Chemical transformations of solvent-derived ozonolysis products: improved synthesis of polycyclic 1,2,4,6-tetroxepanes from α-alkoxy α′-hydroperoxy cyclic ethers and aldehydes

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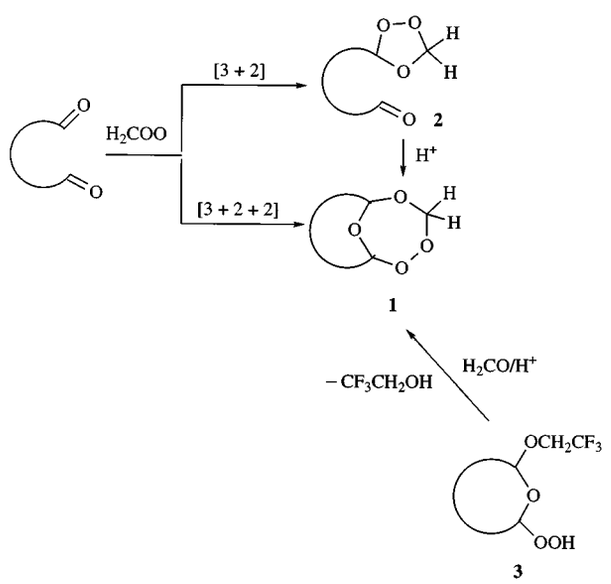
α-Alkoxy α′-hydroperoxy cyclic ethers condense with aliphatic aldehydes under acidic conditions to produce the bicyclic 1,2,4,6-tetroxepanes. By X-ray crystallographic analysis, the tetroxepanes **5b** and **12b**, derived from cyclocondensation of the hydroperoxides **4** and **8** respectively with acetaldehyde, were shown to be *exo*-isomers.

Introduction

The chemistry of mono- and polycyclic peroxides has attracted considerable attention because a significant number of peroxidic natural products possessing interesting pharmacological properties have been isolated.[1,2] Reactions between formaldehyde *O*-oxide and 1,5-keto aldehydes have recently been reported to produce, *via* stepwise [3 + 2 + 2] cycloaddition processes, polycyclic adducts **1** which contain the comparatively rare 1,2,4,6-tetroxepane ring system (Scheme 1).[3] Acid-



Scheme 1

catalysed rearrangements of keto ozonides **2**, derived from intermolecular [3 + 2] cycloaddition reactions between formaldehyde *O*-oxide and keto aldehydes, have also been found to yield structurally similar compounds.[3] Furthermore, by analogy with the preparation of 1,2,4-trioxanes by intramolecular oxymercuriation of the unsaturated hemiperacetals,[4] we have found that acid-catalysed cyclisation reactions between α-alkoxy α′-hydroperoxy cyclic ethers **3** and formaldehyde afford the corresponding 1,2,4,6-tetroxepanes **1** (Scheme 1).[5]

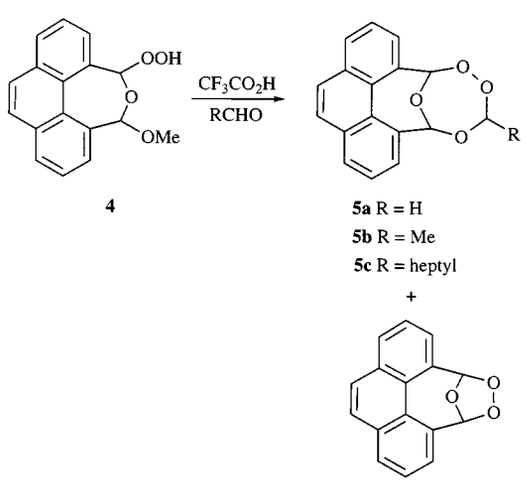
We report herein the results of our recent investigations into the scope of this latter method for the synthesis of 1,2,4,6-tetroxepane derivatives.

