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Transformation of 2-allyl-1,3-diketones to bicyclic compounds containing 1,2-dioxolane and tetrahydrofuran rings using the I_2/H_2O_2 system

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ABSTRACT

A one-pot procedure was developed for the assembly of bicyclic compounds containing 1,2-dioxolane and tetrahydrofuran rings based on the reaction of 2-allyl-1,3-diketones with the I_2/H_2O_2 system. A fivefold molar excess of H_2O_2 and a twofold excess of I_2 are required for the selective formation of tetrahydrofurodioxoles. The synthesis of these structurally complex molecules is unusual in that it does not produce the expected bridged tetraoxanes, products of the addition of several H_2O_2 molecules to a carbonyl group, or the products of double bond iodoperoxidation.

Introduction

The chemistry of peroxides has more than a century of history. During this period, carbonyl compounds, primarily ketones and aldehydes, have gained wide use as reagents for peroxide synthesis due to their availability and the ease of the reaction between the carbonyl carbon atom and the nucleophilic oxygen atom of the hydroperoxide group. Peroxides derived from ketones are produced on an industrial scale and are employed by dozens of companies for the initiation of radical polymerization of unsaturated monomers.[1]

In the 1990s, organic peroxides attracted considerable attention of researchers in the fields of medicinal chemistry and pharmacology since these compounds, particularly ozonides and tetraoxanes, were found to have antimalarial,[2] antihelmintic,[3] and antitumor[4] activities. The two-component drug Synriam containing a molecule with an ozonide ring was approved for marketing.[5] Of particular interest is the development of methods for the synthesis and analysis of peroxides, for instance hexamethylene triperoxide diamine, acetone di- and triperoxides, and other ketone peroxides,[6] to use as explosives.

The synthesis of peroxides from H_2O_2 and monoketones is covered in the literature in hundreds of publications,[7] whereas there are only a few studies concerned with the preparation of peroxides from diketones.[8] There is a reasonable belief that the selectivity of the reactions decreases with an increase in the number of carbonyl groups with similar reactivity in the molecule, resulting in an increase in the number of oxidation products and the formation of difficult-to-separate mixtures of peroxides. The synthesis of a bridged tetraoxane from acetylacetone in a low total yield (18.5%) was described.[8a] In another study,[8b] a bridged tetraoxane was prepared (the yield was not determined) by heating 5-hydroperoxy-3,5-dimethyl-1,2-dioxolan-3-ol, which was synthesized from acetylacetone, in CH_3COOH. Recently, a method was developed for the synthesis of bridged tetraoxanes based on the reaction of H_2O_2 with α-substituted β-diketones catalyzed by strong acids (H_2SO_4, $HClO_4$, HBF_4, or BF_3),[9a] as well as catalyzed by phosphomolybdic acid (PMA) or phosphotungstic acid (PTA).[9b] The synthesis of a series of bridged tetraoxanes was documented and their energy parameters were obtained.[9c]

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The I_2/H_2O_2 system applied in the present study has been used for iodoalkoxylation of alkenes,[10] iodination of arenes,[11] ketones,[12] and alkynes,[13] Baeyer–Villiger oxidation of ketones to lactones,[14] ring contraction of 1,2-quinones to form cyclopentenones,[15] oxidative C–N[16] and C–O[17] coupling, and oxidative cyclization to heterocyclic compounds.[18] Additionally, the I_2/H_2O_2 system was used in peroxide synthesis for double bond iodoperoxidation[19,20] and for the synthesis of geminal bishydroperoxides and tetraoxanes.[21,22]

Results and discussion

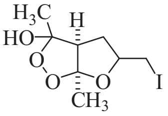
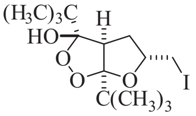
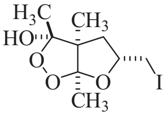
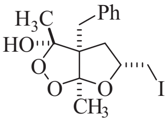
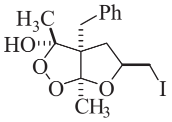
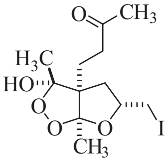
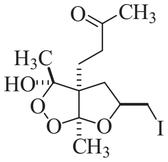
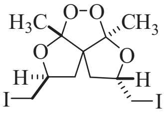
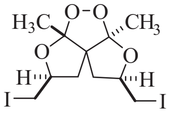
In this study, using the reaction of 2-allyl-1,3-diketones **1**, we obtained bicyclic compounds **2** containing annulated tetrahydrofuran and 1,2-dioxolane rings instead of the expected bridged tetraoxanes, products of the addition of I_2 and H_2O_2 to the double bond or products of the diperoxidation of carbonyl groups[19–22] (Scheme 1).

