

Synthesis and X-Ray Analysis of 2,3,5,6,11-Pentaoxabicyclo[5.3.1]-undecanes

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The reactions of bicyclic ozonides and aldehyde- or ketone-derived peroxides, preformed or generated *in situ*, in the presence of chlorosulphonic acid afford the corresponding 2,3,5,6,11-pentaoxabicyclo[5.3.1]undecanes. In addition, 1,2,4,5-tetroxans are often isolated from the product mixture. Mechanisms are proposed to account for the observed peroxidic products. An X-ray analysis of the crystalline product (4b) confirms the general structure and reveals that it is solely the *exo*-isomer.

The synthesis of structurally novel cyclic peroxides has recently attracted considerable attention since such compounds may exhibit interesting biological or physical properties.¹⁻³ Recently we reported that the reaction of a mixture of 1-phenyl-6,7,8-trioxabicyclo[3.2.1]octane (1a) and 3,5-diphenyl-1,2,4-trioxacyclopentane (1d) in the presence of catalytic amounts of chlorosulphonic acid gives the crossed pentaoxabicycloundecane (4b).⁴ We now report further, more widely applicable synthetic routes to these bicyclic peroxides, in which bis(α -hydroxybenzyl) peroxide (2b) or a mixture of benzaldehyde and 30% hydrogen peroxide is used as an equivalent to the ozonide (1d). An X-ray analysis of one of the bicyclic peroxides (4b) has also been undertaken.

Results and Discussion

Synthesis of Pentaoxabicycloundecanes.—When a mixture of the ozonide (1a) and the peroxide (2a) was treated with chlorosulphonic acid (0.1 mol equiv.) in acetic acid at 20 °C for 20 min, the crossed pentaoxabicycloundecane (4a) in 50% yield was obtained along with 3-(3-benzoylpropyl)-6-(*p*-tolyl)-1,2,4,5-tetroxan (6a) (1% yield), (4g) (20% yield), and 4-benzoylbutanoic acid (7a) (22% yield) [equation (1)]. Since the bicyclic peroxide (4a) did not rearrange to the isomeric tetroxan (6a) under the reaction conditions, then (4a) is not likely to be the precursor of (6a).⁵ More generally, the reaction of the ozonides (1a) or (1c) with the bis(α -hydroxy) peroxides (2a—c) or with a α -hydroxydecyl hydroperoxide (2d) yielded the corresponding pentaoxabicycloundecanes (4a—d) from (1a) and (5a—d) from (1c) (Table 1). Although in some cases configurationally isomeric products (*exo* and *endo* in the case of bicyclic peroxides, and *trans* and *cis* in the case of tetroxans) could be formed, only one isomer was obtained from each of the reactions investigated. A possible mechanistic explanation of the above results is outlined in Scheme 1.

The first step of the reaction would involve heterolytic cleavage of the C—O bond of the peroxide bridge of (1a) to give the reasonably stabilized carboxonium ion (9a).^{4,6} Subsequent attack at C-2 of (9a) by peroxide (2a) would give the intermediate (10). The carbon centre indicated by the asterisk (*) in (10a), being asymmetrically substituted, should have both the *R* and *S* configuration in the absence of any unexpected stereoselection. Ring closure of (10a) by back-side S_N2 type displacement must necessarily produce both the *exo*- and *endo*-isomers of (4a) from the *R* and *S* forms respectively. The latter *endo*-isomer was not observed. Under the reaction conditions, it seems reasonable therefore to postulate the intermediacy of a stabilised carbenium ion (10b). The

Table 1. Reaction of ozonides with α -hydroxy hydroperoxide or bis(α -hydroxy) peroxides^a

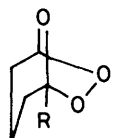
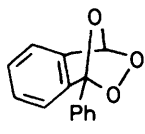
Ozonides	Peroxides	Reaction time (min)	Products [yield (mol %)]
(1a)	(2a)	20	(4a) [50], (6a) [1], (4g) [20], (7a) [22]
(1a)	(2b)	20	(4b) [22], (6d) [3], (4g) [17], (7a) [17]
(1a)	(2c)	20	(4c) [33], (4g) [2], (6e) [10], (7a) [22]
(1a)	(2d)	20	(4d) [18], (4g) [57], (7a) [27]
(1c)	(2a)	20	(5a) [31], (6c) [2], (7c) [25], (8) [13], (3a) [13]
(1c)	(2b)	30	(5b) [31], (6d) [1], (7c) [58], (8) [21]
(1c)	(2c)	30	(5c) [32], (6e) [17], (7c) [37], (8) [19]
(1c)	(2d)	30	(5d) [28], (7c) [51], (8) [7]
(1d)	(2c)	120	(6e) [37], (1d) [9], (7d) [4]
(1d)	(2d)	120	(6g) [11], (6h) [8], (6d) [9], (7d) [16]

^a A mixture of the appropriate ozonide (3 mmol) and peroxide (3 mmol) in acetic acid (30 ml) was treated with chlorosulphonic acid (0.3 mmol) at 20 °C.