Results and discussion

Acid-catalysed condensation of α-alkoxy α′-hydroperoxy cyclic ethers with carbonyl compounds

The required α-alkoxy α′-hydroperoxy cyclic ethers such as **4** were readily prepared by ozonolyses of the corresponding cycloalkenes in the presence of either methanol or trifluoroethanol (see Experimental section for details).

Treatment of the methoxy hydroperoxide **4** with formaldehyde in the presence of trifluoroacetic acid produced the 1,2,4,6-tetroxepane derivative **5a** in 31% yield. From the analogous condensation reactions of **4** with acetaldehyde and octanal, the 3-alkyl-substituted 1,2,4,6-tetroxepanes **5b** and **5c** respectively were also obtained in similar yield (Scheme 2 and Table 1).



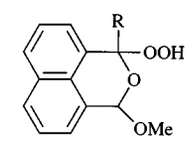
Scheme 2

Although these tetroxepane yields are moderate, they are generally superior to those from the corresponding [3 + 2 + 2] cycloaddition of formaldehyde oxide to phenanthrene-4,5-dicarbaldehyde because in the latter reaction the yield of the tetroxepane **5a** could be as low as 7%. Moreover, it was found that carbonyl oxides which were more highly substituted than formaldehyde *O*-oxide would not undergo the extended

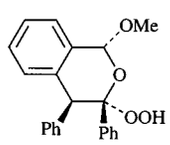
Table 1 Reaction of α-alkoxy α′-hydroperoxy cyclic ethers with aldehydes in the presence of trifluoroacetic acid [a]

Substrate	Aldehyde	Reaction time/h	Tetroxepanes (yield, %)	Other products (yield, %)
4	HCHO	2	**5a** (31)	
4	MeCHO	19	**5b** (61)	
4	octanal	2	**5c** (43)	
4	PhCHO	16		**6** (38)
4	Me_2CO	17		**6** (30)
7a	MeCHO	2	**10a** (18) [b]	
7b	HCHO	3	**10b** (39)	**11** (10)
7b	MeCHO	4	**10c** (41) [c]	**11** (30)
8	HCHO	2	**12a** (8)	**13** (5), **14** (52)
8	MeCHO	1	**12b** (36)	**13** (3), **14** (52)
9	MeCHO	2	**15** (65)	**16** (20)

[a] Treatment of a *ca.* 1:10 mixture of the appropriate alkoxy hydroperoxide and the carbonyl compound with 1 equiv. of trifluoroacetic acid. [b] The unidentified oligomeric products were obtained in significant amounts. [c] A 2:1 mixture of two stereoisomers.



7a R = H
7b R = Me



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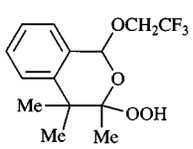

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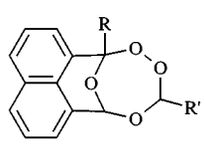
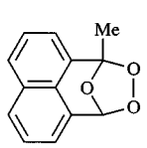


10a R = H, R' = Me
10b R = Me, R' = H
10c R = R' = Me



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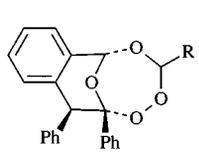
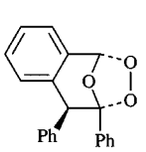


12a R = H
12b R = Me



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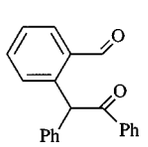

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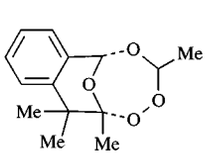

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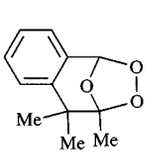

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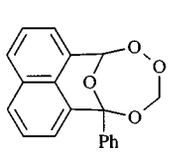

