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Peroxidation

Approach for the Preparation of Various Classes of Peroxides Based on the Reaction of Triketones with H_2O_2: First Examples of Ozonide Rearrangements

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Abstract: The reaction of β,δ-triketones with an ethereal solution of H_2O_2 catalyzed by heteropoly acids in the presence of a polar aprotic co-solvent proceeds via three pathways to form three classes of peroxides: tricyclic monoperoxides, bridged tetraoxanes, and a pair of stereoisomeric ozonides. The reaction is unusual in that produces bridged tetraoxanes and ozonides with one of the three carbonyl groups remaining intact. In the synthesis of bridged tetraoxanes, the peroxide ring is formed by the reaction of hydrogen peroxide with two carbonyl groups at the β positions. The synthesis of ozonides from ketones and hydrogen peroxide is a unique process in which the ozonide ring is formed with the participation of two carbonyl groups at the δ positions. Rearrangements of ozonides were found for the first time after more than one century of their active investigation. Ozonides are interconverted with each other and rearranged into tricyclic monoperoxides, whereas ozonides and tricyclic monoperoxides are transformed into bridged tetraoxanes. The individual reaction products were isolated by column chromatography and characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. One representative of each class of peroxides was characterized by X-ray diffraction.

Introduction

The chemistry of organic peroxides is historically based to a large degree on the reactions of ketones and aldehydes with hydrogen peroxide and hydroperoxides.[1] Aldehydes and ketones have attracted interest as reagents due to their availability and the ease of interaction between the carbonyl carbon atom and the highly nucleophilic oxygen atom of the hydroperoxide group. Organic peroxides based on ketones are produced by dozens of companies on a large scale and are used as initiators for the radical polymerization of unsaturated compounds.[2] In the past three decades, the chemistry of organic peroxides was extensively developed, because these compounds were found to have high antimalarial,[3] anthelmintic,[4] and antitumor activities.[5] The interest in inexpensive and efficient radical polymerization initiators and technologically available biologically active compounds gave impetus to the development of new methods for the synthesis of peroxides starting from ketones and their derivatives, H_2O_2, and hydroperoxides.[6]

The peroxidation of monocarbonyl compounds was studied in most detail.[6,7] The peroxidation of di- and tricarbonyl compounds with H_2O_2 was investigated to a much lesser extent, mainly because these reactions are nonselective and afford a wide diversity of products.[8] In our previous studies,[9] we found an effective and facile route to bridged 1,2,4,5-tetraoxanes starting from β-diketones and H_2O_2 in the presence of acid catalysts. We also showed that, despite the use of hydrogen peroxide in greater than equimolar amounts, the previously unknown tricyclic peroxides containing only one O–O group are selectively assembled from β,δ-triketones and H_2O_2 in the presence of protic acids,[10] Lewis acids,[11] or phosphomolybdic and phosphotungstic acids (PMA, PTA).[10] Thus, it seemed that the only and inevitable pathway of the reaction of triketones results in the formation of tricyclic peroxides containing one peroxide group. In the present study, we showed that the use of polar aprotic (acetonitrile or dichloromethane) co-solvents in the PMA- or PTA-catalyzed peroxidation of β,δ-triketones substantially changes the reaction pathway. Thus, the reaction

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of β,δ-triketones affords different classes of peroxides: tricyclic monoperoxides, bridged tetraoxanes, and two stereoisomers of ozonides. We found that ozonides can be interconverted with each other and rearranged into tricyclic monoperoxides with the peroxide group remaining intact. Tricyclic monoperoxides and ozonides are transformed into bridged tetraoxanes also with retention of the peroxide group.

The known reactions involving the rearrangement of peroxides are usually accompanied by decomposition of the peroxide group. Examples are the Baeyer–Villiger oxidation,[12] the Dakin oxidation,[13] the Elbs oxidation,[14] the Criegee reaction,[15] the Hock rearrangement,[16] the Kornblum–DeLaMare rearrangement,[17] the Wieland rearrangement,[18] and a series of unnamed oxidation reactions involving hydrogen peroxide,[6f,19] hydroperoxides,[20] and peroxides.[21]

Among the diverse transformations of peroxides, only in a few reactions does the hydroperoxide group remain intact. These are mainly the Schenck[22] and Smith[23] rearrangements of allylic hydroperoxides. The acid-catalyzed transformation of acetone triperoxide into diperoxide was documented.[24] To the best of our knowledge, no other transformations of peroxides ROOR′ that are accompanied by R–OO or R′–OO bond cleavage and proceed with retention of the peroxide group were described in the literature.

Table 1. Synthesis of peroxides **2a**, **3a**, **4a**, and **5a** from triketone **1a** and H_2O_2.[a]

Entry	Acid (mol%), co-solvent	Yield of **2a** [%][b]	Yield of **3a** [%][b]	Yield of **4a** [%][b]	Yield of **5a** [%][b]
1	PMA (5.0), CH_2Cl_2	37	16	22	17
2	PMA (10.0), CH_2Cl_2	35	17	20	11
3	PMA (5.0), MeCN	27, 24[c]	25, 22[c]	21, 15[c]	17, 9[c]
4	PMA (10.0), MeCN	33	22	12	10
5	PMA (15.0), MeCN	37, 32[c]	22, 18[c]	13, 9[c]	10, 8[c]
6	PTA (5.0), CH_2Cl_2	30, 26[c]	25, 21[c]	26, 21[c]	14, 11[c]
7[d]	PTA (5.0), CH_2Cl_2	50	14	19	9
8	PTA (5.0), MeCN	25, 21[c]	28, 22[c]	22, 18[c]	16, 12[c]
9[d]	PTA (5.0), MeCN	36	20	22	17

[a] General reaction conditions: A solution of H_2O_2 (5.8 wt% H_2O_2 in Et_2O, 1.5 mol of H_2O_2 per mole of **1a**) and PMA (5–15 mol%) or PTA (5 mol%) were successively added to a solution of β,δ-triketone **1a** in dichloromethane or acetonitrile at 20–25 °C. The mixture was stirred at 20–25 °C for 8 h. [b] Yield based on NMR data. [c] Yield of isolated product. [d] 3 mol of H_2O_2 per mole of **1a**.

Results and Discussion

Peroxidation of β,δ-triketones giving tricyclic monoperoxides, bridged tetraoxanes, and ozonides

The peroxidation of β,δ-triketones **1a–e** with an ethereal solution of H_2O_2 catalyzed by PMA or PTA in the presence of co-solvents (CH_3CN or CH_2Cl_2) afforded tricyclic monoperoxides **2a–e**, bridged tetraoxanes **3a–e**, and stereoisomeric ozonides **4a–e** and **5a–e**; the reactions of β,δ-triketones **1f–h** give only tricyclic monoperoxides **2f–h** (Scheme 1).

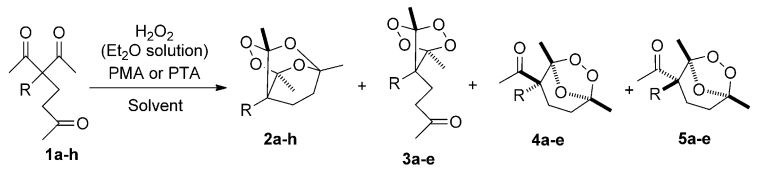
To the best of our knowledge, only one example of the preparative synthesis of an ozonide from a diketone (heptane-2,6-dione) with the use of H_2O_2 was described in the literature.[25] Besides, the possibility of synthesizing this compound from the same reagents in the gas phase was mentioned.[26]

We studied the effect of the amount of the catalyst (PMA or PTA) and the composition of the solvent on the yield of products **2a**, **3a**, **4a**, and **5a** by examining the peroxidation of 3-acetyl-3-benzylheptene-2,6-dione (**1a**; Table 1). The peroxidation was performed under initial homogeneous conditions with CH_2Cl_2 and MeCN as solvents. Since we used an ethereal solution of hydrogen peroxide, all reactions were performed in CH_2Cl_2/Et_2O and $MeCN/Et_2O$ mixtures, with an excess of the former component. In CH_2Cl_2, increasing the amount of PMA was from 5 to 10 mol% gave tricyclic monoperoxide **2a** in higher yield compared to tetraoxane **3a** and ozonides **4a** and **5a** (Table 1, entries 1 and 2). In MeCN (Table 1, entries 3–5), tetraoxane **3a** and ozonides **4a** and **5a** were produced in yields approximately equal to that of tricyclic monoperoxide **2a**.