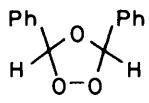
exo-isomer of (4a) presumably results from ring closure of (10b) when it is in its most favoured conformation. If the *endo*- and *exo*-isomers are both formed, the carbenium ion (10b) would also provide a convenient intermediate for the equilibration of the two forms. The absence of significant quantities of the *endo*-isomer of (4a) suggests that the *exo*-isomer is the thermodynamic product.

As illustrated by path b in Scheme 1, attack by (2a) at C(6) of (9a) would ultimately yield *via* intermediates (11a) and (11b) the tetroxan (6a). Isolation of only the thermodynamically favoured *trans*-isomer of (6a) would be entirely consistent with the operation of the equilibration processes discussed above for (4a). Alternatively, a protonated carbonyl oxide (13), formed from (9a) by an electronic rearrangement, may be a key intermediate for the formation of (6a).⁵ This route, which involves the attack by (2a) at the electron deficient carbon of (13), would also be expected to afford the tetroxan (6a) (Scheme 2).

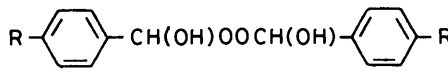
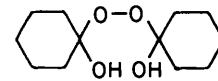
To develop a more convenient, widely applicable method of

(1a) R = Ph
(1b) R = Me

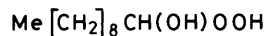
(1c)



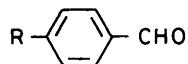
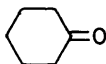
(1d)

(2a) R = Me
(2b) R = H

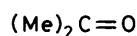
(2c)



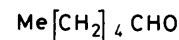
(2d)

(3a) R = Me
(3b) R = OMe

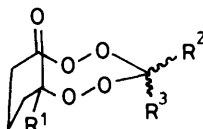
(3c)



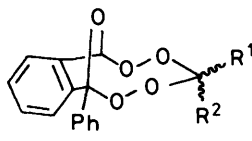
(3d)



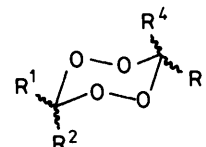
(3e)



(4)



(5)



(6)

a ; R¹ = Ph, R² = MeC₆H₄, R³ = Hb ; R¹ = R² = Ph, R³ = Hc ; R¹ = Ph, R², R³ = -[CH₂]₅-d ; R¹ = Ph, R² = Me[CH₂]₈, R³ = He ; R¹ = Ph, R² = R³ = Meg ; R¹ = Ph, R² = PhCO[CH₂]₃, R³ = Hh ; R¹ = Me, R² = MeC₆H₄, R³ = Hi ; R¹ = Me, R², R³ = -[CH₂]₅-j ; R¹ = R² = R³ = Mek ; R¹ = Me, R² = Me[CH₂]₄, R³ = Hf ; R¹ = Ph, R² = Me[CH₂]₄, R³ = Ha ; R¹ = MeC₆H₄, R² = Hb ; R¹ = Ph, R² = Hc ; R¹ = R² = -[CH₂]₅-d ; R¹ = Me[CH₂]₈, R² = He ; R¹ = R² = Mef ; R¹ = Me[CH₂]₄, R² = Ha ; R¹ = PhCO[CH₂]₃, R³ = MeC₆H₄, R² = R⁴ = Hb ; R¹ = PhCO[CH₂]₃, R³ = R⁴ = Me, R² = Hc ; R¹ = R³ = MeC₆H₄, R² = R⁴ = Hd ; R¹ = R³ = Ph, R² = R⁴ = He ; R¹, R² = R³, R⁴ = -[CH₂]₅-f ; R¹ = R² = R³ = R⁴ = Meg ; R¹ = R³ = Me[CH₂]₈, R² = R⁴ = Hh ; R¹ = Ph, R³ = Me[CH₂]₈, R² = R⁴ = Hi ; R¹ = Ph, R³ = MeOC₆H₄, R² = R⁴ = H

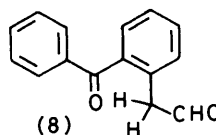
(7)

