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\(^1\) 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.\(^2\)

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.\(^3\) 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 CDCl$_3$ and $^1$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 monoozonides of type $10$.

Ozonolysis of $9a$ and $9b$ on polyethylene afforded the corresponding monoozonides $12a$ 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 monoozonide $12c$ in yield of ca. 14.9%.

The structures of all isolated ozonides were established by $^1$H and $^{13}$C NMR spectroscopy, and by their reduction with triphenylphosphine to give the expected dicarbaldehydes. Characteristic signals in $^1$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 $^{13}$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

$^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker AC-300 spectrometer in 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. Polyethylene (Microthene FN 500 from Serva Feinbiochemica, Heidelberg, Germany; spherical particles, maximum size 20 $\mu$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. 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. The loaded adsorption tower was placed into a bath that had the desired temperature, and an O$_3$/O$_2$ stream (ca. 1 mmol of O$_3$/L of gas) was passed through the tower at a rate of ca. 20 L/h. After completion of the ozon-
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 CDCl₃ was kept at room temperature for 24 hours. The products were analyzed by $^1$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 °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; $^1$H NMR: $\delta$ 1.58-1.67 (m, 2H), 1.90-2.03 (m, 6H), 5.33 (m, 4H); $^{13}$C NMR $\delta$ 20.45, 27.50, 100.05, 104.30. Anal. Calcd for C₈H₁₂O₆ (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; $^1$H NMR: 1.96-2.07 (m, 2H), 5.37 (t, $J$=3 Hz, 4H), $^{13}$C NMR $\delta$ 25.01, 101.99. Anal. Calcd for C₈H₁₂O₆(204): C, 47.05; H, 5.92. Found: C, 46.88; H, 5.98. Reduction of 11b with TPP gave butanedianal [$^1$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 °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 110 mg (0.49 mmol, 12.2%) of diozonide 13a were isolated by column chromatography (silica gel, pentane / diethyl ether, 1 : 1).

Pyrene monoozonide (12a): Colorless crystals; mp 162-164 °C (Lit., 163-165 °C); $^1$H NMR: $\delta$ 6.67 (s, 2H), 7.57-8.05 (m, 8H), $^{13}$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.

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

Pyrene diozonide (13a): Colorless crystals; mp 71 °C; $^1$H NMR: $\delta$ 6.40 (s, 4H), 7.47 (m, 6H), $^{13}$C NMR: $\delta$ 105.73, 128.36, 132.85, 132.96, 138.20. Anal. Calcd for C₁₆H₁₀O₆(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 [$^1$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; $^1$H NMR $\delta$ 6.37 (s, 2H), 7.71-7.95 (m, 6H); $^{13}$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 C₁₀H₈O₃(176): C, 68.26; H, 4.64. Found: C, 68.26; H, 4.64.

Naphthalene diozonide (13b): Colorless liquid; $^1$H NMR $\delta$ 5.63 (s, 2H), 6.11 (s, 2H), 7.44 (m, 4H), $^{13}$C NMR $\delta$ 99.33, 105.53, 131.42, 132.32, 133.30. Anal. Calcd for C₁₀H₈O₆(224): C, 53.57; H, 3.60. Found: C, 53.32; H, 3.48.

Reduction of 13b with TPP gave benzene-1,2-
dicarbaldehyde [\(^1\)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; \(^1\)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); \(^1\)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 C\(_{10}\) H\(_{10}\) 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 [\(^1\)H NMR \(\delta 2.72, 3.31, 9.75, 10.10\)].

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