Stereoelectronic Effects

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Stereoelectronic Control in the Ozone-Free Synthesis of Ozonides

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Abstract: *The value of stereoelectronic guidelines is illustrated by the discovery of a convenient, ozone-free synthesis of bridged secondary ozonides from 1,5-dicarbonyl compounds and H_2O_2. The tetraoxane products generally formed in reactions of carbonyl and dicarbonyl compounds with H_2O_2 were not detected because the structural distortions imposed on the tetraoxacyclohexane subunit in [3.2.2]tetraoxanonanes by the three-carbon bridge leads to the partial deactivation of anomeric effects. The new procedure is readily scalable to produce gram quantities of the ozonides. This reaction enables the selective preparation of ozonides without the use of ozone.*

For a long time, peroxides played secondary roles in organic synthesis. Although they have been very useful in niche applications as initiators of radical polymerization, sources of O-centered radicals, explosives, fuel additives, and oxidative reagents, only recently did peroxides become the primary focus of sustained synthetic efforts. In particular, the interest this functional group is fueled by its expanding role in the development of new therapeutic agents[1] (Figure 1). The impact of peroxides on drug design is illustrated by the Nobel Prize awarded for the development of artemisinin, a natural peroxide antimalarial drug.

Many organic peroxides can be prepared by the reaction of ketones and aldehydes with hydrogen peroxide and organic hydroperoxides. This approach to the preparation of peroxides benefits from the broad availability of such starting materials and opened synthetic access to many classes of organic peroxides, such as geminal bis(hydroperoxides),[2] geminal bisperoxides,[3] tetraoxanes,[4] cyclic triperoxides,[5] and tricyclic monoperoxides.[6] However, synthetic approaches to the 1,2,4-trioxolane moiety (i.e., secondary ozonides) remain limited. Traditionally, ozonides are obtained by the treatment of alkenes with ozone.[7] Lately, the ozonolysis of *O*-methyl oximes in the presence of acyclic or cyclic ketones (Griesbaum coozonolysis)[8] has gained popularity. Potentially, the interaction of two carbonyl groups with one molecule of H_2O_2 can provide a new alternative to the preparation of ozonides. Herein, we evaluate the scope and limitations of this approach and provide a viable strategy based on this concept (Scheme 1).

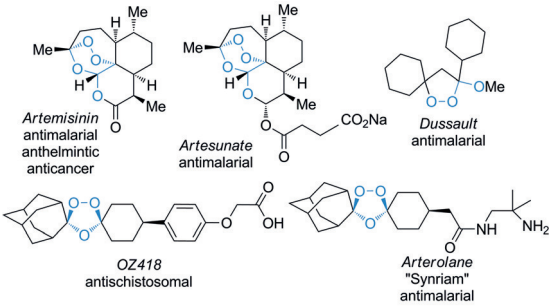
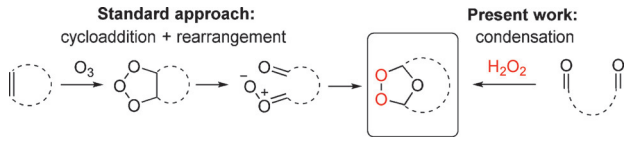


Figure 1. A selection of biologically active ozonides and related compounds.



Scheme 1. Classical and new approaches to ozonide synthesis.

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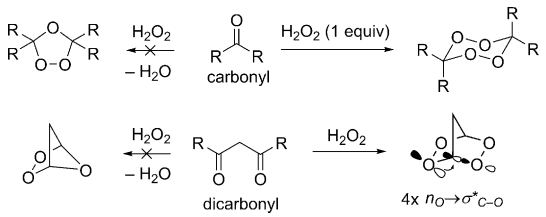
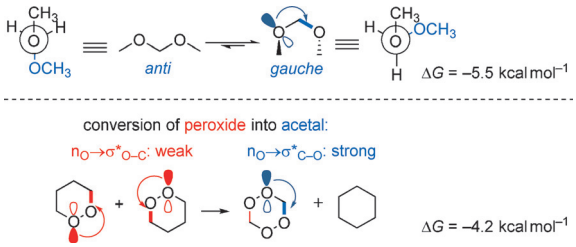
The problem with this attractively simple route to ozonides is that both the interaction of two ketone molecules and the reaction of the more conformationally rigid 1,3-dicarbonyl compounds with H_2O_2 proceed to form bicyclic bisperoxides instead of the desired ozonides (Scheme 2).[4f]



Scheme 2. Alternative cyclic products from reactions of ketones and H_2O_2.

