Ozonolysis of Cyclopentadiene Derivatives. Competitive Participation of [3 + 2] and [3 + 4] Cycloadditions of Carbonyl Oxide Moieties to α,β-Unsaturated Carbonyl Groups

Mitsuyuki Mori,[a] Hideyuki Yamakoshi,[a] Masatomo Nojima,*[,a] Shigekazu Kusabayashi,[a] Kevin J. McCullough,*[,b] Karl Griesbaum,*[,c] Petra Krieger-Beck[c] and In-Chan Jung[c]

[a] *Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan*
[b] *Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, UK*
[c] *Engler-Bunte-Institut, Bereich Petrochemie, Universität Karlsruhe (TH), D-7500 Karlsruhe, Germany*

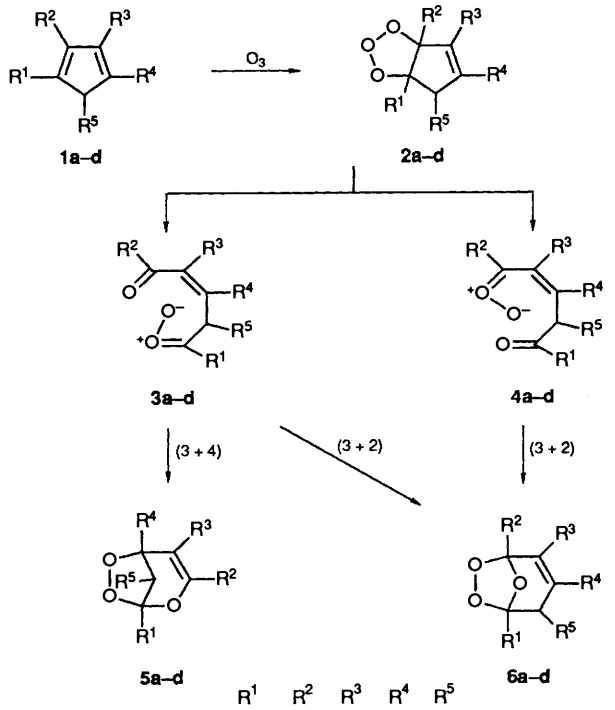
Reactions between cyclopenta-1,3-dienes **1a–i** and ozone, conducted in a variety of solvents including diethyl ether, pentane, CCl_4, CH_2Cl_2, CF_3CH_2OH, AcOH, and MeOH, afforded predominantly monomeric ozonolysis products consisting of either bicyclic endoperoxides **5** containing a 1,2,4-trioxepine ring, or unsaturated bicyclic ozonides **6**, or mixtures of compounds **5** and **6**. From their molecular structures, the novel bicyclic endoperoxides **5** are considered to result from intramolecular recombination of the carbonyl oxide and enone moieties, generated specifically from only one of the two possible decomposition modes of the primary ozonide, *via* stepwise [3 + 4] cycloaddition processes. The product composition was found to be sensitive to the nature of the substituents and the substitution pattern in the cyclopentadiene substrate, and the ozonolysis solvent. In general, protic solvents tended to assist the formation of the endoperoxides **5**. The isomeric peroxides **5** and **6** could, in several instances, be interconverted by treatment with acid catalysts like CF_3CO_2H, or even silica gel.

In the concerted reactions between 4π 1,3-dipoles and dipolarophiles having 4π electrons, the [3 + 4] mode of cycloaddition is thermally disallowed by orbital symmetry. As a consequence, the alternative [3 + 2] mode is generally preferred.[1] Recently, however, Huisgen reported that reaction of thiocarbonyl ylide with tetracyanoethylene proceeds in a stepwise fashion to provide the [3 + 4] cycloadduct together with the expected [3 + 2] cycloadduct.[2] Mayr has also found that both *C,N*-diphenylnitrone and 1,3-diphenyl-2-azaallyl anion undergo [3 + 4] cycloadditions with 3,3,4,4,5,5-hexamethyl-1,2-dimethylenecyclopentane which is highly substituted at the non-terminal positions.[3] It appears, therefore, that under certain favourable circumstances 1,3-dipoles can participate in non-concerted, as well as concerted, cycloaddition reactions and thereby provide direct synthetic routes to the corresponding seven-membered ring compounds.

In this respect, cycloadditions of carbonyl oxides to α,β-unsaturated carbonyl compounds† could produce the novel 1,2,4-trioxepines[5] rather than the more conventional isomeric 3-vinyl-1,2,4-trioxolanes. We report herein that ozonolyses of a number of substituted cyclopenta-1,3-dienes, particularly in protic solvents, afforded products which were formally derived from [3 + 4] cycloaddition processes.[6] Furthermore, it has been found that certain unsaturated ozonides **6**, obtained directly from the ozonolyses of cyclopenta-1,3-dienes, can subsequently undergo acid-catalysed rearrangement to give the corresponding isomeric 1,2,4-trioxepines **5**.

Results and Discussion

Ozonolysis of Cyclopenta-1,3-dienes.—Reactions of 1,4-diphenylcyclopenta-1,3-diene **1a** with ozone (1 mol equiv.) in various solvents including CCl_4, CH_2Cl_2, CF_3OH–CH_2Cl_2, and AcOH–CH_2Cl_2 afforded a 1:1 mixture of two isomeric peroxides (~40% yield), which were readily separated by column chromatography on silica gel (Scheme 1 and Table 1).



	R^1	R^2	R^3	R^4	R^5
a;	Ph	H	H	Ph	H
b;	Ph	H	Ph	Ph	H
c;	Ph	Ph	Ph	Ph	H
d;	H	Ph	Ph	Ph	H
e;	Ph	Ph	Ph	Ph	Ph
f;	Ph	Ph	Ph	Ph	OAc
g;	Me	Ph	Ph	Me	H
h;	Me	Me	Me	Me	Me
i;	Me	Me	Me	Me	H

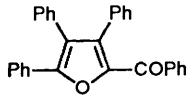
Scheme 1

† The intermolecular combination of carbonyl oxides and α,β-unsaturated carbonyl compounds generally proceeds *via* conventional concerted [3 + 2] cycloaddition processes. Thus, the ozonolysis of 2,3-di-*tert*-butylbuta-1,3-diene on polyethylene, which proceeds selectively through formaldehyde *O*-oxide and *tert*-butyl 1-*tert*-butylvinyl ketone, produces the corresponding ozonide in good yield.[4a] Similarly, the carbonyl oxides derived from the ozonolysis of vinyl ethers react with a variety of α,β-unsaturated compounds, yielding exclusively the corresponding α-vinyl ozonides.[4b]

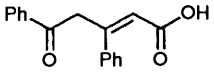
On the basis of ^1H and ^{13}C NMR spectra, the first component eluted from the column was identified as the 1,2,4-trioxepine **5a**, and the second as the 3-vinyl-1,2,4-trioxolane (α-vinyl ozonide) **6a**.*

The ozonolysis of compound **1a** should, in principle, give rise to two carbonyl oxide intermediates **3a** and **4a**,[9] either of which could subsequently produce the bicyclic ozonide **6a** by normal intramolecular [3 + 2] cycloaddition processes. Intermediate **3a** has, however, the additional option of being able to participate in a stepwise intramolecular [3 + 4] addition leading directly to the bicyclic endoperoxide **5a**. If the intermediate **3a** could adopt a more extended *s-trans* conformation, in which the carbonyl oxide would be oriented away from the carbonyl oxide carbon (Fig. 1), the alternative stepwise process would become increasingly more favourable.

The substituents of cyclopenta-1,3-diene derivatives **1b–i** were found to play an important role in determining the outcome of the reaction (Table 1). Ozonolysis of 1,2,4-triphenylcyclopenta-1,3-diene **1b** afforded a mixture of two isomeric peroxides **5b** and **6b**, consistent with a selective attack of ozone at the less hindered double bond of compound **1b**. When the ozonolysis of compound **1b** was carried out in CCl_4, ozonide **6b** was obtained as the sole peroxidic product, whereas the 1,2,4-trioxepine **5b** was the major product from reactions in protic solvent systems such as CF_3CH_2OH–CH_2Cl_2 and AcOH–CH_2Cl_2. Although the ozonide **6b** was still the major product (34% yield) with CH_2Cl_2 as solvent, significant quantities of the isomeric trioxepine **5b** (17% yield) were also produced. The product composition from the ozonolysis of 1,2,3,4-tetraphenylcyclopenta-1,3-diene **1c** exhibited similar variations with solvent; the ratio of products **5c**:**6c**, which was 1:7 in CCl_4, increased to ~3:7 in more polar media such as CH_2Cl_2, CF_3CH_2OH–CH_2Cl_2, and AcOH–CH_2Cl_2. In the case of substrate **1c**, 2-benzoyl-3,4,5-triphenylfuran **7** was also produced in a significant amount (Table 1). As determined by ^1H NMR spectroscopic analysis, it was found that the ratios of the isomeric peroxides **5b**:**6b**, and **5c**:**6c** before and after chromatography on silica gel remained essentially constant, suggesting that there had been no significant interconversion within the respective pairs of isomers.