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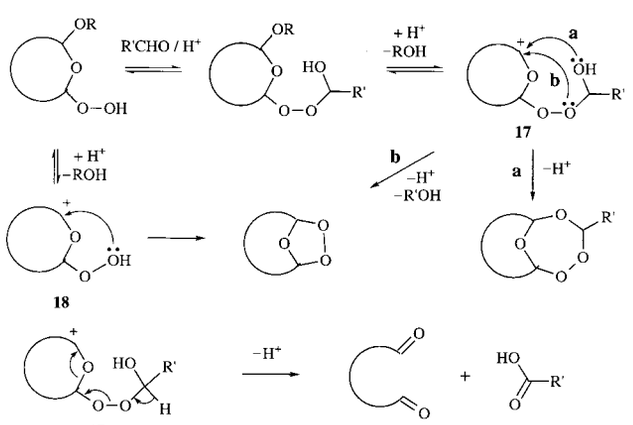
cycloaddition to dialdehydes.[3] There are, however, some limitations on the cyclocondensation process too because the hydroperoxide **4** did not condense with less electrophilic carbonyl compounds such as benzaldehyde or acetone; the sole isolated product was pyrene ozonide **6** (Scheme 2 and Table 1).

The results of a series of reactions involving the hydroperoxides **7**–**9** and either formaldehyde and acetaldehyde are summarised in Table 1. The yields of tetroxepanes vary widely, *e.g.* tetroxepane **10a** was obtained from hydroperoxide **7a** in poor yield (18%) whereas hydroperoxide **7b** afforded the corresponding tetroxepanes **10b** and **10c** in moderate yield (35% for **10b**; 41% for **10c**). Under similar conditions, the reaction of hydroperoxide **8** with formaldehyde gave only small amounts of the tetroxepane **12a** (8%) and the ozonide **13** (5%) with the keto aldehyde **14** (52%) as the major product whereas with acetaldehyde, tetroxepane **12b** was obtained in improved yield (36%). The trifluoroethoxy hydroperoxide **9** gave the best yield of tetroxepane **15** (65%), accompanied by the bicyclic ozonide **16** (20%).

A generalised mechanism for the formation of the 1,2,4,6-tetroxepane derivatives and the bicyclic ozonides discussed above is outlined in Scheme 3. Carbocation **17**, which would



Scheme 3

be expected to be highly resonance stabilised for each of the systems above, could provide a common intermediate to both the tetroxepanes and the ozonides. Competition between the intramolecular cyclisation pathways **a** and **b** should determine the relative ratios of the peroxidic products. Where the yield of the expected 1,2,4,6-tetroxepane was found to be low (Table 1, entries 4 and 5), an alternative route to the ozonide derivative *via* an intermediate carbocation **18** was likely to have been operative.

To account for the relatively high yields of dicarbonyl compound **14** afforded by hydroperoxide **8** (Table 1, entries 9 and 10), or the low mass balance obtained from several of the reactions, it is proposed that intermediate **17**, or the protonated form of the related hemiperacetal, could decompose *via* heterolytic cleavage of the O–O bond (Scheme 3).

Structural studies of tetroxepane derivatives 5b and 12b

Although tetroxepanes **5b** and **5c** could have been formed as mixtures of stereoisomers, in reality only one isomer was isolated in each case. The structure of the crystalline compound **5b** was determined by X-ray crystallographic analysis. The solid state structure of **5b** is shown in Fig. 1 along with the numbering system used in the structural study. The observed bond distances and angles all lie within expected ranges [*e.g.* the bond distance O(1)–O(2) 1.467(2) Å is within the normal range].[3,6] The phenanthrene ring system is non-planar with a pronounced