Previously, we have shown that the increased stability of such cyclic bisperoxides[4a,b] stems from activation of the anomeric effect (AE).[9] Although the AE is deactivated in monoperoxides, it reappears in molecules in which multiple peroxide moieties are separated by a one-atom bridge. This classic stereoelectronic effect explains the paradoxical stabilization of molecules with *multiple* O–O bonds: the very bonds responsible for the instability of monoperoxides (Scheme 3).



Scheme 3. Selected consequences of anomeric interactions.[9,10] Top: Stabilization of acetals in the gauche conformation. Bottom: The increased stability of cyclic bisperoxides originates from their bisacetal nature.

A corollary of this analysis is that the stereoelectronic solution for effective ozonide synthesis should include the selective deactivation of the anomeric effect. If the source of bisperoxide stabilization is removed, ozonides will have a greater chance of winning the thermodynamic tug-of-war between the possible products of the reaction of ketones and H_2O_2.

Similarly to all stereoelectronic effects, the anomeric effect is very sensitive to orbital alignment as a function of molecular geometry.[10] This sensitivity is illustrated by the correlation of the stability of the parent acetal with the magnitude of the $n_O \rightarrow \sigma^*_{C-O}$ interaction quantified by natural bond orbital (NBO) analysis (Figure 2).

Guided by the idea that the selective disruption of anomeric interactions can provide a way to change reaction selectivity, we investigated a direct approach to misaligning orbitals by introducing a variable structural constraint, such as an additional bridge between the interacting orbitals. With

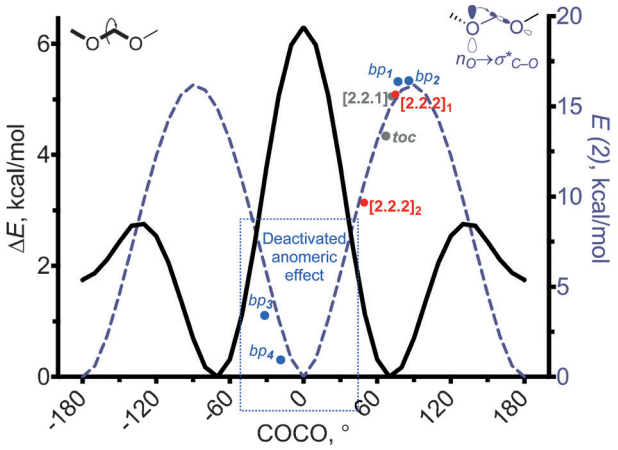


Figure 2. The stability of acetals correlates with the COCO angle and modulations in the magnitude of the $n_O \rightarrow \sigma^*_{C-O}$ interaction. Calculations were carried out at the (SMD = MeCN)/B2PLYP-D2/6-311 + + G-(d,p) level of theory.

the right choice of such a bridge, structural distortions that can disrupt orbital overlap should be possible. To illustrate this premise, let us consider the family of bisperoxides in Figure 3.

