100. Intramolecular Oxygen Transfer on the Ozonolysis of a Diphenylcyclopentene Derivative

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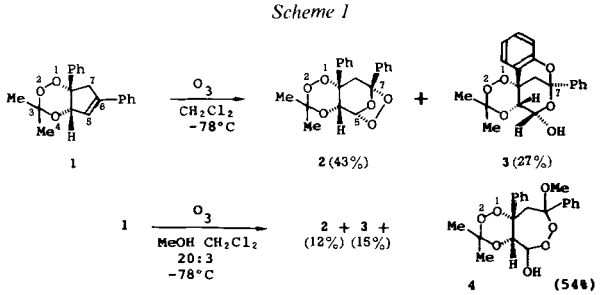
The ozonolysis of *cis*-3,4a,7,7a-tetrahydro-3,3-dimethyl-6,7a-diphenylcyclopenta[1,2-*e*][1,2,4]trioxine (**1**) in CH_2Cl_2 at −78° gave the secondary *endo* ozonide **2** (43% yield) and an acetal **3** (27% yield) derived from O-insertion at the *ortho* position of the C(7a) phenyl substituent. Both structures were elucidated by X-ray. Repetition of the ozonolysis in $MeOH/CH_2Cl_2$ 20:3 at −78° also gave the same two products in 12 and 15% yields, repectively, together with the hemiperacetal **4** (54% yield) formally derived from the secondary ozonide by addition of MeOH.

Introduction. – The unraveling of the mechanism of ozonolysis has been and still remains a major topic of organic chemistry [1] [2]. The chief features of interest are the stereoselectivity of attack by ozone on the double bond [3–5], the direction of scission of the primary ozonide so formed [6], and the configuration [7] [8] and reactivity of the resulting carbonyl oxide [8] [9]. This last intermediate, despite its potential power as an oxidant, generally stays intact during its subsequent reactions. The ozonolyses of phenyl derivatives of cyclopentene [5] and cyclobutene [10] are typical. In non-participating solvents, the reaction proceeds normally in that the *Criegee* intermediate conserves both its O-atoms which are incorporated into the secondary ozonide. The present paper deals with an unusual exception involving a cyclopentene ring where a strategically placed phenyl (Ph) substituent interrupts this smooth cleavage and recombination process by abstracting the distal O-atom of the intermediate carbonyl oxide.

The substrate examined is *cis*-3,4a,7,7a-tetrahydro-3,3-dimethyl-6,7a-diphenylcyclopenta[1,2-*e*][1,2,4]trioxine (**1**). The two rings in **1** are *cis*-fused, and notwithstanding the presence of three O-atoms, the molecule is sufficiently stable and, therefore, amenable to mechanistic study. Moreover, the Ph substituents play an unexpected role in revealing the nature of the intermediate.

Results. – The ozonolysis of **1** in CH_2Cl_2 at −78° gave only two products, the secondary ozonide **2** formed in 43% yield, and the cyclic acetal **3** (27% yield; *Scheme 1*).

Scheme 1



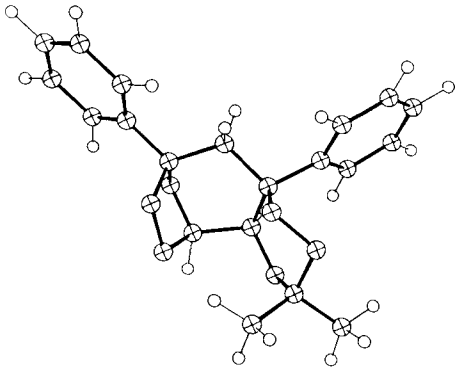


Fig. 1. *Computer-generated perspective drawing of the structure of* **2**

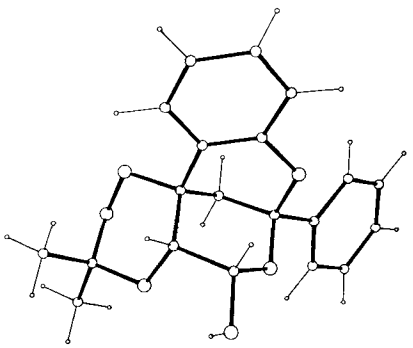


Fig. 2. *Computer-generated perspective drawing of the structure of* **3**

Similar ozonolysis of **1**, but carried out in MeOH containing a small amount of CH_2Cl_2 for solubility purposes, gave products **2** and **3** in diminished yields (12 and 15%, resp.) accompanied by a substantial amount (54%) of the seven-membered cyclic hemiperacetal **4**. The structures of **2** and **3** were determined by X-ray analyses of single crystals *(Figs. 1* and *2)*. The structure of **4** was deduced from its NMR spectra, however, the configuration of the substituents on the seven-membered ring could not be assigned with certainty.

