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Communication

Ozonolysis of Phenanthrene Adsorbed on Polyethylene

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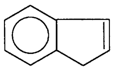
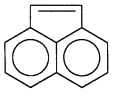
A series of ozonolyses of cycloalkenes **1** carried out in the presence of carbonyl compounds **2** gave product mixture which varied considerably with substrate structure.[1~3] In the cases of indene **1a**,[5,6] acenaphthylene **1b**,[4] pyrene **1c**[4] and 3,4-methylenephenanthrene **1d**,[4] the major product was the corresponding monoozonides **3** and cross-ozonide **4**.



1a



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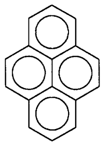

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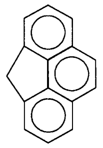

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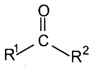
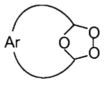


	a	b	c
R^1	H	CH_3	CH_3
R^2	H	CN	Ph

2



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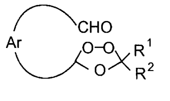

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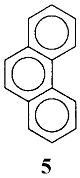
In contrast, the analogous phenanthrene **5** provided 72-74% of cross-ozonides **7** only.[4] The formation of cross-ozonide product **7** is consistent with the expectation that carbonyl oxide **6**, generated from the ozonolysis of phenanthrene **5,** is most likely to adopt a conformation in which the aromatic rings would be essentially orthogonal with respect to each other in order to minimize steric interaction between the ortho-formyl group and the carbonyl oxide group, hence ensuring that these groups are well separated and not available for a [3+2] cycloaddition to form monoozonide **8**.[8] To our knowledge, there is no report about the preparation of monoozonide **8** by the ozonolysis of phenanthrene **5** in non-participating solvents such as ether, dichloromethane or tetrachloromethane.



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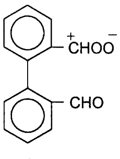

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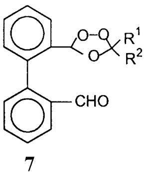

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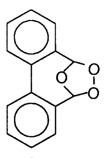

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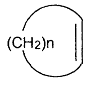
In general, the ozonolysis of olefins in aprotic solvents represents the most versatile method for the preparation of ozonides. Nevertheless, this method failed when applied to a variety of substrates such as larger cyclic olefins **9** and certain bicyclic olefins **10**. The failure of these substrates to afford the corresponding ozonides have been attributed to the no chances for intramolecular ring closures of the intermediates **11**.



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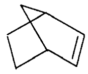

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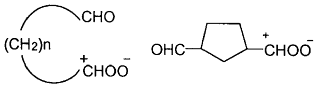

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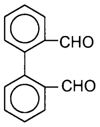
However, it was very recently that Griesbaum et al. have been able to prepare the ozonides of **9** and norbornene **10** by application of the modified ozonolysis on polyethylene.[9] It has been shown that cycloaddition of carbonyl oxides with aldehyde, and hence ozonide formation, can be substantially faciliated by the ozonolysis of olefins adsorbed on powdered polyethylene, presumably due to restricted migration of the primary cleavage fragments.[10-12] we have now tried whether this mode of reaction can be extended to the ozonolysis of phenanthrene **5**.

In the present investigation we have performed the ozonolysis of **5** adsorbed on powdered polyethylene. Commpound **5** (1 g, 5.6 mmol) was loaded on 80 g of polyethylene from an ether solution and ozonized for 10 h at -78 °C. A small sample was extracted with $CDCl_3$. ^1H NMR analysis of the extracted showed the presence of *ca*. 35% of **8**, 4% of **12** and 60% of the unreacted **5**. The remainder of the loaded polyethylene was extracted with ether and the extract was evaporated to leave 1.5 g of the residue. Separation of the residue by column chromatography (silica gel; *n*-pentane/ether, 4 : 1) afforded the colorless liquid ozonide **8**: ^{1}H NMR ($CDCl_3$) δ 6.41 (s, 2H), 7.39-7.55 (m, 6H), 8.03 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 105.32, 129.05, 129.49, 129.92, 130.66, 135.41, 136.04; IR (KBr) 3100, 3000, 1600, 1470, 1110; Anal. calcd for $C_{14}H_{10}O_3$: H, 4.46; C, 74.34. found: H, 4.37; C, 73.98.

Ozonide **8** is unusually stable. Heating of **8** in $CDCl_3$ at 40 °C did not lead to a change in the ^{1}H NMR spectrum within 48 h. Treatment of ozonide **8** with triphenylphosphine in $CDCl_3$ at room temperature, followed by conventional work-up gave 90% of 5,6-biphenylcarbaldehyde **12**. [^{1}H NMR δ 7.39 (d, J = 6.3 Hz, 2H). 7.67 (m, 4H), 8.95 (d, J = 6.3 Hz, 2H), 9.86 (s, 2H). ^{13}C NMR δ 127.67, 128.96,1 132.13, 133.86 136.47, 141.63.]



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The result reported in this paper demonstrate that the ozonolysis of olefins on polyethylene is widely applicable for the preparation of ozonides. In particular, it extends the scope of the formation of ozonides to types that have not been accessible by the hitherto available preparation methods.

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