

## 단 신

### 폴리에틸렌(고체상)에서 사이클로폴리엔들의 오존화반응

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### Ozonolyses of Cyclopolyenes Adsorbed on Polyethylene

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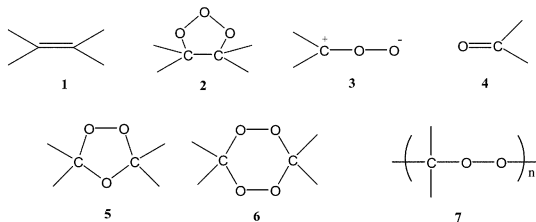
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주제어: 오존화물, 사이클로폴리엔, 폴리에틸렌

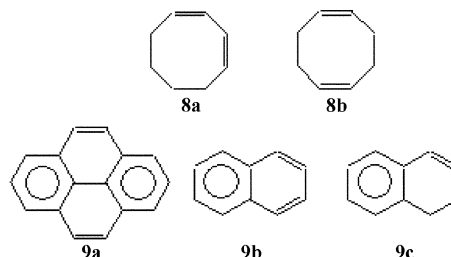
Keywords: Ozonide, Cyclopolyene, Polyethylene

The ozonolyses of olefins **1** in aprotic solvents represents the most versatile method for the preparation of ozonides. While such reactions do proceed according to the Criegee mechanism<sup>1</sup> in the initial steps to give the primary ozonides **2** and the initial fragments **3** and **4**, the latter do undergo [3+2]-cycloaddition to give ozonide **5**. Hence, the carbonyl oxide fragments **3** undergo side reactions which often lead to peroxidic materials other than ozonides, particularly acyclic and cyclic oligomers of **3**, such as dimers of structure **6** and polymers of structure **7**.



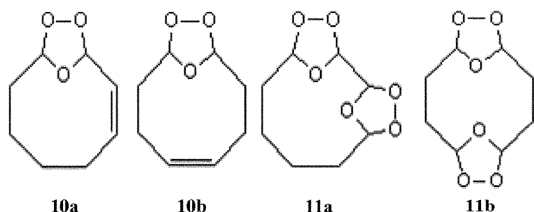
Nevertheless, this method failed when applied to a variety of substrates such as most tetrasubstituted ethylenes, monocyclic olefins except for those having four to six-membered rings, certain bicyclic olefins, certain acyclic conjugated dienes, cyclic polyenes, and aromatic compounds. The failure of

these substrates to afford the corresponding ozonides have been attributed to the low reactivity of ensuing ketone fragments **4** in 1,3-dipolar cycloaddition. However, it was very recently that Griesbaum *et al.* have been able to prepare the ozonides of larger cyclic olefins and bicyclic olefins by application of the modified ozonolysis on polyethylene.<sup>2</sup> It has been shown that cycloaddition of carbonyl oxides with aldehyde, and hence ozonide formation, can be substantially facilitated by the ozonolysis of olefins adsorbed on powdered polyethylene, presumably due to restricted migration of the primary cleavage fragments.<sup>3-7</sup> We have now tried whether this mode of reaction can be extended to the ozonolysis of cyclopolyenes. In the following, we report results from the application of this method to the ozonolysis of cyclopolyenes **8a-b**, and aromatic compounds **9a-c**.



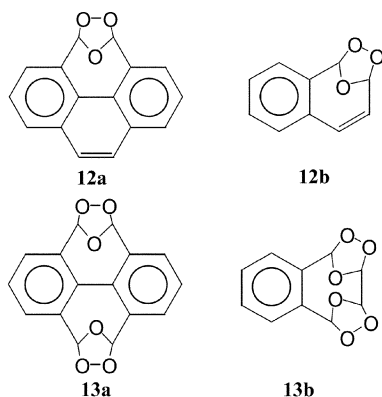
## RESULTS AND DISCUSSION

Ozonolysis of **8a** and of **8b** on polyethylene afforded the corresponding diozonides **11a** and **11b** in yields of ca. 21.2 and 26.3%. A small sample was extracted with  $\text{CDCl}_3$  and  $^1\text{H}$  NMR analysis of the extracted showed the presence of ozonides **11** and unreacted cyclopolyenes **8**. There was no evidence for the formation of the corresponding mono-ozonides of type **10**.

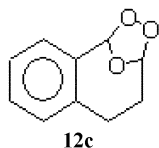


Ozonolysis of **9a** and **9b** on polyethylene afforded the corresponding mono-ozonides **12a** and **12b** and the corresponding diozonides **13a** and **13b** in yields of ca. 9.8, 8.7, 13.3, and 12.2%, respectively.

From these results it can be concluded that, in contrast to cyclopolyenes **8**, the double bonds in aromatic compounds **9a** and **9b** are attacked stepwise by ozone to give equal amounts of mono- and diozonides.



