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Detection of Elusive Chloro- and Bromo Substituted Ozonides by Nucleophilic Substitution Reactions

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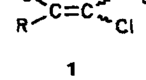
Abstract. Ozonolyses of 2,3-dichloro-2-butene (**4**), 4,5-dichloro-4-octene (**9**) and 2,3-dibromo-1,4-dichloro-2-butene (**12**) on polyethylene gave the corresponding ozonides **5**, **10** and **13a**, respectively, which could not be isolated or unequivocally identified. Their identity could be proven, however, via substitution of the chloro- or bromo substituents at the ozonide rings by stabilizing substituents and subsequent isolation of the substituted ozonides **6**, **11**, **13b** and **13c**. Ozonolysis of 2,3-diacetoxy-2-butene (**14**) on polyethylene, in dichloro methane and in pentane gave mixtures of **16** and **17** but not ozonide **6**.

To our knowledge, bromo substituted ozonides have not yet been reported and the proven existence of chloro substituted ozonides is limited to ozonides derived from polycyclic [1, 2], monocyclic [3] and such acyclic chloroolefins, which bear at least one bromomethyl- or chloromethyl group at the chloro substituted double bond [4]. By contrast, ozonolyses of chloroolefins containing alkyl substituted double bonds like **1a** [3] or **1b** [5] did not result in the isolation or unequivocal identification of the corresponding ozonides of type **2**. However, based on the occurrence of peroxides of type **3**, i.e. acyclic isomers of ozonides **2**, it was suggested that ozonides **2** may have been formed but eluded detection due to rapid isomerization [3, 5].



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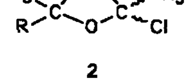

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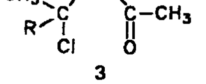

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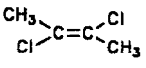
R: **a** = CH_3; **b** = Cl

Although it was demonstrated by others [6, 7], that in the ozonolysis of chloroolefins of type **1**, peroxides of type **3** can be formed by an alternate route without the intermediacy of ozonides of type **2**, we have maintained our interest concerning the existence of monocyclic alkyl substituted chlorinated ozonides. By the combination of two recently developed techniques viz. dry ozonolysis of olefins on polyethylene which has been amply demonstrated to be conducive to ozonide formation [8] and nucleophilic substitution of chlorine at ozonide rings by stabilizing substituents [9], we have now been able to prove for the first time the existence of monocyclic alkyl substituted chlorinated ozonides. In a similar manner, the first representative of the class of bromo substituted ozonides was verified.

Results

In previous work [3] we had ozonized *trans*-2,3-dichloro-2-butene (**4**) on polyethylene, extracted the products with ether and removed the ether at room temperature. In the ^{13}C-NMR spectrum of the residue, there were no signals which could be attributed to C-atoms in an ozonide ring, i.e. ozonide **5** was not present. In the present investigation, the loaded polyethylene was dispersed in a solution of sodium acetate in acetic acid immediately after the ozone treatment of **4** was terminated. Work-up of this mixture afforded ozonide **6** of unknown stereochemical identity in a yield of ca. 12%. Its ozonide structure was established by a positive peroxide test, by correct elemental analysis, by the appearance of a ^{13}C-NMR signal at 120.13 ppm, i.e. in the range which is typical for C-atoms in ozonide rings, by the appearance of ^{17}O-NMR signals at 162 and 310 ppm for the C–O–C- and C–O–O–C moieties, respectively [10], and by reduction with triphenylphosphine to give two molar equivalents of acetic anhydride.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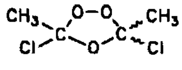
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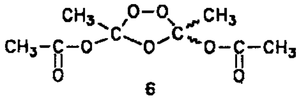
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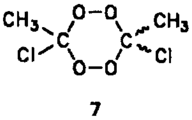
The occurrence of ozonide **6** represents conclusive evidence for the formation of its precursor, the chloro substituted ozonide **5** in the ozonolysis of **4** on polyethylene. The fact, that **5** could not be detected in our previous work [3] when the products of ozonolysis were extracted from polyethylene shows, that this ozonide is obviously very labile and does not survive the usual work-up procedure. By contrast, ozonide **6** is a stable, crystalline compound which melts at 60.5 °C without decomposition. This stabilizing effect of acetoxy groups is in line with our previous experience [9], that substitution of chlorine in the explosive cyclic peroxide **7** – which is a product of the ozonolysis **4** in solution [5, 6] – by acetoxy groups leads to the stable peroxide **8** which melts at 119 °C without decomposition.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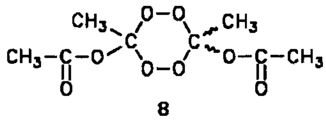
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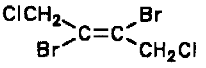
Ozonolysis of *trans*-4,5-dichloro-4-octene (**9**) on polyethylene at –70 °C, followed by immediate extraction of the products with ether and subsequent removal of the solvent gave a residue, which as a neat sample gave a spontaneous exothermic reaction. In CDCl$_3$-solution at 0 °C the original residue showed a signal in the ^{13}C-NMR spectrum at 125.30 ppm which disappeared when the solution warmed up to room temperature. This was indicative of the presence of the labile ozonide **10**, which could, however, not be isolated or unequivocally characterized. In a second experiment, the loaded polyethylene was dispersed in a mixture of AgBF$_4$ and LiF in ether at –70 °C immediately after the ozonolysis of **9** was terminated. This resulted in the formation of ozonide **11** of unknown stereochemistry, which was isolated in a yield of 11%.