Examination of the configuration of **1**, which was determined by X-ray analysis *(Fig. 3)* [1]), indicates that the *endo* face of the double bond is sterically hindered[2]). Experimental confirmation of this hindrance was provided by the reaction of **1** with singlet oxygen. Photo-oxygenation of **1** in CCl_4 solution using *meso*-tetraphenylporphyrin as sensitizer gave a single hydroperoxide **5** *(Scheme 2)*. The bis-nor derivative **6** also gave a single hydroperoxide **7** (62% yield). X-ray analysis showed that the hydroperoxy substituent in **7** possessed the *exo* configuration *(Fig. 4)*. The same *exo* configuration was assumed for **5** by analogy with **7** and by comparison of their spectral properties.

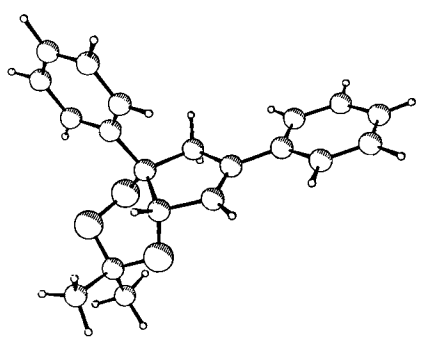


Fig. 3. *Computer-generated perspective drawing of the structure of* **1**

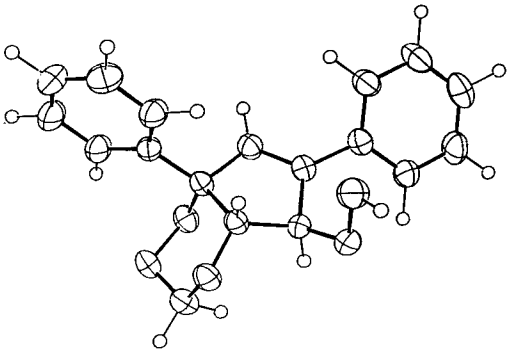
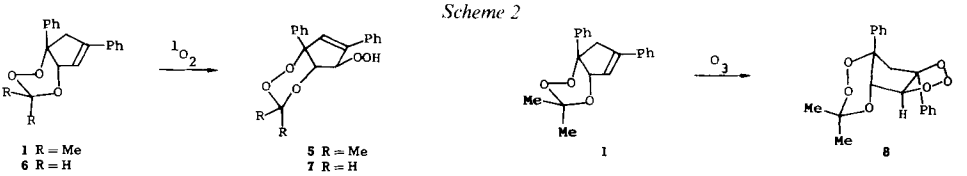


Fig. 4. *Computer-generated perspective drawing of the structure of* **7**

[1]) We thank *O. Kennard, F. H. Allen*, and *S. Bellard*, University Chemical Laboratory, Cambridge, UK, for determining the structure of **1**.

[2]) The prefixes *exo* and *endo* refer to the convex and concave sides, respectively, of the *cis*-fused bicyclic structure.