In MeCN in the presence of 5% of PMA, all four reaction products formed in approximately equal yields (Table 1, entry 3). Similar results were obtained in the presence of 5% PTA in CH_2Cl_2 (Table 1, entry 6) and MeCN (Table 1, entry 8). Increasing the amount of hydrogen peroxide led to an increase in the yield of **2a** (cf. Table 1, entries 6 and 7). The results obtained with PMA and PTA were rather similar; however, application of PMA is more convenient due to its lower molecular weight.

Other tricyclic monoperoxides **2b–h**, bridged tetraoxanes **3b–e**, and stereoisomeric ozonides **4b–e** and **5b–e** were also synthesized under homogeneous conditions starting from β,δ-triketones **1b–h** and H_2O_2 (Table 2). The peroxidation of β,δ-triketones **1b–e** containing a benzyl substituent produced four products **2–5**. The reactions of unsubstituted triketone **1f** and triketones containing aliphatic substituents **1g,h** gave only tricyclic monoperoxides **2f–h**; traces of other peroxides were observed among the reaction products, but attempts to isolate them failed.

The peroxidation of triketones provides the possibility of preparing different classes of compounds (tricyclic monoperoxides, bridged tetraoxanes, and ozo-



a: R = Bn = $C_6H_5CH_2$; **b**: R = 4-$NO_2C_6H_4CH_2$; **c**: R = 4-$CH_3C_6H_4CH_2$; **d**: R = 4-$ClC_6H_4CH_2$; **e**: R = 4-$BrC_6H_4CH_2$; **f**: R = H; **g**: R=*n*-Bu; **h**: R = CH_2CH_2CN

Scheme 1. Peroxidation of β,δ-triketones **1a–h** with H_2O_2.

Table 2. Yields [%] of peroxides **2b–h**, **3b–e**, **4b–e**, and **5b–e**.[a]

Tricyclic monoperoxides **2b–e**	Bridged tetraoxanes **3b–e**	Ozonides **4b–e**	Ozonides **5b–e**
2b, 24	**3b**, 31	**4b**, 15	**5b**, 12
2c, 27	**3c**, 23	**4c**, 18	**5c**, 10
2d, 30	**3d**, 25	**4d**, 20	**5d**, 10
2e, 20	**3e**, 21	**4e**, 15	**5e**, 14
2f, 80	–	–	–
2g, 58	–	–	–
2h, 81	–	–	–

[a] General reaction conditions: An ethereal solution of H_2O_2 (5.8 wt% H_2O_2 in Et_2O, 1.5 mol per mole of β,δ-triketone **1b–h**) and PMA (5 mol%) were added to a solution of β,δ-triketone **1b–h** in MeCN at 20–25 °C. The mixture was stirred at 20–25 °C for 8 h.

nides) in one reaction. It is surprising that the reaction giving tetraoxanes and ozonides proceeds with the retention of one carbonyl group. In the case of tetraoxanes, the peroxide ring is formed as a result of the reaction of two carbonyl groups at the β positions with hydrogen peroxide. In the synthesis of ozonides, the ring is formed with the participation of two carbonyl groups at the δ positions. The synthesis of ozonides from ketones and hydrogen peroxide is a very rare process.[25,26]

Establishment of the structures of peroxides 2–5

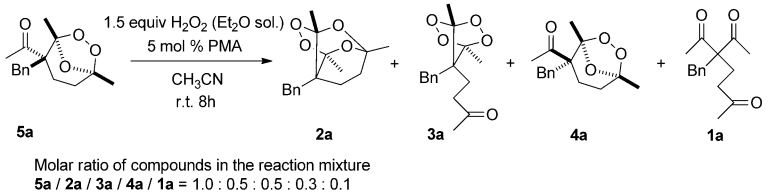
Products **2–5** were separated by column chromatography and characterized by NMR spectroscopy, high-resolution mass spectrometry, and elemental analysis. One representative of each class of peroxides was studied by X-ray diffraction (see Supporting Information). Based on the structures of these peroxides, we obtained the reference NMR chemical shifts by ^1H and ^{13}C NMR spectroscopy using 2D correlation spectroscopic techniques (COSY, NOESY, editing HSQC, and HMBC) and used them to make chemical shift assignments for the other peroxides. The yields of the reaction products were determined from the characteristic signals. For tricyclic monoperoxide **2b**, the characteristic signal in the ^1H NMR spectrum is a singlet at 2.96 ppm (s, 2H, CH_2Ar); for tetraoxane **3b**, a singlet at 3.10 ppm (s, 2H, CH_2Ar); for ozonide **4b**, a doublet at 3.59 ppm (d, 1H, CH_2Ar, $J = 13.2$ Hz); and for ozonide **5b**, a doublet at 3.46 ppm (d, 1H, CH_2Ar, $J = 13.2$ Hz). The ^{13}C NMR spectra of show characteristic signals for tricyclic monoperoxide **2b** at 93.8 (O*C*(CH_2)O) and 107.2 ppm (O*C*(CH_3)O); for tetraoxane **3b** at 111.8 (OCO) and 206.6 ppm (C=O); for ozonide **4b** at 109.2 (OOCCH_2), 110.8 (OO*C*C), and 210.3 ppm (C=O); and for ozonide **5b** at 109.0 (OOCCH_2), 110.6 (OO*C*C), and 209.5 ppm (C=O).

Interconversion of cyclic peroxides

As we have shown earlier,[10,11] the reactions of β,δ-triketones selectively produce tricyclic monoperoxides in a strongly acidic medium in the presence of a large excess of the catalyst (boron trifluoride etherate, sulfuric acid, perchloric acid, or tetrafluoroboric acid), which also serves as a co-solvent medium. A decrease in the amount of the acid led to a substantial decrease in the yield of these products. In the present study, we prepared bridged tetraoxanes and ozonides along with tricyclic monoperoxides by PMA- or PTA-catalyzed reactions of β,δ-triketones with H_2O_2. Initially, we considered bridged tetraoxanes and ozonides to be byproducts that were formed in competitive reactions, because these compounds are very different.

The NMR monitoring of the PMA-catalyzed peroxidation of 3-acetyl-3-benzylheptane-2,6-dione **1a** with an ethereal solution of H_2O_2 in CD_3CN showed that this reaction is a complex process (Figure 5 in the Supporting Information). The multifacetedness of the reaction mechanism is the result of the properties of PMA and PTA. One the one hand, PMA and PTA are protic acids, and on the other hand they form peroxo compounds with M–O–O fragments that influence the direction of peroxidation.[27] In the first few minutes the amounts of ozonides **4a** and **5a** were substantially higher than those of tricyclic compound **2a** and tetraoxane **3a**. One hour after the beginning of the reaction, the amounts of all four products became approximately equal, after which the amount of tetraoxane **3a** remained virtually unchanged, ozonides **4a** and **5a** disappeared, the amount of tricyclic compound **2a** increased, and the conversion of **1a** changed only slightly. The NMR monitoring suggests that ozonides are intermediates in the synthesis of tricyclic compound **2a**. To confirm this suggestion, different reaction conditions were applied for authentic samples of peroxides.

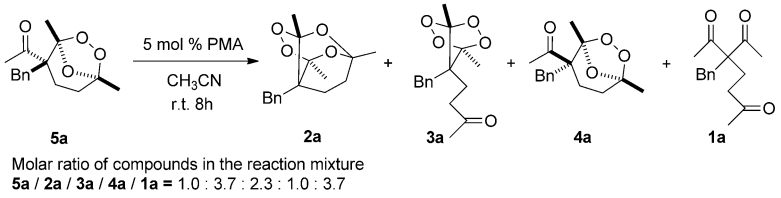
The reaction of ozonide **5a** with hydrogen peroxide gave the same products **2a**, **3a**, and **4a** as those prepared from triketone **1a**; besides, a small amount of triketone **1a** was identified (Scheme 2). In the presence of PMA, the transformation of



Scheme 2. PMA-catalyzed transformation of ozonide **5a** with the use of hydrogen peroxide.

