Synthesis and X-Ray Crystal Structure Analysis of 1,4-Epoxy-4-methyl-1*H*,4*H*-2,3-benzodioxepin

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Ozonolysis of 2-methyl-1*H*-indene (**1**) afforded the stable secondary ozonide 1,4-epoxy-4-methyl-1*H*,4*H*-2,3-benzodioxepin (**2**). This compound crystallizes in two polymorphic forms, depending on the solvent used. The monoclinic form **2a** containing two symmetry-independent molecules (enantiomers) is obtained by crystallization from dichloromethane. In contrast, the orthorhombic modification **2b** is obtained from ethyl acetate solution and crystallizes as a conglomerate of enantiomerically pure single crystals. Additionally, the ring-opened product 2-(2-oxopropyl)benzoic acid (**3**) was obtained and investigated by X-ray crystal structure analysis.

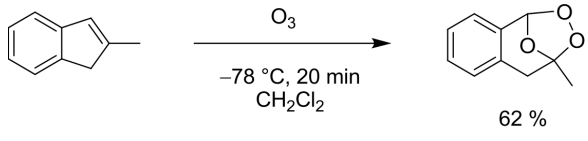
Key words: Ozonolysis, Stable Secondary Ozonide, X-Ray Crystal Structure Analysis

Introduction

Since the early investigations of the oxidative cleavage of unsaturated compounds with ozone by Harries [1] and Staudinger [2], much effort has been dedicated to studies of the actual mechanism of the ozonolysis [3]. According to the widely accepted Criegee mechanism [4], the formation of ozonides (1,2,4-trioxolanes) [5] can be considered the result of a series of three [2+3]-cycloaddition or cycloreversion reactions [6]. The two intermediates, primary ozonide (1,2,3-trioxolane) and carbonyl oxide, have limited lifetimes and are converted into the more stable secondary ozonide, which can be subjected to a hydrolytic, reductive or oxidative workup, giving rise to different products. Particularly ozonides of cyclopentenes [7a] and indenes [7b – c, 8, 9], and their respective derivatives show extraordinary stability. Recently, Jung *et al.* reported the formation of diozonides, triozonides and tetraozonides by ozonolysis of substituted 2-cyclohexenones, followed by treatment with *O*-methyl-hydroxylamine and subsequent co-ozonolysis with different carbonyl compounds [10]. Some secondary ozonides are remarkably stable, but crystal structures are known for only a few compounds of this class [9, 11]. These include two secondary ozonides derived from highly substituted indenes [9a] and two derived from indenones [9b – e]. Furthermore, the crystal structures of a rather complex polycyclic ozonide derived from 1,2,3,6b,7,8-hexahydrobenzo[j]-fluoranthene [11a] and of 3-methoxycarbonyl-5-anisyl-1,2,4-trioxacyclopentane [11b] have been reported. The positions of the peroxide and ether bridges in the latter structure are affected by disorder, so that the interatomic distances and bond angles in this part of the molecule are probably not very reliable. Herein, we report on the synthesis and crystal structure of 1,4-epoxy-4-methyl-1*H*,4*H*-2,3-benzodioxepin (**2**), one of the simplest indene-derived secondary ozonides.

Results and Discussion

Ozonolysis of 2-methyl-1*H*-indene (**1**) at −78 °C in dichloromethane afforded 1,4-epoxy-4-methyl-1*H*,4*H*-2,3-benzodioxepin (**2**) in 62 % yield (Scheme 1). The crystalline product has a melting point of 45 °C and shows remarkable stability. An excess of dimethyl sulfide reduces it rather slowly, and it can be stored, without decomposition, at ambient temperature for several months. Similar observations have been made previously on related compounds [8b, 8e].



Scheme 1. Ozonolysis of 2-methyl-1*H*-indene.