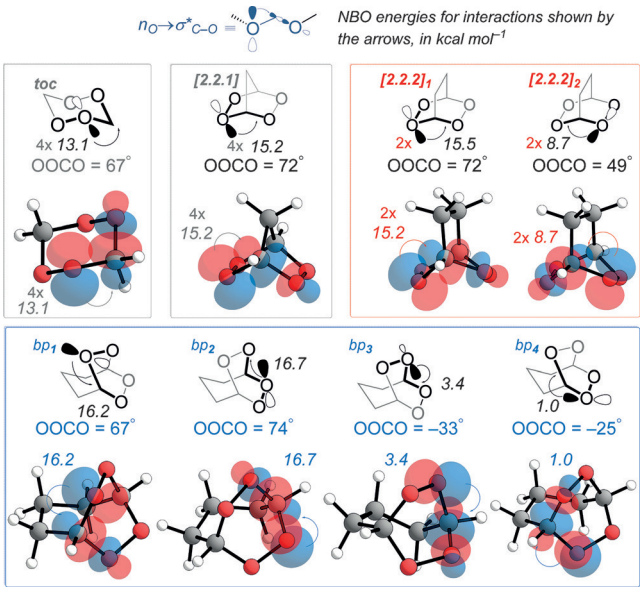


Figure 3. Top: Selective deactivation of anomeric effects by structural constraints. Bottom: Illustrative NBO plots for the key $n_O \rightarrow \sigma^*_{C-O}$ interactions. Calculations at the (SMD = MeCN)/B2PLYP-D2/6–311 + + G(d,p) level of theory.

1,2,4,5-Tetraoxacyclohexane (toc), the parent monocyclic bisperoxide, can pucker from the cyclohexane chair conformation to engage the four relatively strong $n_O \rightarrow \sigma^*_{C-O}$ interactions (the OOCO dihedral angle for each of the four identical $n_O \rightarrow \sigma^*_{C-O}$ interactions is 67°, and the NBO interaction energy is 13.1 kcal mol^{-1}). The addition of a one-carbon-atom bridge leads to the boat geometry of [2.2.1]tetraoxabicycloheptane, in which the $n_O \rightarrow \sigma^*_{C-O}$ interactions are even stronger (15.2 kcal mol^{-1}). In accord with these results,

such bisperoxides are readily formed in the reactions of 1,3-diketones (Figure 3).[4a,b] However, this situation starts to change as the bridge gets longer. In the [2.2.2]tetraoxabicyclooctane, two of the anomeric interactions are considerably weakened (to 8.7 kcal mol^{-1}; Figure 3). A truly dramatic effect is observed for the [3.2.2]tetraoxabicyclononane skeleton, in which two of the $n_O \rightarrow \sigma^*_{C-O}$ interactions nearly disappear (3.4 and 1.0 kcal mol^{-1}) because of the large deviations in the OOCO dihedral from the ideal value of 60° (33 and 25°, respectively).

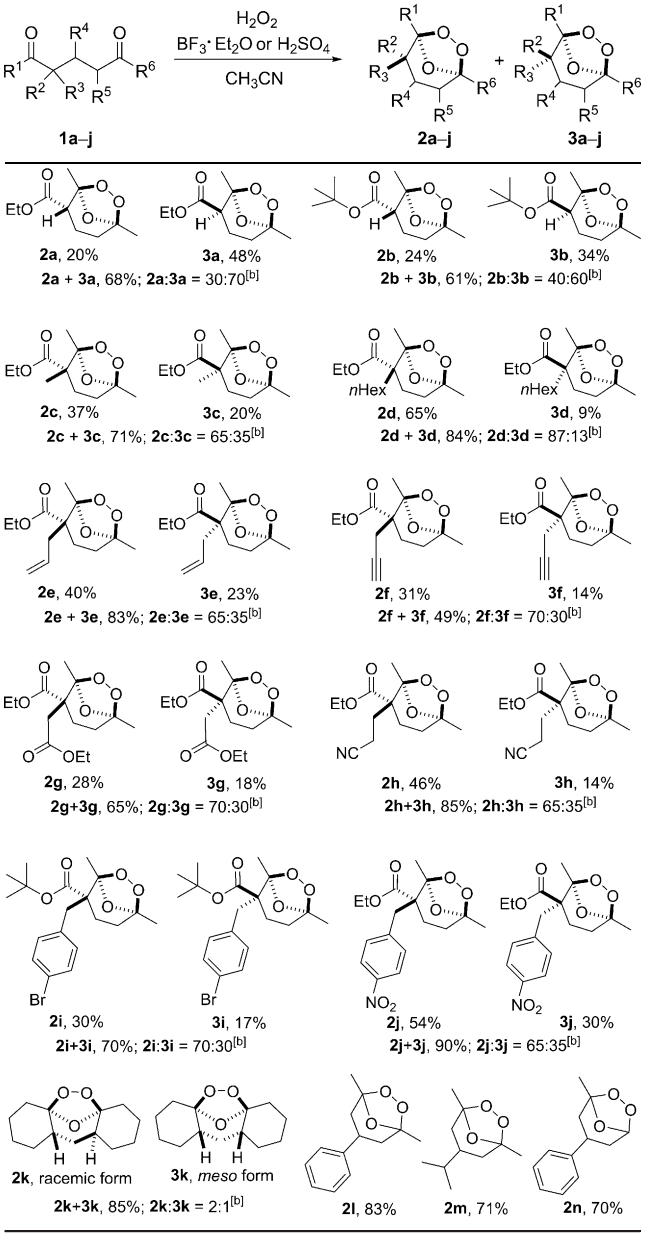
Encouraged by the large stereoelectronic differences between the otherwise very similar bicyclic bisperoxides and earlier reports of the higher stabilities of ozonides obtained by different routes,[11] we investigated the reactivity of 1,5-diketones and H_2O_2. There are only a few scattered reports of this process in the presence of P_2O_5,[12] V_2O_5,[13] and peracetic acid with borone trifluoride.[14] More recently, diketones of the oleanane family were transformed into ozonides by the use of a CH_3COOOH/H_2O_2 system.[15] There is one report of ozonide formation in low yield from 2,6-heptanedione and H_2O_2 in the gas phase at 10^{-2} torr.[16] Finally, an isolated example of ozonide synthesis from an acetal of 1,5-diketone[2e] was followed by a recent study,[17] in which the hidden 1,5-dicarbonyl functionality of artemisinin was transformed into a mixed ketoacetal and then into a pair of stereoisomeric ozonides through a reaction with H_2O_2 under the catalysis of HCl. We found earlier that the acid-catalyzed reaction of branched β′,δ-triketones with H_2O_2 yielded ozonides, but in a mixture with bridged tetraoxanes and tricyclic monoperoxides.[6b,18]