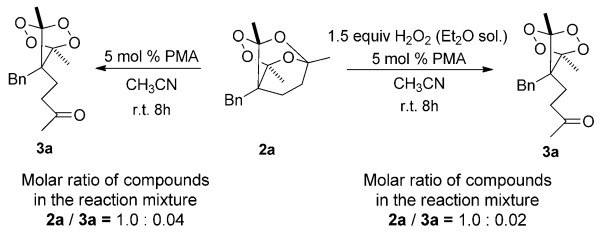
ozonide **5a** takes place even in the absence of hydrogen peroxide to give the same products. The unexpected formation of tetraoxane **3a** containing two peroxide groups can evidently be attributed to the fact that hydrogen peroxide that is eliminated from an ozonide is also involved the reaction (Scheme 3).

Tricyclic monoperoxides and bridged tetraoxanes are more stable products than ozonides. Thus, the transformation of the

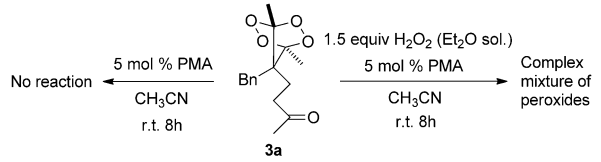


Scheme 3. PMA-catalyzed transformation of ozonide **5a** without hydrogen peroxide.

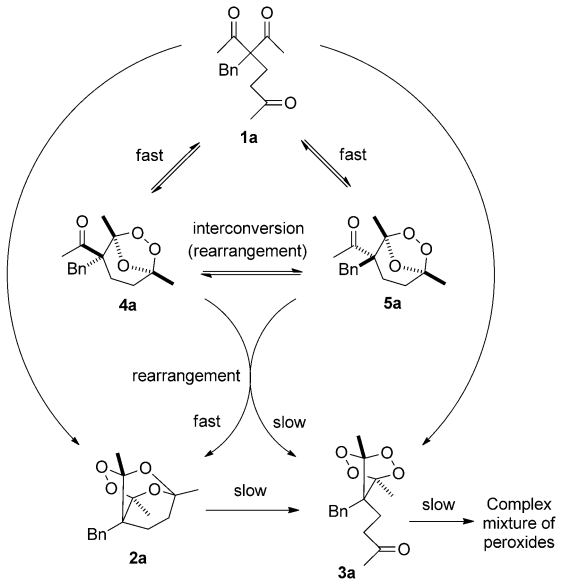
specially prepared tricyclic monoperoxide **2a** into tetraoxane **3a** occurs to a small extent both in the presence and in the absence of hydrogen peroxide (Scheme 4). In the absence of hydrogen peroxide, tetraoxane **3a** remains intact, whereas it is slowly transformed into a complex mixture of peroxides in the presence of hydrogen peroxide (Scheme 5). On the basis of the experimental results, the general scheme of the process can be represented as follows (Scheme 6).



Scheme 4. PMA-catalyzed transformations of tricyclic monoperoxide **2a**.



Scheme 5. PMA-catalyzed transformations of of tetraoxane **3a**.



Scheme 6. Pathways of the peroxidation of 3-acetyl-3-benzylheptane-2,6-dione (**1a**) under the following conditions: a solution of H_2O_2 in Et_2O (1.5 mol of H_2O_2 per mole of **1a**), 5 mol% PMA, CH_3CN, RT, 8 h.

Alternative pathways for the formation of cyclic peroxides **2a** and **3a** from triketone **1a** cannot be ruled out. For example, since the carbonyl carbon atom easily interacts with the highly nucleophilic oxygen atom of the hydroperoxide group, **2a** and **3a** can be generated through the intermediate formation of hydroperoxides, hydroxyhydroperoxides, and hydroxyhydroperoxyperoxides. These intermediates were not observed in the ^1H and ^{13}C NMR spectra, which may be due to their rapid transformation into the final products.

The results of the present and earlier studies[9a,10,11] on the effect of the acidity suggest that tricyclic monoperoxides and bridged tetraoxanes are thermodynamically most favorable peroxidation products. In the presence of a large excess of the acid, the peroxidation of triketones usually gives these compounds as the major products.

Conclusion

The reaction of β,δ-triketones with an ethereal solution of H_2O_2 in acetonitrile or dichloromethane in the presence of PMA or PTA proceeds via three pathways. Thus, it affords tricyclic monoperoxides as the major products along with bridged tetraoxanes and ozonides containing a carbonyl group. The modification of this group can be used to prepare structurally diverse peroxides. Ozonides were found to be intermediates. In the course of the reaction, they are transformed into tetraoxanes and tricyclic monoperoxides. Thus, previously unknown rearrangements of ozonides were found: ozonides are interconverted with each other and rearrange into tricyclic monoperoxides. The observation of ozonide intertransformation may be useful for interpretation of data for the ozonolysis of unsymmetrical unsaturated compounds. Tricyclic monoperoxides, tetraoxanes, and ozonides were isolated by column chromatography and characterized by X-ray diffraction, NMR spectroscopy, mass spectrometry, and elemental analysis. The reaction can be used for the preparative synthesis of these compounds.

Experimental Section

General

Caution! Although we encountered no difficulties in working with peroxides, precautions, such as the use of shields, fume hoods, and the avoidance of transition metal salts, heating, and shaking, should be taken whenever possible.

NMR spectra were recorded on a commercial instrument (300.13 MHz for ^1H, 75.48 MHz for ^{13}C in $CDCl_3$.

High-resolution mass spectra (HRMS) were measured by using electrospray ionization (ESI).[28] The measurements were done in positive-ion mode (interface capillary voltage 4500 V); the spectra were acquired in the *m/z* range of 50–3000; the external/internal calibration was done with Electrospray Calibrant Solution. Solutions in MeCN were injected with a syringe (flow rate 3 μL min^{-1}). Nitrogen was applied as a dry gas; the interface temperature was set at 180 °C.

TLC analysis was carried out on standard silica gel chromatography plates. The melting points were determined on a Kofler hot-stage apparatus. Chromatography was performed on silica gel (0.060–0.200 mm, 60 A, CAS 7631-86-9).

Dichloromethane, diethyl ether, acetonitrile, petroleum ether (PE, 40/70), ethyl acetate (EA), phosphomolybdic acid hydrate (ca. 78% phosphomolybdic acid, PMA), phosphotungstic acid 44-hydrate (PTA), acetylacetone, methyl vinyl ketone, benzyl and alkyl bromides, H_2O_2 (37% aqueous solution), Na_2SO_4, and $NaHCO_3$ were purchased from Acros. A solution of H_2O_2 in Et_2O (5.8%, w/w) was prepared by the extraction with Et_2O (5×100 mL) from a 37% aqueous solution (100 mL) followed by drying over $MgSO_4$.

Synthesis of β,δ-triketones

β,δ-Triketones **1a**[29] and **1b**–**h**[30] were synthesized according to known procedures.

3-Acetyl-3-benzylheptane-2,6-dione (1a): White crystals. R_f=0.34 (PE/EA 5/1); m.p. 79–80 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ=2.06–2.14 (m, 11H, 3×CH_3, CCH_2CH$_2$), 2.27–2.34 (m, 2H, CH_2CO), 3.16 (s, 2H, CH_2Ar), 6.95–7.04 (m, 2H, 2×CH), 7.16–7.27 ppm (m, 3H, 3×CH).

3-Acetyl-3-(4-nitrobenzyl)heptane-2,6-dione (1b): Hazel-colored crystals. R_f=0.31 (PE/EA 2/1); m.p. 113–114 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ=2.11 (m, 11H, 3×CH_3, CCH_2CH$_2$), 2.32 (t, 2H, CH_2CO, J=7.7 Hz), 3.24 (s, 2H, CH_2Ar), 7.19 (d, 2H, 2×CH, J=8.8 Hz), 8.08 ppm (d, 2H, 2×CH, J=8.8 Hz).

3-Acetyl-3-(4-methylbenzyl)heptane-2,6-dione (1c): White crystals. R_f=0.56 (PE/EA 2/1); m.p. 125–126 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ=2.09 (m, 11H, 3×CH_3, CCH_2CH$_2$), 2.24–2.35 (m, 5H, CH_2CO, CH_3C), 3.12 (s, 2H, CCH_2), 6.87 (d, 2H, 2×CH, J=7.3 Hz), 7.03 ppm (d, 2H, 2×CH, J=7.3 Hz).