Finally, ozonolyses of **9c** on polyethylene afforded the corresponding mono-ozonide **12c** in yield of ca. 14.9%.



The structures of all isolated ozonides were established by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, and by their reduction with triphenylphosphine to give the expected dicarbaldehydes. Characteristic signals in  $^1\text{H}$  NMR spectra were those of the CH groups in the ozonide rings appearing in the range of 5.28–5.43 for ozonides **11a-b** and in the range of  $\delta$  5.63–6.67 for ozonides **12a-b** and **13a-b** as singlet. In the  $^{13}\text{C}$  NMR spectra of all ozonides, the two carbon atoms in the ozonide ring exhibited signals in range of  $\delta$  99.33–106.63.

The results reported in this paper demonstrate that the ozonolysis of olefins on polyethylene is widely applicable for the preparation of ozonides that have not been accessible by the hitherto available preparation methods.

## EXPERIMENTAL SECTION

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker AC-300 spectrometer in  $\text{CDCl}_3$  with TMS as internal reference. Chromatographic separations were carried out by flash chromatography on silica gel.

### Procedure for Ozonolyses of Olefins on Polyethylene

**(a) Pretreatment of Polyethylene.**<sup>2</sup> Polyethylene (Microethene FN 500 from Serva Feinbiochemica, Heidelberg, Germany; spherical particles, maximum size 20  $\mu\text{m}$ ) was continuously extracted with ether for 24 h to remove soluble components. Subsequently, it was dried at room temperature and  $10^{-3}$  Torr for 24 h.

**(b) Loading of the Olefin.**<sup>2</sup> The dried polyethylene was placed into a round-bottom flask and admixed with so much of a diethyl ether that the resulting suspension could be stirred. Then the olefin was added, the mixture was stirred for ca. 15 min., the solvent was removed by suction at room temperature, and the loaded polyethylene was transferred into an adsorption tower.

**(c) Ozonolysis of the Olefin.**<sup>3,4</sup> The loaded adsorption tower was placed into a bath that had the desired temperature, and an  $\text{O}_3/\text{O}_2$  stream (ca. 1 mmol of  $\text{O}_3/\text{L}$  of gas) was passed through the tower at a rate of ca. 20 L/h. After completion of the ozo-

nolysis, dried nitrogen was passed through the tower until residual ozone was removed, the tower was warmed up to room temperature, and the polyethylene was transferred into a round-bottom flask and repeatedly extracted with an appropriate solvent.

**Reductions of Ozonides:** A solution of 20-80 mg of an ozonide and an excess of triphenylphosphine in 0.6 mL of  $\text{CDCl}_3$  was kept at room temperature for 24 hours. The products were analyzed by  $^1\text{H}$  NMR spectroscopy.

**Ozonolysis of 1,3-cyclooctadiene (8a):** Compound **8a** (0.5 g, 4.62 mmol) was loaded on 40 g polyethylene and ozonized for 6 h at  $-78^\circ\text{C}$ . The products were extracted with ether, and the combined extracts were distilled at room temperature and 15 Torr to leave 0.45 g of a peroxidic residue. From the residue, 200 mg (0.98 mmol, 21.2%) of ozonide **11a** was isolated by column chromatography (silica gel, pentane / diethyl ether, 1 : 1).

**1,3-Cyclooctadiene diozonide (11a):** Colorless liquid;  $^1\text{H}$  NMR:  $\delta$  1.58-1.67 (m, 2H), 1.90-2.03 (m, 6H), 5.33 (m, 4H);  $^{13}\text{C}$  NMR  $\delta$  20.45, 27.50, 100.05, 104.30. Anal. Calcd for  $\text{C}_8\text{H}_{12}\text{O}_6$  (204): C, 47.05; H, 5.92. Found: C, 47.25; H, 6.04. Reduction of **11a** with TPP gave hexanedial.

**Ozonolysis of 1,5-cyclooctadiene (8b):** Ozonolysis of **8b** (0.5 g, 4.62 mmol) gave a peroxidic residue. From the liquid residue, 250 mg (1.22 mmol, 26.3%) of ozonide **11b** was isolated by column chromatography (silica gel, pentane/diethyl ether, 1 : 2).

**1,5-Cyclooctadiene diozonide (11b):** Colorless liquid;  $^1\text{H}$  NMR: 1.96-2.07 (m, 8H), 5.37 (t,  $J=3$  Hz, 4H);  $^{13}\text{C}$  NMR  $\delta$  25.01, 101.99. Anal. Calcd for  $\text{C}_8\text{H}_{12}\text{O}_6$  (204): C, 47.05; H, 5.92. Found: C, 46.88; H, 5.98.

Reduction of **11b** with TPP gave butanedial [ $^1\text{H}$  NMR  $\delta$  2.67, 9.69].

