The Ozonolysis of Deuterium-Labeled 1-Olefins

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The ozonolysis of either *cis*- or *trans*-1-deuteriohexene-1 gives a 50/50 mixture of *cis*- and *trans*-1-deuteriohexene-1 ozonide. Ozonolysis of 1,1-dideuteriohexene-1 in the presence of a fivefold excess of formaldehyde leads to only 39% incorporation of the formaldehyde in the hexene-1 ozonide. Ozonolysis of an equimolar mixture of 1,1-dideuteriohexene-1 and heptene-1 leads to hexene-1 and heptene-1 ozonides containing 80.3 and 27% dideuterio ozonide, respectively.

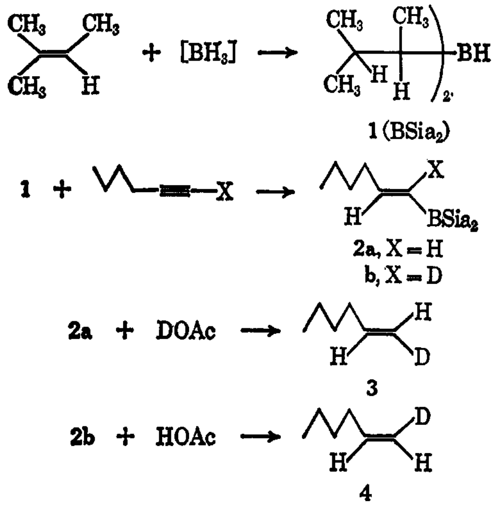
As part of our over-all approach to the problem of the mechanism of ozonolysis we have begun a study of the behavior of 1-olefins in this reaction.[2] These 1-olefin ozonolyses are characterized by a high yield of ozonide in monosubstituted cases,[2] little or no cross-ozonide formation,[2] and, when appropriately substituted, the formation of high yields of epoxides or other products derived from partial cleavage of the double bond.[3–5] Bailey and Lane[5] have shown that the competition between partial and complete cleavage of the double bond is quite sensitive to the size of the olefin substituents.

The formation of high yields of ozonides by monosubstituted 1-olefins is reminiscent of the behavior found in *cis*-olefins and contrasts with that observed in *trans*-olefins.[6,7] It has also been observed that the high yield of ozonide in the case of *cis*-olefins may be accompanied by a predominance of *cis*-ozonide and that this stereoselectivity is more pronounced as substituent size increases.[6,7] It was of interest, therefore, to devise a means of studying the stereochemistry of the olefin to ozonide conversion in the case of a 1-olefin which gave a high yield of ozonide.

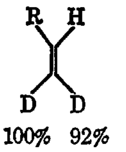
This goal was achieved by suitably substituting an olefin with deuterium and then following the stereochemical course of the reaction by means of nmr. The required olefins were synthesized through the use of the hydroboration technique of Brown and Zweifel.[8,9] The reaction of 2-methylbutene-2 with diborane was used to prepare bis-3-methyl-2-butylborane (disiamylborane), **1**. Because of its large steric requirements only monohydroboration occurred when **1** was treated with 1-hexyne or d_1-1-hexyne to give **2a** or **2b**, respectively. The monohydroboration products **2a** and **2b** are then treated with d_1-acetic acid or acetic acid to give *trans*-1-olefin **3** or *cis*-1-olefin **4**, respectively. A variation of this synthesis was also used to prepare 1,1-dideuteriohexene-1, **5** (Scheme I).

The assignment of configuration to the deuterated olefins is aided by the nmr spectra (Figure 1). The spectra are those of the vinyl protons only. The vinyl proton coupling constants in the *cis*- and *trans*-d_1-hexene-1 isomers are 10 and 18 Hz, respectively. These values are typical of those expected for *cis* and *trans* isomers[10] and follow the expected $J_{cis}/J_{trans} \sim 0.5$ correlation.[10] In each case the vinyl proton doublets have a further minor triplet splitting with $J \sim 1.0$ Hz due to the geminal deuterium atom. Here again, the observed coupling is reasonable for the assigned structure since one expects[11] the deuterium–hydrogen geminal coupling to be approximately one-seventh of the value for the corresponding geminal hydrogen–hydrogen coupling (~12–15 Hz[10]).