	2a	**2b**	**3**
Formula	$C_{10}H_{10}O_3$	$C_{10}H_{10}O_3$	$C_{10}H_{10}O_3$
M_r	178.18	178.18	178.18
T, K	213(2)	120(2)	213(2)
Crystal size, mm^3	$0.3 \times 0.2 \times 0.1$	$0.21 \times 0.18 \times 0.06$	$0.2 \times 0.2 \times 0.08$
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1$	$P2_12_12_1$	$P2_1/c$
a, Å	8.2047(8)	8.9444(3)	11.822(5)
b, Å	19.483(2)	18.6915(6)	6.9490(8)
c, Å	5.4849(5)	5.1152(2)	11.597(6)
β, °	102.30(1)	90	110.46(4)
V, Å^3	856.6(1)	855.16(4)	892.6(6)
Z	4	4	4
D_{calcd}, g cm^{-3}	1.38	1.38	1.33
$\mu(MoK_\alpha)$, mm^{-1}	0.1	0.1	0.1
$F(000)$, e	376	376	376
hkl range	$-10 \le h \le 10$ $-23 \le k \le 23$ $-6 \le l \le 6$	$-11 \le h \le 9$ $-21 \le k \le 17$ $-6 \le l \le 5$	$-14 \le h \le 14$ $-6 \le k \le 8$ $-3 \le l \le 12$
Refl. measured	6132	5061	2099
Refl. unique / R_{int}	3234 / 0.0540	1609 / 0.0216	1128 / 0.1024
Param. refined	315	158	309
$R1$ $[I \ge 2\sigma(I)]$[a]	0.0386[d]	0.0292	0.0508
$wR2$ (all data)[b]	0.0988[d]	0.0796	0.1460
GoF (F^2)[c]	0.912	1.075	0.692
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.17 / −0.15	0.18 / −0.18	0.01 / 0.0

Table 1. Crystal structure data of **2** and **3**.

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$ and A and B are constants adjusted by the program; [c] $\mathrm{GoF} = S = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters; [d] final R values for the alternative refinement in space group $P2_1/a$: $R1$ $[I \ge 2\sigma(I)] = 0.067$ and $wR2$ (all data) = 0.1838.

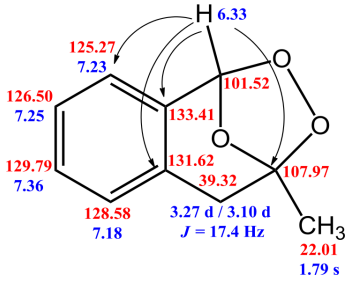


Fig. 1 (color online). Two and three bond coupling in HMBC spectra of ozonide **2**.

The structure of the product was confirmed by spectroscopic methods and by X-ray crystallography. A complete NMR assignment was made by use of ^{1}H, ^{13}C, APT, H,H-COSY, HSQC and HMBC spectra. Most importantly, the bridgehead-proton (^{1}H: 6.33 ppm; ^{13}C(APT): 101.52 ppm) gives cross correlation peaks to the quaternary OCO carbon (107.97 ppm), the quaternary aromatic carbons (133.41 and 131.62 ppm) and an aromatic CH (125.27 ppm) *via* two and three bond coupling in the HMBC spectrum (Fig. 1).

X-Ray crystal structure analyses

The ozonide **2** crystallizes in two polymorphic forms. The monoclinic form **2a** is obtained from dichloromethane solution (see Table 1). Its two crystallographically independent molecules (enantiomers), labelled A and B, are depicted in Fig. 2. The orthorhombic modification **2b** (Fig. 4) crystallizes from ethyl acetate and contains one independent homochiral molecule.

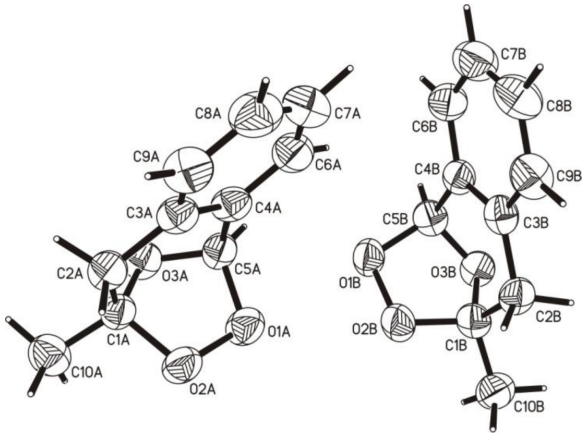


Fig. 2. Molecules A (left) and B (right) of the monoclinic form **2a**.

Form **2a** crystallizes in the space group $P2_1$. Its two independent molecules are related by a pseudo-inversion center, so that the overall molecular arrangement exhibits $P2_1/a$ pseudo-symmetry. In order to test the correctness of the assigned space group, the final

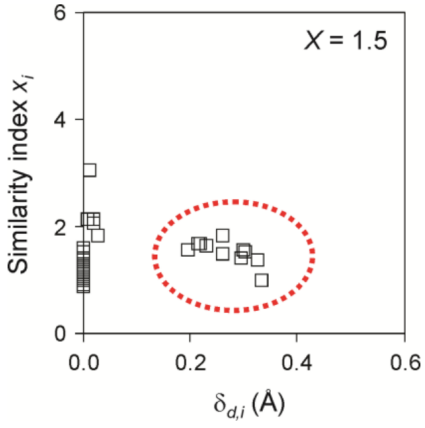


Fig. 3. XPAC plot (see ref. [13]) illustrating a geometrical comparison of the environments of the independent molecules A and B of form **2a**.