3-Acetyl-3-(4-chlorobenzyl)heptane-2,6-dione (1d): White crystals; Yield 84%; R_f=0.49 (PE/EA 2/1); m.p. 130–131 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ=2.04–2.13 (m, 11H, 3×CH_3, CH_2), 2.28 (t, 2H, CH_2C=O, J=7.3 Hz), 3.11 (s, 2H, CH_2Ar), 6.93 (d, 2H, 2×CH, J=8.8 Hz), 7.20 ppm (d, 2H, 2×CH, J=8.8 Hz); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ=24.2, 27.8, 30.0, 36.8, 37.9, 69.9, 128.7, 130.9, 133.0, 134.1, 206.56, 206.61 ppm; HRMS (ESI): *m/z* calcd for $C_{16}H_{19}ClO_3$+Na^+: 317.0915 [*M*+Na^+]; found: 317.0918; elemental analysis calcd (%) for $C_{16}H_{19}ClO_3$: C 65.19, H 6.50, Cl 12.03; found: C 65.27, H 6.41, Cl 12.12.

3-Acetyl-3-(4-bromobenzyl)heptane-2,6-dione (1e): White crystals; Yield 79%; R_f=0.49 (PE/EA 2/1); m.p. 122–123 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ=2.02–2.16 (m, 11H, 3×CH_3, CH_2), 2.29 (t, 2H, CH_2C=O, J=7.3 Hz), 3.11 (s, 2H, CH_2Ar), 6.88 (d, 2H, 2×CH, J=8.1 Hz), 7.36 ppm (d, 2H, 2×CH, J=8.1 Hz); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ=24.3, 27.8, 30.0, 36.9, 37.9, 69.9, 121.1, 131.3, 131.9, 134.6, 206.57, 206.63 ppm; HRMS (ESI): *m/z* calcd for $C_{16}H_{19}BrO_3$+Na^+: 361.0410 [*M*+Na^+]; found: 361.0409; elemental analysis calcd (%) for $C_{16}H_{19}BrO_3$: C 56.65, H 5.65, Br 23.55; found: C 56.63, H 5.67, Br 22.72.

3-Acetylheptane-2,6-dione (1f): Yellow oil; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ=1.97–2.16 (m, 11H, 3×CH_3, CHCH_2), 2.40 (t, 2H, CH_3COCH_2, J=7.0 Hz), 3.63 (t, 0.8H, CH, J=7.0 Hz), 16.64 ppm br s, 0.2H, OH).

3-Acetyl-3-butylheptane-2,6-dione (1g): White crystals; R_f=0.51 (PE/EA 5/1); m.p. 45–46 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ=0.85 (t, 3H, CH_3CH$_2$, J=7.0 Hz), 0.92–1.05 (m, 2H, CH_3CH_2), 1.21–1.34 (m, 2H, CH_3CH_2CH_2), 1.75–1.84 (m, 4H, CCH_2CH$_2$CH$_2$, CCH_2CH$_2$CO), 2.01–2.12 (m, 9H, 3×CH_3), 2.15–2.24 ppm (m, 2H, CH_2CO).

4,4-Diacetyl-7-oxooctanenitrile (1h): Hazel-colored crystals; R_f=0.27 (PE/EA 2/1); m.p. 74–75 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$), δ=2.05–2.31 (m).

Typical reaction for for Table 1 (entries 1–9)

Peroxidation of 3-acetyl-3-benzylheptane-2,6-dione (1a): A 1.10 M ethereal H_2O_2 solution (1.57–3.14 mL, 1.73–3.45 mmol) and PMA (0.014–0.042 g, 5–15 mol%) or PTA (0.037 g, 5 mol%) were successively added with stirring to a solution of β,δ-triketone **1a** (0.30 g, 1.15 mmol) in CH_2Cl_2 or CH_3CN (4 mL) at 20–25 °C. The reaction mixture was stirred at 20–25 °C for 8 h. Then CH_2Cl_2 (20 mL) was added. The organic layer was washed with water (5 mL), a 5% aqueous solution of $NaHCO_3$, and again with water (5 mL). The mixture was dried over Na_2SO_4 and filtered. The solvent was removed with a water-jet vacuum pump. Products **2a**, **3a**, **4a**, and **5a** were isolated by silica-gel column chromatography by gradient elution with 10–80 vol% of EA in PE.

Synthesis of peroxides from β,δ-triketones

An ethereal solution of H_2O_2 (1.5 mol per mole of triketone **1a**–**h**, 1.32–2.64 mmol, 1.10 mol L^{-1}, 1.20–2.40 mL) and PMA (5 mol%) were successively added with stirring to a solution of β,δ-triketone **1a**–**h** (0.30 g, 0.88–1.76 mmol) in CH_3CN (4 mL) at room temperature. The reaction mixture was stirred at 20–25 °C for 8 h. Then CH_2Cl_2 (20 mL) was added. The organic layer was washed with water (5 mL), a 5% aqueous solution of $NaHCO_3$, and again with water (5 mL). The mixture was dried over Na_2SO_4 and filtered. The solvent was removed with a water-jet vacuum pump. Products **2a**–**h**, **3a**–**e**, **4a**–**e**, **5a**–**e** were isolated by silica gel column chromatography by gradient elution with 0–80 vol% EA in PE.

Yields:

2a, 14% (44.6 mg, 0.16 mmol); **3a**, 22% (74.1 mg, 0.25 mmol); **4a**, 15% (47.8 mg, 0.17 mmol); **5a**, 9% (28.7 mg, 0.10 mmol).

2b, 24% (75.8 mg, 0.24 mmol); **3b**, 31% (102.7 mg, 0.30 mmol); **4b**, 15% (47.4 mg, 0.15 mmol); **5b**, 12% (37.9 mg, 0.12 mmol).

2c, 27% (85.7 mg, 0.30 mmol); **3c**, 23% (77.0 mg, 0.25 mmol); **4c**, 18% (57.1 mg, 0.20 mmol); **5c**, 10% (31.7 mg, 0.11 mmol).

2d, 30% (94.9 mg, 0.31 mmol); **3d**, 25% (83.1 mg, 0.25 mmol); **4d**, 20% (63.3 mg, 0.20 mmol); **5d**, 10% (31.6 mg, 0.10 mmol).

2e, 20% (62.8 mg, 0.18 mmol); **3e**, 21% (68.9 mg, 0.19 mmol); **4e**, 15% (47.1 mg, 0.13 mmol); **5e**, 14% (44.0 mg, 0.12 mmol).

2f, 17% (55.8 mg, 0.30 mmol).

2g, 58% (186.3 mg, 0.77 mmol).

2h, 81% (260.4 mg, 1.09 mmol).

Procedure for transformations of peroxides 2a, 3a, and 5a

An ethereal solution of H_2O_2 (1.5 mol per mole of peroxide **2a** (**3a** or **5a**), 0.30 mmol, 1.10 mol L^{-1}, 0.27 mL) and PMA (5 mol%) were successively added with stirring to a solution of peroxide **2a** (**3a** or **5a**) (0.20 mmol) in CH_3CN (0.7 mL) at 20–25 °C. The reaction mixture was stirred at 20–25 °C for 8 h. Then CH_2Cl_2 (5 mL) was added. The organic layer was washed with water (1.5 mL), a 5%

aqueous solution of $NaHCO_3$, and again with water (1.5 mL). The mixture was dried over Na_2SO_4 and filtered. The solvent was removed with a water-jet vacuum pump. The conversion products of peroxides **2a**, **3a**, and **5a** were observed by ^1H NMR and ^{13}C NMR spectroscopy.

3a-Benzyl-3,6,7a-trimethyltetrahydro-3*H*,4*H*-3,6-epoxy-[1,2]dioxolo[3,4-*b*]pyran (2a): White crystals; $R_f = 0.37$ (PE/EA 5/1); m.p. 95–96 °C; ^1H NMR (300.13 MHz, $CDCl_3$): $\delta = 1.39$ (s, 3H, CH_3CCH_2), 1.43 (s, 6H, 2×CH_3), 1.66–1.75 (m, 2H, CH_2CCH_3), 1.81–1.89 (m, 2H, CH_2), 2.87 (s, 2H, CH_2Ar), 7.20–7.31 ppm (m, 5H, 5×CH); ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta = 16.1$ (CH_3), 18.9 (CH_2C), 24.7 (CH_3CCH_2), 30.9 (CH_2CCH_3), 36.8 (CH_2Ar), 51.7 (CH_2CCH_2), 93.7 ($OC(CH_2)O$), 107.5 ($OC(CH_3)O$), 126.8, 128.1, 131.2 (CH), 136.4 ppm (C); HRMS (ESI): *m/z* calcd for $C_{16}H_{20}O_4 + Na^+$: 299.1254 [M+Na^+]; found: 299.1248; elemental analysis calcd (%) for $C_{16}H_{20}O_4$: C 69.54, H 7.30; found: C 69.41, H 7.28.

