which possess attractive pharmacological properties.[1,2] Reactions between formaldehyde *O*-oxide and 1,5-keto aldehydes have been reported[3] to produce, *via* stepwise [3 + 2 + 2] cycloaddition processes, the polycyclic adducts **2** which contain the comparatively uncommon 1,2,4,6-tetroxepane ring system (Scheme 1).[4] Moreover, keto ozonides **1**, derived from the more normal [3 + 2] cycloaddition[5] between formaldehyde *O*-oxide and keto aldehydes, could be rearranged under acidic conditions to give the corresponding 1,2,4,6-tetroxepane derivatives. We now report in detail the results of a more extensive study of the reaction between the carbonyl oxides (formaldehyde, benzaldehyde and octanal *O*-oxides) and a series of dicarbonyl compounds.



Scheme 1

Results and Discussion

Cycloadditions of Formaldehyde O-Oxide with Dicarbonyl Compounds.—A solution of ethyl vinyl ether (3 mmol) and keto aldehyde **3a** (1 mmol) in dichloromethane was ozonised (3 mmol of ozone) at −70 °C. Subsequent rapid column chromatography of the resulting crude product mixture on silica gel afforded the normal [3 + 2] cycloadduct **4a** (21%), two isomeric adducts **5a** (3%) and **6a** (6%), and phenylacenaphthylene ozonide **9** (1%), together with unchanged keto aldehyde **3a** (47%) (Table 1 and Scheme 2).

To differentiate unambiguously between the structures of the isomeric peroxidic adducts **5a** and **6a**, a single crystal of the latter was subjected to X-ray crystallographic analysis. The crystal structure actually consists of two discrete (no intermolecular contacts within 3.2 Å), independent, enantiomeric molecules of compound **6a** per asymmetric unit. The molecular structure of one of the independent molecules of **6a** is depicted in Fig 1. The central seven-membered 1,2,4,6-tetroxepane ring in each independent molecule of compound **6a** adopts a chair conformation which is distorted from ideality to a slightly different extent [C(2)–O(3)–C(3)–O(4) −15.4(4)° as compared with C(2′)–O(3′)–C(3′)–O(4′) 21.2(4)°]. Thus, the tetroxepane ring system in compound **6a**, although highly constrained, does not appear to be conformationally rigid. Corresponding bond lengths and angles around the two molecules of compound **6a** are not significantly different and are also in good agreement with expected values. The O–O bond lengths [1.476(4) and 1.465(4) Å, respectively] are similar to those observed in a range of polycyclic 1,2,4-trioxanes.[6]

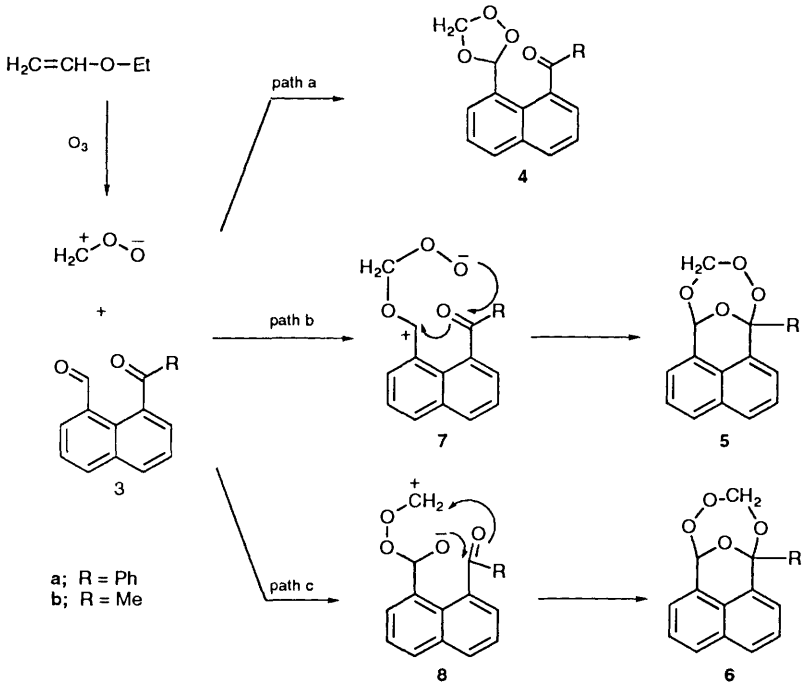
The ^{1}H NMR spectrum of compound **6a** exhibited the presence of a long-range coupling ($^5J_{HH}$ 1.5 Hz) between the two protons at the bridgehead carbons C(1) and C(3) which is similar in magnitude to the long-range coupling ($^5J_{HH}$ 2 Hz) observed in the ^{1}H NMR spectrum of the hemiperacetal obtained from the ozonolysis of indene in methanol.[7]

The mechanism outlined in Scheme 2 tentatively accounts for the formation of the major peroxidic products. Ozonolysis of the unsymmetrical ethyl vinyl ether is known to yield predominantly formaldehyde *O*-oxide.[8] On the basis of the relative dipolarophilicities of formyl and benzoyl groups,[9] formaldehyde *O*-oxide would be expected to attack selectively the former in compound **3a**. Although a normal concerted [3 + 2] cycloaddition process would provide the ozonide **4a** directly (path a),[5] the formation of adducts **5a** and **6a**, albeit as lesser components of the product mixture, indicates that more complex [3 + 2 + 2] cycloaddition processes must also be operative. Since concerted [3 + 2 + 2] cycloadditions would be disallowed by orbital symmetry, the stepwise mechanism[10] shown in Scheme 2 (paths b and c) is consistent with the structures of the adducts **5a** and **6a**. Thus, partial capture of the formaldehyde *O*-oxide by the formal group of compound **3a** would give the betaine intermediates **7a** and **8a**, which on subsequent intramolecular cyclisation with concomitant incorporation of the adjacent benzoyl group would yield compounds **5a** (path b) and **6a** (path c), respectively. The

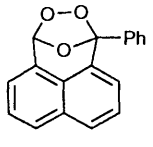
Table 1 Ozonolysis of ethyl vinyl ether in the presence of dicarbonyl compounds[a]

Dicarbonyl compound	Solvent	Products (%)	Recovered starting material (%)
3a	CH_2Cl_2	**4a** (21), **5a** (3), **6a** (6), **9** (1)	(49)
3b	CH_2Cl_2	**5b** (14), **6b** (5)[b]	
10a	CH_2Cl_2	**11a** (2), *endo*-**13a** (21), *exo*-**13a** (4)	(23)
10a	Et_2O	**11a** (40), *endo*-**13a** (9)	(22)
10b	CH_2Cl_2	**11b** (2), *endo*-**13b** (21), *exo*-**13b** (7)	(47)
10b	Et_2O	**11b** (34), *endo*-**13b** (3)	(36)
10c	CH_2Cl_2	**11c** (9), **13c** (17)	(44)
10c	Et_2O	**11c** (46)	(19)
10d	CH_2Cl_2	**12d** (22)	(62)
10e	CH_2Cl_2	**12e** (39)	(40)
10f	CH_2Cl_2		(100)
14	CH_2Cl_2	*b*	
14	Et_2O	**16** (63)	
15	CH_2Cl_2	**17** (6)[b]	
15	Et_2O	**17** (16)[b]	(40)
18	CH_2Cl_2	**19** (12), **20** (8), **21** (48)	
22	CH_2Cl_2	**23** (30), **24** (10)	(35)
22	Et_2O	**23** (37), **24** (15)	(23)
25	CH_2Cl_2	**26** (22)	(19)
25	Et_2O	*b*	(56)

[a] Standard reaction conditions: a solution of ethyl vinyl ether (3 mmol) and the dicarbonyl compound (1 mmol) in the indicated solvent was treated with ozone (3 mmol) at −70 °C. [b] Significant amounts of unidentified products were produced.