R

a ; PhCO[CH₂]₃b ; MeCO[CH₂]₃

c ; o-benzoylbenzyl

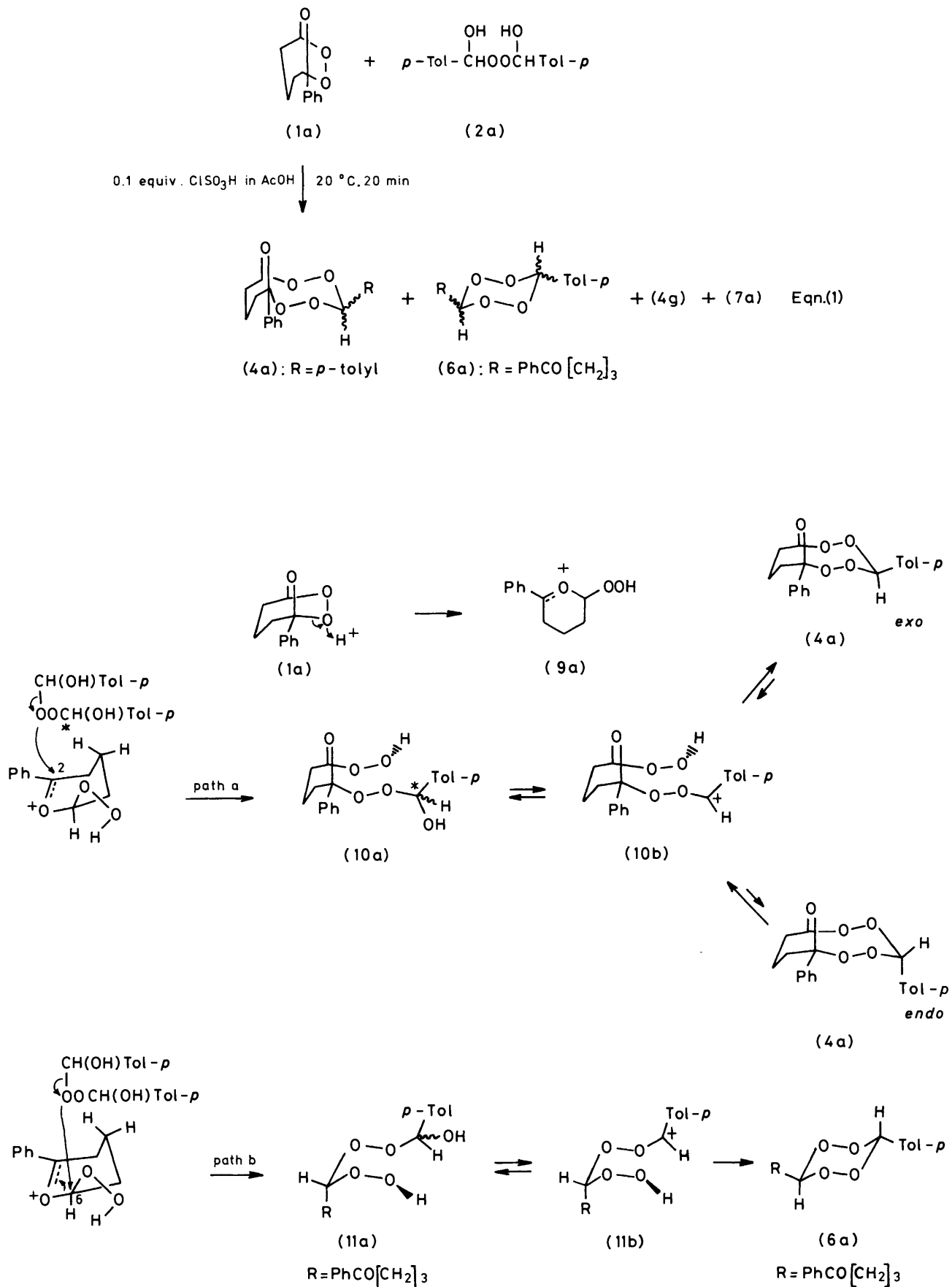
d ; Ph



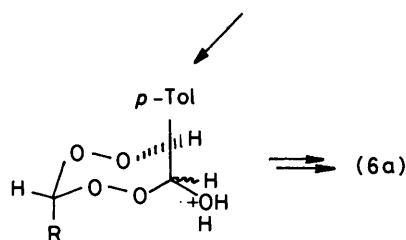
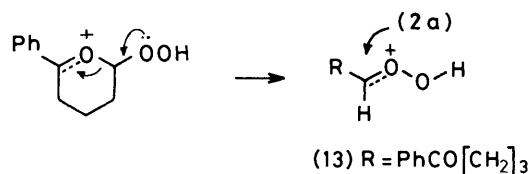
(8)

preparing pentaobicycloundecanes, we have examined a series of reactions between the ozonides (1a—c), carbonyl compounds (3a—e), and 30% hydrogen peroxide in the presence of catalytic amounts of chlorosulphonic acid.

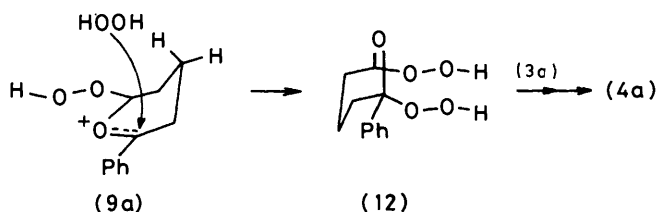
Bicyclic peroxides (4a), (4c), (4e), or (4f) are obtained from (1a), (4h—k) from (1b), and (5a), (5c), (5e), or (5f) from (1c), respectively. In general, yields of the bicyclic peroxides obtained in the above reactions were comparable or slightly



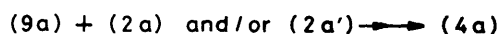
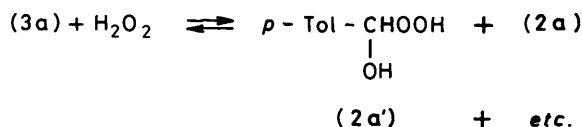
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

lower than those obtained from the reactions using the α -hydroxyhydroperoxide or the bis(α -hydroxy) peroxides (Tables 1 and 2). This latter method is, however, simpler and less hazardous by virtue of not requiring the synthesis and handling of α -hydroxy peroxides, and is potentially applicable to a wide variety of carbonyl compounds.