7



8

Table 1 Ozonolysis of cyclopenta-1,3-diene derivatives

Substrate	Solvent	Reaction temp. (T/°C)	Products (% yield)[a]
1a	CCl_4	0	**5a** (16), **6a** (17)
1a	CCl_4[b]	0	**5a** (21), **6a** (7)
1a	CH_2Cl_2	0	**5a** (20), **6a** (20)
1a	CF_3CH_2OH[c]	0	**5a** (21), **6a** (19)
1a	AcOH[c]	0	**5a** (19), **6a** (19)
1a	MeOH	0	**5a** (21), **6a** (11)
1b	CCl_4	0	**6b** (56)
1b	CH_2Cl_2	0	**5b** (17), **6b** (34)
1b	CF_3CH_2OH[c]	0	**5b** (36), **6b** (12)
1b	AcOH[c]	0	**5b** (30), **6b** (16)
1b	MeOH[c]	0	**5b** (34), **6b** (8)
1c	CCl_4	20	**5c** (5), **6c** (33), **7** (29)
1c	CH_2Cl_2	20	**5c** (8), **6c** (19), **7** (26)
1c	CF_3CH_2OH[c]	20	**5c** (13), **6c** (31), **7** (10)
1c	AcOH[c]	20	**5c** (15), **6c** (34), **7** (8)
1c	MeOH[c]	20	**5c** (18), **6c** (6), **7** (19)
1e	CH_2Cl_2	20	**6e** (29)
1e	CF_3CH_2OH[c]	20	**6e** (43)
1e	AcOH[c]	20	**6e** (52)
1e	MeOH[c]	20	**6e** (48)
1f	CH_2Cl_2	20	**6f** (39)[d]
1f	CF_3CH_2OH[c]	20	**6f** (30)[e]
1f	AcOH[c]	20	**6f** (31)[e]
1g	Et_2O	0	**5g** (40)[f]
1g	CCl_4	0	**5g** (61)[g]
1g	CH_2Cl_2	0	**5g** (47)
1g	CF_3CH_2OH[c]	0	**5g** (51)
1g	AcOH[c]	0	**5g** (49)
1g	MeOH[c]	0	**5g** (38)
1h	Et_2O	−70	**5h** (24), **6h** (48)[f,h]
1h	CH_2Cl_2	−70	**5h** (11), **6h** (41)[f,h]
1h	MeOH[i]	−70	**5h** (10), **6h** (24)[f]
1h	CF_3CH_2OH[i]	−70	**5h** (10), **6h** (41)[f]
1h	AcOH[i]	−70	**5h** (7), **6h** (25)[f]
1i	Et_2O	−70	**5i** (3), **6i** (13)[f,h]
1i	CH_2Cl_2	−70	**5i** (4), **6i** (16)[f,h]
1i	Pentane	−78	**5i** (10), **6i** (15)[h]
1i	Polyethylene	−78	**10i** (26)
1i	CF_3CH_2OH[i]	−70	**5i** (9), **6i** (30)[f]
1i	MeOH[i]	−70	**5i** (2), **6i** (15)[f]

[a] Isolated yield. [b] The reaction in the presence of 0.2 mol equiv. of triethylamine. [c] Methylene dichloride was used as co-solvent (67 vol%). [d] A 5:3 mixture of two stereoisomeric ozonides. [e] The ratio of the two isomers was 4:1. [f] The ^1H NMR spectrum of the crude mixture of the products showed the presence of only ozonide **6g**, **h** or **i**. [g] The **5g**:**6g** ratio in the crude products was 1:1. [h] The yields of **5h**, **i** and of **6h**, **i** were based on the amount of ozone (0.7 mol equiv. of **1h**, **i**) used. [i] Diethyl ether was used as co-solvent (67 vol%).

The predominant formation of ozonides **6b**, **c** from the ozonolyses of cyclopentadienes **1b**, **c** suggests that in non-polar solvent, the corresponding carbonyl oxide intermediates **3b**, **c** must adopt mainly *s-cis* conformations which presumably minimize steric interactions between adjacent phenyl substituents and appear to be particularly favourable arrangements for concerted [3 + 2] cycloadditions. In protic solvents, however, solvation of the most polar carbonyl oxide moiety by the solvents should enhance the electrophilicity of the carbonyl oxide carbon in the intermediates **3b**, **c**, thereby facilitating the intramolecular cyclization *via* the intermediates **9b**, **c** to yield either the endoperoxides **5b**, **c** or the ozonides **6b**, **c** (Scheme 2). Treatment of either product **5c** or **6c** with CF_3CO_2H (TFA) (1 mol equiv.) in CH_2Cl_2 at −70 °C for 30 min produced an equilibrium mixture of the isomeric peroxides, **5c** and **6c**, in the ratio 3:2, respectively (recovered in 60–70% yield). This equilibration process requires that the postulated intermediate hydroperoxy allylic carbocation **9c** may subsequently undergo ring closure in either direction.[10] Although both compounds **5b** and **6b** are stable under the similar acidic conditions, peroxides

* The isomeric bicyclic peroxides **5** and **6** generally gave ^{13}C and ^1H NMR spectra which contained several characteristic differences as exemplified by **5a** and **6a**. The deshielding effect of the oxygen atom at the 2-position in product **5a** gave rise to pronounced differences between ^{13}C NMR chemical shifts for the vinyl carbons in the two compounds;[7] the signals attributable to C-3 and C-4 in compound **5a** appeared at δ_C 146 and 108, respectively, whereas the vinyl carbons (C-2 and C-3) of compound **6a** resonated in the normal region for sp^2 carbon centres. Consistent with the structures of the bicyclic peroxides **5a** and **6a**, the bridgehead carbons of compound **5a**, which are in quite distinctive chemical environments, showed more substantial differences in ^{13}C NMR chemical shift (δ_C 108 and 83, respectively) than the corresponding bridgehead carbons in compound **6a** which are located within a 1,2,4-trioxolane ring (δ_C 98 and 107). In the ^1H NMR spectra of compounds **5a** and **6a**, the magnitude of the geminal coupling constant for the protons at the 8-position of the former [~12 Hz]; the coupling constant between the geminal protons at the 16-position in tetracyclo[7.6.1.$0^{2,7}$.$0^{10,15}$]hexadeca-2,4,6,10,12,14-tetraen-8-ol is as small as 10.7 Hz (ref. 8*a*)] was found to be systematically smaller than that observed for those at the 4-position of the latter [~18 Hz; the coupling constant between the geminal protons in 2,3-diphenylindene ozonide is 18 Hz (ref. 8*b*)].

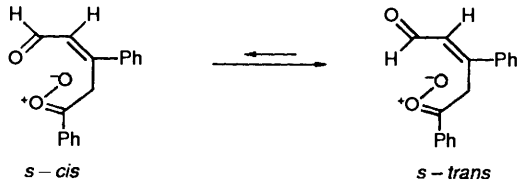
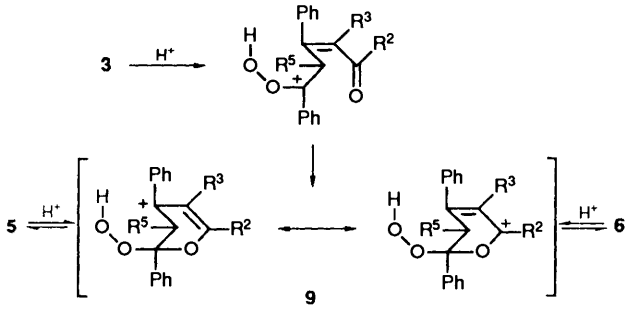


Fig. 1 Conformation of carbonyl oxide **3a**



Scheme 2

5a and **6a** undergo complete decomposition, providing a complex mixture of unidentified products.

Since ozonides **6b**, **c** are the predominant products from the ozonolyses of substrates **1b**, **c** in CCl_4 and the peroxides **5a** and **6a** are very labile toward TFA, the formation of a 1:1 mixture of compounds **5a** and **6a** from the reaction of substrate **1a** with ozone in CCl_4 might simply be due to secondary rearrangement of the ozonide **6a** catalysed by the presence of adventitious acid. When the ozonolysis of compound **1a** in CCl_4 was repeated in the presence of 0.2 mol equiv. of triethylamine, the crude products, as analysed by ^1H NMR spectroscopy, included the isomeric peroxides **5a** and **6a** in the ratio 3:1 (~30% yield). Subsequent column chromatography on silica gel, however, resulted in the isolation of a 1:1 mixture of products **5a** and **6a** in 27% yield. Thus, protic solvents and/or adventitious acid catalysts are not required for the formation of [3 + 4] cycloaddition product **5a** from compound **1a**, though the trioxepine **5a** appears to be less stable than the ozonide **6a** on silica gel. Consistent with the latter observation, treatment of compound **5a** with silica gel in CCl_4 for 1.5 h resulted in the formation of ozonide **6a** in 80% yield. In general, however, the **5**:**6** ratios were not significantly changed following rapid column chromatography of the product mixtures on silica gel.

The ozonide **6a** was unstable towards triethylamine, rearranging to 4-benzoyl-3-phenylbut-2-enoic acid **8** on treatment with triethylamine (0.3 mol equiv.) in $CDCl_3$. The rearrangement process is probably initiated by abstraction of the most acidic proton at the 1-position as noted for the related peroxide system.[11] Under similar conditions, the isomeric peroxide **5a**, lacking corresponding acidic hydrogens, remained intact.

To obtain information for the direction in the cleavage of the primary ozonide **2a**, the reaction of substrate **1a** was conducted in MeOH–CH_2Cl_2. Although the ^1H NMR spectra of the crude product provided evidence for the formation of the methanol-derived product (δ 3.28, s, OMe), it could not be isolated in a pure state. On changing the ozonolysis solvent from CH_2Cl_2 to MeOH–CH_2Cl_2 the yield of ozonide **6a** was significantly decreased (19 to 11%), yet the yield of endoperoxide **5a** remained unchanged (20 to 21%). This may suggest that the ozonolysis intermediate **3a** leading to secondary ozonide **6a** was being selectively captured by MeOH. Similarly, only the yields of the corresponding ozonides **6b**, **c** from the ozonolyses of substrates **1b**, **c** in MeOH–CH_2Cl_2 showed any marked decrease (Table 1).

Since ozonolysis of 1,2,3-triphenylcyclopenta-1,3-diene **1d** in various solvents resulted in the formation of a complex mixture of unidentified products, it is deduced that substituents at both the 1-and 4-position in cyclopentadienes **1** are necessary in order to produce the isolable bicyclic peroxides **5** and/or **6**.