Scheme 2



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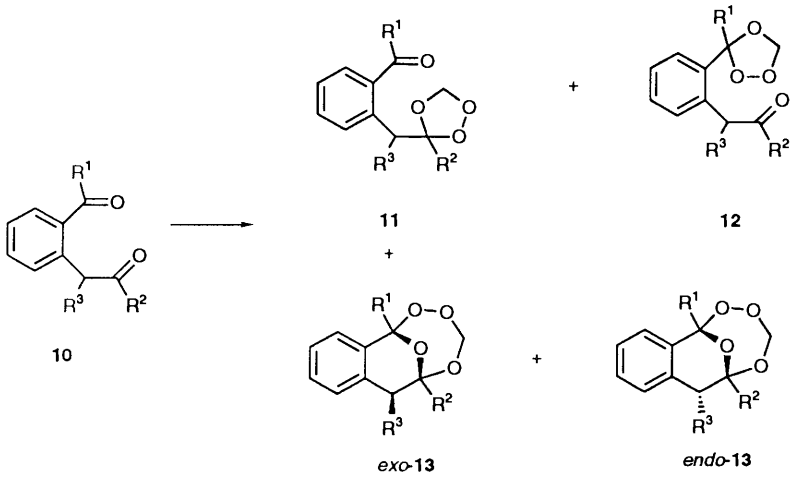
available product and structural data do not, however, preclude the possibilities that (a) the products **5a** and **6a** had been formed *via* an initial attack at the benzoyl group in substrate **3a** or (b) the ozonide **4a** had also been produced *via* stepwise reaction pathways.

In addition to a variety of unidentifiable products, keto aldehyde **3b** afforded the isomeric adducts **5b** (14%) and **6b** (5%; not isolated pure) as the major isolable products. It is presumed that these have also been formed *via* intermediates **7b** and **8b** by a mechanism analogous to that outlined in Scheme 2. Keto ozonide **4b** was not apparently formed.

A further series of ozonolyses of ethyl vinyl ether carried out in the presence of 1,5-dicarbonyl compounds **10a–f** gave product mixtures which varied considerably, if not necessarily predictably, with substrate structure and solvent [Table 1 and eqn. (1)]. In most cases, the major product was the corresponding keto ozonide **11** or **12** as appropriate; formation of ozonide was more favoured when diethyl ether was the reaction



(1)

	R^1	R^2	R^3
a	Ph	H	Ph
b	Ph	H	Me
c	Ph	H	H
d	H	Ph	Ph
e	H	Ph	H
f	Ph	Ph	Me

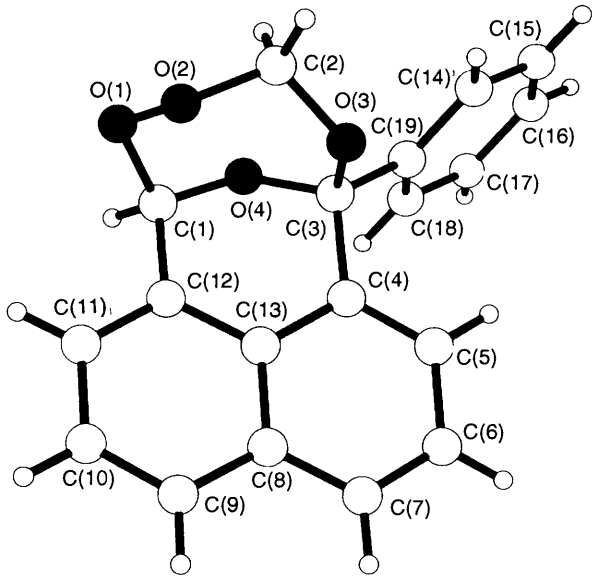


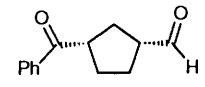
Fig. 1 The X-ray molecular structure and crystallographic numbering scheme of one independent molecule of compound **6a**. The hydrogen labels have been omitted for clarity.

solvent rather than dichloromethane.* Consistent with its structure, the diketone **10f** did not react with formaldehyde *O*-oxide to any significant extent.[9] The reactions involving keto aldehydes **10a–c** in dichloromethane yielded, in addition to the corresponding keto ozonides **11a–c**, a [3 + 2 + 2] cycloaddition product, isolated in yields of ~ 20%, which appeared to be consistently of one type though the adducts derived from substrates **10a** and **10b** were obtained as mixtures of diastereoisomers in each case.†

X-Ray crystallographic analysis of the crystalline major isomer derived from compound **10b** established that it was the 1,2,4,6-tetroxepane derivative illustrated in Fig. 2 and structural formula *endo*-**13b**. The central tetroxepane ring in *endo*-**13b** also adopts a distorted chair conformation [C(2)–O(3)–C(3)–O(4) – 17.3(6)°]. In a similar fashion to tetroxepane **6a**, the observed geometrical parameters around the bicyclic ring system are in good agreement with expected values. Superimposition of the tetroxepane ring from *endo*-**13b** on that of molecule A of compound **6a** shows that there are only minor differences between the two systems (Fig. 3); observed deviations between the two systems were in the range 0.014–0.047 Å.[13]

From their molecular structures, adducts **13a–c** must have been produced exclusively *via* reaction pathways analogous to path b (Scheme 2); no adducts derived from the alternative mode of addition [*cf.* path c (Scheme 2)] were obtained in isolable quantities.

The remaining 1,5-keto aldehydes, **14** and **15**, investigated in this study produced the corresponding keto ozonides **16** and **17** respectively in highly variable yield as the only isolable monomeric peroxidic products. The absence of other types of adducts would tend to suggest that these keto aldehydes adopt extended conformations in which the carbonyl-group oxygen atoms are not in as close proximity to each other as in keto aldehydes **3a**, **b** or **10a–c**.



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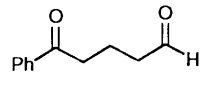

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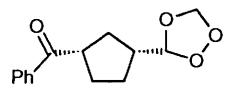

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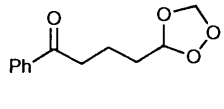

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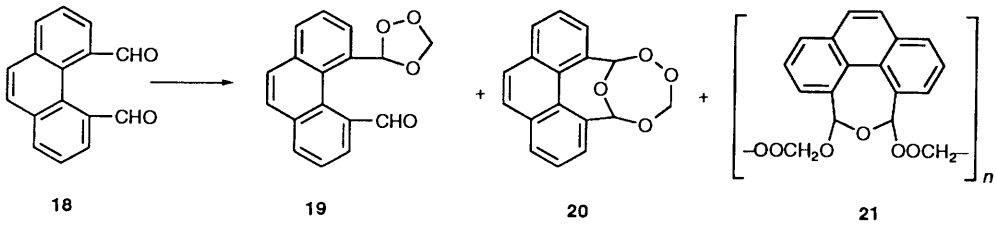
Although the structurally rigid 1,6-dialdehyde **18** gave low but significant quantities of both the mono-ozonide **19** (12%) and the [3 + 2 + 2] cycloadduct **20** (8%), the major isolated product was, on the basis of elemental and ^{1}H NMR spectroscopic analysis, identified as a polymeric peroxide **21** (48%) resulting from the co-polymerisation of dial **18** and formaldehyde *O*-oxide in the ratio of 1:2 respectively [eqn. (2)]. In contrast, the analogous biphenyl-2,2'-dicarbaldehyde **22** provided a mixture of mono-ozonide **23** (37%) and diozonide **24** (15%) [eqn. (3)]. The formation of ozonide products is consistent with the expectation that dial **22** is most likely to

* We had noted previously that diethyl ether tends to promote formation of the ozonide. Ozonolysis of 1,4-dimethyl-2,3-diphenylcyclopentadiene in diethyl ether gave the corresponding bicyclic ozonide *via* an intramolecular [3 + 2] cycloaddition whereas in dichloromethane the isomeric trioxabicyclo[3.2.1]oct-3-ene, arising from an alternative [4 + 3] cycloaddition process, was obtained. See ref. 11.

† The relative stereochemistry of the respective *exo*- and *endo*-isomers of compounds **13a, b** could be assigned on the basis of the magnitude of the vicinal coupling constant between the hydrogen atoms at C-6 and C-7 by analogy with previous assignments made for the *exo*- and *endo*-1,3-diphenylindene ozonides (see ref. 12).



