

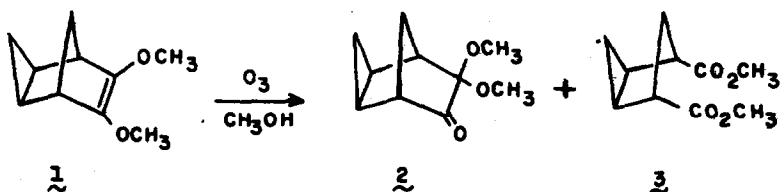
THE ANOMALOUS OZONOLYSIS OF 6,7-DIMETHOXY-EXO-TRICYCLO[3.2.1.0^{2,4}]OCT-6-ENE

Paul G. Gassman and Xavier Creary

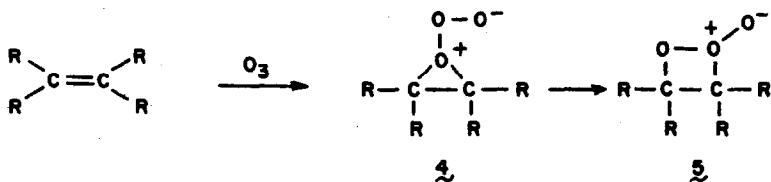
Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

(Received in USA 11 August 1972; received in UK for publication 22 September 1972)

In the preceding communication,¹ we noted that the ozonolysis of 6,7-dimethoxy-exo-tricyclo[3.2.1.0^{2,4}]oct-6-ene (1) in methanol gave 7,7-dimethoxy-exo-tricyclo[3.2.1.0^{2,4}]oct-6-one (2), in addition to the expected ozonolysis product 3. We now wish to report our mechanistic studies related to this anomalous oxidation of 1 to 2.



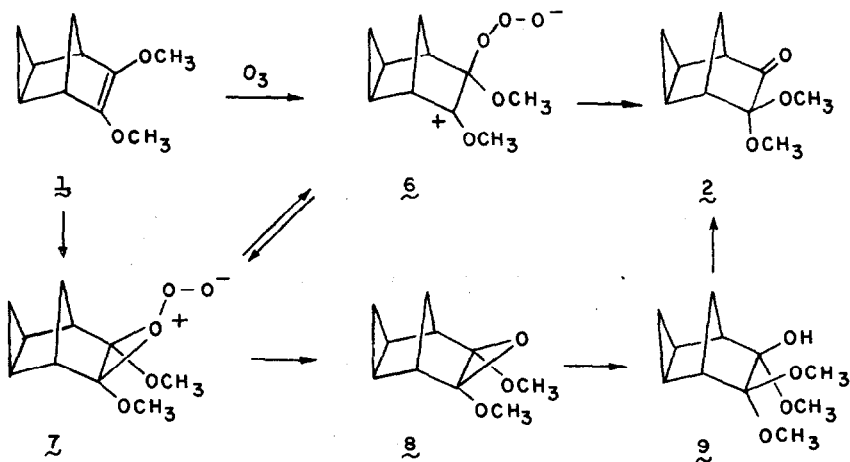
As discussed by Story and coworkers,^{2,3} ozonolysis of olefins can involve a multistep process leading to a variety of products. Most recent evidence supports the intermediacy of peroxy epoxides (4) and Staudinger molozonides (5) in the ozonolysis of simple olefins.



It would appear that all of the known types of ozonolysis products can be rationalized via mechanistic histories involving either 4 or 5.^{2,3} Although the mechanistic and synthetic studies of olefin ozonolysis are extensive, we are unaware of any previously published transformations similar to that of 1 → 2. Thus, we were interested in elucidating whether

this oxidative process was consistent with current mechanistic thinking.