$P2_1$ ($Z' = 2$) structure model was transformed into the corresponding $P2_1/a$ ($Z' = 1$) setting and then re-refined. This alternative structure refinement gave significantly higher R values (see footnotes of Table 1). Moreover, freely refined positional and isotropic displacement parameters of the H atoms were found to be considerably more consistent in the $P2_1$ model ($0.033 \leq U_{iso}(H) \leq 0.092$) than in the $P2_1/a$ alternative ($0.045 \leq U_{iso}(H) \leq 0.142$). A closer inspection of the data for **2a** has shown that one third of all $h0l$ reflections are observed and that their intensities, even though they are weak, are significant. This indicates a (non-centrosymmetric) $P2_1$ structure with an a-glide as a pseudo-symmetry element, whereas the centrosymmetric $P2_1/a$ alternative would require all $h0l$ reflections with $h = 2n + 1$ to be systematically absent.

The program XPAC [12] was used to investigate topological differences between the independent molecules A and B of structure **2a** by comparing the geometries of their respective environments containing 14 surrounding molecules. Using a previously described approach [13], individual similarity indices x_i were calculated for 91 molecular pairs using all 13 non-H positions. The diagram in Fig. 3 illustrates that certain x_i values deviate significantly from 0. These data are the result of an increase of the angular differences between the two packing arrangements, and the overall XPAC index X is 1.5. Additionally, a set of distance parameters $\delta_{d,i}$ was obtained by calculating the distance between two molecular centroids in the cluster around molecule A and comparing these with the corresponding distance in the cluster of B. Remarkably, a subset of $\delta_{d,i}$ values is found in the 0.3 Å range (Fig. 3, encircled area). Hence, the environments of A and B are clearly distinct from one another. In conclusion, the geometrical analysis with XPAC supports the choice of $P2_1$ over $P2_1/a$ as the correct space group symmetry of **2a**.

Table 2. Bond lengths (Å) and angles (deg) for the 1,2,4-trioxolane moieties of **2a** and **2b** with estimated standard deviations in parentheses.

	2a (Molecule A)	**2a** (Molecule B)	**2b**
O1–O2	1.477(4)	1.470(4)	1.479(1)
C1–O2	1.451(5)	1.446(5)	1.472(2)
C1–O3	1.437(4)	1.408(4)	1.419(2)
C5–O1	1.424(5)	1.430(4)	1.430(2)
C5–O3	1.411(5)	1.416(4)	1.412(2)
C1–C2	1.508(5)	1.513(5)	1.517(3)
C2–C3	1.512(5)	1.502(5)	1.512(2)
C3–C4	1.380(5)	1.401(5)	1.397(2)
C4–C5	1.497(4)	1.491(4)	1.509(2)
O2–C1–O3	103.3(3)	104.1(3)	103.6(1)
O2–C1–C2	110.2(3)	108.2(3)	108.1(1)
C1–C2–C3	111.6(3)	111.6(3)	110.9(1)
C2–C3–C4	119.2(3)	118.2(3)	119.2(1)
C3–C4–C5	117.8(3)	117.8(3)	117.4(1)
C4–C5–O1	111.9(3)	113.0(3)	111.5(1)
C4–C5–O3	110.7(3)	111.1(3)	111.6(1)
O1–C5–O3	103.5(3)	102.1(2)	102.6(1)

As described above, molecules A and B of form **2a** have very similar geometries (see Table 2). The Cremer-Pople puckering parameters [14] calculated for the five-membered rings in molecules A [$Q2$ = 0.440(2) Å, $\varphi 2$ = 127.2(3)°] and B [$Q2$ = 0.452(3) Å, $\varphi 2$ = 127.1(3)°] of form **2a** indicate a twist conformation.

The corresponding parameters for the orthorhombic polymorph **2b** are very similar: $Q2$ = 0.451(1) Å and $\varphi 2$ = 129.3(2)°. The six-membered rings with the atoms O3, C1, C2, C3, C4 and C5 adopt an envelope conformation in both independent molecules (A and B) of the form **2a**. As expected, the bond lengths and angles in the orthorhombic form **2b** (Fig. 4) are in concert with the values found in the monoclinic form **2a** (see Table 2).

The bond lengths and angles of the 1,2,4-trioxolan fragment of compound **2** are in good agreement with previously reported bond parameters of secondary ozonides [9, 11].