Peroxides **2a**–**f** and **2d**′–**f**′ were synthesized in DCM at 20–25 °C using a fivefold molar excess of H_2O_2 and a twofold molar excess of I_2 (Table 1).

In entries 1–5, independent of the presence of substituents in the α position, fused cyclic compounds were obtained. Generally, peroxides **2a**, **b** with a CH moiety in the 3a position of the carbon skeleton are less stable in comparison with peroxides **2c**–**f**(**f**′) bearing non-hydrogen substituents in this position.

The introduction of substituents at the α position of the dicarbonyl compounds has little effect on the yield of the reaction but influences the ratio of stereoisomers. The reaction of diketones **1a**–**c** containing a methyl group or a hydrogen atom in the α position gives one stereoisomer. The presence of two bulky substituents at the keto groups of diketone **1b** facilitates the formation of tetrahydrofurodioxole **2b** containing the C(3) atom with a configuration that is different from that in products **2a**,**c**. An increase in the bulkiness of the substituents at the C(3a) atom leads to the formation of two stereoisomers, which differ in the position of the CH_2I group. In the case of sterically hindered 3-allyl-3-benzylpentane-2,4-dione **1d**, the reaction affords an isomer with a *cis* arrangement of CH_2I and $PhCH_2$ groups as the major product. The reaction of 3,3-diallylpentane-2,4-dione **1f** with the I_2/H_2O_2 system produces a mixture of stereoisomers of tricyclic peroxide **2f** and **2f**′ in a 1:1 ratio in a total yield of 72%.

Table 1
Synthesis of tetrahydro-3*H*-furo[2,3-*c*][1,2]dioxoles **2a**–**f** and **2d**′–**f**′ from diketones **1a**–**f**[23]

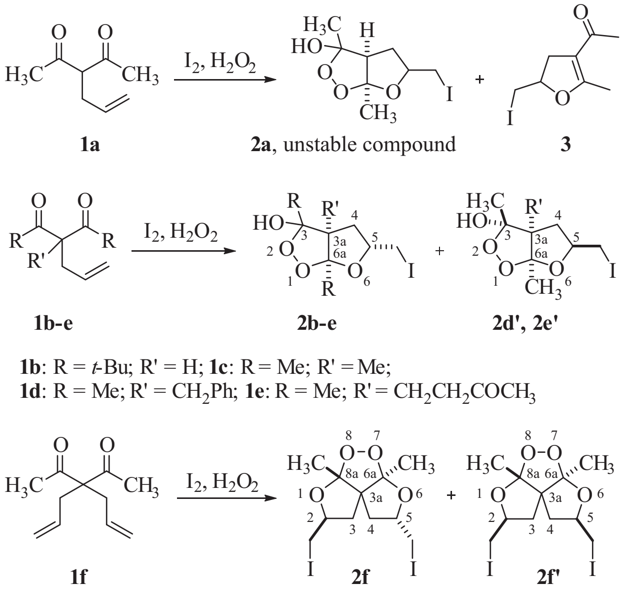
Entry[a]	Product **2a**–**f**	Product **2d**′–**f**′ (yield of **2a**–**f** + **2a**′–**f**′ %; dr)
1	 **2a**[b]	– (50[c])
2	 **2b**	– (81[d])
3	 **2c**	– (50[d])
4	 **2d**	 **2d’** (68 [d]; **2d** / **2d’** (dr 1.8:1))
5	 **2e**	 **2e’** (56 [d]; **2e** / **2e’** (dr 1:1))
6	 **2f**	 **2f’** (72 [d]; **2f** / **2f’** (dr 1:1))

[a] Reagents and conditions: H_2O_2 (5.3 mL, 1.88 M Et_2O, 10 mmol), I_2 (1.015 g, 4 mmol) in DCM (10 mL), diketone **1a**–**f** (2 mmol), 20–25 °C, 1 h.