Irrespective of the solvent, ozonolyses of 1,2,3,4,5-pentaphenylcyclopenta-1,3-diene **1e** and of 5-acetoxy-1,2,3,4-tetraphenylcyclopenta-1,3-diene **1f** gave exclusively the corresponding bicyclic ozonides, **6e** and **6f**, respectively (Table 1). These ozonides were found to be remarkably stable towards acids, *e.g.* treatment of ozonides **6e**, **f** with either TFA (2 mol equiv.) or $ClSO_3H$ (0.1 mol equiv.) in CH_2Cl_2 did not induce rearrangement or decomposition.

In marked contrast, the ozonides **6g–i** obtained from the ozonolyses of 1,4-dimethylcyclopenta-1,3-diene derivatives **1g–i** were unstable even on silica gel. Analysis of the crude product mixture derived from 1,4-dimethyl-2,3-diphenylcyclopenta-1,3-diene **1g** in diethyl ether by ^1H and ^{13}C NMR spectroscopy indicated that the ozonide **6g** had been formed exclusively (see Experimental section). When purification of the crude product mixture was attempted by column chromatography on silica gel, however, only the isomeric trioxepine **5g** was actually isolated.

In an attempt to provide some rationale for the extreme position of the equilibrium between the pairs of isomers **5g**/**6g**, which is in contrast to that of isomers **5a**/**6a**, the structure of the crystalline trioxepine **5g** was determined by X-ray crystallography. The molecular structure of **5g** together with the numbering system adopted in the structural study is illustrated in Fig. 2. In addition to confirming the general features of the bicyclic ring system and its relative stereochemistry, the crystal structure of compound **5g** reveals that the bond distances and angles around the bicyclic skeleton are within the normal ranges, except for the O–O bond distance [1.513(5) Å], which is significantly greater than that found in simple monocyclic peroxide systems (1.470 Å).[12] Since, however, this value is in reasonable agreement with that observed previously in other rigid [2.2.1] and [3.2.1] endoperoxides,[13] it is probably not indicative of excessive strain within the bicyclic ring system of compound **5g** though the O–O bond distances in polycyclic ozonides are generally found to be closer to the expected value.[14] Inspection of molecular models of products **5g** and **6g** suggests that the driving force for the isomerization of ozonide **6g** to compound **5g** could be relief of steric compression between the two adjacent phenyl groups, and also between the bridgehead phenyl group and the nearest oxygen atom of the peroxide bridge in ozonide **6g**. Similar arguments may also be true for the transformation of compound **5a** to ozonide **6a** since the ozonide **6a** has only one bridgehead phenyl substituent whereas the endoperoxide **5a** has two. In general, for those systems which undergo acid catalysed isomerisation without excessive decomposition, the position of the equilibrium between the endoperoxide **5** and the ozonide **6** probably reflects the more favourable packing arrangement of the substituents around the respective bicyclic ring systems. Consequently, the equilibrium ratio of 3:2 observed in the isomerisation of **5c** and **6c** is consistent with the fact that the substitution patterns in these isomers are similar. On the other hand, bulky phenyl and acetoxy substituents located on the methano bridge of the endoperoxides **5e**, **f** would give rise to unfavourable intramolecular steric interactions which would destabilise **5e**, **f** with respect to the corresponding ozonides **6e**, **f**. The endoperoxide system does, however, appear to be able to accommodate a methyl substituent at the methano bridge since ozonide **6h** readily rearranges to **5h** in the presence of silica gel (*vide infra*).

The **5g**:**6g** ratios were subject to solvent effects; ozonolysis of compound **1g** in CCl_4 yielded a 1:1 mixture of products **5g** and **6g**, whereas in polar solvents the isomeric endoperoxide **5g** was

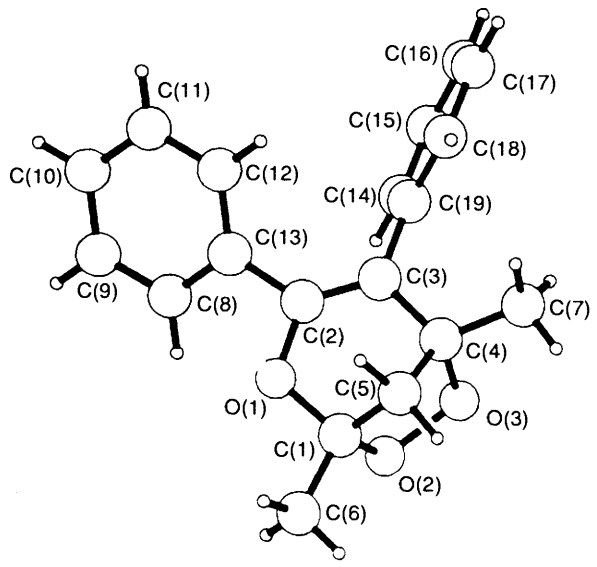


Fig. 2 The molecular structure of bicyclic endoperoxide **5g**

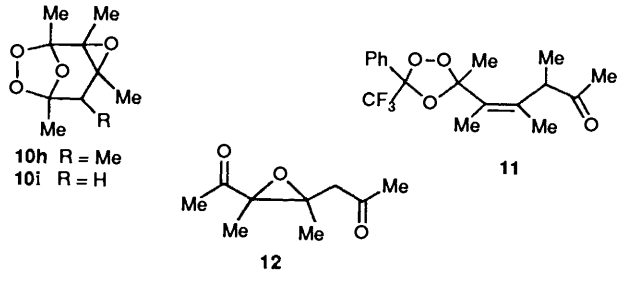


Table 2 Reaction of cyclic peroxides **5**, **6** and **10i** with triphenylphosphine[a]

Substrate	Reaction time (t/h)	Products (% yield)
5a	6	**13a** (25)[b]
6a	0.3	**14a** (100)[c,d]
5b	2	**13b** (75)
6b	0.5	**14b** (90)[c]
5c	24	**13c** (45), **14c** (35)
6c	24	**14c** (100)
6e	15	**14e** (100)
6f[e]	24	**14f** (89)
6f[f]	24	**14f** (37)
5g	24	**14g** (100)[c]
5h	24	**14h** (60)[c,g]
6h	24	**14h** (44)[c]
5i[h]	24	**14i** (40)[c,g]
6i	24	**14i** (24)[c]
6i	4[i]	**14i** (56)[c]
10i	48	**12** (90)[c,g]

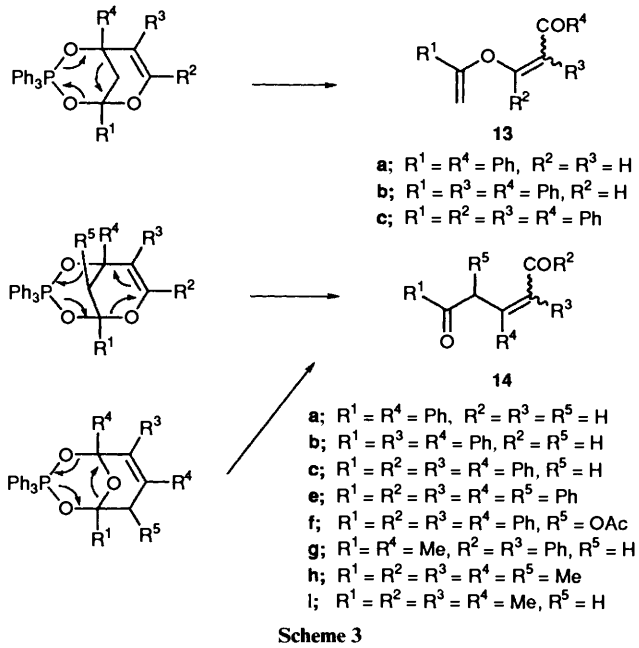
[a] Reaction with 1 mol equiv. of triphenylphosphine in benzene at room temp. unless otherwise noted. [b] The ^{1}H NMR spectra of the crude products showed the formation of a variety of products including dione **14a** together with the ether **13a**. [c] Reaction in $CDCl_3$. [d] The labile dione **14a** could not be isolated. [e] The major isomer. [f] The minor isomer. [g] The yield was determined from the ^{1}H NMR spectra of the crude products. [h] A 1:1 mixture of peroxides **5i** and **6i**. [i] Reaction at 50 °C.

the sole product. Similar solvent effects had been noted previously in the reaction of formaldehyde *O*-oxide with a keto aldehyde; in diethyl ether the keto ozonide, *via* a concerted [3 + 2] process, was produced but in CH_2Cl_2 the 1,2,4,6-tetraoxepane derivative, resulting from a stepwise [3 + 2 + 2] process, was obtained instead.[15] Since ozonide **6g** is very acid labile, however, the alternative possibility that, in a solvent system like AcOH–CH_2Cl_2, **6g** is formed initially and subsequently rearranges rapidly to compound **5g**, cannot be discounted.