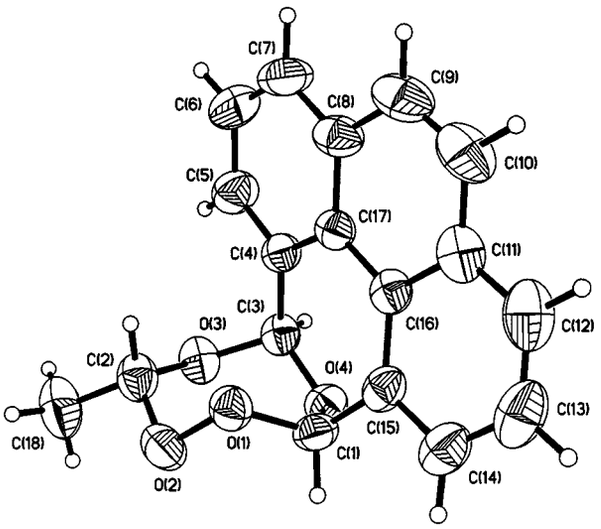


Fig. 1 The solid state structure of one molecule of 1,2,4,6-tetroxepane **5b** (ORTEP,[10] the non-hydrogen atoms are represented by 50% probability ellipsoids and hydrogen atoms by spheres of arbitrary radius).

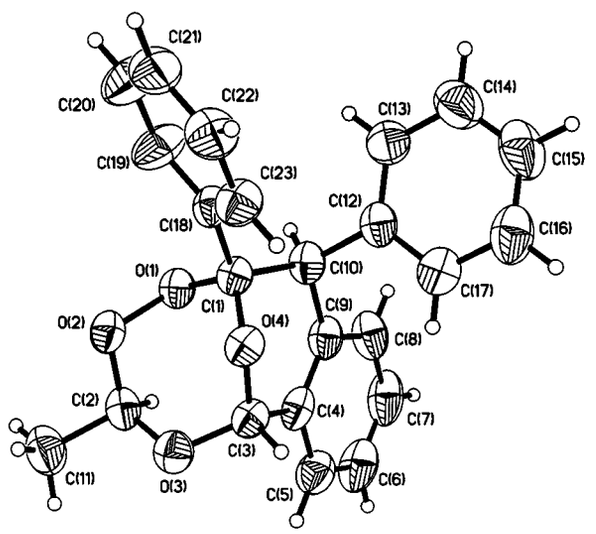


Fig. 2 The solid state structure of one molecule of 1,2,4,6-tetroxepane **12b** (ORTEP,[10] the non-hydrogen atoms are represented by 50% probability ellipsoids and hydrogen atoms by spheres of arbitrary radius).

twist about ring B {torsion angle C(4)–C(17)–C(16)–C(15) −12.7(4)°; atoms C(4) and C(5) are displaced below the least-squares plane through the atoms of ring B by −0.234(3) and −0.250(4) Å whereas atoms C(14) and C(15) lie above the plane by similar distances [0.300(5) and 0.260(4) Å respectively}. The seven-membered 1,2,4,6-tetroxepane ring adopts a distorted chair conformation in which atoms O(1), C(1), O(4) and C(3) are not coplanar as would be required in the idealised arrangement [torsion angle C(3)–O(4)–C(1)–O(1) 26.3(3)°]. This conformation, which is one of several possible chair forms, differs from that observed previously for compound **19**[3] as a result of the structural constraints imposed by the bridging phenanthrene ring system. The methyl group at C(2) occupies a sterically favoured pseudo-equatorial position, *exo* with respect to the bridging oxygen atom O(4).

The crystal structure of tetroxepane **12b**, as determined by X-ray crystallography, consists of two enantiomeric, but independent, molecules per asymmetric unit. The molecular structure of one molecule of **12b** is illustrated in Fig. 2 along with the numbering system adopted. Apart from being mirror images, the two molecules show only minor differences in the relative positions of the non-hydrogen skeletal atoms C(1)–C(10) and O(1)–O(4) [rms deviation ± 0.036 Å] though there are more substantial structural deviations arising from the conformations adopted by the phenyl groups, particularly the one at C(10). The bond distances and angles around **12b** are in reasonable agreement with expected values.[6]

The conformation of the 1,2,4,6-tetroxepane ring in **12b**, which is significantly more distorted away from an idealised chair than that of **5b**, corresponds more closely to a twist-chair in which the C(3)–O(4)–C(1)–O(1) torsion angle has increased to 45.4(4)° with a concomitant decrease in the O(4)–C(1)–O(1)–O(2) torsion angle to 41.1(4)°. As noted previously, there is some conformational flexibility in these kinds of bicyclic systems thus the observed arrangement is probably influenced by the steric interactions between the adjacent *syn*-phenyl groups at C(1) and C(10).[3] In a similar fashion to **5b**, the methyl substituent at C(10) is also located in a pseudo-equatorial position, *exo* with respect to the bridging ether oxygen O(4).