To our delight, the reaction of 1,5-diketones with H_2O_2 in the presence of a Brønsted or Lewis acid led cleanly and efficiently to the exclusive formation of ozonides, even in the case of substrates with alkene or alkyne functionalities, which are not compatible with the classical ozone-based approach to ozonides. No bisperoxides were observed with these dicarbonyl substrates (Table 1). Furthermore, an ozonide could be formed from a 1,5-ketoaldehyde and H_2O_2. Convenient conditions for the peroxidation of 1,5-dicarbonyl compounds **1a–n** involve the combination of ethereal H_2O_2 with either $BF_3{\cdot}Et_2O$ or H_2SO_4 as a promoter.

We tested the scope and limitations of this ring-assembly process by introducing substituents R^1–R^5 at different positions of the 1,5-dicarbonyl compound **1**. The lack of ozonide formed in the reaction of 2,5-heptanedione and inefficient cyclization (18% by NMR spectroscopy) of 4-methylheptane-2,6-dione illustrate the importance of the Thorpe–Ingold effect. We could obtain ozonides with a moderately bulky substituent on the bridge (e.g., the Ph group in **2l**) in up to 90% yield. Importantly, we could prepare ozonides with pendant alkene and alkyne functionalities: compounds impossible to obtain directly by the classical ozonolysis route. Such groups should provide functional handles for bioconjugation through click and other ligation techniques. Interestingly, the transformation of 1,5-ketoaldehyde **1n** into ozonide **2n** proceeded without oxidation of the aldehyde.

The reaction of H_2O_2 with 2-substituted 1,5-diketones created two new stereocenters and yielded a mixture of two diastereomers. The resulting bicyclic ozonides were stable and could be isolated by column chromatography and fully characterized by NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray crystallography (Figure 4; see the Supporting Information).

Table 1: Ozone-free synthesis of ozonides **2a–j**, **3a–j**, and mixtures thereof from diketones **1a–j** and H_2O_2.[a]



[a] Yields are for the isolated individual compound. [b] Yields are for the isolated mixture of stereoisomers of the ozonides separated from the residual diketone reactant by column chromatography on SiO_2. The ratio of stereoisomers of the ozonides was determined from the ^{1}H NMR spectroscopic data.