18 19 20 21 (2)

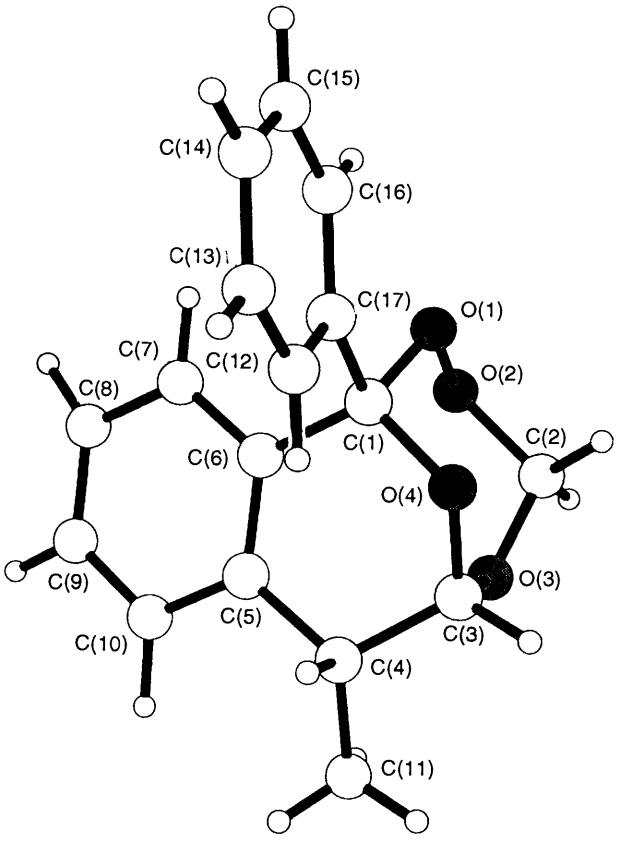


Fig. 2 The X-ray molecular structure and crystallographic numbering scheme of compound **13b**. The hydrogen labels have been omitted for clarity.

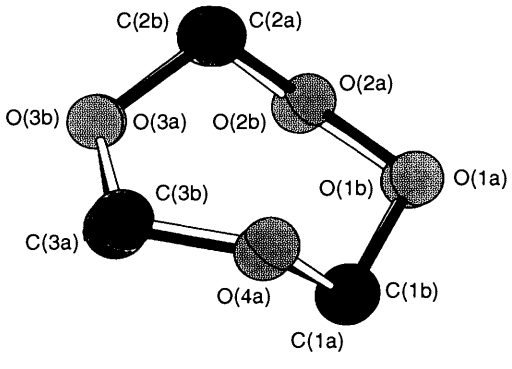
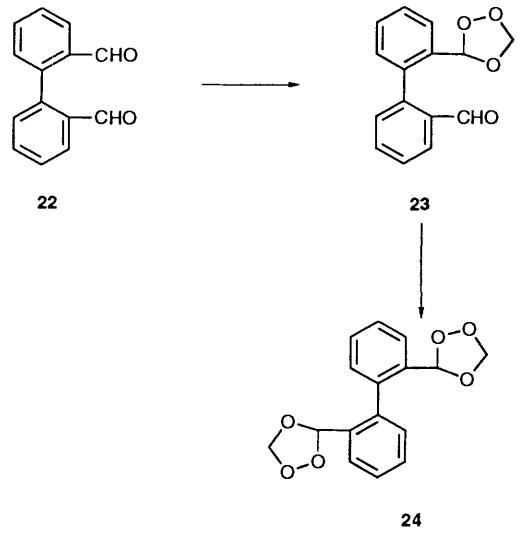


Fig. 3 Superimposition of 1,2,4,6-tetroxepane rings of compounds **6a** and *endo*-**13b**; ring atoms of compound **6a** are denoted by the letter a and are linked by filled bonds

adopt a conformation in which the aromatic rings would be essentially orthogonal with respect to each other in order to minimise steric interactions between the *ortho*-formyl groups, hence ensuring that these groups are well separated and readily

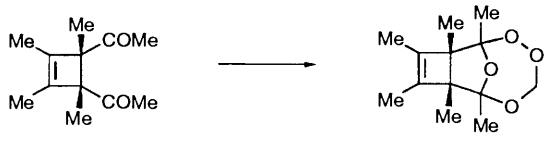


22 23

24 (3)

available for the [3 + 2] cycloaddition with the carbonyl oxide.

cis-3,4-Diacetyl-1,2,3,4-tetramethylcyclobutene **25**, in which the two acetyl groups are necessarily in close proximity to each other, reacted with formaldehyde *O*-oxide in dichloromethane to afford the corresponding tetroxepane **26** in 22% yield [eqn. (4)]. Analogous reactions using diethyl ether as solvent yielded neither compound **26** nor a [3 + 2] cycloadduct; the starting material **25** (56%) was recovered instead.



25 26 (4)

The results discussed above indicated that the observed selectivities of the reactions between formaldehyde *O*-oxide and dicarbonyl compounds are generally consistent with the expected 1,3-dipolarophilic character of the respective carbonyl groups, *i.e.* formyl > acetyl > benzoyl.[9] Although ozonides (1,2,4-trioxolanes) are often the major products, 1,2,4,6-tetroxepanes, arising from more complex [3 + 2 + 2] cycloaddition processes, can also be obtained providing that the two carbonyl groups are located in relatively close proximity to each other. With either conformationally flexible dicarbonyl compounds or reaction solvents such as diethyl ether which might favour extended molecular conformations, the most likely reaction outcome is formation of monomeric or polymeric ozonides.

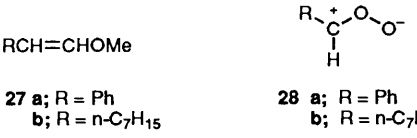
Reactions of Benzaldehyde and Octanal O-*Oxides with Dicarbonyl Compounds.*—Given that 1,2,4,6-tetroxepanes were generally obtained only from reactions between formaldehyde *O*-oxide and keto aldehydes or dialdehydes in which the

Table 2 Ozonolysis of vinyl ethers **27a, b** in the presence of dicarbonyl compounds[a]

Vinyl ether	Dicarbonyl compound	Solvent	Products (%)	Recovered starting material (%)
27a	**3a**	CH_2Cl_2	**9** (6)[b]	
27b	**3a**	CH_2Cl_2	**9** (13), **30** (42)	
27a	**10a**	CH_2Cl_2	**31a** (16)	(56)
27a	**10a**	Et_2O	**31a** (66)	(25)
27a	**10b**	CH_2Cl_2	**31b** (40)	(57)
27a	**10b**	Et_2O	**31b** (87)	
27a	**10c**	CH_2Cl_2	**31c** (15)	(65)
27a	**10c**	Et_2O	**31c** (58)	
27b	**10a**	Et_2O	**31d** (97)	
27b	**10b**	Et_2O	**31e** (58)	
27b	**10c**	Et_2O	**31f** (65)	
27a	**18**	CH_2Cl_2	**32** (7)[b]	

[a] Standard reaction conditions: a solution of the vinyl ether (3 mmol) and dicarbonyl compound (1 mmol) in the indicated solvent was treated with ozone (3 mmol) at −70 °C. [b] Significant amounts of unidentified products were produced.

carbonyl groups were conformationally restricted by steric congestion, the likelihood of substituted carbonyl oxides also participating in the extended [3 + 2 + 2] cycloaddition process was investigated. Thus, the ozonolyses of vinyl ethers **27a, b** were carried out in the presence of a selection of dicarbonyl compounds **3a**, **10a–c** and **18** with either dichloromethane or diethyl ether as solvent (Table 2). Irrespective of the nature of the carbonyl oxide, or the solvent, or the substrate, the desired 1,2,4,6-tetroxepane derivative was not obtained in any case.