The structure of **11** was proven by a positive peroxide test, by its ^{1}H- and ^{13}C-NMR spectrum and by its reduction with dimethyl sulfide to give butyryl fluoride. At room temperature, ozonide **11** undergoes rapid decomposition as a neat sample and gradual decomposition in solution if it is kept in glass vials, but it is stable in Teflon vials [11].

Ozonolysis of *trans*-2,3-dibromo-1,4-dichloro-2-butene (**12**) on polyethylene at –75 °C, followed by immediate extraction of the products with ether gave a mixture of chloro acetic acid and chloro acetic anhydride. In a second experiment, the loaded polyethylene was dispersed in a mixture of AgBF$_4$ and LiF in ether at –70 °C immediately after the ozone treatment of **12** was terminated. This provided a mixture of the fluoro substituted ozonides *cis*- and *trans*-**13b** in a yield of 18% and in a ratio of 1:4. In a third experiment, the loaded polyethylene was dispersed in a solution of AgBF$_4$ in methanol at –70 °C to give the methoxy substituted ozonides *cis*- and *trans*-**13c**. The aforementioned results show that the ozonolysis of **12** on polyethylene has led to the formation of **13a** as the first example of a bromo substituted ozonide.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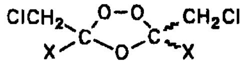
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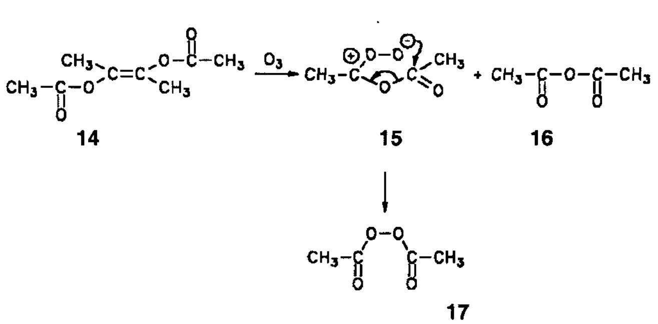
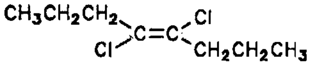
	a	b	c
X	Br	F	OMe

The method of nucleophilic substitutions at ozonides is not only useful for the detection of elusive ozonides, but also for the preparation of ozonides which are not accessible by ozonolysis of the corresponding olefins. A case in point is ozonide **6**. Ozonolysis of the parent olefin **14** did not produce ozonide **6**, but rather acetic anhydride (**16**) and diacetyl peroxide (**17**) in a ratio of ca. 70:30 on polyethylene and in pentane and in a ratio of ca. 50:50 in dichloro methane. This abnormal result is rationalized by ozone cleavage of **14** to give fragments **15** and **16**, and subsequent intramolecular reaction of **15** to give **17**, rather than intermolecular cycload-

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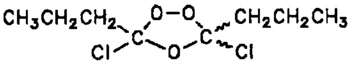
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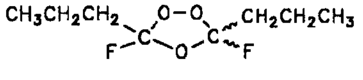
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dition of **15** with the poor dipolarophile acetic anhydride (**16**).