An attempt to crystallize the ozonide **2** from toluene resulted in a rearrangement to the ring-opened product **3** (Fig. 5), which was possibly due to an intramolecular redox reaction [15]. The obtained single crystals were investigated by X-ray structure analysis, and the essential bond parameters of **3** are listed in Table 3.

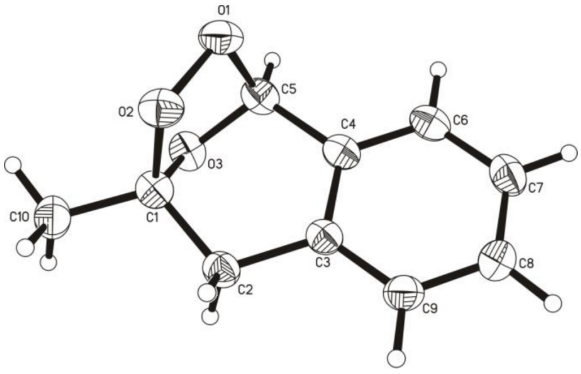


Fig. 4. Molecular structure of the orthorhombic form **2b**.

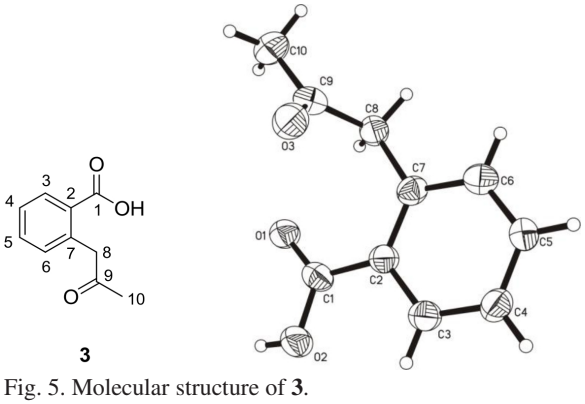


Fig. 5. Molecular structure of **3**.

The crystal structure is composed of O2–H2···O1^{i}-bonded dimers [(i) –*x*+1, –*y*, –*z*+2], where the center of the eight-membered ring coincides with a crystallographic center of symmetry (Fig. 6).

Conclusion

The synthesis of 1,4-epoxy-4-methyl-1*H*,4*H*-2,3-benzodioxepin (**2**) and its structural characterization by spectroscopic methods and X-ray crystallography has been described. In contrast to previously reported, highly substituted indene-derived ozonides, compound **2** has a rather simple structure, but its stability is similar to that of the other compounds. The ring-opened product 2-(2-oxopropyl)benzoic acid (**3**) was also obtained and characterized by X-ray crystallography.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions, using a Varian Mercury plus 400 MHz spectrometer. The signals were referenced to residual chloroform (7.26 ppm, ^{1}H, 77.16 ppm, ^{13}C). Chemical shifts are reported in ppm, multiplicities are labelled s (singulett), d (doublet), t (triplet), q (quartet), p (pentet) and m (multiplet). Melting points were determined on a Boetius hot-stage microscope. IR spectra were obtained with an FTIR spectrometer (Genesis ATI Mattson/Unicam). UV spectra were recorded on a UV spectrometer (DU-650 Beckmann). ESI mass spectra were recorded on a Bruker APEX II FT-ICR. Flash column chromatography was performed using Merck silica gel 60 230 – 400 mesh (0.040 – 0.063 mm).

Table 3. Selected bond lengths (Å) and angles (deg) for **3** with estimated standard deviations in parentheses[a].

C1–O1	1.271(8)	C1–O2	1.315(8)
C2–O3	1.408(8)	C3–C4	1.411(8)
C4–C5	1.371(9)	C5–C6	1.382 (9)
C6–C7	1.400(7)	C7–C8	1.523(9)
C8–C9	1.519(8)	C9–O3	1.242(9)
C9–C10	1.509(9)		
O1–C1–O2	121.6(5)	O1–C1–C2	122.5(6)
O2–C1–C2	115.9(7)	C1–C2–C3	117.5(5)
C1–C2–C7	123.4(6)	C2–C3–C4	122.0(6)
C3–C4–C5	118.1(7)	C4–C5–C6	120.5(6)
C5–C6–C7	122.9(6)	C6–C7–C2	117.6(6)
C6–C7–C8	118.9(6)	C7–C8–C9	115.8(6)
C8–C9–O3	120.8(7)	C8–C9–C10	115.7(7)
O2–H2	0.82	O1^{i} · H2	1.86
O2–O1A	2.667(5)	O2 –H2 ··· O1^{i}	166.3°

[a] Symmetry operation: (i) $-x+1$, $-y$, $-z+2$.