4-(7-Benzyl-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.1]hept-7-yl)-2-butanone (3a): White crystals; $R_f = 0.75$ (PE/EA 1/1); m.p. 69–70 °C; ^1H NMR (300.13 MHz, $CDCl_3$): $\delta = 1.22$ (s, 6H, 2×CH_3), 2.06–2.14 (m, 2H, CCH_2CH_2), 2.28 (s, 3H, CH_3C=O), 2.64–2.71 (m, 2H, CH_2C=O), 3.00 (s, 2H, CH_2Ar), 7.21–7.32 ppm (m, 5H, 5×CH); ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta = 9.2$ (CH_3), 21.5 (CCH_2CH_2), 30.1 (CH_3C=O), 34.1 (CH_2Ar), 38.1 (CH_2C=O), 60.1 (C), 112.0 (OCO), 127.2, 128.4, 130.9 (CH), 135.2 (CHCCH), 206.9 ppm (C=O); HRMS (ESI): *m/z* calcd for $C_{16}H_{20}O_5 + NH_4^+$: 310.1649 [M+NH_4^+]; found: 310.1648; elemental analysis calcd (%) for $C_{16}H_{20}O_5$: C 65.74, H 6.90; found: C 65.61, H 7.04.

1-[(1*R*,2*R*,5*S*)-2-Benzyl-1,5-dimethyl-6,7,8-trioxabicyclo[3.2.1]oct-2-yl]ethanone (4a): Colorless oil; $n_D^{22} = 1.5160$; $R_f = 0.76$ (PE/EA 5/1); ^1H NMR (300.13 MHz $CDCl_3$): $\delta = 1.48$ (s, 3H, CH_3CC), 1.53–1.63 (m, 4H, CH_3CCH_2, CH_2), 1.76–1.86 (m, 1H, CH_2CCH_3), 1.88–2.03 (m, 1H, CH_2CCH_3), 2.15 (s, 3H, CH_3C=O), 2.57–2.71 (m, 1H, CH_2), 2.89 (d, 1H, CH_2Ar, $J = 13.2$ Hz), 3.54 (d, 1H, CH_2Ar, $J = 13.2$ Hz), 7.02–7.10 (m, 2H, 2×CH), 7.15–7.27 ppm (m, 3H, 3×CH); ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta = 18.4$ (CH_3CC), 20.8 (CH_3CCH_2), 22.3 (CH_2), 30.3 (CH_3C=O), 31.0 (CH_2CCH_3), 36.2 (CH_2Ar), 59.2 (C), 109.2 ($OOCCH_2$), 111.4 (OOCC), 126.6, 128.3, 130.2 (CH), 137.7 (CHCCH), 210.9 ppm (C=O); HRMS (ESI): *m/z* calcd for $C_{16}H_{20}O_4 + Na^+$: 299.1254 [M+Na^+]; found: 299.1243; elemental analysis calcd (%) for $C_{16}H_{20}O_4$: C 69.54, H 7.30; found: C 69.49, H 7.39.

1-[(1*R*,2*S*,5*S*)-2-Benzyl-1,5-dimethyl-6,7,8-trioxabicyclo[3.2.1]oct-2-yl]ethanone (5a): White crystals; $R_f = 0.63$ (PE/EA 5/1); m.p. 88–89 °C; ^1H NMR (300.13 MHz, $CDCl_3$): $\delta = 1.50$ (s, 3H, CH_3CCH_2), 1.62–1.76 (m, 4H, CH_3CC, CH_2CCH), 1.87–1.96 (m, 2H, CH_2CCH_3), 2.07 (s, 3H, CH_3C=O), 2.18–2.33 (m, 1H, CH_2), 2.59 (d, 1H, CH_2Ar, $J = 13.2$ Hz), 3.35 (d, 1H, CH_2Ar, $J = 13.2$ Hz), 7.01–7.09 (m, 2H, 2×CH), 7.15–7.29 ppm (m, 3H, 3×CH); ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta = 18.9$ (CH_3CC), 20.5 (CH_3CCH_2), 25.8 (CH_2), 30.0 (CH_3C=O), 33.0 (CH_2CCH_3), 41.4 (CH_2Ar), 58.3 (C), 109.0 ($OOCCH_2$), 111.3 (OOCC), 126.7, 128.2, 130.1 (CH), 136.0 (CHCCH), 210.3 ppm (C=O); HRMS (ESI): *m/z* calcd for $C_{16}H_{20}O_4 + Na^+$: 299.1254 [M+Na^+]; found: 299.1242; elemental analysis calcd (%) for $C_{16}H_{20}O_4$: C 69.54, H 7.30; found: C 69.37, H 7.39.

3,6,7a-Trimethyl-3a-(4-nitrobenzyl)tetrahydro-3*H*,4*H*-3,6-epoxy-[1,2]dioxolo[3,4-*b*]pyran (2b): White crystals; $R_f = 0.20$ (PE/EA 5/1); m.p. 148–149 °C; ^1H NMR (300.13 MHz, $CDCl_3$): $\delta = 1.38$ (s, 3H, CH_3CCH_2), 1.41 (s, 6H, 2×CH_3), 1.68–1.77 (m, 2H, CH_2CCH_3), 1.79–1.88 (m, 2H, CH_2), 2.96 (s, 2H, CH_2Ar), 7.42 (d, 2H, 2×CH, $J = 8.8$ Hz), 8.15 ppm (d, 2H, 2×CH, $J = 8.8$ Hz); ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta = 16.7$ (CH_3), 19.0 (CH_2C), 24.6 (CH_3CCH_2), 30.7 (CH_2CCH_3), 36.8 (CH_2Ar), 51.9 (CH_2CCH_2), 93.8 ($OC(CH_2)O$), 107.2 ($OC(CH_3)O$), 123.3, 131.9 (CH), 144.4 (CH_2C), 147.0 ppm (CNO_2); HRMS (ESI): *m/z* calcd for $C_{16}H_{19}NO_6 + Na^+$: 344.1105 [M+Na^+]; found: 344.1100; elemental analysis calcd (%) for $C_{16}H_{19}NO_6$: C 59.81, H 5.96, N 4.36; found: C 60.08, H 5.74, N 4.38.

4-[1,4-Dimethyl-7-(4-nitrobenzyl)-2,3,5,6-tetraoxabicyclo-[2.2.1]hept-7-yl]-2-butanone (3b): White crystals; $R_f = 0.61$ (PE/EA 1/1); m.p. 120–121 °C; ^1H NMR (300.13 MHz, $CDCl_3$): $\delta = 1.22$ (s, 6H, 2×CH_3), 2.07–2.15 (m, 2H, CH_2), 2.21 (s, 3H, CH_3C=O), 2.67–2.77 (m, 2H, CH_2C=O), 3.10 (s, 2H, CH_2Ar), 7.46 (d, 2H, 2×CH, $J = 8.1$ Hz), 8.17 ppm (d, 2H, 2×CH, $J = 8.1$ Hz); ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta = 9.3$ (CH_3), 21.6 (CCH_2CH_2), 30.2 (CH_3C=O), 34.3 (CH_2Ar), 37.9 (CH_2C=O), 60.2 (C), 111.8 (OCO), 123.5, 131.9 (CH), 143.1 (CHCCH), 147.3 (CNO_2), 206.6 ppm (C=O); HRMS (ESI): *m/z* calcd for $C_{16}H_{19}NO_7 + Na^+$: 360.1054 [M+Na^+]; found: 360.1043; elemental analysis calcd (%) for $C_{16}H_{19}NO_7$: C 56.97, H 5.68, N 4.15; found: C 56.77, H 5.57, N 4.35.