Scheme I



In the case of the 1,1-dideuteriohexene-1 the vinyl proton nmr spectrum shown in Figure 1 has several implications regarding the structural assignments. First of all it is obvious from the top two spectra in Figure 1 that the resonances on the right are those due to the terminal vinyl protons since these are the ones which are reduced by deuterium exchange. It is also clear that the proton exchange with deuterium was not 100% complete. The spectrum for the dideuterated material suggests that deuterium exchange was 100% complete for the terminal proton *trans* to the 2-vinyl proton and ~92% complete for the terminal proton *cis* to the 2-vinyl proton since the residual proton coupling is characteristic of the *cis* geometry (Figure 1).



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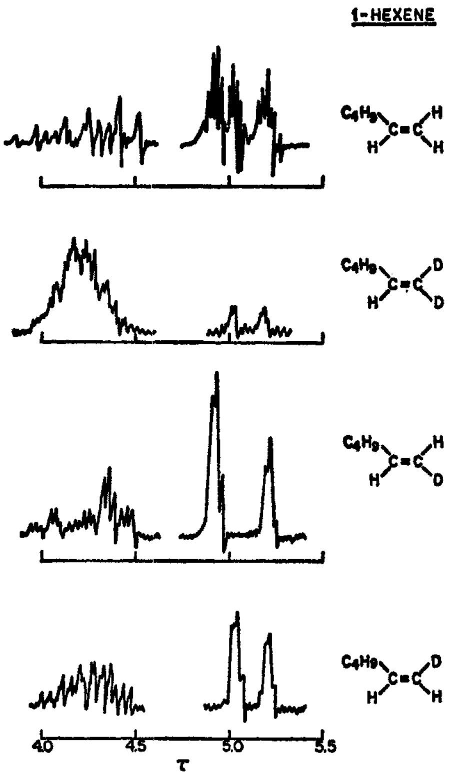


Figure 1.—Vinyl proton nmr spectra of various 1-hexenes.

Ozonolysis of both **3** and **4** gives the same ozonide mixture, the nmr spectrum of which indicates that it is a 50/50 mixture of the ozonide isomers (Figure 2). Only the spectra of the ring protons are shown. In the nondeuterated ozonide (upper spectrum) the methine proton has the expected triplet splitting due to the adjacent methylene group. The geminal methylene protons appear as separate singlets; *i.e.*, the geminal coupling constant is approximately zero. This observation appears to be typical for 1-olefin ozonides and is consistent with the observed change in the value of this coupling constant from a large negative value in cyclopentane to approximately zero for 1,3-dioxolan.[12]

The splitting pattern for the monodeuterated ozonides is the same (lower spectrum) only now the integrated intensities for the three ring protons has changed from a 1:1:1 ratio in the undeuterated ozonide to a ratio of 2:1:1 for the monodeuterated ozonide (Figure 2, center) indicating that this ozonide must be a mixture of the *cis* and *trans* isomers. The 50:50, *cis–trans* ozonide distribution was found not to be dependent upon the extent of ozonolysis nor the concentration of olefin used. It seems fairly certain, therefore, that this ratio is representative of the dominant ozonolysis reaction, and is not the result of a fortuitous combination of separate reaction pathways. Likewise the nmr spectra of the recovered olefins showed that they were not isomerized under the reaction conditions. Thus the loss of stereochemistry was taking place in the ozonolysis reaction.