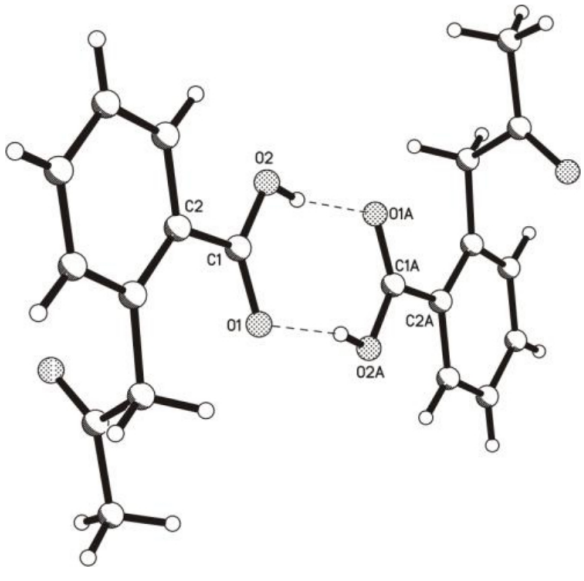


Fig. 6. Dimeric structure of **3**.

*1,4-Epoxy-4-methyl-1H,4H-2,3-benzodioxepin (**2**)*

A solution of 2-methyl-1*H*-indene (98 %, 1.134 g, 8.54 mmol) in 20 mL absolute dichloromethane was cooled to −78 °C and subsequently treated with ozone until the solution became blue in color (20 min). The solvent was removed

in vacuo, and the residue was purified by silica gel chromatography (petroleum ether/diethyl ether, 6 : 1 → 5 : 1) to afford 948.2 mg (62 %; 5.32 mmol) of 1,4-epoxy-4-methyl-1*H*,4*H*-2,3-benzodioxepin (**2**) as a yellowish solid. M. p. 45 °C. – UV/Vis (MeCN): λ_{max} (lg ε_{max}) = 214 nm (3.869). – IR (KBr): $\tilde{\nu}$ = 3417, 3056, 2989, 2936, 1720, 1608, 1586, 1490, 1459, 1425, 1383, 1346, 1287, 1272, 1212, 1193, 1174, 1108, 1094, 1054, 1028, 953, 943, 923, 906, 872, 864, 840, 827, 783, 755, 723, 657, 638, 608, 559, 501, 449, 426 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$, 26 °C): δ = 1.79 (s, 3 H, CH_3), 3.10 (d, J = 17.4 Hz, 1 H, CH_2), 3.27 (d, J = 17.4 Hz, 1 H, CH_2), 6.33 (s, 1 H, CH), 7.18 (m, 1 H, H_{ar}), 7.23 – 7.25 (m, 2 H, H_{ar}), 7.36 (m, 1 H, H_{ar}). – ^{13}C NMR (100 MHz, $CDCl_3$, 26 °C): δ = 22.0 (CH_3), 39.3 (CH_2), 101.5 (CH), 108.0 (C_q), 125.3, 126.5, 128.6, 129.8, 131.6, 133.4 (all C_{ar}). – MS (ESI): m/z = 179 $[M+H]^+$, 185 $[M+Li]^+$, 201 $[M+Na]^+$.

X-Ray structure determination

A sealed vial, containing a solution of 50 mg 1,4-epoxy-4-methyl-1*H*,4*H*-2,3-benzodioxepin (**2**) in 0.2 mL of the respective solvent, was kept at ambient temperature for several days. Single crystals were obtained by slow evaporation of the solvent. Crystallization from dichloromethane gave the monoclinic form **2a**, while from ethyl acetate the orthorhombic form **2b** was obtained. Intensity data for compounds **2a** and **3** were measured on an IPDS1 diffractometer (Fa. Stoe); the data for **2b** were collected on a Bruker P4 diffractometer. The relevant crystallographic data are listed in the Table 1.

The structures were determined using the Direct Methods procedure in SHELXS-97 and refined by full-matrix least-squares on F^2 using SHELXL-97 [16]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of **2b** were located in a difference Fourier map and refined isotropically. In the case of **2a** and **3**, all hydrogen atoms were placed in calculated positions with their isotropic U values set to 1.2 or 1.5 U_{eq} of the parent C or O atom. Refinements of the Flack x parameter for **2a/b** were not deemed necessary because all atoms are only very weak anomalous scatterers and because of the pseudo-centrosymmetry of **2a**. In the case of compound **3**, a significant number of reflections affected by twinning were eliminated during the integration, resulting in a relatively low data/parameter ratio of the corresponding structure refinement.

CCDC 795613 (**2a**), 795451 (**2b**) and 795450 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk /data_request/cif.

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