1-[(1*R*,2*R*,5*S*)-1,5-Dimethyl-2-(4-nitrobenzyl)-6,7,8-trioxabicyclo-[3.2.1]oct-2-yl]ethanone (4b): White crystals; $R_f = 0.50$ (PE/EA 5/1); m.p. 115–116 °C; ^1H NMR (300.13 MHz, $CDCl_3$): $\delta = 1.33$–1.42 (m, 4H, CH_3CC, CH_2), 1.51 (s, 3H, CH_3CCH_2), 1.72–1.95 (m, 2H, CH_2CCH_3), 2.15 (s, 3H, CH_3C=O), 2.58–2.73 (m, 1H, CH_2), 2.94 (d, 1H, CH_2Ar, $J = 13.2$ Hz), 3.59 (d, 1H, CH_2Ar, $J = 13.2$ Hz), 7.21 (d, 2H, 2×CH, $J = 8.8$ Hz), 8.02 ppm (d, 2H, 2×CH, $J = 8.8$ Hz); ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta = 18.2$ (CH_3CC), 20.7 (CH_3CCH_2), 22.2 (CH_2), 29.9 (CH_3C=O), 30.8 (CH_2CCH_3), 35.4 (CH_2Ar), 59.6 (C), 109.2 ($OOCCH_2$), 110.8 (OOCC), 123.4, 131.2 (CH), 145.8 (CHCCH), 146.8 (CNO_2), 210.3 ppm (C=O); HRMS (ESI): *m/z* calcd for $C_{16}H_{19}NO_6 + Na^+$: 344.1105 [M+Na^+]; found: 344.1103; elemental analysis calcd (%) for $C_{16}H_{19}NO_6$: C 59.81, H 5.96, N 4.36; found: C 59.54, H 5.79, N 4.44.

1-[(1*R*,2*S*,5*S*)-1,5-Dimethyl-2-(4-nitrobenzyl)-6,7,8-trioxabicyclo-[3.2.1]oct-2-yl]ethanone (5b): White crystals; $R_f = 0.41$ (PE/EA 5/1); m.p. 132–133 °C; ^1H NMR (300.13 MHz, $CDCl_3$): $\delta = 1.42$–1.52 (m, 4H, CH_3CCH_2, CH_2), 1.57 (s, 3H, CH_3CC), 1.82–2.00 (m, 2H, CH_2CCH_3), 2.06–2.23 (m, 4H, CH_3C=O, CH_2), 2.58 (d, 1H, CH_2Ar, $J = 13.2$ Hz), 3.46 (d, 1H, CH_2Ar, $J = 13.2$ Hz), 7.17 (d, 2H, 2×CH, $J = 8.8$ Hz), 8.01 ppm (d, 2H, 2×CH, $J = 8.8$ Hz); ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta = 18.5$ (CH_3CC), 20.6 (CH_3CCH_2), 25.5 (CH_2), 30.1 (CH_3C=O), 32.7 (CH_2CCH_3) 40.6 (CH_2Ar), 58.3 (C), 109.0 ($OOCCH_2$), 110.6 (OOCC), 123.3, 131.1 (CH), 144.3 (CHCCH), 147.0 (CNO_2), 209.5 ppm (C=O). HRMS (ESI): *m/z* calcd for $C_{16}H_{19}NO_6 + Na^+$: 344.1105 [M+Na^+]; found: 344.1100; elemental analysis calcd (%) for $C_{16}H_{19}NO_6$: C 59.81, H 5.96, N 4.36; found: C 59.95, H 5.94, N 4.35.

3,6,7a-Trimethyl-3a-(4-methylbenzyl)tetrahydro-3*H*,4*H*-3,6-epoxy-1,2-dioxolo[3,4-*b*]pyran (2c): White crystals; $R_f = 0.26$ (PE/EA 20/1); m.p. 107–108 °C; ^1H NMR (300.13 MHz, $CDCl_3$): $\delta = 1.38$ (s, 3H, CH_3CCH_2), 1.42 (s, 6H, 2×CH_3), 1.65–1.75 (m, 2H, CH_2CCH_3), 1.77–1.87 (m, 2H, CH_2), 2.31 (s, 3H, CH_3Ar), 2.82 (s, 2H, CH_2Ar), 7.07–7.10 ppm (m, 4H, 4×CH); ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta = 16.6$ (CH_3), 18.9 (CH_2), 21.0 (CH_3Ar), 24.7 (CH_3CCH_2), 30.9 (CH_2CCH_3), 36.3 (CH_2Ar), 51.7 (C), 93.7 (CH_2CCH_3), 107.5 ($CCCH_3$), 128.8, 131.1 (CH), 133.2 (CH_3CCH), 136.4 ppm (CH_2CCH); HRMS (ESI): *m/z* calcd for $C_{17}H_{22}O_4 + Na^+$: 313.1410 [M+Na^+]; found: 313.1407; elemental analysis calcd (%) for $C_{17}H_{22}O_4$: C 70.32, H 7.64; found: C 70.28, H 7.51.

4-[1,4-Dimethyl-7-(4-methylbenzyl)-2,3,5,6-tetraoxabicyclo-[2.2.1]hept-7-yl]butan-2-one (3c): Pale yellow crystals; $R_f = 0.31$ (PE/EA 5/1); m.p. 79–80 °C; ^1H NMR (300.13 MHz, $CDCl_3$): $\delta = 1.23$ (s, 6H, 2×CH_3), 2.01–2.21 (m, 5H, CH_3C=O, CH_2), 2.31 (s, 3H, CH_3Ar), 2.62–2.73 (m, 2H, CH_2C=O), 2.96 (s, 2H, CH_2Ar), 7.04–7.15 ppm (m, 4H, 4×CH); ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta = 9.3$ (CH_3), 21.0 (CH_3), 21.5 (CCH_2CH_2), 30.1 (CH_3C=O), 33.7 (CH_2Ar), 38.1 (CH_2C=O), 60.1 (C), 112.0 (OCO), 129.1, 130.8 (CH), 132.0 ($CHCCH_3$), 136.8 (CHCCH), 206.6 ppm (C=O); HRMS (ESI): *m/z* calcd for $C_{17}H_{22}O_5 + Na^+$: 329.1359 [M+Na^+]; found: 329.1357; elemental analysis calcd (%) for $C_{17}H_{22}O_5$: C 66.65, H 7.24; found: C 66.59, H 7.21.

1-[(1*R*,2*R*,5*S*)-1,5-Dimethyl-2-(4-methylbenzyl)-6,7,8-trioxabicyclo[3.2.1]oct-2-yl]ethanone (4c): Yellow oil; $n_D^{22}=1.5215$; $R_f=0.50$ (PE/EA 20/1); ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta=1.48$ (s, 3H, CH_3CC), 1.51–1.65 (m, 4H, CH_3CCH_2, CH_2), 1.75–1.86 (m, 1H, CH_2CCH_3), 1.91–2.03 (m, 1H, CH_2CCH_3), 2.14 (s, 3H, CH_3C=O), 2.28 (s, 3H, CH_3Ar), 2.56–2.70 (m, 1H, CH_2), 2.85 (d, 1H, CH_2Ar, $J=13.2$ Hz), 3.49 (d, 1H, CH_2Ar, $J=13.2$ Hz), 6.95 (d, 2H, 2×CH, $J=8.1$ Hz), 7.01 ppm (d, 2H, 2×CH, $J=8.1$ Hz); ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta=18.4$ (CH_3CC), 20.8 (CH_3CCH_2), 21.0 (CH_3Ar), 22.3 (CH_2), 30.3 (CH_3C=O), 30.9 (CH_2CCH_3), 35.8 (CH_2Ar), 59.1 (C), 109.1 ($OOCCH_2$), 111.4 (OOCC), 129.0, 130.0 (CH), 134.5 ($CHCCH_3$), 136.1 (CHCCH), 211.0 ppm (C=O); HRMS (ESI): *m/z* calcd for $C_{17}H_{22}O_4+K^+$: 329.1150 [M+K$^+$]; found: 329.1155; elemental analysis calcd (%) for $C_{17}H_{22}O_4$: C 70.32, H 7.64; found: C 70.35, H 7.70.