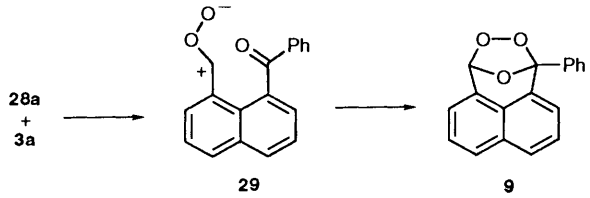
27 a; R = Ph
b; R = n-C_7H_{15}

28 a; R = Ph
b; R = n-C_7H_{15}

Reaction of benzaldehyde *O*-oxide **28a** with compound **3a** did not even yield the normal [3 + 2] cycloadduct but instead the ozonide **9**, which had been observed previously (see Table 1, entry 1), was obtained in small quantities (~7%) as the only isolable peroxidic product. Under similar conditions, the reaction of octanal *O*-oxide **28b** with compound **3a** in dichloromethane gave the corresponding [3 + 2] cycloadduct **32** in 42% yield together with ozonide **9** (13%). With the conformationally more flexible keto aldehydes **10a–c**, the corresponding normal [3 + 2] cycloaddition products **31a–f** were obtained in reasonable yields, particularly when the reactions were conducted in diethyl ether. Ozonide **32** was the sole detectable product from the reaction of dialdehyde **18** with carbonyl oxide **28b**.

The formation of ozonide **9** can be rationalised by an initial oxygen-atom transfer[14] from carbonyl oxides **28a, b** to the sterically congested keto aldehyde **3a** generating the corresponding carbonyl oxide intermediates such as **29**, which in turn undergo intramolecular [3 + 2] cycloaddition [eqn. (5)]. Analogous processes must also be operating in the transformation of dialdehyde **18** to ozonide **32**.

The results obtained thus far suggest that the [3 + 2 + 2] cycloaddition process is highly sensitive to the steric requirements of both the substrate and the carbonyl oxide. Although conformationally restricted dicarbonyl compounds had been found to favour the formation of 1,2,4,6-tetroxepanes (*vide supra*), substituents attached to the carbonyl oxide appear to inhibit the more extended cycloaddition process completely. As a consequence, less sterically demanding processes such as



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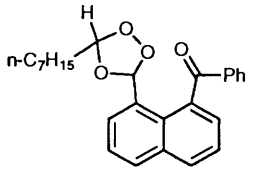
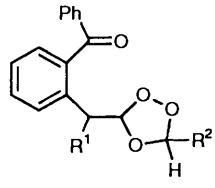
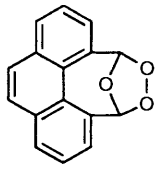






	R^1	R^2
a	Ph	Ph
b	Me	Ph
c	H	Ph
d	Ph	n-C_7H_{15}
e	Me	n-C_7H_{15}
f	H	n-C_7H_{15}

[3 + 2] cycloaddition or oxygen transfer tend to predominate.

Acid-catalysed Rearrangement of Keto and Aldehydo Ozonides.—Although direct reaction of carbonyl oxides with dicarbonyl compounds in general produced the normal [3 + 2] adducts rather than the isomeric 1,2,4,6-tetroxepanes, it was considered possible that acid-catalysed rearrangement of the former under mild conditions might provide an alternative route to additional derivatives of the latter. Thus, treatment of ozonide **4a** with trifluoroacetic acid (TFA) (1 mol equiv.) at 20 °C for 2 h led to the formation of a mixture of compounds **5a** (25%) and **6a** (16%), together with keto aldehyde **3a** (20%). Since the ratio of isomers **5a** to **6a** in the acid-catalysed rearrangement is significantly different from that in the ozonolysis experiment, compounds **5a** and **6a** are unlikely to be secondary ozonolysis products resulting from adventitious acid-catalysed rearrangement of the ozonide **4a**.

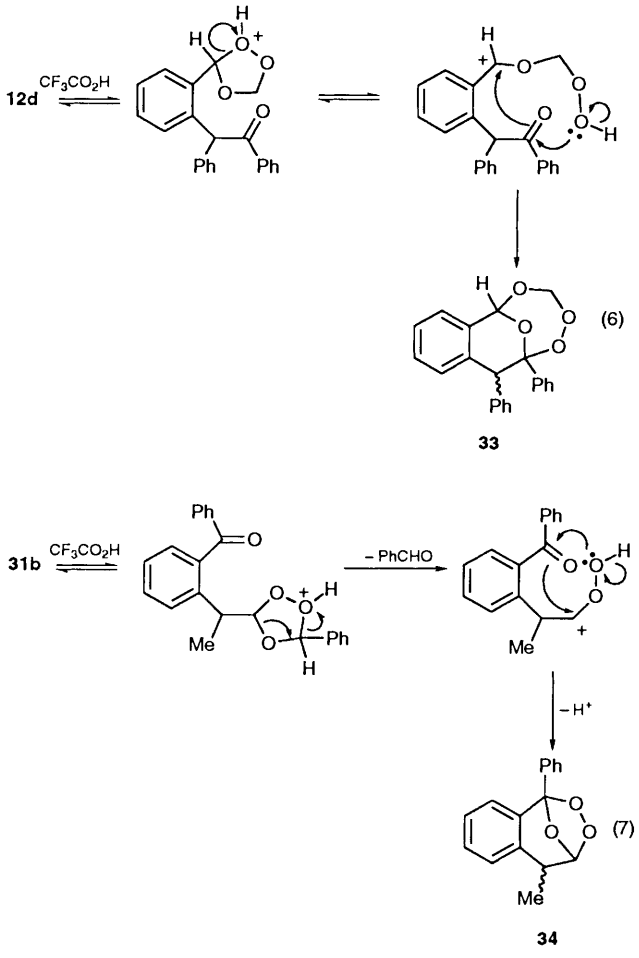
The results for the acid-catalysed rearrangement reactions are summarised in Table 3. Treatment of ozonide **12d** with TFA gave the isomeric tetroxepane **33** [eqn. (6)], whereas ozonide **12e** afforded a complex mixture of unidentified products. Under similar reaction conditions, the series of keto ozonide **31a–c** gave variable results; **31a** was recovered unchanged, **31b** afforded 1-methyl-3-phenylindene ozonide **34** *via* an elimination–recombination process [eqn. (7)], and **31c** gave the keto aldehyde **10c**. Like compound **31a**, keto ozonides **11a–c** and **31d–f** were also stable and were recovered in quantitative yield.

Acidolysis of the rigid ozonide **19** in TFA led to the formation of the tetroxepane **20**. Under similar conditions, the polyperoxide **21** also yielded compound **20** together with ozonide **32**. Treatment of the mono-ozonide **23** with chlorosulfonic acid afforded the dialdehyde **22** as the sole isolable product.

Table 3 Acidolysis of keto and aldehydo ozonides[a]

Ozonide	Products (%)	Recovered ozonide (%)
4a[b]	**5a** (25), **6a** (16), **9** (1), **3a** (20)	
12d	**10d** (16), **33** (21)	
12e	*d*	(43)
16[c]	**14** (17)	(10)
19	**20** (51)	
21	**20** (10), **32** (13)	
23[c]	**22** (22)	
31b	**34** (51)	(14)
31c	**10c** (31)	(31)

[a] An equimolar mixture of the ozonide and TFA in dichloromethane was stirred at room temperature for 15 h. [b] The reaction time was 2 h. [c] Reaction with 0.1 mol equiv. of chlorosulfonic acid at room temperature for 15 h. [d] Considerable amounts of unidentified products were produced.



Following acid-catalysed opening of the trioxolane ring in the systems above, a variety of processes may take place, including intramolecular recombination to give the desired tetroxepane [*cf.* eqn. (6)], elimination of a carbonyl compound such as benzaldehyde followed by recombination to give an indene ozonide [*cf.* eqn. (7)], and elimination of a carbonyl oxide fragment to regenerate the dicarbonyl compound. For several of the systems mentioned above, these processes appear to be competitive and their respective contributions are clearly influenced by minor changes in the structure of the ozonides.

Experimental

General.—^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-PS-100 and JNM-GSX-400 spectrometers respectively with $CDCl_3$ as solvent (unless otherwise stated). *J* Values are given in Hz. Mass spectral data were obtained with an Hitachi RMU-6H spectrometer, and IR spectra with an Hitachi 215 spectrometer.