Scheme 2



1 R = Me
6 R = H

5 R = Me
7 R = H

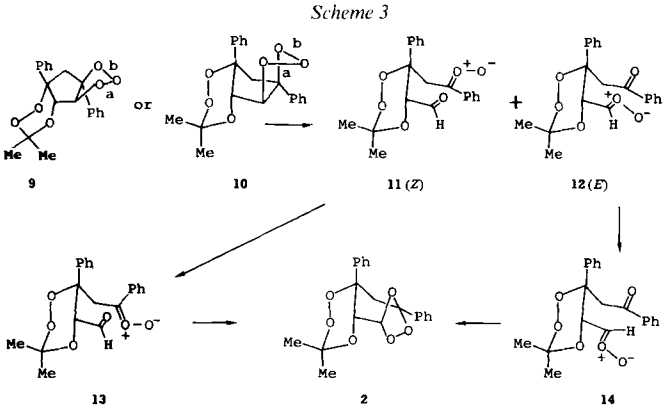
1

8

Discussion. – As ozone and singlet oxygen are both electrophiles and similar in size, their mode of attack on olefins might be thought to be the same. In fact, if experiments with the silyl enol ether of camphor can be taken as a guide, ozone displays greater steric discrimination towards a highly hindered double bond than does singlet oxygen [11]. This means that ozone adds to a double bond with a concerted two-point attack, whereas singlet oxygen adds to just one terminus. As the *cis*-fused cyclopentene is relatively open on its *exo* face, unlike the bornene fragment, ozone might favor an *exo* approach. The result will be the formation of the *exo* primary ozonide **8**. The subsequent evolution of **8** has to accommodate the conventional formation of a single secondary ozonide and two unusual events, the reaction of the Ph group and MeOH with some intermediate.

A plausible and comprehensive explanation is forthcoming if it is assumed that the primary ozonide **8** undergoes cleavage to the *Criegee* intermediate. Two such cleavages are possible, the proportions of which will reflect the ability of substituents to stabilize the resulting carbonyl oxides. In addition, conformational effects will also operate. However, bicyclic primary ozonides may be less amenable to stereochemical arguments than monocyclic ones. The *Bauld-Baily* mechanism [12] is inapplicable as the constraints on the cyclopentane ring prevent the *cis*-fused 1,2,3-trioxolane ring from adopting the C–C half-chair conformation. Moreover, inspection of *Dreiding* models reveals that **8** can adopt two conformations in both of which the ozonide exists as an envelope conformation (**9** and **10**) similar to that proposed by *Kuczkowski* [13]. In each case, cleavage of the two alternative O–O bonds (a and b, *Scheme 3*) necessarily produces the (*Z*)-phenylcarbonyl oxide **11** and the (*E*)-formyl oxide **12**[3]). The relative amounts of these two intermediates are difficult to gauge, as hyperconjugative and inductive effects often

Scheme 3



9 **10** **11** (*Z*) **12** (*E*)

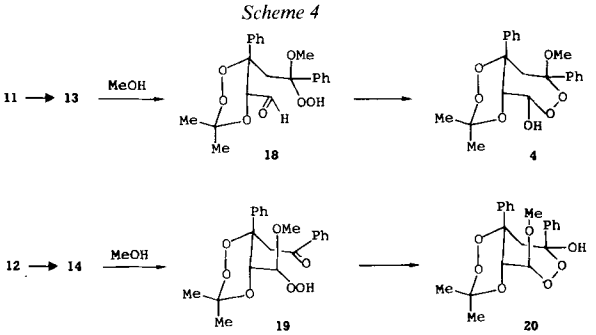
13 **2** **14**

[3]) The prefixes *E* and *Z* denote configurations about the double bond of the carbonyl oxide.

outweigh the stabilization conferred by conjugation [14]. All that can be said is that both **11** and **12** will form. Once formed, neither **11** nor **12** retain their initial conformations as no closure to the secondary *exo* ozonide is observed. Steric compression undoubtedly obliges the carbonyl oxides to undergo rapid rotation about the C–C bond to adopt the two *endo* conformations **13** and **14** which then cyclize to the same *endo* ozonide **2**.

Aside from this common fate, another is also shared. Instead of submitting to conformational change, the (*Z*)- and (*E*)-carbonyl oxides **11** and **12**, respectively, are equally well placed to sacrifice their distal O-atom to the contiguous 1,3-disposed Ph substituent *(Scheme 4)*. Presumably, the first common intermediate formed is the benzene epoxide **15**, which on NIH shift [15] to the ketone **16** and aromatization furnishes the *o*-phenol **17**. As soon as it is formed, the phenolic function in **17** produces the acetal **3**.