1-[(1*R*,2*S*,5*S*)-1,5-Dimethyl-2-(4-methylbenzyl)-6,7,8-trioxabicyclo[3.2.1]oct-2-yl]ethanone (5c): White crystals; $R_f=0.35$ (PE/EA 20/1); m.p. 90–91 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta=1.50$ (s, 3H, CH_3CCH_2), 1.63–1.77 (m, 4H, CH_3CC, CH_2), 1.87–1.95 (m, 2H, CH_2CCH_3), 2.08 (s, 3H, CH_3C=O), 2.14–2.34 (m, 4H, CH_3Ar, CH_2), 2.56 (d, 1H, CH_2Ar, $J=13.2$ Hz), 3.30 (d, 1H, CH_2Ar, $J=13.2$ Hz), 6.94 (d, 2H, 2×CH, $J=8.1$ Hz), 7.04 ppm (d, 2H, 2×CH, $J=8.1$ Hz); ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta=18.9$ (CH_3CC), 20.5 (CH_3CCH_2), 21.0 (CH_3Ar) 25.8 (CH_2), 30.0 (CH_3C=O), 33.1 (CH_2CCH_3) 41.0 (CH_2Ar), 58.3 (C), 109.0 ($OOCCH_2$), 111.3 (OOCC), 128.9, 130.0 (CH), 132.8 ($CHCCH_3$), 136.3 (CHCCH), 210.4 ppm (C=O); HRMS (ESI): *m/z* calcd for $C_{17}H_{22}O_4+Na^+$: 313.1410 [M+Na$^+$]; found: 313.1411; elemental analysis calcd (%) for $C_{17}H_{22}O_4$: C 70.32, H 7.64; found: C 66.95, H 7.89.

3a-(4-Chlorobenzyl)-3,6,7a-trimethyltetrahydro-3*H*,4*H*-3,6-epoxy-[1,2]dioxolo[3,4-*b*]pyran (2d): White crystals; $R_f=0.49$ (PE/EA 5/1); m.p. 121–122 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta=1.40$ (s, 3H, CH_3CCH_2), 1.43 (s, 6H, 2×CH_3), 1.68–1.77 (m, 2H, CH_2CCH_3), 1.78–1.88 (m, 2H, CH_2), 2.85 (s, 2H, CH_2Ar), 7.18 (d, 2H, 2×CH, $J=8.8$ Hz), 7.28 ppm (d, 2H, 2×CH, $J=8.8$ Hz); ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta=16.7$ (CH_3), 18.9 (CH_2), 24.6 (CH_3CCH_2), 30.8 (CH_2CCH_3), 36.2 (CH_2Ar), 51.7 (C), 93.7 (CH_2CCH_3), 107.4 ($CCCH_3$), 128.3, 132.4 (CH), 132.9 (CCl), 134.9 ppm (CHCCH); HRMS (ESI): *m/z* calcd for $C_{16}H_{19}ClO_4+Na^+$: 333.0864 [M+Na$^+$]; found: 333.0854; elemental analysis calcd (%) for $C_{16}H_{19}ClO_4$: C 61.84, H 6.16, Cl 11.41; found: C 61.75, H 6.30, Cl 11.51.

4-[7-(4-Chlorobenzyl)-1,4-dimethyl-2,3,5,6-tetraoxabicyclo-[2.2.1]hept-7-yl]butan-2-one (3d): White crystals; $R_f=0.19$ (PE/EA 5/1); m.p. 97–98 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta=1.23$ (s, 6H, 2×CH_3), 2.04–2.14 (m, 2H, CH_2), 2.19 (s, 3H, CH_3C=O), 2.63–2.72 (m, 2H, CH_2C=O), 2.97 (s, 2H, CH_2Ar), 7.19 (d, 2H, 2×CH, $J=8.8$ Hz), 7.28 ppm (d, 2H, 2×CH, $J=8.8$ Hz); ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta=9.3$ (CH_3), 21.6 (CCH_2CH_2), 30.2 (CH_3C=O), 33.7 (CH_2Ar), 38.1 (CH_2C=O), 60.1 (C), 111.9 (OCO), 128.6, 132.3 (CH), 133.3 (CCl), 133.7 (CHCCH), 206.9 ppm (C=O); HRMS (ESI): *m/z* calcd for $C_{16}H_{19}ClO_5+Na^+$: 349.0813 [M+Na$^+$]; found: 349.0823; elemental analysis calcd (%) for $C_{16}H_{19}ClO_5$: C 58.81, H 5.86, Cl 10.85; found: C 58.75, H 5.90, Cl 10.95.

1-[(1*R*,2*R*,5*S*)-2-(4-Chlorobenzyl)-1,5-dimethyl-6,7,8-trioxabicyclo-[3.2.1]oct-2-yl]ethanone (4d): White crystals; $R_f=0.74$ (PE/EA 5/1); m.p. 120–121 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta=1.44$ (s, 3H, CH_3CC), 1.48–1.60 (m, 4H, CH_3CCH_2, CH_2), 1.76–1.99 (m, 2H, CH_2CCH_3), 2.17 (s, 3H, CH_3C=O), 2.58–2.73 (m, 1H, CH_2), 2.85 (d, 1H, CH_2Ar, $J=13.2$ Hz), 3.51 (d, 1H, CH_2Ar, $J=13.2$ Hz), 7.01 (d, 2H, 2×CH, $J=8.8$ Hz), 7.19 ppm (d, 2H, 2×CH, $J=8.8$ Hz); ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta=18.3$ (CH_3CC), 20.8 (CH_3CCH_2), 22.2 (CH_2), 30.2 (CH_3C=O), 30.9 (CH_2CCH_3), 35.2 (CH_2Ar), 59.3 (C), 109.2 ($OOCCH_2$), 111.1 (OOCC), 128.4, 131.6 (CH), 132.5 (CCl), 136.2 (CHCCH), 210.7 ppm (C=O); HRMS (ESI): *m/z* calcd for $C_{16}H_{19}ClO_4+Na^+$: 333.0864 [M+Na$^+$]; found: 333.0868; elemental analysis calcd (%) for $C_{16}H_{19}ClO_4$: C 61.84, H 6.16, Cl 11.41; found: C 61.90, H 6.20, Cl 11.50.

1-[(1*R*,2*S*,5*S*)-2-(4-Chlorobenzyl)-1,5-dimethyl-6,7,8-trioxabicyclo-[3.2.1]oct-2-yl]ethanone (5d): White crystals; $R_f=0.62$ (PE/EA 5/1); m.p. 105–106 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta=1.49$–1.74 (m, 7H, CH_3CCH_2, CH_3CC, CH_2), 1.88–2.00 (m, 2H, CH_2CCH_3), 2.08–2.31 (m, 4H, CH_3C=O, CH_2), 2.54 (d, 1H, CH_2Ar, $J=13.2$ Hz), 3.35 (d, 1H, CH_2Ar, $J=13.2$ Hz), 6.99 (d, 2H, 2×CH, $J=8.8$ Hz), 7.20 ppm (d, 2H, 2×CH, $J=8.8$ Hz); ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta=18.7$ (CH_3CC), 20.6 (CH_3CCH_2), 25.6 (CH_2), 30.1 (CH_3C=O), 32.9 (CH_2CCH_3) 40.5 (CH_2Ar), 58.2 (C), 109.0 ($OOCCH_2$), 111.0 (OOCC), 128.4, 131.5 (CH), 132.7 (CCl), 134.6 (CHCCH), 210.1 ppm (C=O); HRMS (ESI): *m/z* calcd for $C_{16}H_{19}ClO_4+Na^+$: 333.0864 [M+Na$^+$]; found: 333.0863; elemental analysis calcd (%) for $C_{16}H_{19}ClO_4$: C 61.84, H 6.16, Cl 11.41; found: C 61.95, H 6.20, Cl 11.55.

3a-(4-Bromobenzyl)-3,6,7a-trimethyltetrahydro-3*H*,4*H*-3,6-epoxy-[1,2]dioxolo[3,4-*b*]pyran (2e): White crystals; $R_f=0.41$ (PE/EA 5/1); m.p. 124–125 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta=1.38$ (s, 3H, CH_3CCH_2), 1.41 (s, 6H, 2×CH_3), 1.65–1.74 (m, 2H, CH_2CCH_3), 1.76–1.86 (m, 2H, CH_2), 2.81 (s, 2H, CH_2Ar), 7.10 (d, 2H, 2×CH, $J=8.8$ Hz), 7.41 ppm (d, 2H, 2×CH, $J=8.8$ Hz); ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta=16.7$ (CH_3), 18.9 (CH_2), 24.6 (CH_3CCH_2), 30.8 (CH_2CCH_3), 36.3 (CH_2Ar), 51.7 (C), 93.7 (CH_2CCH_3), 107.4 ($CCCH_3$), 120.9 (CBr), 131.3, 132.8 (CH), 135.4 ppm (CHCCH); HRMS (ESI): *m/z* calcd for $C_{16}H_{19}BrO_4+Na^+$: 377.0359 [M+Na$^+$]; found: 377.0344; elemental analysis calcd (%) for $C_{16}H_{19}BrO_4$: C 54.10, H 5.39, Br 22.49; found: C 54.09, H 5.35, Br 22.47.