Ozone was generated using a Nippin Ozone ON-I-2 Ozonator (50 dm^3 h^{-1} O_2).

Silica gel YMC-Gel (70–230 mesh) was used for column chromatography.

The following starting materials: 8-benzoylnaphthalene-1-carbaldehyde **3a**,[15] 8-acetylnaphthalene-1-carbaldehyde **3b**,[15] 2-(*o*-benzoylphenyl)-2-phenylacetaldehyde **10a**,[15] 2-(*o*-benzoylphenyl)propanal **10b**,[12] (*o*-benzoylphenyl)acetaldehyde **10c**,[12] *o*-(α-phenylphenacyl)benzaldehyde **10d**,[15] *o*-phenacylbenzaldehyde **10e**,[15] α-(*o*-benzoylphenyl)propiophenone **10f**,[12] *cis*-3-benzoylcyclopentanecarbaldehyde **14**,[16] 5-oxo-5-phenylpentanal **15**,[17] phenanthrene-4,5-dicarbaldehyde **18**,[15] biphenyl-2,2′-dicarbaldehyde **22**,[18] and *cis*-3,4-diacetyl-1,2,3,4-tetramethylcyclobutene **25**,[19] were prepared by the literature methods cited.

CAUTION: Since organic ozonides and peroxides are potentially hazardous compounds, they must be handled with due care; avoid exposure to strong heat or light, or mechanical shock, or oxidisable organic materials, or transition metal ions. No particular difficulties were experienced in handling any of the new organic ozonides or peroxides synthesized in this work using the reaction scales and procedures described below together with the safeguards mentioned above.

Ozonolysis of Ethyl Vinyl Ether in the Presence of Keto Aldehyde **3a**.—A slow stream of ozone (3 mmol) was passed through a cooled solution (−70 °C) of ethyl vinyl ether (216 mg, 3 mmol) and compound **3a** (260 mg, 1 mmol) in dichloromethane (15 cm^3). After evaporation of the solvent under reduced pressure, the products were separated by column chromatography on silica gel to give, in successive fractions, with benzene–hexane (1:1), ozonide **9**[20] (3 mg, 1%); with benzene–hexane (3:2), compound **6a** (18 mg, 6%); with benzene–hexane (7:3), compound **5a** (9 mg, 3%); with benzene, keto ozonide **4a** (64 mg, 21%); and with diethyl ether–benzene (1:2), keto aldehyde **3a** (128 mg, 49% recovery).

1-Phenyl-1,4-epoxy-1*H*,4*H*-naphtho[1,8-*de*][1,2]dioxepine **9**. Recrystallised from methanol, m.p. 130–131 °C (lit.,[20] 130–131 °C); δ_H 6.78 (1 H, s) and 7.1–7.9 (11 H, m) (Found: C, 78.2; H, 4.4. Calc. for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38%).

6-*Phenyl*-1,6-*epoxy*-1H,6H-*naphtho*[1,8-fg][1,2,4]*trioxonine* **6a**. Recrystallised from methanol, m.p. 120 °C (decomp.) (Found: C, 74.5; H, 4.6. $C_{19}H_{14}O_4$ requires C, 74.50; H, 4.61%); δ_H 5.35 (1 H, dd, *J* 10.0 and 1.5), 5.83 (1 H, d, *J* 10.0), 6.68 (1 H, d, *J* 1.5), 6.90 (1 H, d, *J* 7.0) and 7.1–8.0 (10 H, m); δ_C 97.21 (t, CH_2), 101.70 (d, CH), 104.42 (s) and 125.54–140.82 (16 aromatic C); ν_{max}/cm^{-1} 1310 and 1090; *m/z* (CI; isobutane) 307 [(M + 1)$^+$].

1-*Phenyl*-1,6-*epoxy*-1H,6H-*naphtho*[1,8-fg][1,2,4]*trioxonine* **5a**. M.p. 141–143 °C (from MeOH) (Found: C, 74.0 H, 4.55%); δ_H 5.36 (1 H, d, *J* 10), 5.53 (1 H, d, *J* 10), 6.63 (1 H, s), 7.01 (1 H, d, *J* 7) and 7.2–8.1 (10 H, m); δ_C 96.59 (d, CH), 97.12 (t, CH_2), 107.47 (s) and 125.39–138.34 (16 aromatic C); ν_{max}/cm^{-1} 1270, 1080, 1040 and 1020.

Phenyl 8-(1,2,4-*trioxolan*-3-*yl*)*naphthyl ketone* **4a**. An oil (Found: C, 74.65; H, 4.65%); δ_H 4.92 (1 H, s), 4.99 (1 H, s), 6.58 (1 H, s) and 7.2–8.0 (11 H, m); ν_{max}/cm^{-1} 1660 and 1270.

Ozonolysis of Ethyl Vinyl Ether in the Presence of Keto Aldehyde **3b**.—The basic procedure was similar to that used for

compound **3a**. The following products were isolated by column chromatography on silica gel.

1-*Methyl*-1,6-*epoxy*-1H,6H-*naphtho*[1,8-fg][1,2,4]*trioxonine* **5b**. M.p. 107–108 °C (from MeOH) (Found: C, 68.7; H, 4.9. $C_{14}H_{12}O_4$ requires C, 68.85; H, 4.95%); δ_H 1.95 (3 H, s), 5.17 (1 H, d, *J* 10), 5.60 (1 H, d, *J* 10), 6.34 (1 H, s) and 7.2–7.9 (6 H, m).

6-Methyl-1,6-epoxy-1*H*,6*H*-naphtho[1,8-*fg*][1,2,4]trioxonine **6b** (in admixture with 30% of **5b**). An oil; δ_H 2.01 (3 H, s), 5.08 (1 H, dd, *J* 10 and 2), 5.66 (1 H, d, *J* 10), 6.43 (1 H, d, *J* 2) and 7.2–7.9 (6 H, m).

Ozonolysis of Mixtures of Ethyl Vinyl Ether and Dicarbonyl Compounds.—The general procedure, which was used for dicarbonyl compounds **10a–f**, **14**, **15**, **18**, **22** and **25**, is illustrated for keto aldehyde **10a**. A cooled (−70 °C) solution of ethyl vinyl ether (216 mg, 3 mmol) and compound **10a** (330 mg, 1 mmol) in dichloromethane (15 cm^3) was treated with ozone (3 mmol). After removal of the solvent, the reaction products were separated by column chromatography on silica gel by using the indicated solvents to give the following fractions in succession: (a) benzene–hexane (7:3), *endo*-**13a** (79 mg, 21%); (b) benzene–hexane (4:1), *exo*-**3a** (14 mg, 4%); (c) benzene, keto ozonide **11a** (7 mg, 2%); (d) diethyl ether–benzene (1:9), unchanged keto aldehyde **10a** (76 mg, 23%).

6,7-*Dihydro*-1,7-*diphenyl*-1,6-*epoxy*-1H-2,3,5-*benzotrioxonine*, endo-**13a**. Recrystallised from methanol, m.p. 158–163 °C (Found: C, 76.4; H, 5.1. $C_{22}H_{18}O_4$ requires C, 76.28; H, 5.24%); δ_H 4.45 (1 H, d, *J* 3), 5.26 (1 H, d, *J* 11), 5.76 (1 H, d, *J* 3), 5.84 (1 H, d, *J* 11) and 6.8–7.8 (14 H, m); ν_{max}/cm^{-1} 1130 and 1040.

6,7-Dihydro-1,7-diphenyl-1,6-epoxy-1*H*-2,3,5-benzotrioxonine, *exo*-**13a**. An oil; δ_H 4.22 (1 H, s), 5.13 (1 H, d, *J* 10), 5.70 (1 H, d, *J* 10), 5.78 (1 H, s) and 6.9–7.8 (14 H, m); ν_{max}/cm^{-1} 1150, 1140, 1060 and 1005.

o-[α-(1,2,4-*Trioxolan*-3-*yl*)*benzyl*]*benzophenone* **11a**. An oil (Found: C, 77.0; H, 5.2. $C_{22}H_{18}O_4$ requires C, 76.28; H, 5.19%); δ_H 4.60 (1 H, d, *J* 7), 4.9–5.0 (2 H, m), 5.67 (1 H, d, *J* 7) and 6.9–7.9 (14 H, m); ν_{max}/cm^{-1} 1660, 1265 and 1250.