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Experimental

^{1}H, ^{13}C and ^{17}O NMR: Bruker AC 250. Unless mentioned otherwise, the ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ with TMS as internal reference. The ^{17}O NMR spectra were recorded in C_6D_6 with H_2O as external reference and under previously reported conditions [10]. – MS: Hewlett Packard 5985B. – Chromatographic separations: Flash chromatography [12] on silica gel. Ozonolyses on polyethylene have been performed according to a procedure which has been published in detail [13].

Ozonolysis of *trans*-2,3-dichloro-2-butene (4)

3,5-Bis-(acetoxy)-3,5-dimethyl-1,2,4-trioxolane (**6**)
With the method applied for volatile olefins [13], 62 g of polyethylene was loaded with 1.82 g (14.6 mmol) of **4** and treated with ozone at –70 °C for 90 min. Residual ozone was flushed off with nitrogen at –70 °C and the loaded polyethylene was dispersed in a solution of 5.98 g (72.9 mmol) of anhydrous sodium acetate in 100 ml of acetic acid at room temp. The mixture was stirred for 16 h, 300 ml of ether was added, the solid was filtered off and from the filtrate the solvent was evaporated at 38 °C and reduced pressure. The solid residue (4.97 g) was extracted with 80 ml of ether and from the extract the solvent was evaporated at room temp. and reduced pressure. The liquid residue (994 mg) was chromatographed in two equal portions (column 1.8 × 45 cm, 55 g of silica gel, 400 ml of pentane/ether, 3:1, 300 ml of ether) to give a total of 402 mg (12.5%) of **6**. Colorless solid; m.p. 60.5 °C. – ^{1}H NMR: δ = 2.02 (s), 2.09 (s). – ^{13}C NMR (BB): δ = 19.49, 21.59, 120.13, 168.00. – ^{13}C NMR (GD, C_6D_6, TMS): δ = 19.52 (q, J = 131.6 Hz), 20.96 (q, J = 129.8 Hz), 120.47 (q, J = 6.1 Hz), 167.41 (q, J = 7.0 Hz). – ^{17}O NMR: δ = 161.8 (s, -O-), 218.3 (s, O–Ac), 309.7 (s, -O–O-), 386.5 (s, C=O). – CI MS (CH_4), *m/z* (%): 221 (2) [M^++1]. – $C_8H_{12}O_7$ (220.2): calcd. C 43.64, H 5.49; found C 43.33, H 5.37.

Reduction of 6

A solution of 12 mg (0.06 mmol) of **6** and 10 µl of 1,1,2,2-tetrachloroethane in 0.6 ml of $CDCl_3$ was admixed with 25 mg (0.1 mmol) of triphenylphosphine and the reaction was monitored by ^{1}H NMR spectroscopy. After 30 min **6** had disappeared and ca. 2 molar equivalents of acetic anhydride (δ = 2.22, s) had been formed.

Ozonolysis of *trans*-4,5-dichloro-4-octene (9)

With the method applied for nonvolatile olefins [13], 60 g of polyethylene was loaded with 0.94 g (5.2 mmol) of **9** [14] (*cis:trans* = 1:52) in 120 ml of pentane and treated with ozone at –75 °C for 3.5 h. Residual ozone was flushed off with nitrogen at –70 °C, the products were extracted with 200 ml of ether at room temp. and the extract was concentrated by distillation of the ether at room temp. and reduced pressure. The remaining liquid residue underwent a spontaneous strongly exothermic reaction.