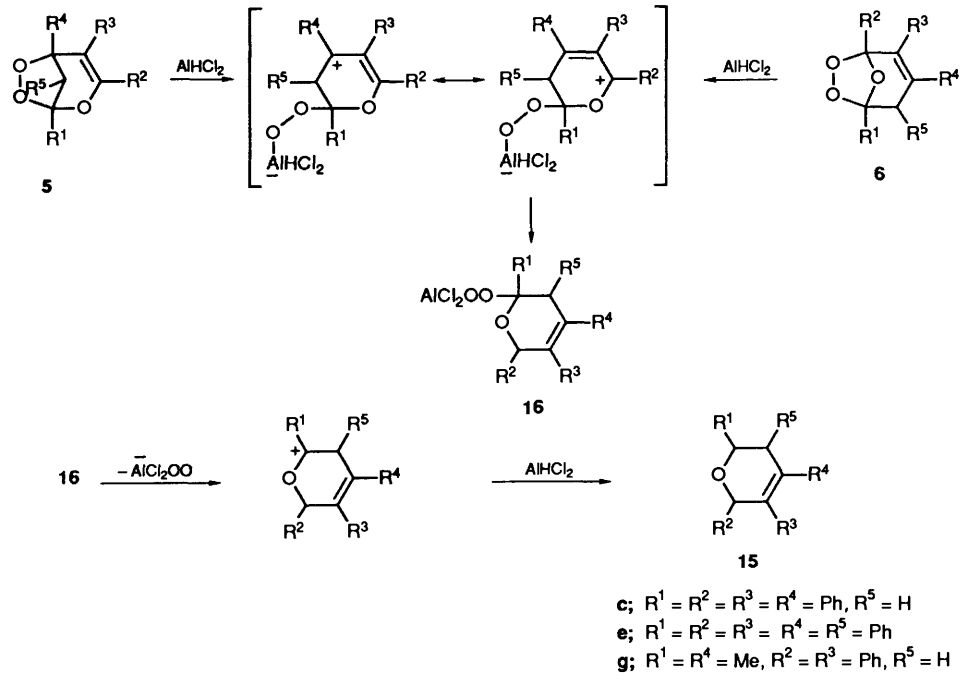
Compared with compound **6g**, ozonide **6h**, obtained from the ozonolysis of 1,2,3,4,5-pentamethylcyclopenta-1,3-diene **1h** was found to be more stable towards silica gel. Irrespective of the solvent, ozonolyses of substrate **1h** produced exclusively ozonide **6h**, which on attempted isolation by column chromatography on silica gel underwent partial isomerization, with the ozonide **6h** (~40% yield) being eluted first followed by the trioxepine **5h** (~20% yield). Treatment of ozonide **6h** with silica gel in pentane for 1 h resulted in the production of the isomer **5h** (68% yield). Reaction of compound **6h** with *m*-chloroperbenzoic acid (*m*-CPBA) in CH_2Cl_2 afforded the epoxy ozonide **10h**, as expected. When the ozonolysis of compound **1h** was conducted in diethyl ether containing α,α,α-trifluoroacetophenone, the monocyclic ozonide **11** (36% yield) was obtained together with ozonide **6h** (35% yield).

The ozonolysis of 1,2,3,4-tetramethylcyclopenta-1,3-diene **1i** in CF_3CH_2OH–Et_2O gave the corresponding ozonide **6i** as the sole detectable bicyclic peroxide. As with compound **6h** above, ozonide **6i** undergoes partial isomerization either on column chromatography on silica gel [**5i** (9% yield), **6i** (30% yield)] or on treatment with a slurry of silica gel in pentane for 1 h [1:1 mixture of **5i** and **6i** (42% yield)]. With aprotic ozonolysis solvents, the yield of unidentified polymeric products tended to increase with a concomitant decrease in the yield of **6i** (Table 1). Instead of the expected bicyclic peroxides **5i** or **6i**, ozonolysis of compound **1i** on polyethylene gave the epoxy ozonide **10i** (~26% yield), whose structure was established by a combination of ^{1}H and ^{13}C NMR spectroscopy, independent preparation of compound **10i** by epoxidation of the unsaturated ozonide **6i**, and the nature of the epoxy diketone **12** obtained on reduction of tricycle **10i**.

Reactions of Bicyclic Peroxides, **5** *and* **6**, *with Triphenylphosphine.*—In addition to marked differences in their respective spectroscopic properties, the bicyclic isomeric peroxides **5** and **6** could, in some cases, be distinguished by their reaction with triphenylphosphine. Treatment of compound **5c** with 1 mol equiv. of triphenylphosphine in benzene gave a mixture of



Scheme 3



Scheme 4

Table 3 Reduction of bicyclic peroxides, **5** or **6**, with $AlHCl_2$[a]

Peroxide	Product (% Yield)	Ratio of two isomers
5c	**15c** (30)	63:37
6c	**15c** (32)	63:37
6e	**15e** (31)	100:0
5g	**15g** (66)	77:23

[a] Reaction with 8 mol equiv. of $AlHCl_2$ in diethyl ether at 20 °C for 1 h.

ketone **13c** and diketone **14c** in yields of 45 and 35%, respectively, while only diketone **14c** was obtained from ozonide **6c**. Similar differences in the behaviour were also observed for the isomeric pairs **5a**, **b** and **6a**, **b** (Table 2). The aforementioned results can be rationalized in terms of the insertion/cyclic elimination mechanism outlined in Scheme 3. From trioxepines **5g–i**, however, only the corresponding diketones **14g–i** were obtained in each case.

Reactions of Bicyclic Peroxides, **5** *and* **6**, *with* $AlHCl_2$.—$AlHCl_2$ is well known to act as a Lewis acid and a hydride reducing agent.[16] In accordance with this, treatment of either ozonide product **5c** or **6c** with $AlHCl_2$ (8 mol equiv.) in diethyl ether gave 2,3,4,6-tetraphenyl-5,6-dihydro-2*H*-pyran **15c** as a mixture of two stereoisomers (Table 3 and Scheme 4). Reductions of other bicyclic peroxides, **5g** and **6e**, also proceeded in a similar fashion to give in each case the corresponding 5,6-dihydro-2*H*-pyran derivatives **15g**, **e** in moderate yields. To account for the formation of the 5,6-dihydro-2*H*-pyran **15** from substrate **5** or **6**, a mechanistic sequence involving an initial heterolytic cleavage of the C–O bond of the peroxide bridge would be the most probable (Scheme 4).[16]

Experimental

General.—^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ (unless otherwise noted) with $SiMe_4$ as standard, with a JNM-PS-100 spectrometer and a JEOL JNM-GSX-400 spectrometer, respectively, or with a Bruker AC 250 spectrometer. *J* Values are given in Hz. Mass data were obtained with a Hitachi RMU-6H or Hewlett-Packard 5985B spectrometer, and IR spectra with an Hitachi 215 spectrometer.

*Preparation of Cyclopenta-*1,3*-dienes* **1a–i**.—The substrates 1,2,3,4-tetraphenyl-**1c**,[17] 1,4-dimethyl-2,3-diphenyl-**1g**,[18] 1,2,4-triphenyl-**1b**,[19] 1,4-diphenyl-**1a**,[20] 1,2,3-triphenyl-**1d**,[21] 1,2,3,4,5-pentaphenyl-**1e**,[22] 1,2,3,4,5-pentamethyl-**1h**,[23] and 1,2,3,4-tetramethyl-cyclopenta-1,3-diene **1i**[24] were prepared by reported methods. 5-Acetoxy-1,2,3,4-tetraphenylcyclopenta-1,3-diene **1f** was prepared by treatment of 2,3,4,5-tetraphenylcyclopenta-2,4-dienol with acetyl chloride in diether ether in the presence of pyridine.[25] Compound **1f** had m.p. 185–187 °C (from diethyl ether–hexane); δ_H 2.02 (3 H, s), 5.12 (1 H, s) and 6.9–7.5 (20 H, m).

*Ozonolysis of Cyclopenta-*1,3*-dienes* **1a–f**.—To a solution of a cyclopenta-1,3-diene **1** (300 mg) in an appropriate solvent (30 cm^3) was passed a slow stream of ozone (1 mol equiv.) (20 mmol of ozone and 50 dm^3 of oxygen h^{-1}) at 0 or 20 °C (see Table 1). When the solvent system was a 1:2 mixture of a protic solvent and CH_2Cl_2, the reaction mixture was poured into ice-cold aq. $NaHCO_3$ and extracted with diethyl ether. When the solvent was an aprotic one, the solvent was evaporated off immediately after the reaction. Then, the products were separated by column chromatography [column, 2 × 50 cm; silica gel (20 g); elution with benzene–hexane (1:1)]. The endoperoxide **5** was eluted first and then the ozonide **6**. They were purified by recrystallization from methanol. From compound **1c** was obtained also 2-benzoyl-3,4,5-triphenylfuran **7** (Table 1).

1,5-*Diphenyl*-2,6,7-*trioxabicyclo*[3.2.1]*oct*-3-*ene* **5a**. M.p. 95–96 °C (Found: C, 76.4; H, 5.2. $C_{17}H_{14}O_3$ requires C, 76.69; H, 5.26%); δ_H 3.09 (1 H, dd, *J* 12 and 1.5), 3.24 (1 H, d, *J* 12), 5.54 (1 H, dd, *J* 6 and 1.5), 6.78 (1 H, d, *J* 6) and 7.2–7.7 (10 H, m); δ_C 51.08, 83.02, 108.56 (2 C), 125.79–135.52 (12 C) and 145.60.

1,4,5-*Triphenyl*-2,6,7-*trioxabicyclo*[3.2.1]*oct*-3-*ene* **5b**. M.p. 105–108 °C (Found: C, 80.3; H, 5.2. $C_{23}H_{18}O_3$ requires C, 80.70; H, 5.26%); δ_H 3.12 (1 H, d, *J* 11), 3.45 (1 H, d, *J* 11), 6.79 (1 H, s) and 6.9–7.7 (15 H, m); δ_C 53.20, 85.77, 108.30, 122.39, 126.09–135.71 (19 C) and 143.83.

1,3,4,5-*Tetraphenyl*-2,6,7-*trioxabicyclo*[3.2.1]*oct*-3-*ene* **5c**. M.p. 125–127 °C (Found: C, 83.3; H, 5.3%; M^+, 418. $C_{29}H_{22}O_3$ requires C, 83.23; H, 5.20%); δ_H 3.63 (1 H, d, *J* 11), 4.17 (1 H, d, *J* 11) and 6.8–8.1 (20 H, m); δ_C 51.42, 87.45, 107.78, 118.75, 126.28–136.55 (24 C) and 150.38; ν_{max}(KBr)/cm^{-1} 1600, 1480, 1438, 1320, 1280, 1221, 1141, 1096, 1060, 1024, 920, 877, 742 and 680.