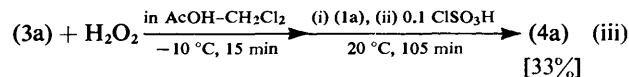
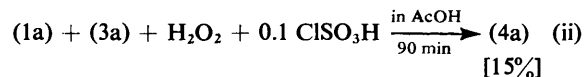
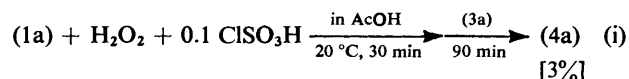
The reaction could proceed *via* an initial attack by hydrogen peroxide at C-2 of (9a) to give the intermediate (12), which on condensation with, for example, *p*-tolualdehyde (3a), would yield (4a) (Scheme 3). On the other hand, it has been shown that the reaction between hydrogen peroxide and an aldehyde or a ketone usually gives rise to an equilibrium mixture of monomeric and oligomeric peroxides, depending markedly on a variety of reactions conditions including pH, solvent, and so on.⁷ Under our reaction conditions, it is possible that aldehyde or ketone peroxides could be formed and therefore participate in the reaction sequence yielding the bicyclic peroxides (Scheme 4). In an attempt to distinguish between the possible pathways, the following experiments have been performed. (a) A mixture of (1a), 30% hydrogen peroxide, and catalytic amounts of chlorosulphonic acid in acetic acid was kept stirred at 20 °C for 30 min. The aldehyde (3a) was then added and the reaction continued for a further 90 min

Table 2. Reaction of a mixture of ozonides, carbonyl compounds, and hydrogen peroxide^a

Ozonides	Carbonyl compds.	Reaction time (h)	Products [yield (mol %)]
(1a)	(3a)	2	(4a) [15], (6a) [3], (4g) [21], (6c) [3], (7a) [19]
(1a)	(3c)	4	(4c) [17], (4g) [34], (6e) [19], (7a) [7]
(1a)	(3d)	2	(4e) [4], (6f) [3], (7a) [14]
(1a)	(3e)	4	(4f) [22], (4g) [30], (7a) [21]
(1b)	(3a)	4	(4h) [23], (7b) [15]
(1b)	(3c)	4	(4i) [7], (7b) [51]
(1b)	(3d)	4	(4j) [10], (7b) [5]
(1b)	(3e)	36	(4k) [20], (7b) [20]
(1c)	(3a)	4	(5a) [27], (7c) [48]
(1c)	(3c)	2	(5c) [13], (7c) [70]
(1c)	(3d)	2	(5e) [7], (7c) [26]
(1c)	(3e)	2	(5f) [35], (7c) [9]
(1d)	(3b)	1	(6i) [13], (1d) [20], (7d) [8]
(1d)	(3e)	2	(1d) [25], (7d) [26]

^a The reaction of a mixture of an ozonide (3 mmol), a carbonyl compound (3 mmol), and 30% hydrogen peroxide (3 mmol) in the presence of chlorosulphonic acid (0.3 mmol) in acetic acid (30 ml) was performed at 20 °C.

[the yield of (4a) 3%] (reaction i). (b) An equimolar mixture of (1a), (3a), and 30% hydrogen peroxide in the presence of 0.1 mol equiv. of chlorosulphonic acid in acetic acid was stirred at 20 °C for 2 h [the yield of (4a) 15%] (reaction ii; the standard reaction). (c) The aldehyde (3a) was treated with an equimolar amount of 30% hydrogen peroxide at -10 °C for 15 min. To this solution, (1a) and then 0.1 mol equiv. of chlorosulphonic acid were added, as the mixture was stirred at 20 °C for 105 min [the yield of (4a) 33%] (reaction iii). The reaction conditions in experiment (i) would certainly favour the formation of the intermediate bis-hydroperoxide (12) whereas those in (ii) and (iii) would be more conducive



to the build-up of concentrations of the α -hydroxyhydroperoxides and/or its equivalents. Our preliminary results, based solely on the isolated yields of (4a), suggest that a reaction sequence similar to that outlined in Scheme 4 represents a favoured route to the formation of the bicyclic peroxide systems.

The present methods used for the synthesis of pentaoxabicycloundecanes are also applicable to the preparation of unsymmetrically substituted tetroxans other than (6a—b). The reaction of a monocyclic ozonide (1d) with the peroxide (2d) gave 3-phenyl-6-nonyl-1,2,4,5-tetroxan (6h) in a yield of 8% (Table 1). Treatment of (1d) with a mixture of 4-methoxybenzaldehyde (3b) and 30% hydrogen peroxide also afforded the crossed tetroxan (6i) (13% yield) (Table 2). However, the