Isolated from the ozonolysis of ethyl vinyl ether with keto aldehyde **10b**: 6,7-*Dihydro*-7-*methyl*-1-*phenyl*-1,6-*epoxy*-1H-2,3,5-*benzotrioxonine*, endo-**13b**: (59 mg, 21%), recrystallised from methanol, m.p. 145–147 °C (Found: C, 71.7; H, 5.65. $C_{17}H_{16}O_4$ requires C, 71.82; H, 5.67%); δ_H 1.46 (3 H, d, *J* 7), 3.22 (1 H, qd, *J* 7 and 3), 5.19 (1 H, d, *J* 10), 5.62 (1 H, d, *J* 3), 5.81 (1 H, d, *J* 10) and 6.9–7.6 (9 H, m); ν_{max}/cm^{-1} 2940, 1150 and 1040.

6,7-*Dihydro*-7-*methyl*-1-*phenyl*-1,6-*epoxy*-1H-2,3,5-*benzotrioxonine*, exo-**13b**: (20 mg, 7%) recrystallised from methanol, m.p. 115–117 °C (Found: C, 71.5; H, 5.7%); *m/z* 284 (M^+); δ_H 1.39 (3 H, d, *J* 7), 3.07 (1 H, q, *J* 7), 5.19 (1 H, d, *J* 10), 5.62 (1 H, s), 5.80 (1 H, d, *J* 10) and 6.9–7.6 (9 H, m).

o-[1-(1,2,4-*Trioxolan*-3-*yl*)*ethyl*]*benzophenone* **11b**: (6 mg, 2%), an oil isolated as a mixture of two stereoisomers in the ratio ~1:2 (Found: C, 71.5; H, 5.8. $C_{17}H_{16}O_4$ requires C, 71.82; H, 5.67%); δ_H 1.35 (d, *J* 7, Me for the minor isomer), 1.36 (d, *J* 7, Me for the major isomer), 3.4–3.7 (1 H, m), 4.77 (s, minor), 4.90 (s, major), 4.91 (s, minor), 5.10 (s, major), 5.2–5.3 (1 H, m) and 7.2–8.0 (9 H, m); ν_{max}/cm^{-1} 1662, 1285, 1260 and 1080.

Isolated from the ozonolysis of ethyl vinyl ether with keto aldehyde **10c**: 6,7-*Dihydro*-1-*phenyl*-1,6-*epoxy*-1H-2,3,5-*benzotrioxonine* **13c**: (44 mg, 17%), recrystallised from methanol, m.p. 148–150 °C (Found: C, 71.1; H, 5.2. $C_{16}H_{14}O_4$ requires C, 71.10; H, 5.22%); δ_H 3.03 (1 H, d, *J* 16), 3.29 (1 H, dd, *J* 16 and 3), 5.25 (1 H, d, *J* 10), 5.83 (1 H, d, *J* 10), 5.96 (1 H, d, *J* 3) and 7.1–7.5 (9 H, m); ν_{max}/cm^{-1} 1125, 1045, 1000 and 965.

o-[(1,2,4-*Trioxolan*-3-*yl*)*methyl*]*benzophenone* **11c**: (23 mg, 9%), an oil (Found: C, 71.5; H, 5.3. $C_{16}H_{14}O_4$ requires C, 71.10; H, 5.22%); δ_H 3.12 (1 H, d, *J* 5), 3.15 (1 H, d, *J* 5), 4.91 (2 H, s), 5.38 (1 H, t, *J* 5) and 7.1–7.7 (9 H, m); ν_{max}/cm^{-1} 1660, 1265 and 1090.

Isolated from the ozonolysis of ethyl vinyl ether with keto aldehyde **10d**: α-*phenyl*-α-[o-(1,2,4-*trioxolan*-3-*yl*)*phenyl*]-*acetophenone* **12d**: (76 mg, 22%), an oil (Found: C, 76.9; H, 5.3. $C_{22}H_{18}O_4$ requires C, 76.29; H, 5.24%); ν_{max}/cm^{-1} 1680, 1205 and 1055; δ_H 5.12 (1 H, s), 5.35 (1 H, s), 6.21 (1 H, s), 6.52 (1 H, s) and 7.0–8.2 (14 H, m).

Isolated from the ozonolysis of ethyl vinyl ether with keto aldehyde **10e**: α-[o-(1,2,4-*trioxolan*-3-*yl*)*phenyl*]*acetophenone* **12e**: (101 mg, 39%) an oil (Found: C, 71.15; H, 5.35. $C_{16}H_{14}O_4$ requires C, 71.10; H, 5.22%); $\delta_H(CCl_4)$ 4.37 (2 H, s), 5.16 (1 H, s), 5.26 (1 H, s), 6.10 (1 H, s) and 7.0–8.0 (9 H, m); ν_{max}/cm^{-1} 1690, 1330, 1210 and 1060.

Isolated from the ozonolysis of ethyl vinyl ether with keto aldehyde **14** in diethyl ether: phenyl *cis*-3-(1,2,4-trioxolan-3-yl)cyclopentyl ketone **16**: (149 mg, 63%), an oil; δ_H 1.3–2.5 (7 H, m), 3.3–4.3 (1 H, m), 4.97 (1 H, s), 5.06 (2 H, br s) and 7.3–8.2 (5 H, m); ν_{max}/cm^{-1} 2950, 2890, 1680, 1600, 1580, 1450, 1365, 1220, 1060 and 695.

Isolated from the ozonolysis of ethyl vinyl ether with keto aldehyde **15**: γ-(1,2,4-trioxolan-3-yl)butyrophenone **17**: (13 mg, 6%) an oil; δ_H 1.7–2.1 (4 H, m), 2.8–3.2 (2 H, m), 5.00 (1 H, s), 5.13 (1 H, s), 5.13 (1 H, t, *J* 4) and 7.3–8.0 (5 H, m); ν_{max}/cm^{-1} 3060, 2890, 1685, 1600, 1450, 1370, 1105, 960, 740 and 685.

Ozonolysis of Ethyl Vinyl Ether in the Presence of Dialdehyde **18**.—A cooled (−70 °C) solution of ethyl vinyl ether (324 mg, 4.5 mmol) and dialdehyde **18** (352 mg, 1.5 mmol) in dichloromethane (15 cm^3) was treated with ozone (4.5 mmol). After removal of the solvent under reduced pressure, the products were separated by column chromatography on silica gel and elution with the indicated solvents to give the following fractions: (a) dichloromethane–benzene (1:9), tetroxepane **20** (34 mg, 8%); (b) dichloromethane, mono-ozonide **19** (50 mg, 12%); (c) diethyl ether–dichloromethane (2:3), polyperoxide **21** (237 mg, 48%).

9,14-*Dihydro*-9,14-*epoxyphenanthro*[4,5-fgh][1,2,4]*trioxecine* **20**: Recrystallised from ethyl acetate–hexane, m.p. 159–160 °C (Found: C, 73.1; H, 4.2. $C_{17}H_{12}O_4$ requires C, 72.85; H, 4.32%); δ_H 5.36 (1 H, d, *J* 10), 5.67 (1 H, d, *J* 10), 6.64 (2 H, s) and 7.4–8.3 (8 H, m); δ_C 93.10, 100.39, 107.76, 126.13, 126.42, 127.43, 127.57, 128.47, 128.69, 128.76, 128.84, 129.07, 130.33, 131.13, 134.51, 134.60 and 136.54; ν_{max}/cm^{-1} 2930, 1435, 1350, 1245, 1175, 1140, 1105, 1050, 1015, 960, 940, 830 and 720.