In summary, the acid-catalysed cyclocondensation of α-alkoxy α′-hydroperoxy cyclic ethers with aliphatic aldehydes provides a convenient method for the synthesis of a variety of polycyclic 1,2,4,6-tetroxepane derivatives. The yields of tetroxepanes were found to vary considerably with the nature of both the hydroperoxides and the aldehydes.

Experimental

General

^{1}H (270 MHz) and ^{13}C NMR (67.5 MHz) spectra were obtained in $CDCl_3$ with $SiMe_4$ as standard.

The α-alkoxy α′-hydroperoxy cyclic ethers **4**,[7] **7a**,[7] **7b**[7] and **8**[8] were prepared according to the literature procedures cited. The physical properties of the products **5a**,[3] **10b**,[3] **12a**,[3] **6**,[7] **11**,[7] **13**[8] and **14**[7,8] have been previously reported.

CAUTION: Since organic 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 peroxides synthesised in this work using the reaction scales and procedures described below together with the safeguard mentioned above.

Ozonolysis reactions must be carried out in a well ventilated fume cupboard.

Preparation of the α-alkoxy α′-hydroperoxy cyclic ether 9

A slow stream of ozone (1.5 equiv.) was passed through a cooled (0 °C) solution of 1,1,2-trimethylindene (342 mg, 2.16 mmol) in trifluoroethanol (3 cm^3) and dichloromethane (12 cm^3). Diethyl ether (30 cm^3) was added and the separated organic layer was washed in turn with saturated aqueous $NaHCO_3$ and saturated brine, and dried (anhydrous $MgSO_4$). After evaporation of the solvent under reduced pressure, the products were separated by column chromatography on silica gel. Elution with benzene–hexane gave the ozonide **16** (19 mg, 4%). Subsequent elution with benzene gave the isochroman derivative **9** (509 mg, 77%).

1,1,2-Trimethylindene ozonide 16. Mp 84–86 °C (from methanol) (Found: C, 70.1; H, 6.8. $C_{12}H_{14}O_3$ requires: C, 69.9; H, 6.8%); δ_H 1.29 (3 H, s), 1.38 (3 H, s), 1.60 (3 H, s), 6.09 (1 H, s), 7.0–7.7 (4 H, m).

3,4,4-Trimethyl-3,4-dihydro-1-(2,2,2-trifluoroethoxy)-1*H*-2-benzopyran-3-yl hydroperoxide 9. Mp 85–86 °C (from diethyl ether–hexane) (Found: C, 54.45; H, 5.7. $C_{14}H_{17}F_3O_4$ requires: C, 54.9; H, 5.6%); δ_H 1.20 (3 H, s), 1.41 (3 H, s), 1.62 (3 H, s), 4.23 (1 H, q, *J* 9), 4.30 (1 H, q, *J* 9), 5.75 (1 H, s), 7.1–7.5 (4 H, m) and 8.46 (1 H, s); δ_C 17.29, 22.52, 27.91, 43.60, 60.71 (q, *J* 35), 101.46, 112.51, 124.26 (q, *J* 278), 124.58, 126.02, 126.15, 130.08, 131.23 and 142.14.