4-[7-(4-Bromobenzyl)-1,4-dimethyl-2,3,5,6-tetraoxabicyclo-[2.2.1]hept-7-yl]butan-2-one (3e): White crystals; $R_f=0.14$ (PE/EA 10:1); m.p. 82–83 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta=1.23$ (s, 6H, 2×CH_3), 2.00–2.13 (m, 2H, CH_2), 2.19 (s, 3H, CH_3C=O), 2.62–2.73 (m, 2H, CH_2C=O), 2.95 (s, 2H, CH_2Ar), 7.13 (d, 2H, 2×CH, $J=8.8$ Hz), 7.43 ppm (d, 2H, 2×CH, $J=8.8$ Hz);^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta=9.3$ (CH_3), 21.5 (CCH_2CH_2), 30.2 (CH_3C=O), 34.8 (CH_2Ar), 38.0 (CH_2C=O), 60.0 (C), 111.9 (OCO), 121.3 (CBr), 131.6, 132.6 (CH), 134.2 (CHCCH), 206.9 ppm (C=O); HRMS (ESI): *m/z* calcd for $C_{16}H_{19}BrO_5+Na^+$: 393.0308 [M+Na$^+$]; found: 393.0296; elemental analysis calcd (%) for $C_{16}H_{19}BrO_5$: C 51.77, H 5.16, Br 21.52; found: C 51.80, H 5.25, Br 21.63.

1-[(1*R*,2*R*,5*S*)-2-(4-Bromobenzyl)-1,5-dimethyl-6,7,8-trioxabicyclo-[3.2.1]oct-2-yl]ethanone (4e): White crystals; $R_f=0.74$ (PE/EA 10/1); m.p. 110–111 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta=1.39$–1.64 (m, 7H, CH_3CC, CH_3CCH_2, CH_2), 1.76–2.00 (m, 2H, CH_2CCH_3), 2.18 (s, 3H, CH_3C=O), 2.59–2.74 (m, 1H, CH_2), 2.84 (d, 1H, CH_2Ar, $J=13.2$ Hz), 3.50 (d, 1H, CH_2Ar, $J=13.2$ Hz), 6.96 (d, 2H, 2×CH, $J=8.1$ Hz), 7.35 ppm (d, 2H, 2×CH, $J=8.1$ Hz); ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta=18.3$ (CH_3CC), 20.8 (CH_3CCH_2), 22.2 (CH_2), 30.2 (CH_3C=O), 30.9 (CH_2CCH_3), 35.3 (CH_2Ar), 59.2 (C), 109.2 ($OOCCH_2$), 111.1 (OOCC), 120.6 (CBr), 131.4, 132.0 (CH), 136.8 (CHCCH), 210.8 ppm (C=O); HRMS (ESI): *m/z* calcd for $C_{16}H_{19}BrO_4+Na^+$: 377.0359 [M+Na$^+$]; found: 377.0351; elemental analysis calcd (%) for $C_{16}H_{19}BrO_4$: C 54.10, H 5.39, Br 22.49; found: C 54.15, H 5.44, Br 22.56.

1-[(1*R*,2*S*,5*S*)-2-(4-Bromobenzyl)-1,5-dimethyl-6,7,8-trioxabicyclo-[3.2.1]oct-2-yl]ethanone (5e): White crystals; $R_f=0.59$ (PE/EA 10/1); m.p. 108–109 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta=1.53$–1.70 (m, 7H, CH_3CCH_2, CH_3CC, CH_2), 1.88–1.98 (m, 2H, CH_2CCH_3), 2.11 (s, 3H, CH_3C=O), 2.13–2.28 (m, 1H, CH_2), 2.52 (d, 1H, CH_2Ar, $J=13.2$ Hz), 3.33 (d, 1H, CH_2Ar, $J=13.2$ Hz), 6.93 (d, 2H, 2×CH, $J=8.8$ Hz), 7.35 ppm (d, 2H, 2×CH, $J=8.8$ Hz); ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta=18.7$ (CH_3CC), 20.6 (CH_3CCH_2), 25.6 (CH_2), 30.1 (CH_3C=O), 32.9 (CH_2CCH_3) 40.6 (CH_2Ar), 58.1 (C), 109.0 ($OOCCH_2$), 111.0 (OOCC), 120.8 (CBr), 131.4, 131.9 (CH), 135.2 (CHCCH), 210.0 ppm (C=O);

HRMS (ESI): *m/z* calcd for $C_{16}H_{19}BrO_4+Na^+$: 377.0359 [*M*+Na^+]; found: 377.0352; elemental analysis calcd (%) for $C_{16}H_{19}BrO_4$: C 54.10, H 5.39, Br 22.49; found: C 54.18, H 5.35, Br 22.57.

3,6,7a-Trimethyltetrahydro-3*H*,4*H*-3,6-epoxy[1,2]dioxolo[3,4-*b*]pyran (2 f): White crystals; R_f = 0.54 (PE/EA 5/1); m.p. 75–76 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.38 (s, 3H, CH_3CCH_2), 1.52 (s, 6H, 2×CH_3), 1.60–1.70 (m, 2H, H_3CCH_2), 1.79–1.91 (m, 2H, CH_2), 2.30–2.38 ppm (m, 1H $CHCH_2$); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 13.1 (CH_2CH), 17.7 (CH_3), 24.6 (CH_3CCH_2), 29.2 (CH_2CCH_3), 47.8 (CH), 95.3 ($OC(CH_2)O$), 104.8 ppm ($OC(CH_3)O$).

3a-Butyl-3,6,7a-trimethyltetrahydro-3*H*,4*H*-3,6-epoxy[1,2]-dioxolo[3,4-*b*]pyran (2 g): White crystals; R_f = 0.27 (PE/EA 10:1); m.p. 60–61 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.89 (t, 3H, CH_3CH_2, J = 7.0 Hz), 1.20–1.52 (m, 15H, $CH_3CH_2CH_2CH_2$, 2×CH_3, CH_3CCH_2), 1.67–1.71 ppm (m, 4H, CCH_2CH_2C); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 13.8 (CH_3CH_2), 16.1 (CH_3), 18.9 ($CCCH_2CH_2C$), 23.6 (CH_3CH_2), 24.8 (CH_3CCH_2), 26.3, 30.87 ($CH_2CH_2CH_2CH_3$), 30.94 (CH_3CCH_2), 50.6 (CH_2CCH_2), 94.0 ($OC(CH_2)O$), 107.3 ppm ($OC(CH_3)O$).

3-(3,6,7a-Trimethylhexahydro-3,6-epoxy[1,2]dioxolo[3,4-*b*]-pyran-3a-yl)propanenitrile (2 h): White crystals; R_f = 0.13 (PE/EA 5/1); m.p. 114–115 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.38 (s, 3H, CH_3CCH_2), 1.47 (s, 6H, 2×CH_3), 1.67–1.73 (m, 4H, CCH_2CH_2C), 1.80–1.88 (m, 2H, CCH_2CH_2CN), 2.56–2.64 ppm (m, 2H, CH_2CN); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 12.9 (CH_2CN), 15.6 (CH_3), 20.5 (CH_2CC), 24.5 (CH_2CH_2CN), 28.1 (CH_3CCH_2), 30.5 (CH_3CCH_2), 50.2 (CH_2CCH_2), 94.3 ($OC(CH_2)O$), 106.2 ($OC(CH_3)O$), 119.5 ppm (CN).

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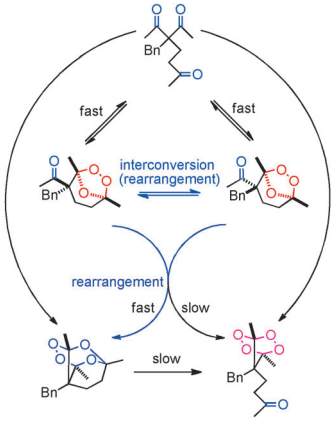
FULL PAPER

Tricyclic monoperoxides, bridged tetraoxanes, and ozonides can all be prepared by the peroxidation of β,δ-triketones (see scheme). The synthesis of ozonides from ketones and hydrogen peroxide is an unprecedented process, and rearrangements of ozonides were found for the first time after more than one century of their active investigation.



Peroxidation

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Approach for the Preparation of Various Classes of Peroxides Based on the Reaction of Triketones with H_2O_2: First Examples of Ozonide Rearrangements