Scheme 4

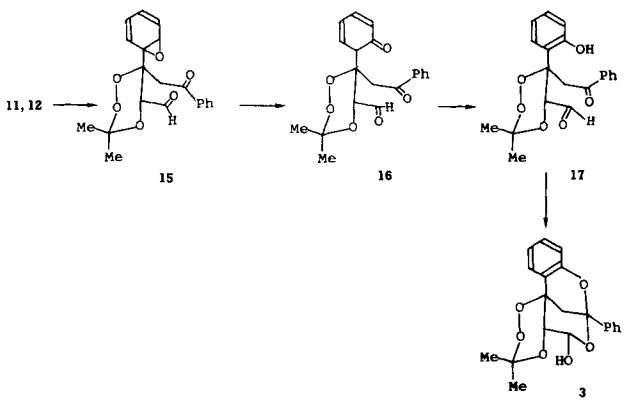


This O-transfer vies with secondary ozonide formation. Despite apparent similarities, the two cyclizations will probably not occur to the same extent. The intramolecular capture of the carbonyl oxide in **11** by the carboxaldehyde group should be more efficient than that experienced by the carbonyl oxide in **12** with the ketone function [16]. An exact parallel is provided by the mechanistically homologous zwitterionic peroxides produced by the photooxygenation of enol ethers. They are captured only by aldehydes to give 1,2,4-trioxanes. The usual ketones are not electrophilic enough to react [17]. Consequently, carbonyl oxide **12** will be expected to undergo a greater degree of O-transfer to produce more phenol than **11**.

Such intramolecular functionalization of the benzene ring is reminiscent of the homogentisic-acid rearrangement in which an oxenoid engendered by enzymatic oxygenation behaves just like a carbonyl oxide [18]. Precedence exists for similar behavior by secondary ozonides. An intermolecular example is the oxidation of mesitylene in good yield by the stable transannular ozonide of anthracene [19]. The photo-sensitized autooxidation of paracyclophanofuran also caused a small amount (~ 5%) of intramolecular epoxidation [20]. However, it is unlikely that phenol **17** could have arisen by direct abstraction of the central O-atom of the primary *exo* ozonide **8** as it is too far away from the Ph substituent. Furthermore, the secondary ozonide **2** proved to be thermally stable in refluxing benzene. There was no conversion to **3**. It can, therefore, be safely concluded that an intermediate carbonyl oxide is responsible for the insertion of an O-atom into the benzene ring.

Further support for the carbonyl-oxide intermediate comes from the results obtained in $MeOH/CH_2Cl$. The ozonide **2** and acetal **3** are obtained as before, but in differently

Scheme 5



diminished quantities with a corresponding amount of the hemiperacetal **4** being formed in their stead. The compensatory effect is greater for **2** than for **3**. This difference may be rationalized as follows: the more efficient or better precursor to the ozonide **2**, namely **13**, is also better intercepted by MeOH than **14**, which is a bad precursor to **2**, but in its initial conformation **12** is a good one for the acetal **3**. The result is that **13** reacts with MeOH to give initially the hemiperacetal **18** which subsequently undergoes acetalization to **4** *(Scheme 5)*. Although a doubt exists about the configurations of the MeO and Ph groups in **4**, which could possibly be interchanged, the alternative structure **20** is simply not observed. The absence of **20**, which would have been derived from the hemiperacetal **19**, may be interpreted in two ways. Either the (*E*)-configurated formyl oxide **12** is entirely intercepted by the Ph group to give **3** or it is not formed at all, so denying the conformation **14** the opportunity to give **19**.

Lastly, a word needs to be said about the possibility of ozonation on the *endo* side of **1**. Some *endo* addition is difficult to exclude. Indeed, cleavage of the primary *endo* ozonide would immediately generate the two carbonyl oxides in their *endo* conformations **13** and **14** in a state of readiness to give all products except the acetal **3**. Production of the latter would require reversion to the *exo* conformations **11** and **12**, the chances of which are hard to predict.

Conclusion. – Few cases of intramolecular oxenoid oxidation have been reported so far [21] [22]. Perhaps the most relevant one is the ozonolysis of 1-(1-phenanthryl)-1-phenyl-2-methylprop-1-ene which led to cleavage of the double bond with formation of 1-benzoyl-9,10-epoxy-9,10-dihydrophenanthrene in 4.2% yield [23]. Ozonolysis of our cyclopentene derivative **1** now provides the first example of the intramolecular oxidation of a Ph substituent. Unlike the phenanthrene nucleus which is easily epoxidized at the 9,10 position [24], the oxidation of an unactivated benzene ring requires the action of a highly electrophilic reagent. The formation of the acetal **3** in 27% yield constitutes the first unambiguous example of the intramolecular oxidation of a Ph substituent by a carbonyl oxide arising from ozonolysis.