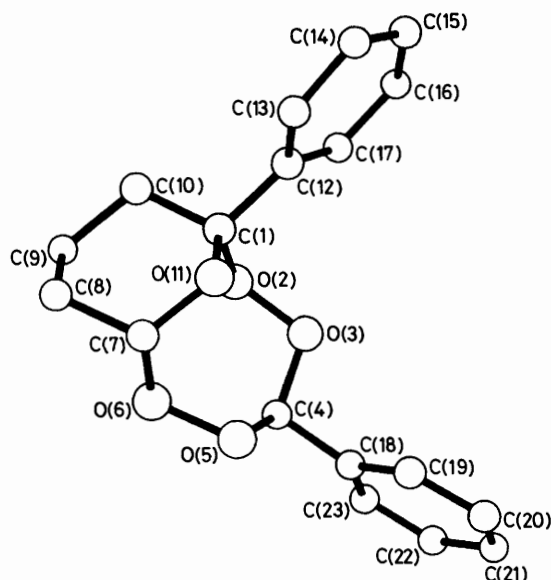
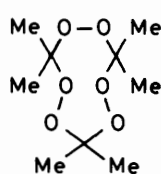
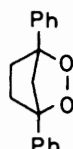


Figure.



(14)



(15)

reactions of (1d) with either (2c) or a mixture of (3e) and hydrogen peroxide did not give the expected crossed products (Tables 1 and 2).

Crystal Structure of the Peroxide (4b).—A computer-generated diagram (PLUTO)⁸ of the crystal structure of (4b), indicating the numbering system adopted for this study, is depicted in the Figure. Interatomic distances and bond angles are listed in Tables 3 and 4 respectively. No significantly short intermolecular contacts were observed.

The peroxide bond distances [1.474(4) and 1.476(4) Å] are comparable with those observed in the benzo-derivative (5c) [1.474(6) and 1.463(7) Å]⁹ and in good agreement with the O—O bond lengths reported by Groth for stable monocyclic peroxides such as tetraoxans (6d)¹⁰ and (6e)¹¹ and hexoxan (14)¹¹ though substantially shorter than the value of 1.501(2) Å found in the more thermally labile endoperoxide (15).¹² Similarly, the mean C—O (peroxide) and C—O (epoxide) distances [1.426(3) and 1.412(a) Å respectively] are consistent with previous results.^{9–11} The remaining bond distances around the molecule lie within the expected ranges.

The Figure shows clearly that the molecule (4b) possesses the [5.3.1]bicyclic skeleton which is approximately bisected by the plane through atoms C(4), C(9), and O(11). The eight-membered ring adopts the thermodynamically favoured boat-chair conformation as found previously in bicyclopentaoxaundecane (5c).⁹ In addition to being slightly twisted, the six-membered pyranoid ring is flattened around the atoms C(9) and O(11). Since the bond angle C(8)—C(9)—C(10) is close to tetrahedral, this flattening of the pyranoid ring may be

Table 3. Bond distances with estimated standard deviations

O(2)—O(3)	1.470(4)
O(5)—O(6)	1.476(5)
C(1)—O(2)	1.434(5)
C(4)—O(3)	1.418(4)
C(4)—O(5)	1.413(5)
C(7)—O(6)	1.443(6)
C(1)—O(11)	1.416(5)
C(7)—O(11)	1.408(5)
C(7)—C(8)	1.513(8)
C(8)—C(9)	1.513(7)
C(9)—C(10)	1.522(6)
C(1)—C(10)	1.534(7)
C(1)—C(12)	1.506(5)
C(4)—C(18)	1.497(7)
C(12)—C(13)	1.388(6)
C(13)—C(14)	1.388(6)
C(14)—C(15)	1.380(8)
C(15)—C(16)	1.380(8)
C(16)—C(17)	1.393(5)
C(12)—C(17)	1.384(6)
C(18)—C(19)	1.376(7)
C(19)—C(20)	1.384(9)
C(20)—C(21)	1.378(7)
C(21)—C(22)	1.380(8)
C(22)—C(23)	1.386(9)
C(18)—C(23)	1.376(6)

Table 4. Selected bond angles with estimated standard deviations

Angle	(°)
C(1)—O(11)—C(7)	116.7(3)
O(11)—C(1)—O(2)	110.9(3)
C(10)—C(1)—O(11)	112.7(4)
C(10)—C(1)—C(2)	102.5(3)
C(1)—O(2)—O(3)	108.2(3)
O(2)—O(3)—C(4)	107.1(3)
O(3)—C(4)—O(5)	113.3(3)
C(4)—O(5)—O(6)	106.4(3)
O(5)—O(6)—C(7)	108.4(3)
O(6)—C(7)—O(11)	112.0(4)
C(8)—C(7)—O(11)	113.9(4)
C(8)—C(7)—O(6)	103.7(4)
C(7)—C(8)—C(9)	111.0(4)
C(8)—C(9)—C(10)	109.1(4)
C(9)—C(10)—C(1)	112.8(3)

attributed to the wider angle of 116.7(3)° at the epoxide oxygen O(11).

