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# OZONOLYSIS. VI. EXISTENCE OF THE CIS MOLOZONIDE. LACK OF STEREOSELECTIVITY IN THE MOLOZONIDE-OZONIDE REARRANGEMENT.

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Evidence has been reported (1) which indicated that ozonation of trans alkenes in ether at -112° gave rise to a stable trans molozonide, whereas under similar conditions cis alkenes did not form a stable molozonide. We have now found that a white solid formed during the ozonation of a dilute solution of cis-3-hexene in pentane at -112°. The ozonide is much, much less explosive than this white solid, and it is assumed to be the molozonide. By permitting this solid to warm slowly, it was hoped that the molozonide would rearrange to the ozonide, and thereby information could be obtained on the stereochemistry of this rearrangement. Such experiments resulted in explosions of considerable vigor.

The addition of 36.8 mmoles of ozone to a solution of 38.7 mmoles of cis-3-hexene in 250 ml. of pentane at -70° gave a reaction solution which was separated into three fractions. For Fraction I the reaction flask was rotated in a bath at -50°, the system was evacuated to 0.1 mm. and the vapor was condensed in a liquid nitrogen-cooled trap. This condensate was shown by

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vapor phase chromatography (v.p.c.) to contain 1.58 mmoles of propionaldehyde and pentane. Rotation of the reaction flask in a bath at 25°and evaporation as just described gave Fraction II, 4.22 g. Distillation of this material gave 30.2 mmoles of ozonide, b.p. 45°/22 mm., $n_D^{25}$ 1.4012, mol. wt. 132 (cryoscopic, $C_6H_6$). Lit. (2) values for the ozonide from trans-3-hexene: b.p. 46.5°/26 mm., $n_D^{20}$ 1.4050. The residue in the reaction flask was Fraction III, 0.40 g., mol. wt. 627.

Ozonation of 40.8 mmoles of trans-3-hexene in pentane with 38.8 mmoles of ozone at -70° and fractionation of the reaction solution as described above gave: Fraction I, 3.18 mmoles of propionaldehyde; distilled Fraction II, 4.0 mmoles of ozonide, b.p. 41°/21 mm., $n_D^{25}$ 1.4015, mol. wt. 126; Fraction III, 3.64 g.

Ozonation of 42.4 mmoles of trans-3-hexene in pentane with 40.3 mmoles of ozone at -30° and fractionation of the reaction solution as described above gave: Fraction I, 7.1 mmoles of propionaldehyde; distilled Fraction II, 9.1 mmoles of ozonide, b.p. 44.5°/23 mm.; Fraction III, 3.04 g., mol. wt. 512.

The infrared spectra (Perkin-Elmer Model 421) of the ozonides from the cis and trans alkenes were superimposable except for absorption at 1716 cm.$^{-1}$. This absorption was weak for the ozonide from the trans alkene and almost nonexistent for the ozonide from the cis alkene. Comparison of the ozonide and di-n-propyl peroxide spectra showed the similarities to be very strong absorption at 950, 1380 and 1460 cm$^{-1}$ for the ozonides and 955, 1375 and 1453 cm$^{-1}$ for the peroxide.

Schröder (3) reported that by v.p.c. a silicone GE SF 96 column separated cis and trans ozonides, but our experience was that a similar column effected no separation of the ozonides from the 3-hexenes. However, a cyanosilicone and a diethyleneglycol succinate column showed each ozonide to be composed of two components, supposedly, the cis and trans ozonides. There was some overlap of the two peaks. The v.p.c. tracings indicated that the ozonide from the cis alkene was a 50-50 mixture of the stereoisomeric ozonides, and that the ozonide from the trans alkene was about a 55-45 mixture of the two stereoisomers.

Nuclear magnetic resonance (n.m.r.) spectra of the ozonides confirmed the v.p.c. findings. There were some differences in intensities of some of the peaks of the n.m.r. spectra of the ozonides (35 wt. % in $CCl_4$) from the cis and trans alkenes, but the structures of the corresponding peaks were identical. There were two overlapping triplets one of which was centered at 4.90 and the other at 4.94 ppm., a multiplet centered at 1.55 ppm. and two, unresolved, overlapping triplets centered at 0.82 ppm. The integrated areas of these three peaks were in the ratio 1.00:2.04:3.12 for the ozonide from the cis alkene and 1.00:2.07:3.18 for the ozonide from the trans alkene. Accordingly, these peaks were assigned to the methine, methylene and methyl protons, respectively. For the 4.94 methine triplets J = 5.0 cps., for the 4.90 triplet J = 4.4 cps. The methine triplets clearly indicated a mixture of the two stereoisomers in each ozonide. The overlapping of these triplets was so serious that no meaningful integration of the relative areas of the two triplets could be made.

The evidence supports Staudinger's (4) molozonide as the first species formed during the ozonation of straight-chain alkenes, and the evidence suggests also that such molozonides are transformed to the ozonides. The results from *cis*- and *trans*-3-hexene surely indicate the lack of stereoselectivity in this transformation.

Other workers have studied the relation between alkene geometry and ozonide geometry. Schröder (3) reported that *trans*-di-*t*-butylethylene gave the *trans* ozonide stereospecifically, whereas the *cis*-alkene gave the *cis* ozonide stereoselectively. With methyl oleate and methyl elaidate Riezebos (5) and Privett (6) reported no stereoselectivity in the formation of the stereoisomeric ozonides.

There are striking differences in the ozonation of *cis*- and *trans*-3-hexene, and these may be explained by the difference in stability between a *cis* and a *trans* molozonide. Because of the instability of the *cis* molozonide it will rearrange immediately to the ozonide, with the result that one obtains an excellent yield of ozonide and little material is diverted to polymeric product and aldehyde. The *trans* molozonide is a more stable species. Consequently, there is an appreciable concentration of rearranging species, and this results in little ozonide with most of the material being diverted to polymeric product and aldehyde. The results of the ozonation of *trans*-3-hexene at -70° and at -30° support this explanation.

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