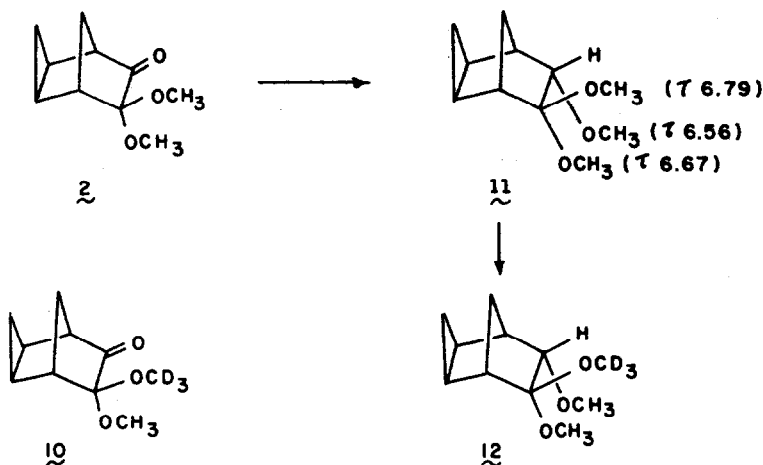
In principle, the formation of 2 could arise via at least two alternate routes. As shown below, initial addition of ozone to 1 could yield either the zwitterion 6 or the peroxy epoxide 7.⁴ Either of these intermediates could eventually yield 2. Loss of oxygen from 6 with concerted shift of the endo methoxyl group would yield 2 directly. A somewhat more complicated route would involve loss of oxygen from 7 to produce the



epoxide 8, followed by addition of methanol to 8 in a stepwise process to give 9. Loss of methanol from 9 would yield 2. A distinction can be made between these two processes, since the direct route from 6 to 2 does not involve the addition of solvent whereas the route involving 8 and 9 does incorporate solvent into the final product.

When 1 was ozonized in methanol- d_4 we obtained 10 instead of 2. It could be shown that 2 did not undergo exchange under the reaction conditions to yield 10. Even in the presence of *p*-toluenesulfonic acid, the exchange of 2 was found to be extremely slow. Thus, the possibility of intramolecular methoxyl group shift was eliminated. Whereas 2 showed three proton absorptions in the nmr at τ 6.67 and 6.60, 10 showed only the latter peak. Since exo-methoxyl groups generally appear at higher field in the nmr spectra of ketals of 2-norcamphor,⁵ the deuterated methoxyl group was initially assigned to the exo-position. This stereochemical assignment was confirmed by the sequence shown below. Reduction of 2 with sodium borohydride, followed by methylation with sodium hydride and methyl iodide

gave 11, which showed methoxyl peaks in the nmr spectrum at τ 6.56, 6.67, and 6.79. When 11 was treated with *p*-toluenesulfonic acid in methanol- d_4 , the peak at τ 6.79 disappeared



rapidly, the peak at τ 6.67 decreased slowly, and the peak at τ 6.56 underwent no change. On the basis of the extensive studies of exchange rates carried out by Traylor and Perrin,⁵ the peaks were assigned as shown above. When 10 was reduced with sodium borohydride followed by treatment with sodium hydride and methyl iodide, we obtained 12, which showed methoxyl peaks at τ 6.56 and 6.67. Thus, the deuterated methoxyl group of 10 must have been in the *exo*-position.

The studies outlined above would implicate the epoxide 8 as an intermediate in the formation of 2. If this were correct, epoxidation of 1 in methanol should also yield 2. Confirmation of this idea was obtained when 1 was treated with *m*-chloroperbenzoic acid in methanol buffered with sodium carbonate. No trace of the epoxide, 8, could be found. Instead, 2 was isolated and shown to be identical to the ozonolysis product in all respects.

In conclusion, the anomalous ozonolysis of 1 is consistent with the initial formation of a peroxy epoxide which loses oxygen to form a highly reactive epoxide. In view of the high percentage of product derived from this route, it would appear that the electron-rich double bond of 1 is particularly susceptible to this type of reaction.

Acknowledgement. We are indebted to the National Science Foundation for partial support of this investigation and to the B.F. Goodrich Corporation for a fellowship (X.C.).

REFERENCES

1. P.G. Gassman and X. Creary, Tetrahedron Letters, preceding communication.
2. For a leading reference see P.R. Story, E.A. Whited, and J.A. Alford, J. Amer. Chem. Soc., 94, 2143 (1972).
3. P.R. Story, J.A. Alford, J.R. Burgess, and W.C. Ray, J. Amer. Chem. Soc., 93, 3042, 3044 (1971) and references contained therein.
4. Structures 6 and 7 could easily be interconvertible under the reaction condition. The methoxyl substituted tertiary carbenium ion of 6 would be expected to be a stabilizing influence on the overall zwitterionic species.
5. T.G. Traylor and C.L. Perrin, J. Amer. Chem. Soc., 88, 4934 (1966).