Acid-catalysed condensation of α-alkoxy α′-hydroperoxy cyclic ethers, 4a–e with aldehydes

The general procedure, which was used for the reaction of hydroperoxides and aldehydes, is illustrated for the hydroperoxide **4** and acetaldehyde. A solution of the hydroperoxide **4** (241 mg, 0.85 mmol) and acetaldehyde (374 mg) in CH_2Cl_2 (10 cm^3) was stirred at 0 °C for 2 h. After the addition of a solution of trifluoroacetic acid (97 mg, 0.85 mol) in CH_2Cl_2 (10 cm^3), the reaction was continued at room temperature for 19 h. Subsequently, the reaction mixture was poured into ice-cold aqueous $NaHCO_3$ and was extracted with diethyl ether (3 × 25 cm^3). After the organic extracts were combined, dried (anhydrous $MgSO_4$) and concentrated, the products were isolated by column chromatography on silica gel (column, 2 × 50 cm; 20 g silica gel; elution with diethyl ether–hexane; the ratio was changed from 5:95 to 15:85) to give the tetroxepane **5b** (153 mg, 61%).

4,9-Dihydro-7-methyl-4,9-epoxyphenanthro[4,5-*fgh*][1,2,4]trioxecine 5b. Mp 134–139 °C (from diethyl ether–hexane) (Found: C, 73.5; H, 4.7. $C_{18}H_{14}O_4$ requires: C, 73.5; H, 4.8%); δ_H 1.1–1.5 (3 H, m), 5.72 (1 H, q, *J* 5.5), 6.47 (2 H, s) and 7.3–8.1 (8 H, m); δ_C 17.07, 98.87, 99.49, 107.69, 126.05, 126.33, 127.20, 127.33, 127.51, 127.54, 128.28, 128.31, 128.78, 130.05, 131.03, 134.48 and 137.46.

4,9-Dihydro-7-heptyl-4,9-epoxyphenanthro[4,5-*fgh*][1,2,4]trioxecine 5c. Mp 74 °C (from diethyl ether–hexane) (Found: C, 76.5; H, 6.9. $C_{24}H_{26}O_4$ requires: C, 76.8; H, 6.9%); δ_H 0.7–1.8 (15 H, m), 5.56 (1 H, t, *J* 4), 6.47 (1 H, s), 6.50 (1 H, s) and 7.4–8.1 (8 H, m); δ_C 14.06, 22.60, 24.55, 29.07, 29.31, 31.17, 31.72, 99.57, 101.87, 107.69, 126.06, 126.37, 127.24, 127.34, 127.56, 127.59, 128.35, 128.82, 130.07, 131.05, 133.36, 134.53, 137.54.

4-Methyl-1,6-epoxy-1*H*,6*H*-naphtho[1,8-*fg*][1,2,4]trioxonine 10a. Mp 81–83 °C (from diethyl ether–hexane) (Found: C, 68.8; H, 4.9. $C_{14}H_{12}O_4$ requires: C, 68.85; H, 4.95%); δ_H 1.15 (3 H, d, *J* 6), 5.94 (1 H, q, *J* 6), 6.56 (2 H, s) and 7.2–8.1 (6 H, m).

1,4-Dimethyl-1,6-epoxy-1*H*,6*H*-naphtho[1,8-*fg*][1,2,4]trioxonine 10c (minor isomer). Mp 178–180 °C (from diethyl ether–hexane) (Found: C, 69.8; H, 5.5. $C_{15}H_{14}O_4$ requires: C, 69.8; H, 5.5%); δ_H 1.23 (3 H, d, *J* 5), 2.00 (3 H, s), 5.00 (1 H, q, *J* 5), 6.37 (1 H, s) and 7.4–8.0 (6 H, m).

1,4-Dimethyl-1,6-epoxy-1*H*,6*H*-naphtho[1,8-*fg*][1,2,4]trioxonine 10c (major isomer). Mp 87–89 °C (from diethyl ether–hexane) (Found: C, 69.8; H, 5.3. $C_{15}H_{14}O_4$ requires: C, 69.8; H, 5.5%); δ_H 1.11 (3 H, d, *J* 5.5), 1.92 (3 H, s), 5.95 (1 H, q, *J* 5.5), 6.52 (1 H, s) and 7.5–8.1 (6 H, m).