3,5-Difluoro-3,5-dipropyl-1,2,4-trioxolane (**11**)

As described above for the ozonolysis of **9**, 1.01 g (5.6 mmol) of **9** on 60 g of polyethylene was ozonized at –75 °C for 2.5 h. The products were extracted with 140 ml of ether, and the extract was dropwise added to a stirred mixture of 1.61 g (8.3 mmol) of $AgBF_4$ and 1.95 g (75.2 mmol) of LiF in 20 ml of ether. After 30 min the mixture was decanted, the ether solution was washed with an aqueous solution of NaCl and $NaHCO_3$ and dried with $MgSO_4$ in a Teflon flask. From the decanted solution ether was distilled off at room temp. and reduced pressure, and the liquid residue (628 mg) was chromatographed (column 1.8×55 cm, 66 g of silica gel, pentane/ether, 60:1) to give 123 mg (11%) of **11**. It was further purified by distillation at room temp. and 0.1 Torr from a Teflon flask and fractional condensation of the distillate in a series of three Teflon traps kept at –20 °C, –78 °C and –198 °C. The trap kept at –20 °C contained 78 mg (7%) of **11**. Colorless liquid. – ^{1}H NMR (Teflon tube): δ = 0.99 (t, J = 7.4 Hz, 6 H), 1.52 – 1.67 (m, 4 H), 2.04 – 2.13 (m, 4 H). – ^{13}C NMR (BB, Teflon tube): δ = 13.56 (s), 16.41 (s), 33.30 (m), 125.80 (d, J = 271.5 Hz). – CI MS (CH_4), *m/z* (%): 177 (1) [M^+–F].

Reduction of 11

A solution of 18 mg (0.09 mmol) of **11** in 0.4 ml of $CDCl_3$ was admixed with 15 µl of dimethyl sulfide in a Teflon NMR tube. ^{1}H NMR analysis after 2.5 h showed the presence of **11** and of butyryl fluoride in a molar ratio of ca. 2.5:1, whereas after 20 h ozonide **11** had disappeared and dimethyl sulfoxide (δ = 2.62) and butyryl fluoride [δ = 1.02 (td, J = 7.4 and 1.0 Hz), 1.72 (sextet, J = 7.4 Hz), 2.50 (td, J = 7.2 and 0.9 Hz] were present in a molar ratio of ca. 1:2. To this mixture 6 µl of methanol was added. ^{1}H NMR analysis showed the formation of methyl butyrate [δ = 0.95 (t, J = 7.4 Hz), 1.66 (sextet, J = 7.4 Hz), 2.30 (t, J = 7.4 Hz), 3.68 (s)] as the sole product.

Decomposition of 11

A solution of 20 mg (0.1 mmol) of **11** in 0.6 ml of $CDCl_3$ was kept in a glass NMR tube at room temp. After 16 h ozonide **11** had disappeared to give as the sole product dibutyryl peroxide: ^{1}H NMR: δ = 1.02 (t, J = 7.4 Hz), 1.76 (sextet, J = 7.4 Hz), 2.42 (t, J = 7.3 Hz). – ^{13}C NMR (BB): δ = 13.43, 18.42, 31.89, 169.03.

Ozonolysis of *trans*-2,3-dibromo-1,4-dichloro-2-butene (12) on Polyethylene

With the method applied for nonvolatile olefins [13], 64 g of polyethylene was loaded with 610 mg (2.1 mmol) of **12** in 100 ml of pentane and treated with ozone at –75 °C for 8 h. Residual ozone was flushed off with nitrogen at –75 °C, the products were extracted with 200 ml of ether at room temp. and the extract was concentrated by distillation of the ether at room temp. and reduced pressure. ^{1}H NMR analysis of the residue showed the presence of 71% of chloroacetic acid (δ =

4.14), of 14% of chloroacetic anhydride ($\delta = 4.25$) and of 15% of unreacted **12** ($\delta = 4.54$).