As already mentioned, there is the possibility of conformational isomerism at the carbon centre C(4) in several of the bicyclic systems (4) though only one isomer was actually isolated in each instance. From this structural determination, compound (4b) is unambiguously identified as the *exo*-isomer in which the phenyl group at C(4) occupies a *pseudo*-equatorial position. The plane of the phenyl group makes an angle of *ca.* 12° with the mirror plane through atoms C(4), C(9), and O(11). The above situation is analogous to the thermodynamically favoured conformations adopted by aromatic substituents in six-membered ring systems such as tetraoxan (6d),¹³ 1-phenylcyclohexane and 2-aryl-1,3-dioxans.¹⁴ In the latter systems, the aromatic groups preferentially adopt equatorial positions with similar small angles between the aromatic ring plane and the mirror plane of the six-membered ring. The observed rotational conformation observed in the crystalline state may however be simply determined by crystal packing forces.¹⁴

Experimental

¹H N.m.r. spectra were obtained with a JEOL LNM 4P 100 instrument, mass spectra with a Hitachi RMU-6H spectrometer, and i.r. spectra with a Hitachi 215 spectrometer.

Ozonides (1a—d)⁵ and peroxides (2a),¹⁵ (2b),¹⁵ (2c),¹⁵ and (2d)¹⁶ were prepared according to the reported methods. The experimental details given below may be regarded as typical procedures. The physical properties of all new peroxides are given in Table 5.

Reaction of the Ozonide (1a) with Bis(α-hydroxy-4-methylbenzyl) Peroxide (2a) in the Presence of Chlorosulphonic Acid.—A mixture of the ozonide (1a) (3 mmol), the peroxide (2a) (3 mmol), and chlorosulphonic acid (0.3 mmol) in acetic acid (30 ml) was stirred at 20 °C for 20 min. Work-up of the reaction mixture was carried out by pouring it into water,

extracting the latter with ether, and washing the organic extracts with portions of aqueous potassium hydroxide and water. After evaporation of the solvent, the neutral products were isolated by column chromatography on silica gel using ether–benzene–light petroleum as eluant (the solvent polarity was increased gradually by increasing the proportion of ether). The first fraction contained the pentaoxabicycloundecane (4a) (50%), from the second fraction the crossed tetraoxan (6a) was obtained (1%) and the final fraction contained (4g) (20%). Acidification of the potassium hydroxide extract afforded 4-benzoylbutanoic acid (7a) (22%).

Reaction of a Mixture of (1a) and Hydrogen Peroxide with p-Tolualdehyde (3a) in the Presence of Chlorosulphonic Acid (Reaction i).—An equimolar mixture of (1a) (3 mmol) and hydrogen peroxide (30%; 3 mmol) in the presence of chloro-

Table 5. Physical properties of peroxidic products ^a

Peroxide	M.p. ^b (°C)	Molecular formula	Calc. (%)		Found (%)		(m/z) M ⁺	¹ H N.m.r. (δ)
			C	H	C	H		
(4a)	145–147	C ₁₉ H ₂₀ O ₅	69.5	6.15	69.6	5.85	328	2.32 (3 H, s), 1.48–2.48 (6 H, m), 5.75 (1 H, bs), 6.63 (1 H, s), 7.02–7.72 (9 H, m)
(4c)	140–142	C ₁₇ H ₂₂ O ₅	65.55	7.25	66.25	7.15	306	1.42–1.70 (10 H, m), 1.70–2.45 (6 H, m), 5.60 (1 H, bs), 7.20–7.60 (5 H, m)
(4e)	134–135	C ₁₄ H ₁₈ O ₅	63.15	6.8	63.25	6.85	266	1.24 (3 H, s), 1.45 (3 H, s), 1.30–2.30 (6 H, m), 5.60 (1 H, bs), 7.20–7.60 (5 H, m)
(4h)	109–110	C ₁₄ H ₁₈ O ₅	63.15	6.8	62.85	6.75	266	1.50 (3 H, s), 1.63–1.92 (6 H, m), 2.33 (3 H, s), 5.47 (1 H, bs), 6.45 (1 H, s), 7.04–7.38 (4 H, m)
(4i)	114–116	C ₁₂ H ₂₀ O ₅	59.0	8.25	59.3	8.3	244	1.48 (3 H, s), 1.44–2.40 (16 H, m), 5.36 (1 H, bs)
(4j)	Oil	C ₉ H ₁₆ O ₅	52.95	7.90	53.2	7.65	204	1.36 (3 H, s), 1.45 (3 H, s), 1.52 (3 H, s), 1.6–2.0 (6 H, m), 5.39 (1 H, bs)
(5a)	199–201	C ₂₃ H ₂₀ O ₅	73.4	5.35	73.25	5.2	376	2.28 (3 H, s), 3.03 (1 H, d, J 21 Hz), 3.60 (1 H, dd, J 21 Hz and 6 Hz), 6.07 (1 H, d, J 6 Hz), 6.55 (1 H, s), 6.78–7.72 (13 H, m)
(5c)	125–128	C ₂₁ H ₂₂ O ₅	71.2	6.25	71.0	6.25	354	1.31–1.89 (8 H, m), 2.04–2.25 (2 H, m), 2.96 (1 H, d, J 6 Hz), 3.51 (1 H, dd, J 21 and 6 Hz), 5.90 (1 H, d, J 6 Hz), 6.68–7.68 (9 H, m)
(5d)	103–105	C ₂₃ H ₃₂ O ₅	72.8	7.8	72.55	7.8	412	0.85 (3 H, bt), 1.20–1.60 (16 H, m), 2.92 (1 H, d, J 18 Hz), 3.50 (1 H, dd, J 18 and 6 Hz), 5.63 (1 H, bt), 5.94 (1 H, d, J 6 Hz), 6.75–7.75 (9 H, m)
(5e)	144–146	C ₁₈ H ₁₈ O ₅	68.8	5.75	68.8	5.7	314	1.36 (3 H, s), 1.64 (3 H, s), 2.96 (1 H, d, J 21 Hz), 3.56 (1 H, dd, J 21 and 6 Hz), 5.96 (1 H, d, J 6 Hz), 6.77–7.72 (9 H, m)
(6a)	110–111	C ₁₉ H ₂₀ O ₅	69.5	6.15	69.3	6.1	— ^c	1.40–2.10 (4 H, m), 2.40 (3 H, s), 3.10 (2 H, t, J 6 Hz), 6.11 (1 H, t, J 4.5 Hz), 6.7 (1 H, s), 7.14–8.04 (9 H, m)
(6b)	66–68	C ₁₄ H ₁₈ O ₅	63.15	6.8	62.85	7.5	— ^c	1.32 (3 H, s), 1.40 (3 H, s), 1.55–1.90 (4 H, m), 3.00 (2 H, t, J 6 Hz), 5.44 (1 H, t, J 4.5 Hz), 7.20–7.64 (3 H, m), 7.84–8.02 (2 H, m)
(6g)	47–50	C ₂₀ H ₄₀ O ₄	69.85	11.6	69.7	11.7	— ^c	0.92 (6 H, t, J 6 Hz), 1.12–1.72 (32 H, m), 6.16 (2 H, t, J 4.5 Hz)
(6h)	Oil	C ₁₇ H ₂₆ O ₄	69.35	8.9	69.95	9.15	— ^c	0.88 (3 H, t, J 6 Hz), 1.0–1.30 (14 H, m), 1.28–1.75 (2 H, m), 6.04 (1 H, t, J 4.5 Hz), 6.72 (1 H, s), 7.20–7.60 (5 H, m)
(6i)	158–159	C ₁₂ H ₂₀ O ₅	65.75	5.15	65.75	5.0	— ^c	3.82 (3 H, s), 6.80–7.00 (4 H, m), 7.32–7.55 (7 H, m)