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Experimental Part

General. Solvents: *Merck* anal. grade. Column chromatography: *Merck* silica *60* (70–230 mesh) and *Fluka Florisil* (100–200 mesh). TLC and prep. TLC: *Merck* silica gel *60* F_{254} (0.2 mm and 2 mm, resp.). M.p.: *Reichert* hot-stage microscope; uncorrected. IR spectra: *Perkin-Elmer-681* spectrometer. ^{1}H- (360 Mz) and ^{13}C-NMR (90.6 MHz) spectra. *Bruker-FT-360* spectrometer; chemical shifts in ppm downfield from tetramethylsilane and coupling constants (J) in Hz. MS (m/z (rel. abundance)): *CH-4-MAT* and *Finnigan-GC/MS-4023* instruments using the INCOS data system. Elemental analyses were carried out by Dr. *H.J. Eder*, service de microchimie, institut de chimie pharmaceutique, University of Geneva.

cis-*3,4a,7,7a-Tetrahydro-3,3-dimethyl-6,7a-diphenylcyclopenta[1,2-e][1,2,4]trioxine* (**1**). The reaction of 1,4-diphenyl-1,4-epidioxycyclopent-2-ene and acetone according to our procedure [25] gave **1** as colorless crystals, m.p. 95–97° (recrystallized from Et_2O/pentane at −78°). ^{1}H-NMR ($CDCl_3$): 1.38 (*s*, 3 H); 1.64 (*s*, 3 H); 3.02 (br. *d*, J = 16.5, 1 H); 3.32 (br. *d*, J = 16.5, 1 H); 5.03 (br. *s*, 1 H); 6.37 (br. *ddd*, J = 2, 2, 2, 1 H); 7.25–7.45 (*m*, 6 H); 7.49 (*d*, J = 7, 2 H); 7.57 (*d*, J = 6, 2 H). ^{13}C-NMR ($CDCl_3$): 23.4 (*q*); 24.9 (*q*); 44.7 (*t*); 79.6 (*d*); 88.4 (*s*); 102.6 (*s*); 124.2 (*d*); 125.4 (*d*); 126.0 (*d*); 127.5 (*d*); 128.4 (*d*); 128.5 (*d*); 134.8 (*s*); 142.9 (*s*); 144.7 (*s*). MS: 308 (4, M^+), 234 (5), 233 (8), 222 (9), 219 (17), 218 (100). Anal. calc. for $C_{20}H_{20}O_3$: C 77.90, H 6.54; found: C 77.69, H 6.79.

cis-*3,4a,7,7a-Tetrahydro-6,7a-diphenylcyclopenta[1,2-e][1,2,4]trioxine* (**6**). To a soln. of 1,4-diphenyl-1,4-epidioxycyclopent-2-ene (345 mg, 1.38 mmol) in THF (6 ml), aq. 37% formaldehyde (4 ml) was added followed by aq. 20% H_2SO_4 (0.5 ml) with stirring at 20° [26]. After 15 h, aq. sat. NaCl soln. (30 ml) was added followed by Et_2O extraction (5 × 40 ml). The combined Et_2O extracts were dried ($MgSO_4$), and after evaporation of the solvent, prep. TLC (CH_2Cl_2) of the residue gave pure **6** (318 mg, 85%); colorless plates, m.p. 102–103° (recrystallized from CH_2Cl_2/hexane). ^{1}H-NMR ($CDCl_3$): 3.00 (br. *s*, 2 H); 5.12 (*d*, J = 8, 1 H); 5.45 (br. *d*, J = 1, 1 H); 5.70 (*d*, J = 8, 1 H); 6.26 (br. *d*, J = 1, 1 H); 7.28–7.50 (*m*, 8 H); 7.66 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 44.8 (*t*); 80.2 (*d*); 88.2 (*s*); 91.5 (*t*); 122.7 (*d*); 125.8 (*d*); 126.7 (*d*); 127.9 (*d*); 128.4 (*d*); 143.6 (*s*); 140.4 (*s*); 143.0 (*s*). MS: 280 (8, M^+), 279 (4), 250 (3), 222 (17), 221 (5), 167 (5), 149 (11), 130 (6), 115 (8), 105 (100), 77 (26). Anal. calc. for $C_{18}H_{16}O_3$: C 77.11, H 5.76; found: C 76.98, H 6.02.