3,5-*Diphenyl*-6,7,8-*trioxabicyclo*[3.2.1]*oct*-2-*ene* **6a**. M.p. 103–105 °C (Found: C, 76.5; H, 5.2. $C_{17}H_{14}O_3$ requires C, 76.69; H, 5.26%); δ_H 3.24 (1 H, dd, *J* 18 and 1.5), 3.27 (1 H, dd, *J* 18 and 1.5), 6.21 (1 H, d, *J* 4), 6.45 (1 H, dt, *J* 4 and 1.5) and 7.2–7.7 (10 H, m); δ_C 39.02, 98.39, 106.84 and 119.31–138.39 (14 C).

2,3,5-*Triphenyl*-6,7,8-*trioxabicyclo*[3.2.1]*oct*-2-*ene* **6b**. M.p. 109–112 °C (Found: C, 80.3; H, 5.3. $C_{23}H_{18}O_3$ requires C, 80.70; H, 5.26%); δ_H 3.15 (1 H, d, *J* 18), 3.37 (1 H, d, *J* 18), 6.30 (1 H,), 7.1–7.2 (10 H, m), 7.4–7.5 (3 H, m) and 7.6–7.7 (2 H, m); δ_C 42.07, 102.45, 107.16 and 125.72–138.56 (20 C).

1,2,3,5-*Tetraphenyl*-6,7,8-*trioxabicyclo*[3.2.1]*oct*-2-*ene* **6c**. M.p. 116–119 °C (Found: C, 83.3; H, 5.3%; M^+, 418. $C_{29}H_{22}O_3$ requires C, 83.23; H, 5.26%); δ_H 3.63 (1 H, d, *J* 18), 4.03 (1 H, d, *J* 18) and 6.8–8.1 (20 H, m); δ_C 42.11, 108.51, 109.03 and 125.89–139.57 (26 C); ν_{max}(KBr)/cm^{-1} 1485, 1440, 1355, 1320, 1222, 1160, 1105, 1000, 940, 918, 758 and 690.

1,2,3,4,5-*Pentaphenyl*-6,7,8-*trioxabicyclo*[3.2.1]*oct*-2-*ene* **6e**. M.p. 138–140 °C (Found: C, 84.1; H, 5.3. $C_{35}H_{26}O_3$ requires C, 85.02; H, 5.26%); δ_H 4.13 (1 H, s) and 6.7–7.4 (25 H, m); δ_C 57.46, 108.91, 110.86 and 125.32–139.61 (32 C).

4-*Acetoxy*-1,2,3,5-*tetraphenyl*-6,7,8-*trioxabicyclo*[3.2.1]*oct*-2-*ene* **6f**. (Minor isomer); m.p. 160–163 °C (Found: C, 77.8; H, 5.05. $C_{31}H_{24}O_5$ requires C, 78.15; H, 5.04%); δ_H 1.56 (3 H, s), 4.86 (1 H, s) and 7.1–8.0 (20 H, m); δ_C 19.86, 58.07, 106.56, 110.23, 125.98–140.76 (26 C) and 167.47; ν_{max}(KBr)/cm^{-1} 1770 and 1200.

4-*Acetoxy*-1,2,3,5-*tetraphenyl*-6,7,8-*trioxabicyclo*[3.2.1]*oct*-2-*ene* **6f**. (Major isomer); m.p. 152–154 °C (Found: C, 77.6; H, 5.1%); δ_H 1.62 (3 H, s), 4.32 (1 H, s) and 7.1–8.0 (20 H, m); δ_C 19.96, 57.58, 106.80, 111.11, 125.30–140.76 (26 C) and 168.20; ν_{max}(KBr)/cm^{-1} 1770 and 1200.

2-*Benzoyl*-3,4,5-*triphenylfuran* **7**. M.p. 165–167 °C (lit.,[26] 166.5–167 °C) (Found: C, 87.7; H, 5.1%; M^+, 400. Calc. for $C_{29}H_{20}O_2$: C, 86.97; H, 5.03%); ν_{max}(KBr)/cm^{-1} 1640, 1528, 1470, 1443, 1392, 1335, 1252, 1218, 1180, 1153, 1075, 1028, 1010, 997, 779, 761, 733 and 688.

Ozonolysis of 1,4-*Diphenylcyclopenta*-1,3-*diene* **1a** *in* CCl_4 *in the Presence of Triethylamine*.—A mixture of compound **1a** (218 mg, 1 mmol) and triethylamine (20 mg, 0.2 mmol) in CCl_4 (15 cm^3) was treated with ozone (1 mmol) at 0 °C. The reaction mixture was then poured into ice-cold aq. $NaHCO_3$ and was extracted with diethyl ether. The ^{1}H NMR spectrum of the mixture of the crude products showed the presence of compounds **5a** and **6a** in ~30% yield, the ratio of **5a**:**6a** being 3:1. Subsequent column chromatography on silica gel [elution with benzene–hexane (3:7)] gave a 1:1 mixture of compounds **5a** and **6a** (72 mg, 27%). A CCl_4 solution (15 cm^3) of this mixture of compounds **5a** and **6a** in the presence of silica gel (7 g) was stirred at 15 °C for 1.5 h. After filtration, the silica gel was washed with diethyl ether and the combined organic layers were concentrated. From the residue, compound **6d** was isolated in 61% yield (44 mg).

Reaction of Ozonide **6a** *with Triethylamine*.—Treatment of ozonide **6a** (44 mg, 0.18 mmol) with triethylamine (5 mg, 0.05 mmol) in $CDCl_3$ (5 cm^3) for 24 h, followed by conventional work-up, gave 90% yield (40 mg) of 4-benzoyl-3-phenylbut-2-enoic acid **8**.

Reaction of a 1:1 *Mixture of Compounds* **5a** *and* **6a** *with Triethylamine*.—A 1:1 mixture of compounds **5a** and **6a** (301 mg, 1.13 mmol) was treated with triethylamine (30 mg, 0.3 mmol) in $CDCl_3$ (1 cm^3). The ^{1}H NMR spectra of the reaction mixture showed that compound **6a** had been converted into acid **8**, while compound **5a** remained intact. After 15 min, the reaction mixture was poured into aq. $NaHCO_3$ and was extracted with diethyl ether. Then, the solvent was evaporated off and the residue was recrystallized from methanol to afford pure substrate **5a** (56 mg, 37%). From the aqueous layer was isolated compound **8** (66 mg, 50%).

A CCl_4 solution (15 cm^3) of compound **5a** (50 mg) in the presence of silica gel (7 g) was stirred at room temp. for 1 h. From the filtrate was isolated pure **6a** (45 mg, 80%).

4-*Benzoyl*-3-*phenylbut*-2-*enoic acid* **8**. M.p. 128–130 °C (from diethyl ether–hexane) (Found: C, 76.85; H, 5.25. $C_{17}H_{14}O_3$ requires C, 76.67; H, 5.31%); δ_H 4.87 (2 H, s), 6.43 (1 H, s), 7.3–7.8 (8 H, m) and 8.0–8.3 (2 H, m); ν_{max}(KBr)/cm^{-1} 3100–2300, 1680, 1608, 1230 and 1210.

TFA-Catalysed Interconversion of Isomers **5c** *and* **6c**.—To a solution of compound **5c** (105 mg, 0.25 mmol) in CH_2Cl_2 (5 cm^3) kept at −70 °C was added a solution of TFA (30 mg, 0.25 mmol) in CH_2Cl_2 (5 cm^3) and the reaction was continued at −70 °C for 30 min. Then, the reaction mixture was poured into ice-cold aq. $NaHCO_3$ and was extracted with diethyl ether. After evaporation of the solvent, the products were separated by column chromatography on silica gel [elution with benzene–hexane (1:1)]. The first fraction contained a 7:3 mixture of isomers **5c** and **6c** (74 mg, 70%). Treatment of compound **6c** with TFA in CH_2Cl_2 under the same conditions resulted in the isolation of a 7:3 mixture of isomers **5c** and **6c** (60%).

Ozonolysis of 1,4-*Dimethyl*-2,3-*diphenylcyclopenta*-1,3-*diene* **1g**.—An ethereal solution (20 cm^3) of compound **1g** (246 mg, 1 mmol) was treated with ozone (1 mol equiv.) at 0 °C. The ^{1}H and ^{13}C NMR spectra of the mixture of the crude products after evaporation of the solvent suggested the formation of ozonide **6g** in ~60% yield; 3,5-dimethyl-1,2-diphenyl-6,7,8-trioxabicyclo[3.2.1]oct-2-ene **6g** (not isolated in a pure state) had δ_H 1.57 (3 H, s), 1.63 (3 H, s), 2.32 (1 H, d, *J* 18), 2.80 (1 H, d, *J* 18) and 6.7–7.7 (10 H, m); δ_C 19.19, 22.02, 43.22, 108.26, 109.19, 127.17 (2 C), 127.22, 128.15, 128.21 (2 C), 128.37 (2 C), 129.09 (2 C), 129.51 and 130.32. However, by column chromatography on silica gel [elution with benzene–hexane (1:1)] only the 1,2,4-trioxepine **5g** (118 mg, 40%) was eluted. 1,5-*Dimethyl*-3,4-*diphenyl*-2,6,7-*trioxabicyclo*[3.2.1]*oct*-3-*ene* **5g** had m.p. 104–106 °C (from MeOH) (Found: C, 77.55; H, 6.2. $C_{19}H_{18}O_3$ requires C, 77.55; H, 6.12%); δ_H 1.24 (3 H, s), 1.77 (3 H, s), 2.58 (1 H, d, *J* 11), 2.97 (1 H, d, *J* 11) and 7.1–7.4 (10 H, m); δ_C 17.99, 19.86, 49.95, 81.99, 106.64, 117.77, 126.86–136.36 (12 C) and 149.77.