[b] In the case of H_2O_2 (2 mmol; 1 equiv) dihydrofuran **3** was obtained in 69% yield. Product **2a** was detected in trace amounts.

[c] NMR data.

[d] Isolated yield.

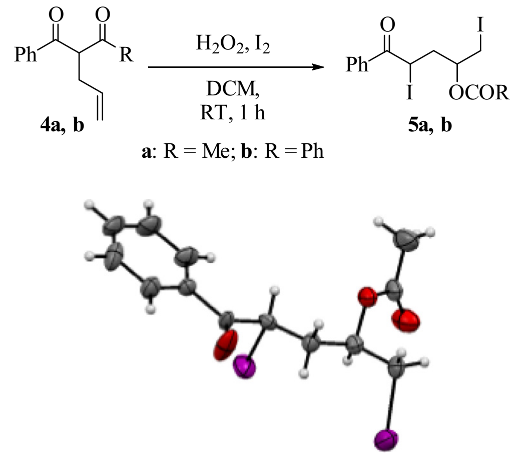


Scheme 1. Reaction of **1a**–**f** with the I_2/H_2O_2 system. Descriptors **b**–**e** indicate *cis*-, R, CH_2I, stereochemistry, while **d**′, **f** indicate *trans*-, CH_3, CH_2I, stereochemistry.

The reaction of ketones **4a**,**b** containing an aromatic ring adjacent to the carbonyl group with the I_2/H_2O_2 system gives, instead of cyclization products **2**, only oxidation and iodination products **5a**,**b** in 11% and 24% yields, respectively (Scheme 2).

Taking into account the published data[24] on the reactions of 2-allyl-1,3-diketones with molecular iodine, we propose the following mechanism for the formation of products **2**, **3**, and **5** (Scheme 3).

The first step involves the reaction of iodine with a double bond to form iodonium cation **I**, which undergoes cyclization to tetrahydrofuran intermediate **II** and is stabilized by a lone pair of the oxygen atom. Then, addition of H_2O_2 to **II** followed by the cyclization of **III** gives bicyclic compound **2**. The reaction of monosubstituted diketone **2a** in the presence of only one equivalent of hydrogen peroxide proceeds via an alternative pathway involving the deprotonation of cation **II** to form product **3**. In the case of compounds **4** the large substituent R = Ph prevents cyclization. After

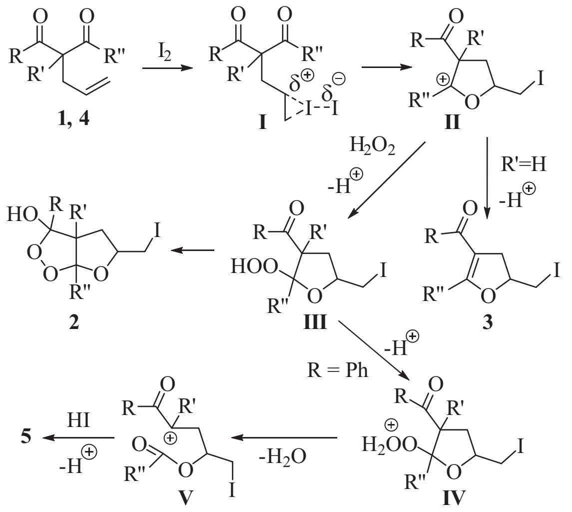


Scheme 2. Reaction of ketones **4a**,**b** with the I_2/H_2O_2 system. Single crystal X-ray diffraction structure of product **5a**.

the protonation of **III**, product **IV** undergoes a Baeyer–Villiger rearrangement with formation of cation **V**, which is iodinated by, for example HI, to give products **5**.

The structures of bicyclic compounds **2** were established by NMR spectroscopy and HRMS. The ^{1}H NMR spectra show a multiplet for δ 4.0–4.5 ppm assigned to the CHO group. Signals of protons at the endocyclic C(6) atom are in the range of δ 1.5–2.5 ppm. In the ^{13}C NMR spectra, the signals of the monoperoxyacetal moieties are well distinguished by the chemical shift difference. The signal of the carbon atom C(6a) at the ring junction is observed at δ 112–123 ppm, and the signal of the carbon atom C(3) appears at δ 106–110 ppm. The signal of the CHO group is at δ 75–80 ppm. The CH_2I group was identified based on the characteristic high-field signal at δ 8–10 ppm. The signals of the C(3a) and C(4) atoms appear at δ 14–60 ppm.

