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OZONIDE FORMATION BY TRANSANNULAR CYCLOADDITION BETWEEN A CARBONYL OXIDE AND A CARBONYL GROUP

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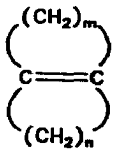
Abstract: Ozonolysis of bicyclo[10.3.0]pentadec-1(12)-en-13-one (9a) on polyethylene gave the corresponding ozonide 11a. The structure of the labile ozonide was proved by its transformation into the stable O-methyl oxime 11b, and by independent synthesis of 11b by ozonolysis of the O-methyl oxime of 9a.

To our knowledge, ozonolyses of bicyclic olefins of type 1 have never resulted in the formation of the corresponding tricyclic ozonides 3. A case in point is the ozonolysis of 1a, which provided the dimeric peroxide 4a to the exclusion of ozonide 3a.[1] Obviously, the carbonyl oxide moiety in 2 evades a transannular cycloaddition with the carbonyl group in the same molecule. This could be due to steric reasons and/or to the known poor dipolarophilicity of ketone groups in cycloadditions with carbonyl oxides.[2] In recent years we have demonstrated that both steric restraints and poor dipolarophilicity can be surmounted by performing ozonolysis reactions of unsaturates on polyethylene rather than in solution.[3] Furthermore, we have found, that ozonolysis of 5 gave in a high overall yield the isomeric ozonides 7 and 8, probably due to mutual activation of the two adjacent carbonyl groups in intermediate 6.[4] Encouraged by these observations we have now ozonized the bicyclic α-oxo-olefin 9a, hoping that the combined effects of the use of polyethylene and of the adjacent carbonyl groups in the expected intermediate 10 may favor a transannular cycloaddition.

Ozonolysis of 9a on polyethylene at -78°C gave an ozonide which was isolated in 14% yield. As expected on the basis of previous experience with α-oxo-ozonides, the neat ozonide was thermally labile and was, hence, only amenable to preliminary characterization based on its peroxidic properties and on the appearance of ^{13}C NMR signals at δ 107.54 and 111.01 ppm, which are typical for C-atoms in ozonide rings. Treatment of the ozonide with O-methyl hydroxylamine gave, however, a stable product. Its ozonide structure was proven based on its ^{17}O NMR- (δ_O 128.1, δ_{OCH_3} 154.2, $\delta_{O\text{-}O}$ 310.2 ppm) and ^{13}C NMR spectrum ($CDCl_3$, TMS; δ 17.61, 21.31, 21.70, 24.61, 25.25, 25.78, 26.06, 26.56, 27.04, 27.46, 31.96, 32.26, 61.96, 108.45, 110.72 and 152.58 ppm) on the appearance of a M+1 peak at m/e = 298 (39%) in the CI mass



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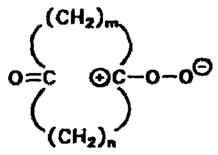

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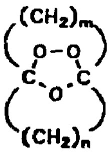

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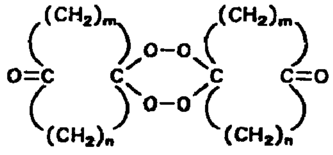

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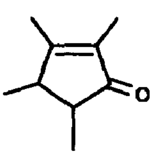
a:m=n=4



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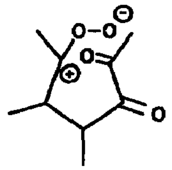

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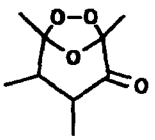

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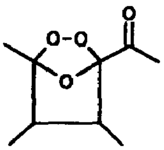

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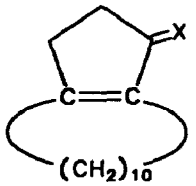
spectrum and on correct elemental analysis (Calcd for $C_{18}H_{27}NO_4$: C 64.62, H 9.15, N 4.71. Found: C 65.00, H 9.27, N 4.84). However, these data did not allow to distinguish unequivocally between the ozonides 11b and 12b, which would be derived from the a priori possible isomeric ozonides 11a and 12a. In order to clarify this question, we have ozonized the cycloolefin 9b, in which the α-carbonyl group is no longer available for transannular cycloaddition with carbonyl oxide and, hence, can only provide ozonide 11b. Ozonolysis of 9b on polyethylene gave in 3% yield an ozonide, which was in all properties identical with the product obtained from ozonolysis of 9a and subsequent treatment with O-methyl hydroxylamine. We can conclude, therefore, that the product isolated from the ozonolysis of 9a was 11a.



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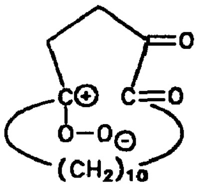

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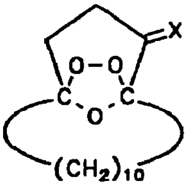

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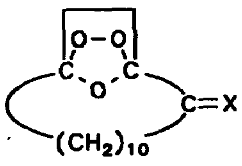

12

a:X=O; b:X=NOCH$_3$

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