X-Ray Crystal Structure Determination of the Bicyclic Endoperoxide **5g**.—A single crystal of compound **5g** (from ethyl acetate–hexane, approximate size 0.3 × 0.7 × 0.5 mm), mounted in a Lindemann tube, was used for X-ray data collection.

Crystal data. $C_{19}H_{18}O_3$, M = 294.3, colourless prisms, monoclinic, space group *C*2/*c* (No. 15), *a* = 36.752(3), *b* = 5.8433(14), *c* = 16.4633(14) Å, *β* = 113.987(7)°, *V* = 3230.2(9) Å^3, *Z* = 8, D_c = 1.210 g cm^{-3}, *F*(000) 1248, *μ*(Mo-Kα) 0.76 cm^{-1}.

Data collection, structure solution and refinement. The intensity data were collected on a Enraf-Nonius CAD4 diffractometer over the hemisphere (*θ* range: 1.0–25.0°; *h*: 0 to +43, *k*: 0 to +6, *l*: −19 to +19) using Mo-Kα X-radiation (*λ* 0.710 693 Å) and *ω*–2*θ* scanning. Of the 1980 unique data measured, 1399 had $I > 2\sigma(I)$ and were used in subsequent

structural solution and refinement. The data were collected for Lorentz and polarization effects, but not for absorption. The structure was solved by direct methods (SHELXS86)[27a] and refined by full-matrix least-squares methods (SHELX76)[27a] using 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 with refined group isotropic temperature factors. At convergence, the discrepancy factors R and R_w were 0.056 and 0.067, respectively. The weighting scheme, $w^{-1} = [\sigma^2(F) + 0.000\,259(F)^2]$ was found to give satisfactory analyses of variance. The final difference Fourier map was essentially featureless (general noise level less than +0.24 e Å^{-3}). Incidental crystallographic calculations and compilation of tables were carried out using the computer program CALC and Fig. 2 was prepared using a locally modified version (Dr. J. A. Hunter, Heriot-Watt University) of PLUTO.[27c]

Ozonolysis of 1,2,3,4,5-*Pentamethylcyclopenta*-1,3-*diene* **1h**.—An ethereal solution (15 cm^3) of compound **1h** (324 mg, 2.4 mmol) was treated with ozone (0.7 mol equiv.) at −70 °C. After evaporation of the solvent, the products were separated by column chromatography on silica gel [elution with diethyl ether–hexane (8:92)]. The first fraction contained ozonide **6h** (175 mg, 48%). From the second fraction was obtained endoperoxide **5h** (85 mg, 24%).

Ozonide **6h** (240 mg, 1.3 mmol) was treated with silica gel (7 g) in pentane (15 cm^3) at 23 °C for 1 h. After filtration, the silica gel was washed with diethyl ether. The combined organic solvent was then evaporated off and the residue was separated by column chromatography on silica gel [elution with diethyl ether–hexane (8:92)] to give endoperoxide **5h** in 68% yield (163 mg).

1,3,4,5,8-*Pentamethyl*-2,6,7-*trioxabicyclo*[3.2.1]*oct*-3-*ene* **5h** was an oil (Found: C, 65.2; H, 8.8. $C_{10}H_{16}O_3$ requires C, 65.18; H, 8.77%); $\delta_H(CCl_4)$ 0.95 (3 H, d, *J* 7), 1.20 (3 H, s), 1.37 (3 H, s), 1.57 (3 H, s), 1.71 (3 H, s) and 2.00 (1 H, q, *J* 7); δ_C 9.20, 12.30, 15.37, 15.41, 18.52, 50.52, 82.95, 104.03, 106.22 and 145.83.

1,2,3,4,5-*Pentamethyl*-6,7,8-*trioxabicyclo*[3.2.1]*oct*-2-*ene* **6h** was an oil (Found: C, 65.4; H, 8.9%); $\delta_H(CCl_4)$ 1.01 (3 H, d, *J* 7), 1.43 (3 H, s), 1.50 (3 H, s), 1.67 (6 H, s) and 1.93 (1 H, q, *J* 7); δ_C 13.19, 14.56, 16.54, 16.61, 20.65, 45.45, 106.70, 110.75, 125.72 and 131.93.

Reaction of Ozonide **6h** *with MCPBA*.—Treatment of the ozonide **6h** (260 mg, 1.4 mmol) with MCPBA (1 mol equiv.) in CH_2Cl_2 at room temperature for 24 h, followed by column chromatography of the crude neutral products [silica gel; elution with diethyl ether–hexane (8:92)], gave, first, the unchanged ozonide **6h** (67 mg, 26% recovery) and then the epoxy ozonide **10h** (68 mg, 24%). 1,2,4,5,6-*Pentamethyl*-3,7,8,9-*tetraoxatricyclo*[4.2.1.0^{2,4}]*nonane* **10h** was an oil (Found: C, 60.0; H, 8.15. $C_{10}H_{16}O_4$ requires C, 59.97; H, 8.07%); δ_H 1.11 (3 H, d, *J* 7), 1.34 (3 H, s), 1.38 (3 H, s), 1.42 (3 H, s), 1.58 (3 H, s) and 1.96 (1 H, q, *J* 7); δ_C 10.40, 12.54, 15.16, 19.26, 19.90, 41.81, 60.88, 63.21, 107.24 and 110.76.

Ozonolysis of Compound **1h** *in the Presence of Trifluoroacetophenone*.—The reaction of compound **1h** (272 mg, 2 mmol) with ozone (1 mol equiv.) was conducted in diethyl ether (15 cm^3) in the presence of trifluoroacetophenone (348 mg, 2 mmol, 1 mol equiv.) at −70 °C. After evaporation of the solvent, the products were separated by column chromatography on silica gel [elution with diethyl ether–hexane (8:92 to 15:85)]. The first fraction contained ozonide **5h** (103 mg, 35%). Then, ozonide **11** was eluted (260 mg, 36%).

3,4-*Dimethyl*-5-[3-*methyl*-5-*phenyl*-5-*trifluoromethyl*-1,2,4-*trioxolan*-3-*yl*]*hex*-4-*en*-2-*one* **11** was obtained as an oily 1:1 mixture of two isomers (Found: C, 60.2; H, 6.3. $C_{18}H_{21}F_3O_4$ requires C, 60.32; H, 5.92%); $\delta_H(CCl_4)$ 0.95 (3 H, d, *J* 7), 1.22 (s), 1.40 (s), 1.52 (s), 1.60 (s), 1.77 (s), 1.97 (s), 2.10 (s), 3.81 (0.5 H, q, *J* 7), 4.07 (0.5 H, br q, *J* 7) and 7.3–7.8 (5 H, m); ν_{max}(neat)/cm^{-1} 1720, 1450, 1180 and 1080.

Ozonolyses of 1,2,3,4-*Tetramethylcyclopenta*-1,3-*diene* **1i**.—(a) *Ozonolysis in* CF_3CH_2OH. A CF_3CH_2OH–diethyl ether solution (15 cm^3; 1:2 v/v) of compound **1i** (244 mg, 2 mmol) was treated with ozone (2 mmol) at −70 °C. The reaction mixture was poured into ice-cold aq. $NaHCO_3$ and was extracted with diethyl ether. After evaporation of the solvent, the crude products were separated by column chromatography on silica gel [elution with diethyl ether–hexane (5:95 and then 8:92)]. Ozonide **6i** (70 mg, 21%) was eluted first and then a 1:1 mixture of ozonide **6i** and the trioxepine **5i** (61 mg, 18%).

Ozonide **6i** (53 mg, 0.31 mmol) was treated with silica gel (7 g) in pentane (10 cm^3) at room temperature for 1 h. After filtration, the silica gel was washed with diethyl ether. The combined organic phases were concentrated and the residue was chromatographed on silica gel [elution with diethyl ether–hexane (8:92)] to give a 1:1 mixture of compounds **5i** and **6i** (22 mg, 42%).

(b) *Ozonolysis in pentane*. A solution of compound **1i** (250 mg, 2.1 mmol) in pentane (40 cm^3) was treated with ozone (0.7 mol equiv.) at −78 °C. The solvent was evaporated off (room temp.; 12 mmHg) to leave a liquid residue (400 mg). Separation by flash chromatography [column 1.5 × 30 cm; silica gel 60 (23 g); pentane–diethyl ether (11:1) (400 cm^3) followed by diethyl ether] gave compound **6i** (23 mg, 10%), a mixture of isomers **5i** and **6i** (35 mg, 10%), and compound **5i** (15 mg, 6%). Repeated separation of the mixture of compounds **5i** and **6i** afforded **5i** (9 mg, 4%) and **6i** (12 mg, 5%).

1,3,4,5-Tetramethyl-2,6,7-trioxabicyclo[3.2.1]oct-3-ene **5i** (as a 1:1 mixture with **6i**) an oil (Found: C, 63.7; H, 8.3. Calc. for $C_9H_{14}O_3$: C, 63.50; H, 8.31%); δ_H 1.42 (3 H, s), 1.62 (3 H, s), 1.64 (3 H, br s), 1.77 (3 H, s), 2.37 (1 H, d, *J* 10) and 2.64 (1 H, d, *J* 10); δ_C 12.12, 15.72, 16.43, 19.88, 49.95, 81.07, 105.98, 107.43 and 146.46.