3,5-Bis-(chloromethyl)-3,5-difluoro-1,2,4-trioxolane (**13b**)

As described above for the ozonolysis of **12**, 1.30 g (4.6 mmol) of **12** on 51 g of polyethylene was ozonized at –75 °C for 4 h. After the removal of residual ozone, the cold polyethylene was dispersed in a mixture of 2.10 g (10.8 mmol) of $AgBF_4$ and 1.3 g (50.5 mmol) of LiF in 150 ml of ether at –70 °C. After warming up to room temp. the slurry was filtered, the filtrate was washed with an aqueous solution of NaCl and $NaHCO_3$, dried with $MgSO_4$ and concentrated by distillation at room temp. and reduced pressure. From the residue (450 mg) one obtained 175 mg (18%) of ozonide **13b** by flash chromatography (column 2 × 30 cm, 25 g silica gel, 300 ml of pentane/dichloromethane, 20:1). Colorless liquid, 1:4-mixture of *cis*- and *trans*-isomer. - ^1H NMR: $\delta = 3.88$–3.97 (m). – ^{13}C NMR (BB): $\delta = 38.37$–39.93 (m, CH_2 in *cis*- and *trans*-**13b**), 124.71 (dd, $J = 275.1$ and 1.0 Hz, C-F in *cis*-**13b** [9]), 123.44 (d, $J = 276.1$ Hz, C-F in *trans*-**13b** [9]).

3,5-Bis-(chloromethyl)-3,5-dimethoxy-1,2,4-trioxolane (**13c**)

With the method applied for nonvolatile olefins [13], 17 g of polyethylene was loaded with 580 mg (2.1 mmol) of **12** in 27 ml of pentane and treated with ozone at –75 °C for 3.3 h. Residual ozone was flushed off with nitrogen at –75 °C and the cold polyethylene was dispersed in a solution of 0.9 g (4.6 mmol) of $AgBF_4$ in 35 ml of methanol, kept at –70 °C. The stirred mixture was allowed to warm up to –10 °C within 2 h. Then, 963 mg (7 mmol) of K_2CO_3 was added, the mixture was stirred for 14 h, filtered and the filtrate was concentrated by distillation at room temp. and reduced pressure. The remaining solid residue was leached with ether and the ether was distilled off to leave 137 mg of a colorless semisolid residue. Chromatographic separation of the residue (column 1.5×30 cm, 25 g of silica gel, 320 ml of pentane/ether, 15:1) afforded 17 mg (3.5%) of *trans*-**13c** and 7 mg (1.5%) of a mixture containing 89% of *cis*-**13c** and 11% of *trans*-**13c**. They were identified with the help of authentic samples [9].

cis-3,5-Bis-(chloromethyl)-3,5-dimethoxy-1,2,4-trioxolane (*cis*-**13c**): ^{13}C NMR: $\delta = 42.14, 51.85, 120.72$.

trans-3,5-Bis-(chloromethyl)-3,5-dimethoxy-1,2,4-trioxolane (*trans*-**13c**): ^{13}C NMR: $\delta = 42.92, 51.22, 120.04$.

Ozonolyses of 2,3-diacetoxy-2-butene (14)

a) *On Polyethylene*: With the method applied for nonvolatile olefins [13], 21 g of polyethylene was loaded with 218 mg (1.3 mmol) of **14** [15] in 40 ml of ether and treated with ozone at –70 °C for 2 h. Residual ozone was flushed off with nitrogen, the products were extracted from polyethylene with 80 ml of ether, and the extract was concentrated by distillation of ether at room temp. and reduced pressure. ^1H NMR analysis of the residue showed the presence of unreacted **14** [77%; $\delta = 1.81$ (s); 2.17 (s)], of **16** [7%; $\delta = 2.23$ (s)] and of **17** [16%; $\delta = 2.20$ (s)], whereas the signals of ozonide **6** at $\delta = 2.02$ and 2.09 did not appear.

b) *In Pentane*: A solution of 201 mg (1.2 mmol) **14** in 220 ml of pentane was ozonized at –40 °C until **14** had disappeared. Residual ozone was flushed out with nitrogen and pentane was distilled off at room temp. and reduced pressure. ^1H NMR analysis of the residue showed the presence of **16** (30%) and **17** (70%), to the exclusion of ozonide **6**.

c) *In Dichloromethane*: A solution of 490 mg (2.9 mmol) of **14** in 30 ml of dichloromethane was ozonized at –75 °C and worked up as described above. ^1H NMR analysis showed the presence of **16** (48%) and **17** (52%) as the sole products. ^{13}C NMR analysis confirmed the presence of **16** [$\delta = 21.98$ and 166.30] and of **17** [$\delta = 16.37$ and 165.98].

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