In order to more accurately identify the resulting compounds, we used 2D NMR techniques (COSY, NOESY, HMBC, and HSQC), which allowed us to not only determine the structures of products **2** but to study their stereochemistry. The reactions of diketones **1b**, **c** produce one stereoisomer, viz., bicyclic compounds **2b**, **c**, whereas two stereoisomers—**2d**–**f** and **2d**′–**f**′—in different ratios are generated from diketones **1d**–**f**. The yield of compound **2a** was determined based on C*H*O NMR data (4.16–4.30 ppm) using *p*-dinitrobenzene as an internal standard. Diastereomeric ratios were calculated by dividing the integral intensity of the characteristic C*H*O signals in the ^{1}H NMR spectra: **2d** (4.22–4.36 ppm)/**2d**′ (4.00–4.13 ppm), **2f** (3.94–4.06 ppm) / **2f**′ (4.22–4.32 ppm), and the ratio of **2e** / **2e**′ was similarly determined by comparison of $CH_3C(6a)$ signals integral intensity (1.41 and 1.44 ppm, respectively). The structure of rapidly decaying bicyclic compound **2a** was determined using ^{1}H NMR, ^{13}C NMR, and HRMS data without stereochemical information.



Scheme 3. Proposed mechanism for the formation of products **2**, **3**, and **5** by the reaction of 2-allyl-1,3-diketones **1** and **4** with the I_2/H_2O_2 system.

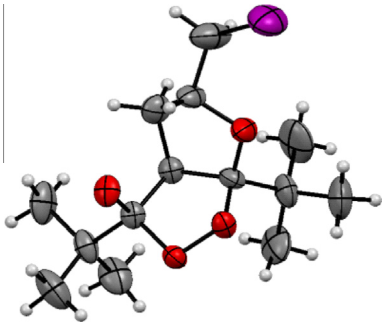


Figure 1. Single crystal X-ray diffraction structure of product **2b**.

Since the COOC and COC functional groups are characterized by similar NMR spectroscopic data, we determined the structure of compound **2b** by single crystal X-ray diffraction in order to confirm the presence of the COOC group rather than the COC group (Fig. 1).[25]

Conclusion

A one-pot procedure was developed for the selective assembly of complex bicyclic structures—tetrahydrofurodioxoles—by the reaction of 2-allyl-1,3-diketones with a fivefold molar excess of H_2O_2 and a twofold excess of I_2. The process is unusual in that it does not afford the expected bridged tetraoxanes, products of double bond iodoperoxidation or dihydroperoxidation of the carbonyl groups.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2016.01.061.

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23. *Caution:* Although we have encountered no difficulties in working with peroxides, precautions such as the use of a safety shield and fume hood should be taken. The use of redox-active transition-metal salts, heating and vigorous shaking should be avoided!
    *Preparation of **2a**–**f**, **2d**′–**f**′, **3**, **5a**,**b** by the reaction of 2-allyl-1,3-diketones **1a**–**f**, **4a**,**b** with the I_2/H_2O_2 system.* Iodine (1.015 g, 4 mmol) was dissolved in CH_2Cl_2 (10 mL), a 1.88 M ether solution of H_2O_2 (5.3 mL, 10 mmol; in the case of compound **3**—1.05 mL, 2 mmol) was added, and then diketone **1a**–**f**, **4a**,**b** (2 mmol) was added with stirring at room temperature. The reaction mixture was stirred for one hour at room temperature. Petroleum ether (20 mL) and finely powdered $Na_2S_2O_3 \cdot 5H_2O$ (3 g) were added to the reaction mixture, and the mixture was stirred until the solution turned colorless. The precipitate was filtered off and the solvents were evaporated on a rotary vacuum evaporator (10–15 mm Hg) at 15–20 °C. The products were isolated by silica gel column chromatography using PE–EA as the eluent (5:1, v/v).
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25. Crystallographic data for **2b** and **5a** have been deposited—CCDC Nos. 1423151 and 1423152, respectively—with the Cambridge Crystallographic Data Center, and they can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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