1,2,3,5-*Tetramethyl*-6,7,8-*trioxabicyclo*[3.2.1]*oct*-2-*ene* **6i** was an oil (Found: C, 63.65; H, 8.4%); δ_H 1.57 (3 H, s), 1.61 (3 H, s), 1.67 (3 H, br s), 1.72 (3 H, br s), 2.21 (1 H, br d, *J* 22) and 2.54 (1 H, br d, *J* 22); δ_C 13.10, 17.07, 17.61, 21.98, 43.42, 106.64, 107.64, 127.33 and 127.39.

(c) *Ozonolysis on polyethylene*. A solution of compound **1i** (1.5 g, 12.3 mmol) in diethyl ether (200 cm^3) was admixed with powdered polyethylene (120 g). The slurry was stirred and subsequently evaporated (room temp.; 12 mmHg) to remove the solvent. The loaded polyethylene was treated with a O_3–O_2-gas stream containing 1 mmol of O_3 per dm^3 for 4 h at −78 °C. Residual ozone was flushed out with N_2 and the products were recovered from polyethylene by extraction with diethyl ether. After evaporation of the solvent (room temp.; 12 mmHg) there remained a liquid residue (2.3 g). Separation by flash chromatography [column 2.5 × 50 cm; silica gel 60 (80 g); pentane–diethyl ether (85:15)] gave compound **10i** (590 mg, 26%).

Reaction of Compound **6i** *with MCPBA*.—A pentane solution (20 cm^3) of compound **6i** (0.8 g, 6.56 mmol) was treated with ozone (0.7 mol equiv.) at −78 °C. The solvent was evaporated off (room temp.; 18 mmHg) to leave a residue (1.05 g); δ_H 1.56 (s), 1.58 (s), 1.64 (s), 1.69 (s), 1.77 (s), 1.88 (s), 2.47 (s) and 2.70 (s).

A mixture of this residue (0.11 g) and MCPBA (0.12 g, 0.71 mmol) in CH_2Cl_2 (30 cm^3) was stirred at room temp. for 18 h. The organic layer washed successively with aq. NaOH and water, and was dried over anhydrous $MgSO_4$. CH_2Cl_2 was removed (room temp.; 15 mmHg) to leave a residue (0.3 g). Separation by column chromatography [column 2.5 × 50 cm;

silica gel (60 g); pentane–diethyl ether (85:15)] gave the epoxy ozonide **10i** (50 mg, 40%).

1,2,4,6-*Tetramethyl*-3,7,8,9-*tetraoxatricyclo*[4.2.1.$0^{2,4}$]*nonane* **10i** was a liquid (Found: C, 58.1; H, 7.5. $C_9H_{14}O_4$ requires C, 58.05; H, 7.58%); δ_H 1.36 (3 H, s), 1.39 (3 H, s), 1.48 (3 H, s), 1.60 (3 H, s), 1.92 (1 H, d, *J* 15.5) and 2.28 (1 H, d, *J* 15.5); δ_C 12.27 (q), 15.64 (q), 20.53 (q), 22.01 (t), 40.45 (t), 59.68 (s), 60.51 (s), 107.15 (s) and 107.86 (s); ν_{max}(neat)/cm^{-1} 3010, 2948, 1730, 1460, 1413, 1387, 1362, 1285, 1220, 1180, 1155, 1130, 1105, 954, 892, 877, 832, 800, 717 and 628.

Reaction of Bicyclic Peroxides, **5** *and* **6**, *with Triphenylphosphine.*—The reaction of an equimolar mixture of a bicyclic peroxide, **5** or **6**, and triphenylphosphine was conducted in benzene or $CDCl_3$ (for the conditions, see Table 2). The products were separated by column chromatography on silica gel (elution with benzene). In the case that both the ketone **13** and the diketone **14** were produced, the ketone **13** was eluted first and then the diketone **14**.

1-*Phenyl*-3-(1-*phenylvinyloxy*)*prop*-2-*en*-1-*one* **13a** was an oil (Found: C, 81.9; H, 5.5%; M$^+$, 250. $C_{17}H_{14}O_2$ requires C, 81.60; H, 5.60%); δ_H 4.03 (1 H, d, *J* 3), 5.02 (1 H, d, *J* 3), 5.93 (1 H, d, *J* 7), 6.93 (1 H, d, *J* 7), 7.2–7.6 (8 H, m) and 7.7–7.9 (2 H, m); ν_{max}(neat)/cm^{-1} 1670, 1635, 1607, 1494, 1449, 1285, 1222, 1182, 1128, 1072, 1029 and 1005.

1,2-*Diphenyl*-3-(1-*phenylvinyloxy*)*prop*-2-*en*-1-*one* **13b** was an oil (Found: C, 84.55; H, 5.5. $C_{23}H_{18}O_2$ requires C, 84.66; H, 5.52%); δ_H 4.56 (1 H, d, *J* 3), 4.87 (1 H, d, *J* 3) and 7.1–8.0 (16 H, m); ν_{max}(neat)/cm^{-1} 1668, 1635, 1600, 1494, 1448, 1355, 1280, 1222, 1160, 1075, 1040 and 1016.

1,2,3-*Triphenyl*-3-(1-*phenylvinyloxy*)*prop*-2-*en*-1-*one* **13c** had m.p. 124–126 °C (from MeOH) (Found: C, 86.6; H, 5.4. $C_{29}H_{22}O_2$ requires C, 86.57; H, 5.47%); δ_H 4.44 (1 H, d, *J* 3), 4.79 (1 H, d, *J* 3), 6.9–7.7 (18 H, m) and 7.9–8.2 (2 H, m); ν_{max}(KBr)/cm^{-1} 1660, 1640, 1600, 1490, 1442, 1312, 1263, 1214, 1175, 1116, 1070 and 1011.

4-Benzoyl-3-phenylbut-2-en-1-one **14a** (not isolated in a pure state); δ_H 4.70 (2 H, s), 6.62 (1 H, d, *J* 7), 7.2–8.0 (10 H, m) and 9.90 (1 H, d, *J* 7).

4-*Benzoyl*-2,3-*diphenylbut*-2-*en*-1-*one* **14b** was an oil (Found: C, 84.35; H, 5.6. $C_{23}H_{18}O_2$ requires C, 84.66; H, 5.52%); δ_H 4.72 (2 H, s), 7.0–8.0 (15 H, m) and 9.98 (1 H, s); ν_{max}(neat)/cm^{-1} 1680, 1595, 1491, 1480, 1386, 1320, 1265, 1209, 1176, 1074 and 1024.

4-Benzoyl-1,2,3-triphenylbut-2-en-1-one **14c** [(*Z*)-isomer] had m.p. 113–114 °C;[28] δ_H 4.23 (2 H, s) and 7.0–8.0 (20 H, m); ν_{max}(KBr)/cm^{-1} 1674, 1650 and 1410; *m*/*z* 402 (M$^+$).[26] The (*Z*)-diketone (*Z*)-**14c** was labile on silica gel, and consequently, by column chromatography, a mixture of the (*Z*)- and (E)-isomer of dione **14c** was obtained. (*E*)-**14c** had m.p. 147–148 °C; δ_H 4.19 (2 H, s) and 7.0–8.0 (20 H, m); ν_{max}(KBr)/cm^{-1} 1675 and 1655.[26]

4-Benzoyl-1,2,3,4-tetraphenylbut-2-en-1-one **14e** was an oil; δ_H 5.97 (1 H, s) and 6.7–8.1 (25 H, m); ν_{max}(neat)/cm^{-1} 1688, 1660, 1595, 1587, 1487, 1476, 1446, 1255, 1210, 1173, 1072, 1023, 1000 and 974.

4-*Acetoxy*-4-*benzoyl*-1,2,3-*triphenylbut*-2-*en*-1-*one* **14f** had m.p. 148.5–150.5 °C (from MeOH) (Found: C, 80.8; H, 5.3. $C_{31}H_{24}O_4$ requires C, 80.87; H, 5.21%); δ_H 2.08 (3 H, s), 6.75 (1 H, s) and 7.1–8.2 (20 H, m).

3-Methyl-1,2-diphenylhex-2-ene-1,5-dione **14g** was an oil; δ_H 1.87 (3 H, s), 1.98 (3 H, s), 3.15 (2 H, s) and 7.1–8.0 (10 H, m).

3,4,5-Trimethylhept-3-ene-2,6-dione **14h** was an oil; δ_H(CCl_4) 1.05 (3 H, d, *J* 7), 1.55 (3 H, s), 1.88 (3 H, s), 2.02 (3 H, s), 2.20 (3 H, s) and 3.90 (1 H, q, *J* 7); ν_{max}(neat)/cm^{-1} 1720, 1680 and 1360.

3,4-Dimethylhept-3-ene-2,6-dione **14i** was an oil; δ_H 1.83 (3 H, br s), 1.97 (3 H, br s), 2.20 (3 H, s), 2.23 (3 H, s) and 3.43 (2 H, s); δ_C 15.85, 21.81, 29.28, 29.63, 50.51, 133.33, 137.40, 202.31 and 205.86; ν_{max}(neat)/cm^{-1} 1710, 1675, 1450, 1160 and 960; CI–MS *m*/*z* 155 (100%) [M + 1]$^+$.

3,4-Epoxy-3,4-dimethylheptane-2,6-dione had δ_H 1.39 (3 H, s), 1.59 (3 H, s), 2.09 (3 H, s), 2.23 (3 H, s), AB-system with δ_A 2.83, δ_B 2.56 (2 H, J_{AB} 17.6).

Reaction of Bicyclic Peroxides, **5** *or* **6**, *with* $AlHCl_2$.—To anhydrous $AlCl_3$ (12 mmol) at 0 °C was added anhydrous diethyl ether (40 cm^3), followed by $LiAlH_4$ (4 mmol). To this solution was added a solution of a compound **5** or **6** (2 mmol) in diethyl ether (40 cm^3) during 5 min. The reaction mixture was kept at 0 °C for 15 min and then the reaction was allowed to continue at room temperature for a further 45 min. The products were chromatographed on a column of silica gel [elution with benzene–hexane (1:1)].