6,7-Dihydro-6,7-diphenyl-3-methyl-1,6-epoxy-1*H*-2,4,5-benzotrioxonine 12b. Mp 134–135 °C (from diethyl ether–hexane) (Found: C, 76.5; H, 5.6. $C_{23}H_{20}O_4$ requires: C, 76.65; H, 5.6%); δ_H 1.26 (3 H, d, *J* 5.5), 4.09 (1 H, s), 5.41 (1 H, q, *J* 5.5), 6.58 (1 H, s) and 6.9–7.6 (14 H, m).

6,7-Dihydro-3,6,7,7-tetramethyl-1,6-epoxy-1*H*-2,4,5-benzotrioxonine 15. Mp 72 °C (from diethyl ether–hexane) (Found: C, 66.9; H, 7.2. $C_{14}H_{18}O_4$ requires: C, 67.2; H, 7.25%); δ_H 1.28 (3 H, s), 1.33 (3 H, d, *J* 5.6), 1.35 (3 H, s), 1.57 (3 H, s), 5.21 (1 H, q, *J* 5.6), 6.08 (1 H, s) and 7.3–7.5 (4 H, m).

X-Ray crystallographic structure determination of 1,2,4,6-tetroxepane 5b

The crystal of **5b** used for X-ray data collection (approx. dimensions 0.46 × 0.58 × 0.68 mm) was grown by slow evaporation from a dichloromethane/hexane (1:1) solution and mounted in a sealed Lindemann capillary tube.

Crystal data. $C_{18}H_{14}O_4$, $M = 294.3$, colourless block, monoclinic, space group $P2_1/n$ (non-standard setting of No. 14), $a = 10.4490(10)$, $b = 8.8350(10)$, $c = 15.2790(10)$ Å, $\beta = 91.030(10)°$, $U = 1410.3(2)$ Å^3, $Z = 4$, $D_c = 1.386$ g cm^{-3}, $F(000)$ 616, μ(Mo-Kα) 0.098 mm^{-1}.

Data collection. The intensity data were collected on a Siemens P4 diffractometer over the quadrant $-1 \leqslant h \leqslant 12$, $-1 \leqslant k \leqslant 10$, $-18 \leqslant l \leqslant 18$ temperature 293(2) K; θ range: 2.34 to 25.00° using graphite monochromated Mo-Kα X-radiation (λ 0.710 73 Å) and ω-scanning. Of the 2488 unique data [R(int) = 0.025] measured, 1666 had $I > 2\sigma(I)$. The data were corrected for Lorentz and polarisation effects, but not for absorption.

Structure solution. The approximate positions of the non-hydrogen atoms were determined by direct methods (SHELXS-86[9]). The structure was refined by full-matrix least-squares methods on F^2 (SHELXTL/PC[10]) using all F^2 data and anisotropic temperature factors for all the non-hydrogen atoms. All the hydrogen atoms were located on difference Fourier maps and included in the refinement process at idealised positions with isotropic temperature factors ($1.5 \times U_{iso}$ of the bonded atom). At convergence, the discrepancy factors R [$F > 4\sigma(F)$] and wR^2 were 0.055 and 0.098 respectively. The weighting scheme, $w = \{1/[\sigma^2(F_o^2) + (0.0515\ P)^2 + 0.1696\ P]\}$ where $P = (F_o^2 + 2F_c^2)/3$ was found to give satisfactory analyses of variance. The final difference Fourier map was essentially featureless (general noise level less than ±0.10 e Å^{-3}) with largest different peak and hold of 0.16 and −0.15 e Å^{-3} respectively.

X-Ray crystallographic structure determination of 1,2,4,6-tetroxepane 12b

Details of the procedures for data collection and structure solution were similar to those described above for **5b**.