^a The physical properties of compounds (4b),⁴ (4f),⁴ (4g),⁵ (4k),⁴ (5b),⁴ (5f),⁴ (6c),¹⁹ (6d),¹⁹ (6e),¹⁵ and (6f)²⁰ ^b All solid peroxides recrystallised from methanol. ^c Molecular ion not observed.

sulphonic acid (0.3 mmol) in acetic acid (25 ml) was stirred at 20 °C for 30 min. A solution of (3a) (3 mmol) in acetic acid (5 ml) was then added, and the mixture was stirred for a further 90 min and worked up as described above. Column chromatography on silica gel afforded (4a) (3%), the tetraoxan (6a) (40%), and (4g) (36%). Acidification of the alkaline extract gave the keto acid (7a) (19%).

Reaction of a Mixture of (1a), (3a), and Hydrogen Peroxide in the Presence of Chlorosulphonic Acid (Reaction ii, a Standard Method).—An equimolar mixture of (1a) (3 mmol), (3a) (3 mmol), and hydrogen peroxide (30%; 3 mmol) in acetic acid (30 ml) was stirred at 20 °C for 2 h. The product mixture was separated by column chromatography on silica gel to afford the following neutral products; (6c) (3%), (4a) (15%), (6a) (3%), and (4g) (21%) in order of elution. The keto acid (7a) was also isolated (13%).

Reaction of (1a) with a Mixture of (3a) and Hydrogen Peroxide in the Presence of Chlorosulphonic Acid (Reaction iii).—A mixture of (3a) (3 mmol) and hydrogen peroxide (30%; 3 mmol) in acetic acid–methylene chloride (30 ml; 2:1, v/v) was maintained at –10 °C for 15 min. A solution of (1a) (3 mmol) in acetic acid (5 ml) was then added, followed by addition of a solution of chlorosulphonic acid (0.3 mmol) in acetic acid (5 ml). The mixture was warmed to 20 °C in 5 min, and the reaction was continued for a further 100 min. From the reaction mixture (4a), (4g), and (7a) were isolated in yields of 33, 28, and 8%, respectively.

X-Ray Crystal Structure Determination of 1,4-Diphenyl-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane, C₁₈H₁₈O₅ (4b).—Crystals suitable for X-ray analysis were grown by slow evaporation from a methylene chloride–methanol solution. A colourless, irregular fragment of approximate dimensions 0.30 × 0.30 × 0.15 mm was used for data collection.