2,3,4,6-*Tetraphenyl*-5,6-*dihydro*-2H-*pyran* **15c** (*major isomer*) had m.p. 141–143 °C (from diethyl ether–hexane) (Found: C, 89.5; H, 6.2. $C_{29}H_{24}O$ requires C, 89.69; H, 6.19%); δ_H 2.5–3.0 (2 H, m), 4.73 (1 H, dd, *J* 10 and 5), 5.81 (1 H, br s) and 6.9–7.5 (20 H, m); ν_{max}(KBr)/cm^{-1} 1493, 1450, 1377, 1252, 1130, 1079, 1031, 1006, 768, 753, 745, 722 and 698.

Compound **15c** (minor isomer) had an oil; δ_H 2.5–3.2 (2 H, m), 5.03 (1 H, dd, *J* 10 and 3), 5.64 (1 H, br s) and 6.9–7.5 (20 H, m); ν_{max}(neat)/cm^{-1} 1482, 1438, 1353, 1337, 1235, 1200, 1141, 1118, 1061, 1019, 755, 740, 715 and 684; *m*/*z* 388 (M$^+$).

4,6-*Dimethyl*-2,3-*diphenyl*-5,6-*dihydro*-2H-*pyran* **15g** (*major isomer*) was an oil (Found: C, 86.1; H, 7.6. $C_{19}H_{20}O$ requires C, 86.30; H, 7.58%); δ_H 1.36 (3 H, d, *J* 6), 1.58 (3 H, br s), 1.9–2.5 (2 H, m), 3.8–4.1 (1 H, m), 5.30 (1 H, br s) and 6.9–7.5 (10 H, m).

Compound **15g** (minor isomer) was an oil; δ_H 1.19 (3 H, d, *J* 6), 1.73 (3 H, s), 2.0–2.3 (2 H, m), 3.7–4.0 (1 H, m), 5.51 (1 H, br s) and 6.9–7.5 (10 H, m); *m*/*z* 264 (M$^+$).

2,3,4,5,6-*Pentaphenyl*-5,6-*dihydro*-2H-*pyran* **15e** had m.p. 144–146 °C (from diethyl ether–hexane) (Found: C, 90.2; H, 6.1. $C_{35}H_{28}O$ requires C, 90.52; H, 6.03%); δ_H 3.81 (1 H, dd, *J* 4 and 2), 5.44 (1 H, d, *J* 4), 5.76 (1 H, d, *J* 2) and 6.7–7.4 (25 H, m).

Acknowledgements

We thank Professor M. B. Hursthouse (University of Wales, Cardiff) for access to X-ray crystallographic facilities *via* the SERC Crystallographic Service.

References

1 J. N. Crabb and R. C. Storr, in *1,3-Dipolar Cycloaddition Chemistry*, ed. A. Padwa, Wiley, New York, 1984, vol. 2, ch. 15.
2 R. Huisgen, G. Mloston and E. Langhals, *J. Am. Chem. Soc.*, 1986, **108**, 6401; *J. Org. Chem.*, 1986, **51**, 4087; R. Huisgen, J. Penelle, G. Mloston, A. B. Padias and H. K. Hall, Jr., *J. Am. Chem. Soc.*, 1992, **114**, 266; R. Huisgen, in *Advances in Cycloaddition*, ed. D. P. Curran, JAI Press, Greenwich, Connecticut, 1988, vol. 1.
3 H. Mayr, J. Baran and U. W. Heigl, *Gazz. Chim. Ital.*, 1991, **121**, 373; J. Baran and H. Mayr, *J. Am. Chem. Soc.*, 1987, **109**, 6519; *J. Org. Chem.*, 1989, **54**, 5012, 5774; J. Baran, H. Mayr, V. Ruster and F.-G. Klarner, *J. Org. Chem.*, 1989, **54**, 5016.
4 (*a*) K. Griesbaum, W. Volpp, R. Greinert, H. Greunig, J. Schmid and H. Henke, *J. Org. Chem.*, 1989, **54**, 383; (*b*) M. Mori, T. Tabuchi, M. Nojima and S. Kusabayashi, *J. Org. Chem.*, 1992, **57**, 1649.
5 For the synthesis of 1,2,4-trioxepane; W. Adam and N. Duran, *J. Chem. Soc., Chem. Commun.*, 1972, 798; S. Futamura and Y. Kamiya, *J. Chem. Soc., Chem. Commun.*, 1988, 1053.
6 A part of this work was published in preliminary form; N. Mori, N. Nojima and S. Kusabayashi, *J. Am. Chem. Soc.*, 1987, **109**, 4407.
7 E. Breitmaier and W. Voelter, *Carbon-13 NMR Spectroscopy*, 3rd edn., VCH, Weinheim, 1987.
8 (*a*) W. Grugel, *Handbook of NMR Spectral Parameters*, Heyden, London, 1979, vol. 1; (*b*) K. J. McCullough, N. Nakamura, T. Fujisaka, M. Nojima and S. Kusabayashi, *J. Am. Chem. Soc.*, 1991, **113**, 1786.

9 (*a*) P. S. Bailey, *Ozonation in Organic Chemistry*, Academic Press, New York, 1978, vol. 1; 1982, vol. 2; (*b*) R. L. Kuczkowski, in *1,3-Dipolar Cycloaddition Chemistry*, ed. A. Padwa, Wiley, New York, 1984, vol. 2, ch. 11; W. H. Bunnelle, *Chem. Rev.*, 1991, **91**, 335; R. L. Kuczkowski, in *Advances in Oxygenated Processes*, ed. A. L. Baumstark, JAI Press, Greenwich, Connecticut, 1991, vol. 3.
10 M. Miura, S. Nagase, M. Nojima and S. Kusabayashi, *J. Org. Chem.*, 1983, **48**, 2366 and references therein.
11 See, for example, C. W. Jefford, J.-C. Rossier and J. Boukouvalas, *J. Chem. Soc., Chem Commun.*, 1986, 1701; 1987, 713; 1987, 1593; T. Fujisaka, M. Miura, M. Nojima and S. Kusabayashi, *J. Chem. Soc., Perkin Trans. 1*, 1989, 1031.
12 F. H. Allen, S. Bellard, B. A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B. G. Hummelink-Peters, O. Kennard, W. D. S. Motherwell, J. R. Rodgers and D. G. Watson, *Acta Crystallogr., Sect. B*, 1979, **35**, 2331.
13 D. A. Langs, M. G. Erman, G. T. DeTitta, D. J. Coughlin and R. G. Salamon, *J. Cryst. Mol. Struct.*, 1978, **8**, 239; A. J. Bloodworth, H. J. Eggelte, H. M. Dawes, M. B. Hursthouse and N. P. C. Walker, *J. Chem. Soc., Perkin Trans. 2*, 1986, 991.
14 M. Miura, A. Ikegami, M. Nojima, S. Kusabayashi, K. J. McCullough and S. Nagase, *J. Am. Chem. Soc.*, 1983, **105**, 2414; A. Syed, G. P. Kirschenheuter, V. Jain, G. W. Griffin and E. D. Stevens, *Acta Crystallogr., Sect. C*, 1986, **42**, 1239.
15 T. Sugimoto, M. Nojima, S. Kusabayashi and K. J. McCullough, *J. Am. Chem. Soc.*, 1990, **112**, 3690. For a general discussion of solvent effects in ozonolysis: see ref. 9(*a*); R. W. Murray and M. M. Morgan, *J. Org. Chem.*, 1991, **56**, 6123.
16 E. L. Eliel and F. W. Nader, *J. Am. Chem. Soc.*, 1970, **92**, 3045; E. C. Ashby and J. Prather, *J. Am. Chem. Soc.*, 1966, **88**, 729; T. Fujisaka, M. Nojima and S. Kusabayashi, *J. Org. Chem.*, 1985, **50**, 275.
17 M. P. Cava and K. Narasimhan, *J. Org. Chem.*, 1969, **34**, 3641.
18 P. Bladon, S. McVey, P. L. Pauson, G. D. Broadhead and W. M. Horspool, *J. Chem. Soc. C*, 1966, 306.
19 F. H. Newmann, *Justus Liebig's Ann. Chem.*, 1898, **302**, 236.
20 S. G. Cohen, R. Zand and C. Steel, *J. Am. Chem. Soc.*, 1961, **83**, 2895.
21 P. L. Pauson and B. J. Williams, *J. Chem. Soc.*, 1961, 4153.
22 K. Ziegler and B. Schnell, *Justus Liebig's Ann. Chem.*, 1925, **445**, 266.
23 F. X. Kohl and P. Sutzi, *J. Organomet. Chem.*, 1983, **243**, 119.
24 G. Schmitt and S. Ozman, *Chem.-Ztg.*, 1976, **100**, 143.
25 F. Fleck, A. Rossi, M. Hinder and H. Sehinz, *Helv. Chim. Acta*, 1950, **33**, 134.
26 P. Yates and G. H. Stout, *J. Am. Chem. Soc.*, 1954, **76**, 5110.
27 (*a*) G. M. Sheldrick, SHELXS86, University of Göttingen, Germany, 1986; SHELX76, University of Cambridge, England, 1976; (*b*) R. O. Gould and P. J. Taylor, CALC, University of Edinburgh, Scotland, 1983; (*c*) W. D. S. Motherwell, PLUTO, University of Cambridge, England, 1976.
28 G. Rio and Y. Fellion, *Tetrahedron Lett.*, 1962, 1213.

Paper 2/06882F
Received 30*th December* 1992
Accepted 26*th February* 1993