**Ozonolysis of pyrene (9a):** Compound **9a** (0.5 g, 2.47 mmol) was loaded on 40 g polyethylene and

ozonized for 4 h at  $-78^\circ\text{C}$ . The products were extracted with ether, and the combined extracts were distilled at room temperature and 15 Torr to leave 0.45 g of a peroxidic residue. From the residue, 60 mg (0.24 mmol, 9.8%) of monoozonide **12a** and 100 mg (0.34 mmol, 13.3%) of diozonide **13a** were isolated by column chromatography (silica gel, pentane / diethyl ether, 1 : 1).

**Pyrene monoozonide (12a):** Colorless crystals; mp  $162\text{--}164^\circ\text{C}$  (Lit.<sup>8</sup>,  $163\text{--}165^\circ\text{C}$ );  $^1\text{H}$  NMR:  $\delta$  6.67 (s, 2H), 7.57-8.05 (m, 8H);  $^{13}\text{C}$  NMR:  $\delta$  106.63, 125.36, 126.20, 126.51, 127.81, 128.20, 129.18, 131.56, 135.06. The data are identical to those reported.<sup>8</sup>

Reduction of **12a** with TPP gave phenanthrene-4,5-dicarbaldehyde [ $^1\text{H}$  NMR:  $\delta$  7.41-8.14(m), 10.03].

**Pyrene diozonide (13a):** Colorless crystals; mp  $71^\circ\text{C}$ ;  $^1\text{H}$  NMR:  $\delta$  6.40 (s, 4H), 7.47 (m, 6H);  $^{13}\text{C}$  NMR:  $\delta$  105.73, 128.36, 132.85, 132.96, 138.20. Anal. Calcd for  $\text{C}_{16}\text{H}_{10}\text{O}_4$  (298): C, 64.44; H, 3.38. Found: C, 64.66; H, 3.42.

Reduction of **13a** with TPP gave biphenyl-2,2',6,6'-tetracarbaldehyde [ $^1\text{H}$  NMR  $\delta$  7.20-8.21 (m), 9.69].

**Ozonolysis of naphthalene (9b):** Ozonolysis of **9b** (0.5 g, 3.08 mmol) gave a peroxidic residue. From the residue, 60 mg (0.34 mmol, 8.7%) of monoozonide **12b** and 110 mg (0.49 mmol, 12.2%) of diozonide **13b** were isolated by column chromatography (silica gel, pentane / diethyl ether, 1 : 1).

**Naphthalene monoozonide (12b):** Colorless liquid;  $^1\text{H}$  NMR  $\delta$  6.37 (s, 2H), 7.71-7.95 (m, 6H);  $^{13}\text{C}$  NMR 98.25, 102.74, 123.67, 123.81, 124.43, 125.83, 127.60, 129.78, 131.17, 134.78. Anal. Calcd for  $\text{C}_{10}\text{H}_8\text{O}_3$  (176): C, 68.17; H, 4.58. Found: C, 68.26; H, 4.64.

**Naphthalene diozonide (13b):** Colorless liquid;  $^1\text{H}$  NMR  $\delta$  5.63 (s, 2H), 6.11 (s, 2H), 7.44 (m, 4H);  $^{13}\text{C}$  NMR  $\delta$  99.33, 105.53, 131.42, 132.32, 133.30. Anal. Calcd for  $\text{C}_{10}\text{H}_8\text{O}_6$  (224): C, 53.57; H, 3.60. Found: C, 53.32; H, 3.48.

Reduction of **13b** with TPP gave benzene-1,2-

dicarbaldehyde [ $^1\text{H NMR } \delta$  7.21-7.69, 10.51].

**Ozonolysis of 1,2-dihydronaphthalene (9c):** Ozonolysis of **9c** (0.5 g, 3.84 mmol) gave a peroxidic residue. From the residue, 100 mg (0.56 mmol, 14.9%) of ozonide **12c** was isolated by column chromatography (silica gel, pentane / diethyl ether, 1 : 1).

**1,2-Dihydronaphthalene monoozonide(12c):** Yellow crystal; mp 123~124 °C;  $^1\text{H NMR } \delta$  2.04-2.16 (m, 2H), 2.71-2.77 (m, 1H), 3.53 (m, 2H), 5.91 (s, 1H), 6.15 (s, 1H), 7.20-7.30 (m, 5H);  $^{13}\text{C NMR } \delta$  30.11, 33.03, 103.93, 105.96, 126.68, 128.81, 130.13, 130.89, 136.82, 141.02. Anal. Calcd for  $\text{C}_{10}\text{H}_{10}\text{O}_3$ (178): C, 67.40; H, 5.66. Found: C, 67.55; H, 5.55.

Reduction of **12c** with TPP gave o-(2-formyl-ethyl)benzaldehyde [ $^1\text{H NMR } \delta$  2.72, 3.31, 9.75, 10.10].

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