Crystal Data for C₁₈H₁₈O₅.—*M* = 314.33; *a* = 10.727(1), *b* = 11.858(5), *c* = 13.602(2) Å, β = 115.07(1)°, *V* = 1567.2 Å³, *Z* = 4, *D_c* = 1.33 g cm⁻³, *D_o* = 1.34 g cm⁻³, Space group, monoclinic *P*2₁/*c* (No. 14); Mo-*K*_α radiation, λ = 0.71069 Å; μ = 1.05 cm⁻¹.

The intensity data were collected on an Enraf-Nonius CAD 4 four-circle diffractometer using the ω–2θ scanning mode and Mo-*K*_α radiation (θ < 25°). Of the 2 728 reflections measured, 1 422 had *I* > 2.5σ(*I*) where σ is the standard deviation of the background corrected count. Periodic monitoring of two standard reflections indicated no significant crystal decay. The intensities were corrected for Lorentz and polarisation effects, but not for absorption. Systematic absences [*h*0*l*, *l* = 2*n* + 1; 0*k*0, *k* = 2*n* + 1] showed the space group to be *P*2₁/*c*.

Structure Solution and Refinement.—The positions of all the non-hydrogen atoms were determined by direct methods using the program MULTAN.¹⁷ All subsequent structural refinement was undertaken using SHELX.¹⁸ After several cycles of least-squares refinement of the atomic co-ordinates and isotropic temperature factors for the carbon and oxygen atoms the conventional *R*-factor fell to 0.13. The hydrogen atoms were located on a difference Fourier map and included in the calculations with fixed temperature and positional parameters. Structural refinement was continued using

Table 6. Fractional co-ordinates of atoms with standard deviations

	<i>X</i>	<i>Y</i>	<i>Z</i>
C(1)	0.938 3(4)	0.142 8(4)	0.712 8(3)
O(2)	0.852 9(3)	0.045 3(2)	0.697 3(2)
O(3)	0.758 1(2)	0.067 5(2)	0.747 6(2)
C(4)	0.623 3(4)	0.070 8(4)	0.662 7(3)
O(5)	0.592 4(3)	0.173 7(3)	0.604 9(2)
O(6)	0.662 6(3)	0.170 1(3)	0.532 2(2)
C(7)	0.771 3(4)	0.253 0(4)	0.568 8(4)
C(8)	0.843 8(5)	0.234 1(4)	0.496 0(4)
C(9)	0.919 1(4)	0.122 4(4)	0.520 6(4)
C(10)	1.013 3(4)	0.116 5(4)	0.641 3(4)
O(11)	0.857 6(3)	0.242 0(3)	0.680 2(2)
C(12)	1.038 2(4)	0.159 2(4)	0.829 6(3)
C(13)	1.109 7(4)	0.260 0(4)	0.862 7(4)
C(14)	1.209 9(5)	0.273 5(5)	0.967 9(4)
C(15)	1.239 4(5)	0.184 8(5)	1.040 0(4)
C(16)	1.169 5(5)	0.083 9(5)	1.008 9(4)
C(17)	1.069 0(4)	0.071 3(4)	0.903 1(3)
C(18)	0.530 0(4)	0.062 4(4)	0.718 8(3)
C(19)	0.521 0(5)	0.149 9(4)	0.781 9(4)
C(20)	0.442 8(5)	0.139 7(4)	0.840 3(4)
C(21)	0.371 6(4)	0.041 4(4)	0.834 8(4)
C(22)	0.376 8(5)	–0.045 5(4)	0.769 1(4)
C(23)	0.457 1(5)	–0.035 0(4)	0.712 2(4)
H(5)	0.6121	0.0172	0.6081
H(7)	0.7354	0.3284	0.5763
H(8A)	0.9093	0.2903	0.5179
H(8B)	0.7722	0.2551	0.4262
H(9A)	0.9878	0.1253	0.4721
H(9B)	0.8586	0.0607	0.5018
H(10A)	1.0872	0.1767	0.6546
H(10B)	1.0414	0.0494	0.6577
H(13)	1.0947	0.3261	0.8158
H(14)	1.2544	0.3625	0.9808
H(15)	1.3260	0.1898	1.1275
H(16)	1.1772	0.0056	1.0438
H(17)	1.0324	0.0017	0.8879
H(19)	0.5810	0.2404	0.7950
H(20)	0.4368	0.1979	0.9026
H(21)	0.3041	0.0216	0.8828
H(22)	0.3139	–0.1371	0.7668
H(23)	0.4467	–0.1027	0.6564

anisotropic temperature factors for the non-hydrogen atoms. At convergence, the conventional and weighted *R*-factors were 0.0568 and 0.0499 respectively. The application of the weighting scheme was found to give satisfactory variances of $|F|$ analysed both in ranges of $|F|$ and sin θ. The final difference Fourier map contained no features greater than ±0.32 e⁻ Å⁻³ with a general noise level of ±0.15 e⁻ Å⁻³. The final values of the refined fractional atomic co-ordinates are listed in Table 6. Tables of the thermal vibrational parameters and the observed and calculated structure factor amplitudes have been deposited as Supplementary Publication No. SUP. 23602 (11 pp).*

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* For details of the Supplementary publications scheme, see 'Instructions for Authors (1983),' *J. Chem. Soc., Perkin Trans. 1*, 1983, Issue 1.

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