5-(1,2,4-Trioxolan-3-yl)phenanthrene-4-carbaldehyde **19**: Isolated as an oil; δ_H 5.47 (2 H, br s), 6.55 (1 H, s), 7.6–8.4 (8 H, m) and 10.26 (1 H, s); δ_C 96.13, 101.17, 126.60, 126.94, 127.08, 127.25, 127.40, 127.63, 128.16, 128.23, 130.35, 133.07, 133.28, 133.46, 134.11, 134.38 and 191.32; ν_{max}/cm^{-1} 3050, 2960, 2890, 1685, 1370, 1270, 1250, 1220, 1070, 820 and 720.

Polyperoxide **21**: Recrystallised from ethyl acetate–hexane, m.p. 124–134 °C [Found: C, 66.5; H, 4.4. $(C_{18}H_{14}O_6)_n$ requires C, 66.26; H, 4.32%]; δ_H 4.5–5.8 (br s), 6.0–6.8 (br s) and 7.0–8.3 (br s), the proportions of the peak areas being 2:1:4; ν_{max}/cm^{-1} 3400, 1690w, 1170, 1055, 945, 825, 760, 720 and 675; *m/z* (vapour-pressure osmometry, CH_2Cl_2) 3395.

Ozonolysis of Ethyl Vinyl Ether in the Presence of Dialdehyde **22**.—The basic procedure was similar to that for dial **18**. The following products were isolated by column chromatography on silica gel: 2′-(1,2,4-trioxolan-3-yl)biphenyl-2-carbaldehyde **23**: (115 mg, 30%), an oil (a 1:1 mixture of two diastereoisomers); δ_H[4.83 (s) + 5.06 (s) + 5.15 (s) + 5.18 (s)] (2 H), [5.68 (s) + 5.72 (s)] (1 H), 7.0–8.1 (8 H, m) and [9.65 (s) + 9.72 (s)] (1 H); δ_C 94.95, 95.11, 100.80, 101.21, 127.22, 127.37, 127.66, 128.02, 128.25, 128.39, 128.46, 128.55, 128.60,

129.77, 129.85, 130.86, 130.95, 131.00, 131.04, 131.49, 133.03, 133.24, 134.10, 134.48, 138.51, 138.58, 142.39, 142.65, 191.32 and 191.39.

Treatment of a solution of monoacetal **23** in $CDCl_3$ with triphenylphosphine (1 mol equiv.) at room temp. for 15 h gave the dialdehyde **22** in quantitative yield.

2,2'-Bis-(1,2,4-trioxolan-3-yl)biphenyl **24**: (45 mg, 10%) isolated as a mixture of diastereoisomers, recrystallised from methanol, m.p. 95 °C; δ_H[4.97 (s) + 5.01 (s) + 5.17 (s) + 5.20 (s) + 5.22 (s) + 5.26 (s) + 5.28 (s) + 5.30 (s)] (4 H, relative proportions of the peak areas 9:2:3:2:8:9:3:8), [5.69 (s) + 5.73 (s) + 5.76 (s) + 5.80 (s)] (2 H, relative proportions of the peak areas 7:3:2:8) and 7.2–7.8 (8 H, m); δ_C 94.89, 95.00, 95.19, 95.24, 100.75, 100.84, 100.98, 101.12, 127.29, 127.37, 127.60, 127.64, 128.24, 128.33, 128.60, 128.65, 129.47, 129.50, 129.71, 129.76, 130.36, 130.49, 130.57, 130.79, 131.09, 131.11, 131.29, 139.51, 139.64, 139.79 and 139.97.

On treatment of a solution of compound **24** in $CDCl_3$ with triphenylphosphine (1 mol equiv.) at room temp. for 15 h, the dialdehyde **22** was regenerated in quantitative yield.

Ozonolysis of Ethyl Vinyl Ether in the Presence of Diketone **25**.—A slow stream of ozone (5.76 mmol) was passed into a cooled solution (−70 °C) of ethyl vinyl ether (414 mg, 5.76 mmol) and diketone **25** (372 mg, 1.92 mmol) in dichloromethane (15 cm^3). After evaporation of the solvent, the products were separated by column chromatography on silica gel, and eluted first with diethyl ether–hexane (1:20) to give tetroxepane **26** (102 mg, 22%) followed by unchanged diketone **25** (72 mg, 19%) on further elution with diethyl ether–hexane (15:85).

1,2,3,4,5,6-*Hexamethyl*-7,8,10,11-*tetraoxatricyclo*[4.4.1.$0^{2,5}$]-*dec*-3-*ene* **26**: recrystallised from methanol, m.p. 109 °C (Found: C, 64.6; H, 8.45. $C_{13}H_{20}O_4$ requires C, 64.98; H, 8.93%); δ_H 1.03 (6 H, s), 1.27 (3 H, s), 1.31 (3 H, s), 1.57 (6 H, s), 5.08 (1 H, d, *J* 10) and 5.47 (1 H, d, *J* 10); δ_C 10.10, 10.51, 11.49, 12.15, 17.77, 22.92, 57.30, 59.92, 96.95, 109.45, 113.81, 141.10 and 141.71; ν_{max}/cm^{-1} 2950, 1450, 1380, 1285, 1250, 1135, 1095, 1065, 975, 860, 665 and 610.

Ozonolysis of Vinyl Ethers **27a**, **b** *in the Presence of Dicarbonyl Compounds* **3a**, **10a–c** *and* **18**.—The general procedure is exemplified by the ozonolysis of compound **27a** in the presence of keto aldehyde **10a**. A slow stream of ozone (3 mmol) was passed into a cooled (−70 °C) solution of the vinyl ether **27a** (400 mg, 3 mmol) and keto aldehyde **10a** (330 mg, 1 mmol) in diethyl ether (15 cm^3). After removal of the solvent under reduced pressure, the products were separated by column chromatography on silica gel with the indicated solvents to give the following fractions: (a) benzene, benzaldehyde (70 mg); (b) benzene, keto ozonide **31a** (279 mg, 66%), and (c) diethyl ether–benzene (1:9), keto aldehyde **10a** (82 mg, 25%).

Ozonide **31a** (a 1:1 mixture of two diastereoisomers): an oil (Found: C, 79.8; H, 5.4. $C_{28}H_{22}O_4$ requires C, 79.60; H, 5.25%); $\delta_H(CCl_4)$ [5.07 (d, *J* 2) + 5.08 (d, *J* 2)] (1 H), 5.46 (1 H, d, *J* 2), [5.83 (s) + 5.94 (s)] (1 H) and 6.9–7.9 (19 H, m); ν_{max}/cm^{-1} 1660, 1290, 1270 and 1050.

From ozonolysis of the vinyl ether **27a** in the presence of keto aldehyde **10b**: *ozonide* **31b** (313 mg, 87%), an oil (Found: C, 76.5; H, 5.7. $C_{23}H_{20}O_4$ requires C, 76.65; H, 5.59%); δ_H 1.40 (3 H, d, *J* 7), 3.5–3.8 (1 H, m), 5.45 (1 H, d, *J* 5), 5.90 (1 H, s) and 7.1–7.9 (14 H, m); ν_{max}/cm^{-1} 1660, 1290, 1270, 1060 and 920.

From ozonolysis of the vinyl ether **27a** in the presence of keto aldehyde **10c**: *ozonide* **31c** (a 3:2 mixture of two diastereoisomers) (201 mg, 58%), an oil (Found: C, 76.2; H, 5.5. $C_{22}H_{18}O_4$ requires C, 76.28; H, 5.5%); $\delta_H(CCl_4)$ [3.27 (br d, *J* 4) + 3.30 (br d, *J* 4)] (2 H), 5.58 (t, *J* 4, CH, minor), 5.67 (t, *J* 4, CH, major), 5.76 (s, CH, minor), 5.89 (s, CH, major) and 7.2–7.8 (14 H, m).

From ozonolysis of the vinyl ether **27a** in the presence of dialdehyde **18**: ozonide **32** (18 mg, 7%), m.p. 162–164 °C (lit.,[20] 163–165 °C); $\delta_H(CDCl_3)$ 6.70 (2 H, s) and 7.2–8.0 (8 H, m).