Crystal data. $C_{24}H_{20}O_4$, $M = 360.4$, colourless block, approx. size (0.44 × 0.46 × 0.74 mm), monoclinic, space group $P2/c$ (No. 13), $a = 8.4710(10)$, $b = 10.1800(10)$, $c = 21.821(3)$ Å, $\beta = 98.82(2)°$, $U = 1859.5(4)$ Å^3, $Z = 8$ (2 independent molecules per asymmetric unit), $D_c = 1.287$ g cm^{-3}, $F(000)$ 760, μ(Mo-Kα) 0.088 mm^{-1}.

Data collection. The intensity data were collected on a Siemens P4 diffractometer [$-10 \leqslant h \leqslant l$, $-12 \leqslant k \leqslant 1$, $-25 \leqslant l \leqslant 25$; temperature 293 (2) K; θ range: 1.89 to 24.99°; Mo-Kα X-radiation (λ 0.710 73 Å) and ω-scanning]. Of the 3958 unique data [R(int) = 0.027] measured, 3153 had $I > 2\sigma(I)$.

Structure solution. The structure was solved by direct methods (SHELXS-86[9]) and was refined by full-matrix least-squares methods on F^2 (SHELXTL/PC[10]) using all F^2 data and anisotropic temperature factors for all the non-hydrogen atoms. The phenyl groups were treated as idealised regular hexagons (k_{C-C} 1.39 Å). At convergence, the discrepancy factors R [$F > 4\sigma(f)$] and wR^2 were 0.044 and 0.114 respectively. The weighting scheme, $w = \{1/[\sigma^2(F_o^2) + (0.0625\ P)^2 + 0.3287\ P]\}$ where $P = (F_o^2 + 2F_c^2)/3$ was found to give satisfactory analyses of variance. The final difference Fourier map was essentially featureless (general noise level less that ±0.10 e Å^{-3}) with largest difference peak and hold of 0.15 and −0.18 e Å^{-3} respectively.

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/246.

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References

1 D. A. Casteel, *Nat. Prod. Rep.*, 1992, **9**, 290.
2 (*a*) *The Chemistry of Peroxides*, ed. S. Patai, Wiley, New York, 1983; (*b*) *Organic Peroxides*, ed. W. Ando, Wiley, New York, 1992.

3 (*a*) T. Sugimoto, M. Nojima, S. Kusabayashi and K. J. McCullough, *J. Am. Chem. Soc.*, 1990, **112**, 3690; (*b*) K. J. McCullough, T. Sugimoto, S. Tanaka, S. Kusabayashi and M. Nojima, *J. Chem. Soc.*, *Perkin Trans. 1*, 1994, 643.
4 (*a*) A. J. Bloodworth and A. Shah, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 947; (*b*) A. J. Bloodworth and N. A. Tallant, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 428.
5 Y. Ushigoe, S. Tanaka, M. Nojima and K. J. McCullough, *Tetrahedron Lett.*, 1994, **35.** 9741.
6 (*a*) F. H. Allen, S. A. Bellard and O. Kennard, *Acta Crystallogr.*, *Sect. C*, 1986, **42**, 829; (*b*) G. Bernardelli, C. W. Jefford, J. Boukouvalas, D. Jaggi and S. Kohmoto, *Acta Crystallogr.*, *Sect. C*, 1987, **43**, 701.
7 T. Sugimoto, M. Nojima and S. Kusabayashi, *J. Org. Chem.*, 1990, **55**, 3816.
8 T. Sugimoto, K. Teshima, N. Nakamura, M. Nojima, S. Kusabayashi and K. J. McCullough, *J. Org. Chem.*, 1993, **58**, 135.
9 SHELXS-86, G. M. Sheldrick, *Acta Crystallogr.*, 1990, **A46**, 467.
10 SHELXTL/PC (Vers. 5.03), G. M. Sheldrick, Siemens Analytical X-ray Instruments Inc., Madison, W.I. USA.

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