This process is readily scalable (gram quantities of the starting diketones can be used) with only a small negative effect on the yields of the ozonides. The reaction of H_2O_2 with 3.0 g of diketone **1d** provided the isolated mixture of stereoisomeric ozonides **2d** and **3d** in 66% combined yield.

The synthesis of these new bicyclic ozonides gave us an opportunity to explore the chemistry of this functionality. For

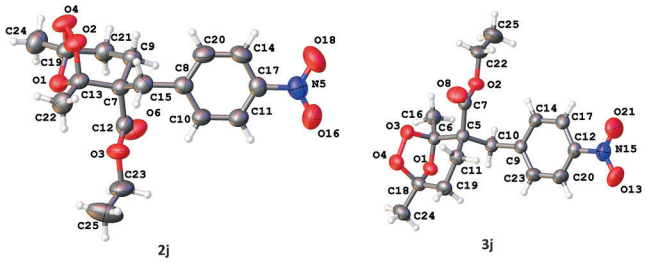
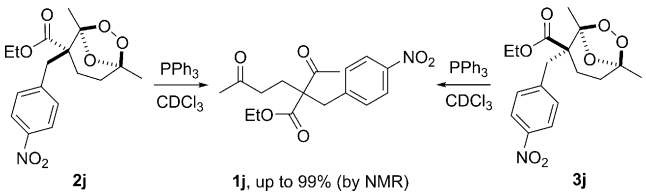


Figure 4. Molecular structures of **2j** and **3j**. Atoms are presented as atomic displacement parameter ellipsoids (50% probability).

example, ozonides **2j** and **3j** could be selectively reduced to the starting diketone **1j** with triphenylphosphine in $CDCl_3$ (Scheme 4). Formation of the starting diketone was complete after 8 h at room temperature. This transformation suggests that the ozonide ring can be used as an atom-economical protecting group for dicarbonyl functionalities.

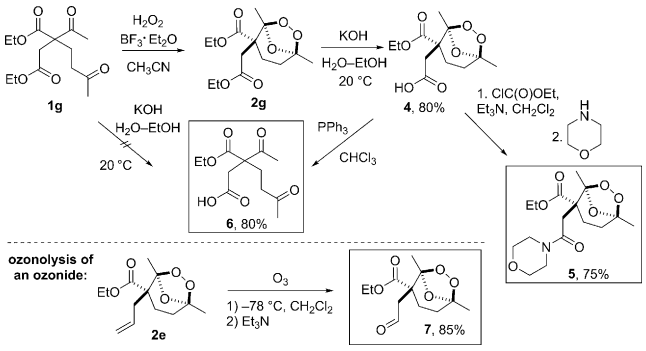


Scheme 4. Reduction of ozonides **2j** and **3j** by PPh_3.

The potential utility of the new protecting group in synthesis is illustrated by the selective hydrolysis of the less hindered ester group in the ozonide derived from the tetracarbonyl compound **1g**. The ozonide moiety is sufficiently stable in the presence of bases and nucleophiles to allow the transformations illustrated in Scheme 5.

An alkenyl-substituted ozonide **2e** can undergo ozonolysis to give aldehyde **7** after a mild reductive (Et_3N) workup. Because this process should proceed via an intermediate with two structurally distinct ozonide moieties, it provides direct experimental evidence that bicyclic ozonides are much more stable than "normal" ozonides.

In summary, the value of stereoelectronic guidelines was illustrated by the discovery of a convenient, scalable, and ozone-free synthesis of bridged secondary ozonides from 1,5-dicarbonyl compounds. This approach is applicable to ozonides with pendant alkene and alkyne functionalities, which are useful as potential functional handles for bioconjugation and further synthetic transformations. The structural distortions imposed on the tetraoxacyclohexane subunit in [3.2.2]tetraoxanonanes by the three-carbon-atom bridge lead to the partial deactivation of anomeric effects. Other stereoelectronic strategies for the control of peroxide synthesis and reactivity are under investigation.



Scheme 5. Transformations of ozonides **2g**, **2e**, and **4**.

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Conflict of interest

The authors declare no conflict of interest.

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