From ozonolysis of the vinyl ether **27b** in the presence of keto aldehyde **3a**: ozonide **30** (170 mg, 42%), an oil; $\delta_H(CCl_4)$ 0.8–2.5 (15 H, m), 5.03 (1 H, t, *J* 4.5), 6.67 (1 H, s) and 7.3–7.8 (11 H, m); ν_{max}/cm^{-1} 2930, 1660, 1460, 1270, 1100 and 1055; *m/z* (CI) 405 ([M + 1]$^+$, 5%).

From ozonolysis of the vinyl ether **27b** in the presence of keto aldehyde **10a**: *ozonide* **31d** (430 mg, 97%), an oil (Found: C, 77.9; H, 7.3. $C_{29}H_{32}O_4$ requires C, 78.35; H, 7.25%); $\delta_H(CCl_4)$ 0.7–1.9 (15 H, m), 4.70 (1 H, d, *J* 5), 5.01 (1 H, t, *J* 5), 5.61 (1 H, d, *J* 5) and 6.9–7.8 (14 H, m); ν_{max}/cm^{-1} 2930, 1660, 1450, 1260 and 1100.

From ozonolysis of the vinyl ether **27b** in the presence of keto aldehyde **10b**: ozonide **31e** (222 mg, 58%), an oil (Found: C, 74.5; H, 8.2. $C_{24}H_{30}O_4$ requires C, 75.36; H, 7.91%); δ_H 0.7–1.8 (18 H, m), 3.3–3.6 (1 H, m), 4.7–5.3 (2 H, m) and 7.1–8.0 (9 H, m); ν_{max}/cm^{-1} 2930, 1670, 1450, 1285, 1270 and 1105.

From ozonolysis of the vinyl ether **27b** in the presence of keto aldehyde **10c**: ozonide **31f** (a 1:1 mixture of two isomers) (239 mg, 65%), an oil (Found: C, 74.1; H, 8.0. $C_{23}H_{28}O_4$ requires C, 74.97; H, 7.66%); δ_H 0.7–1.9 (15 H, m), 3.0–3.3 (2 H, m), [4.86 (t, *J* 5) + 4.95 (t, *J* 5)] (1 H), [5.24 (t, *J* 5) + 5.42 (t, *J* 5)] (1 H) and 7.2–7.8 (9 H, m); *m/z* (CI) 369 ([M + 1]$^+$, 10%).

Acidolysis of Ozonides **4a**, **12d**, **e**, **16**, **19**, **21**, **23** *and* **31b**, **c**.—The general procedure is exemplified by the acidolysis of ozonide **12d**. An equimolar solution of ozonide **12d** (135 mg, 0.39 mmol) and TFA (44 mg, 0.39 mmol) in dichloromethane (15 cm^3) was stirred at room temp. for 15 h. Diethyl ether (50 cm^3) was added and the resulting reaction mixture was washed in turn with aq. $NaHCO_3$ and saturated brine, and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the products were separated by column chromatography on silica gel, and eluted first with benzene–hexane (7:3) to give tetroxepane **33** (28 mg, 21%) and subsequently with diethyl ether–benzene (1:50) to give the keto aldehyde **10d** (18 mg, 16%).

6,7-Dihydro-6,7-diphenyl-1,6-epoxy-1*H*-2,4,5-benzotrioxonine **33**: an oil; δ_H 4.04 (1 H, s), 5.04 (1 H, d, *J* 10), 5.17 (1 H, d, *J* 10), 6.49 (1 H, s) and 6.5–7.5 (14 H, m); ν_{max}/cm^{-1} 3040, 1480 and 1040; *m/z* (EI) 346 (M$^+$).

From the acidolysis of ozonide **31b**. After conventional work-up described above, the following products were isolated by column chromatography on silica gel with the indicated solvents to give the following fractions: (a) benzene–hexane (3:7), *endo*-**34**[12] (36 mg, 20%); (b) benzene–hexane (1:1), *exo*-**34**[12] (56 mg, 31%); and (c) benzene, unchanged ozonide **31b** (25 mg, 14% recovery).

X-Ray Crystal-structure Determination of the 1,2,4,6-*Tetroxapine Derivative* **6a**.*—A single crystal of compound **6a** (from ethyl acetate–hexane, approximate size 0.525 × 0.325 × 0.25 mm), mounted in a Lindemann tube, was used for X-ray data collection.

Crystal data. $C_{19}H_{14}O_4$, *M* = 306.3, prisms, monoclinic, space group $P2_1/n$ (non-standard setting of No. 14), *a* = 16.5350(21), *b* = 9.7445(16), *c* = 18.120(3) Å, β = 98.163(12)°, *V* = 2890.0(8) Å^3, *Z* = 8, D_c = 1.408 g cm^{-3}, *F*(000) 1280, μ(Mo-Kα) = 0.92 cm^{-1}.

Data collection, structure solution and refinement. The intensity data were collected on an Enraf–Nonius CAD4

* Atomic coordinates, bond lengths and angles, and thermal parameters for compounds **6a** and **13b** have been deposited at the Cambridge Crystallographic Data Centre. For details of the deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1994, Issue 1.

diffractometer over the hemisphere (θ-range: 1.0–25.0°; h: 0 to +19, k: 0 to +11, l: −21 to +21) using Mo-Kα X-radiation (λ 0.710 693 Å) and ω–2θ scanning. Of the 5087 unique data measured, 2435 had $I > 2\sigma(I)$ and were used in subsequent structural solution and refinement. The data were corrected for Lorentz and polarisation effects, but not for absorption. The structure was solved by direct methods (SHELXS86)[21] and refined by full-matrix least-squares methods (SHELX76)[22] using anisotropic temperature factors for all the non-hydrogen atoms. All the hydrogen atoms were located on difference Fourier maps and were included in the refinement process at idealised positions (d_{C-H} 0.95 Å) with a fixed isotropic temperature factor (U_{iso} 0.10 Å^2). At convergence, the discrepancy factors R and W_w were 0.044 and 0.067 respectively. The weighting scheme, $w^{-1} = [\sigma(F) + 0.0044 (F)^2]$, was found to give satisfactory analyses of variance. The final difference Fourier map was essentially featureless (general noise level less than +0.12 e Å^{-3}). Incidental crystallographic calculations and compilation of tables were carried out using the computer program CALC.[23] Figs. 1 and 2 were prepared by using the plotting program Ball & Stick (Version 3.0).[24]

X-Ray Crystal-structure Determination of the 1,2,4,6-*Tetroxepine Derivative* endo-**13b**.*—A single crystal of compound *endo*-**13b** (from ethyl acetate–hexane, approximate size 0.275 × 0.35 × 0.125 mm), mounted in a Lindemann tube, was used for X-ray data collection.

Crystal data. $C_{17}H_{16}O_4$, M = 284.3, prisms, monoclinic, space group $P2_1/n$ (non-standard setting of No. 14), a = 11.3735(12), b = 7.7273(16), c = 16.4224(19) Å, β = 106.679(12)°, V = 1382.6(8) Å^3, Z = 4, D_c = 1.366 g cm^{-3}, $F(000)$ 600, μ(Mo-Kα) 0.91 cm^{-1}.

Data collection, structure solution and refinement. Details of data collection (CAD-4, ω–2θ scanning, $1.5 < \theta < 25.0°$; h: 0 to +13, k: −9 to 0, l: −19 to +19; Mo-Kα X-radiation), structure solution and refinement were similar to those mentioned above for compound **6a**. The phenyl groups were treated as regular hexagons (d_{C-C} 1.395 Å and d_{C-H} 0.95 Å). Hydrogen atoms were included in the refinement process at observed positions with fixed isotropic temperature factors (U_{iso} 0.10 Å^2). At convergence, the discrepancy factors R and R_w were 0.047 and 0.0456 respectively for 982 intensity data with $I > 2\sigma(I)$ where $w^{-1} = [\sigma^2(F) + 0.000\,05\ (F)^2]$ was found to give satisfactory analyses of variance. The general noise level of the final difference Fourier map was ~ ±0.13 e Å^{-3}.

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