Ozonolysis of **1** *in* CH_2Cl_2. A soln. of **1** (160 mg, 0.52 mmol) in CH_2Cl_2 (50 ml) was submitted to ozonolysis for 20 min at −78°. The resulting mixture was stirred for an additional 15 min while N_2 was passed through the soln. for 30 min to expel excess O_3 (reaction control by TLC). The solvent was evaporated and the residue chromatographed over silica gel (CH_2Cl_2) to yield **2** (80 mg, 43%) and **3** (50 mg, 27%). *3,4aβ,5,7,8,8a-Hexahydro-3,3-dimethyl-7β,8aβ-diphenyl-5α,7α-epidioxypyrano[3,4-e][1,2,4]trioxine* (**2**). Colorless plates, m.p. 133–135° (recrystallized from Et_2O/pentane at −78°). ^{1}H-NMR ($CDCl_3$): 1.25 (*s*, 3 H); 1.91 (*s*, 3 H); 2.59 (*d*, J = 15, 1 H); 2.90 (*d*, J = 15, 1 H); 4.78 (*d*, J = 2.5, 1 H); 6.10 (*d*, J = 2.5, 1 H); 7.3–7.7 (*m*, 10 H). ^{13}C-NMR ($CDCl_3$): 25.3 (*q*); 26.3 (*q*); 47.2 (*t*); 69.8 (*d*); 78.7 (*s*); 101.6 (*d*); 102.6 (*s*); 106.2 (*s*); 125.2 (*d*); 125.5 (*d*); 127.6 (*d*); 128.47 (*d*); 128.54 (*d*); 129.8 (*d*); 134.4 (*s*); 143.6 (*s*). MS: 356 (2, M^+), 340 (1), 338 (2), 324 (1), 250 (10), 203 (8), 147 (9), 105 (100). Anal. calc. for $C_{20}H_{20}O_6$: C 67.41, H 5.66; found: C 67.18, H 5.84.

3,4aβ,5,7,8,8a-Hexahydro-3,3-dimethyl-7α-phenyl-7,8a-(epoxy-o-benzeno)pyrano[3,4-e][1,2,4]trioxin-5α-ol (**3**). Colorless plates, m.p. 135–143° (recrystallized from hexane at −78°). IR (CCl_4): 3560*m* (OH). ^{1}H-NMR ($CDCl_3$): 1.54 (*s*, 3 H); 1.83 (*s*, 3 H); 2.17 (*dd*, J = 12, 1, 1 H); 3.28 (*d*, J = 12, 1 H); 3.77 (*d*, J = 12, 1 H); 4.08 (*dd*, J = 3, 1, 1 H); 5.11 (*dd*, J = 12, 3, 1 H); 7.1 (*m*, 2 H); 7.3–7.55 (*m*, 5 H); 7.75 (*m*, 2 H); a peak at 3.77 was exchanged by D_2O. MS: 357 (5, M^+ + 1), 356 (16, M^+), 340 (7), 223 (14), 147 (11), 121 (40), 106 (23), 105 (100), 77 (37). Anal. calc. for $C_{20}H_{20}O_6$: C 67.41, H 5.66; found: C 67.21, H 5.91.

