The *cis*-Molozonide

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THE formation, by the interaction of a *trans*-alkene and ozone, of a *trans*-molozonide as an intermediate in ozonolysis has been well established, but the *cis*-molozonide has been more elusive. Bailey, *et al.*,[1] could find no evidence for the presence of a molozonide by an n.m.r. spectral study of a *cis*-di-t-butylethylene–ozone reaction mixture. Also, α-glycols could not be detected[2] in the reaction products which resulted from the reduction of *cis*-alkene ozonization solutions. A few years ago the results of some inelegant experiments were reported[2a] which were thought to indicate that the *cis*-molozonide was a stable species but less stable than the corresponding *trans*-isomer. We can now report more sophisticated data to support this.

The initial n.m.r. spectra (−130°) of the solutions resulting from the ozonation at −130° of dichlorodifluoromethane solutions of each of the *cis*-isomers of but-2-ene, pent-2-ene, and hex-3-ene had two methine absorptions, one in the 5·05—4·87 δ range and the second in the 4·52—4·35 δ range. The first can be assigned to ozonide-methine by comparison with the spectra of the authentic ozonides of but-2-ene and hex-3-ene. The behaviour of these *cis*-alkenes was analogous to that, which was found by similar low temperature n.m.r. spectral studies, of the corresponding *trans*-alkenes,[3] and thus the second methine peak was assigned to molozonide. As the solutions from the *cis*-alkenes were allowed to stand at −130°, the ozonide methine peak increased at the expense of the molozonide methine peak. With the *trans*-alkenes, however, warming the solutions to −100° was necessary before the molozonide methine absorption began to disappear. With the *cis*-alkenes the lowest initial (about 30 min. after starting ozonization) ozonide–molozonide methine

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† F. G. thanks the Department of Chemistry, Stanford University, and particularly Dr. Harry S. Mosher for their hospitality and the Petroleum Research Fund of the American Chemical Society for partial financial support during sabbatical leave from Tufts University. Present address: Department of Chemistry, Tufts University, Medford, Massachusetts 02155.

TABLE

N.m.r. spectral data[a]

Alkene	Aldehyde CHO, δ[b]	Ozonide CH, δ	Molozonide CH, δ	Ethanal Me, δ	Methylene δ	Methyl δ
−130° Spectra						
cis-But-2-ene	9·50(u)	5·05(q), 4·97(q)[c]	4·52(u)[d]	1·80(d)		1·17(d), 1·08(d)
cis-Pent-2-ene	9·65—9·56(m)	4·93(m)[c]	4·35(m)		Overlapping multiplets 2·02—0·42	
cis-Hex-3-ene		4·95(t), 4·87(t)[c]	4·53(u)[d]		1·48(u)	0·80(u)
−50° Spectra						
cis-But-2-ene		5·17(q), 5·10(q)[e]		2·00(d)		1·23(d)
cis-Pent-2-ene		5·70—4·80(m)[e]			2·27—1·30(m)	1·27(d), 0·87(t)
cis-Hex-3-ene		5·05(t), 5·00(t)[e]			1·58(m)	0·88(t)

[a] Authentic ozonides of but-2-ene and hex-3-ene, authentic hex-3-ene ozonization oligomer and aldehydes were used for peak assignments.

[b] All δ values related to internal Me_4Si, 0·00; dichlorofluoromethane used as internal standard.

[c] Oligomer evidenced by broad, weak absorption on low-field side of ozonide CH peak.

[d] Gianni, *et al.* (ref. 5b) have observed multiplicity of *cis* vicinal methine absorption in other cyclic systems.

[e] Oligomer absorption increased markedly.

(d), doubtlet; (m), multiplet; (q) quartet; (t), triplet; (u), unresolved.

peaks ratio was realized with pent-2-ene, and somewhat more than 2 hr. elapsed before the molozonide peak disappeared completely. After the molozonide-methine absorption disappeared the solutions were warmed, and the spectra at −50° indicated the usual ozonolysis products of aldehyde, oligomer, and ozonide. The spectral data are recorded in the Table.

Under the usual ozonization conditions, *trans*-alkenes gave high yields of oligomer, whereas *cis*-alkenes gave very little oligomer.[4] It has been suggested[4] that the molozonide is the principal source of the ozonation oligomer, and that the different behaviours of *cis*- and *trans*-alkenes may be explained by the relative stability of *cis*- and *trans*-molozonides. If the experimental conditions were such that the *cis*-molozonide were stable for some time, then one might expect reasonable amounts of oligomer from the ozonation of *cis*-alkenes. Our studies support this thesis. In the −130° spectra the oligomer is evidenced by broad, weak absorption on the low-field side of the ozonide-methine peak. When warmed to −50° the solutions gave spectra in which this low-field absorption was markedly increased in intensity. When recooled to −130° the spectra again had weak, low-field absorption. This behaviour may be explained by the oligomer coming into and going out of solution.

The addition of ozone to the alkenes which have been studied appeared to be stereospecifically *cis*. This may be deduced from the *trans*-molozonide-methine absorption[3] (4·1 δ) and that of the *cis*-molozonide (4·5 δ). No appreciable isomerization occurred during ozonization, for no indication of *trans*-molozonide-methine absorption was observed with the *cis*-alkenes, and *vice versa*. The published facts[1],[2] support the 1,2,3-trioxolane structure for the *trans*-molozonide. There are a number of instances[5] where with cyclic compounds, having vicinal methine protons, the *cis*-isomer absorbs at a lower field than the *trans*-isomer. While the evidence for a 1,2,3-trioxolan structure for the *cis*-molozonide is not unambiguous, we suggest this structure by analogy with the *trans*-molozonide for the intermediate that is formed in the ozonolysis of the simpler *cis*-alkenes.

For the ozonizations the theoretical amount of 2—3 vol. % ozone–oxygen was bubbled into an n.m.r. tube which was cooled to −130° and which contained 0·30 ml. of liquid dichlorodifluoromethane, 0·24 mmole of alkene, and a small amount of dichlorofluoromethane as an internal standard. After the ozonation, helium was bubbled through the solution (−130°) for 10 min. to remove dissolved oxygen, and the n.m.r. tube was transferred to an n.m.r. probe which was precooled to −130°. Spectra were recorded (Varian HR-60 instrument) at −130° at various intervals until the molozonide-methine absorption disappeared. The solutions were then warmed to −50°, and the spectra recorded at this temperature.

(*Received, October 30th, 1967; Com.* 1171).

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