Ozonolysis of **1** *in MeOH/*CH_2Cl_2. A soln. of **1** (100 mg, 0.32 mmol) in MeOH (20 ml) and CH_2Cl_2 (3 ml) was subjected to ozonation for 15 min at −78°. Stirring was continued for a further 15 min while N_2 was passed for 30 min to expel excess O_3. The solvent was evaporated and the residue chromatographed over silica gel (CH_2Cl_2) to give **2** (13 mg, 12%) and a mixture **3**/**4**. Prep. TLC (Et_2O/hexane 7:3) of **3**/**4** gave pure **3** (17 mg, 15%) and **4** (68 mg, 54%). *3,4aβ,5,8,9,9a-Hexahydro-8-methoxy-3,3-dimethyl-8,9aβ-diphenyl[1,2,4]trioxino[5,6-d][1,2]dioxepin-5-ol* (**4**): Colorless plates, m.p. 134–136° (recrystallized from hexane at −30°). IR (CCl_4): 3550*m* (OH). ^{1}H-NMR ($CDCl_3$): at r.t. **4** is a dynamic molecule; at −22°, 2 conformers, ratio 3:1 (by integration of the CH_3 signals). Major conformer (−22°): 1.00 (*s*, 3 H); 1.11 (*s*, 3 H); 2.59 (*d*, J = 16.5, 1 H); 2.97 (*s*, 3 H); 3.06 (*d*, J = 16.5, 1 H); 4.06 (*d*, J = 4.5, 1 H); 5.22 (*d*, J = 11, 1 H); 5.85 (*dd*, J = 11, 4.5, 1 H); 7.3–7.6 (Ph, overlapping with those of minor conformer). Minor conformer (−22°): 1.73 (*s*, 3 H); 1.81 (*s*, 3 H); 2.83 (*d*, J = 16.5, 1 H); 3.26 (*s*, 3 H); 3.65 (*d*, J = 16.5, 1 H); 4.71 (br., *d*, J = 4.5, 1 H); 4.77 (br. *d*, J = 11, 1 H); 4.95 (br. *m*, 1 H); 7.3–7.6 (Ph, overlapping with those of major conformer). MS: 388 (0.2, M^+), 355 (0.2), 239 (2), 223 (2), 147 (2), 131 (2), 115 (4), 105 (100), 91 (13), 77 (52), 69 (6), 59 (12), 51 (20). Anal. calc. for $C_{21}H_{24}O_7$: C 64.93, H 6.24; found: C 64.71, H 6.48.

Photooxygenation of **1**. A soln. of **1** (100 mg, 0.32 mmol) in CCl_4 (10 ml) was irradiated with a 500-W high-pressure Na lamp at −15° using *meso*-tetraphenylporphin (TPP, 3 mg) as sensitizer while O_2 was bubbled through the soln. After 5 h, **1** was completely oxidized. TLC (CH_2Cl_2) indicated one spot corresponding to cis-*3,4a,5,7a-tetrahydro-3,3-dimethyl-6,7a-diphenylcyclopenta[1,2-e][1,2,4]trioxin-5β-yl hydroperoxide* (**5**). Colorless plates, m.p. 144–146° (recrystallized from hexane/CH_2Cl_2 at −78°). IR (CCl_4): 3550*m* (OOH). ^{1}H-NMR ($CDCl_3$): 1.50 (*s*, 3 H); 1.52 (*s*, 3 H); 4.70 (*s*, 1 H); 5.60 (*s*, 1 H); 6.33 (*s*, 1 H); 7.3–7.55 (*m*, 6 H); 7.6–7.7 (*m*, 4 H); 8.10 (*s*, 1 H). MS: 266 (3), 248 (7), 233 (16), 220 (3), 207 (4), 191 (15), 178 (4), 159 (2), 141 (2), 131 (6), 115 (11), 105 (100), 91 (6), 77 (59). Anal. calc. for $C_{20}H_{20}O_5$: C 70.58, H 5.92; found: C 70.30, H 5.84.

Reduction of **5**. A sample of **5** was prepared by photooxygenation of **1** (109 mg, 0.35 mmol). The solvent was evaporated and replaced by THF (10 ml). Next $NaBH_4$ (200 mg) was added and the resulting mixture stirred overnight at r.t. Insoluble material was filtered, the solvent evaporated, and the residue purified by chromatography over silica gel (CH_2Cl_2/EtOAc) affording the corresponding allylic alcohol (107 mg, 93%) cis-*3,4a,5,7a-tetrahydro-3,3-dimethyl-6,7a-diphenylcyclopenta[1,2-e]trioxine-5β-ol*. Colorless plates, m.p. 109–110° (recrsytallized from hexane at −78°). IR (CCl_4): 3610*m* (OH). ^{1}H-NMR ($CDCl_3$): 1.50 (*s*, 6 H); 1.85 (br. *d*, *J* = 6, 1 H); 4.38 (*s*, 1 H); 5.27 (*d*, *J* = 6, 1 H); 6.26 (*s*, 1 H); 7.3–7.5 (*m*, 6 H); 7.65 (*m*, 4 H). MS: 257 (1), 249 (7), 243 (22), 221 (7), 209 (3), 191 (21), 178 (6), 156 (4), 131 (8), 115 (17), 105 (100), 91 (13), 77 (78), 69 (14), 51 (24). Anal. calc. for $C_{20}H_{20}O_4$: C 74.06, H 6.22; found: C 73.88, H 6.22.

Photooxygenation of **6**. A soln. of **6** (141 mg, 0.49 mmol) in CCl_4 (15 ml) and TPP (3 mg) was irradiated with a 500-W *Sylvania-FFX* lamp equipped with a UV cut-off filter (> 418 nm) for 6 h at −20° while O_2 was bubbled through. Oxidation was complete after 6 h. TLC (CH_2Cl_2) revealed one spot corresponding to 7. Evaporation and recrystallization of the residue from hexane/Et_2O gave cis-*3,4a,5,7a-tetrahydro-6,7a-diphenylcyclopenta[1,2-e][1,2,4]trioxin-5β-yl hydroperoxide* (7) as a pure compound (98 mg, 62%). Colorless plates, m.p. 128–130° (recrystallized from hexane/Et_2O at −78°). IR ($CHCl_3$): 3525*m* (OOH). ^{1}H-NMR ($CDCl_3$): 5.11 (*d*, *J* = 5, 1 H); 5.33 (*d*, *J* = 8, 1 H); 5.62 (*d*, *J* = 8, 1 H); 5.82 (br. *d*, *J* = 5, 1 H); 6.21 (*d*, *J* = 1, 1 H); 7.35–7.5 (*m*, 6 H); 7.63 (*m*, 4 H); 7.87 (*s*, 1 H). MS: 312 (1, M^+), 294 (2), 264 (3), 248 (17), 236 (24), 235 (44), 220 (17), 191 (24), 105 (100), 77 (68). Anal. calc. for $C_{18}H_{16}O_5$: C 69.22, H 5.16; found: C 69.14, H 5.38.

Crystal Data for **1**, **2**, **3**, *and* **7**. *Cyclopentatrioxine* **1**[4]): $C_{20}H_{20}O_3$; *M* 308.4; monoclinic, $P2_1/c$; a = 17.144(4), b = 5.771(1), c = 17.720(4) Å; β = 110.64(2)°, V = 1640.7 Å^3; Z = 4; D_c = 1.25 g·cm^{-3}; μ = 5.84 cm^{-1} for Cu$K\alpha$ radiation; R = 0.042 for 2577 observed reflections ($|F|^2 \geq 3\sigma(F^2)$).

Peroxide **2**[5]): $C_{20}H_{20}O_6$; *M* 356.4; triclinic, $P\bar{1}$; a = 5.634(1), b = 10.079(3), c = 16.785(3) Å; α = 104.48(4), β = 93.48(3), γ = 103.93(1)°; V = 888.3 Å^3; Z = 2; D_c = 1.33 g·cm^{-3}; μ = 0.920 cm^{-1} for Mo$K\alpha$ radiation; R = 0.055 for 1171 observed reflections ($|F_o| \geq 3\sigma(F_o)$ and $|F_o| \geq 4.0$).

Alcohol **3**[5]): $C_{20}H_{20}O_6$; *M* 356.4; monoclinic, $C2/c$; a = 30.962(4), b = 6.126(1), c = 18.862(3) Å; β = 104.52(1)°, V = 3463.3 Å^3; z = 8; D_c = 1.37 g·cm^{-3}; μ = 0.944 cm^{-1} for Mo$K\alpha$ radiation; R = 0.066 for 1163 observed reflections ($|F_o| \geq 3\sigma(F_o)$ and $|F_o| \geq 8.0$).

Hydroperoxide **7**[5]): $C_{18}H_{16}O_5$; *M* 312.3; monoclinic, $P2_1/c$; a = 8.9185(12), b = 22.595(3), c = 8.0069(12) Å; β = 111.01(2)°, V = 1506.2 Å^3; Z = 4; D_c = 1.38 g·cm^{-3}; μ = 0.941 cm^{-1} for Mo$K\alpha$ radiation; R = 0.038 for 1047 observed reflections ($|F_o| \geq 3\sigma(F_o)$ and $|F_o| \geq 7.0$).

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