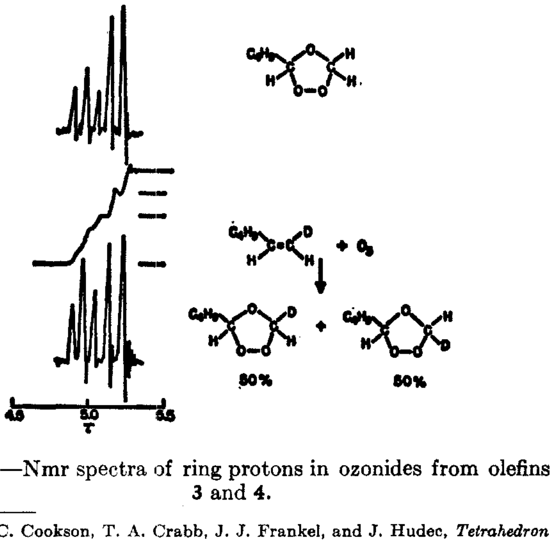
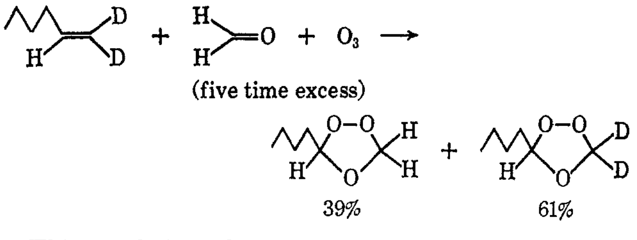


Figure 2.—Nmr spectra of ring protons in ozonides from olefins **3** and **4**.

It seems clear, therefore, that while these ozonolyses are proceeding in high yield, they are also proceeding with complete loss of olefin stereochemistry. These results would seem to rule out any concerted, stereospecific path as being largely responsible for the high yield. Apparently the ozonide-forming fragments are produced and recombine rapidly, perhaps in a solvent cage, with little chance for side reactions. This would also be consistent with the view of Greenwood and coworkers[13,14] that ozonide yield is in large part dependent upon the stability of the molozonide and that 1-olefins are expected to have molozonides with stabilities intermediate between those of *cis-* and *trans*-olefins.[15]

In order to learn more about the ozonide-forming reaction in these cases we have ozonized 1,1-dideuteriohexene-1 in the presence of a large excess of added formaldehyde. This kind of experiment tests the accessibility of the ozonide precursor to diversion by the added aldehyde. It was found that even with a fivefold excess of added formaldehyde only 39% of the hexene-1 ozonide produced had been diverted to the nondeuterated material.



This result is to be contrasted with the cases of the internally unsaturated olefins, *cis-* and *trans*-hexene-3, where ozonolysis in the presence of a fivefold excess of added butyraldehyde led to 84 and 89% diversion of the intermediate, respectively.[16]

Again these results indicate a striking difference between the ozonolysis of 1-olefins and internally unsaturated olefins. In the 1-olefin cases the ozonide precursor is particularly difficult to divert to a new ozonide by the added aldehyde technique.

Evidence that 1-olefin ozonolyses do allow for some fragment interchange comes from the ozonolysis of a mixture of 1,1-dideuteriohexene-1 and heptene-1. Here an nmr analysis of the hexene-1 and heptene-1 ozonides produced indicates a fair amount of fragment

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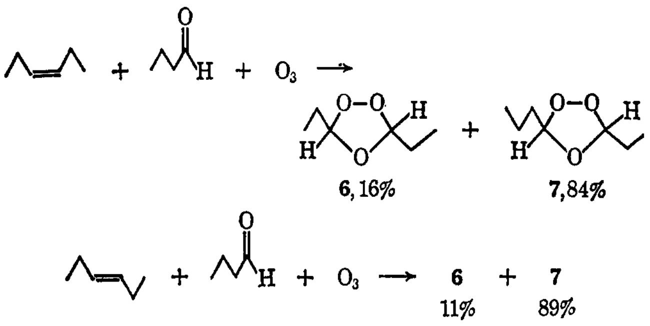
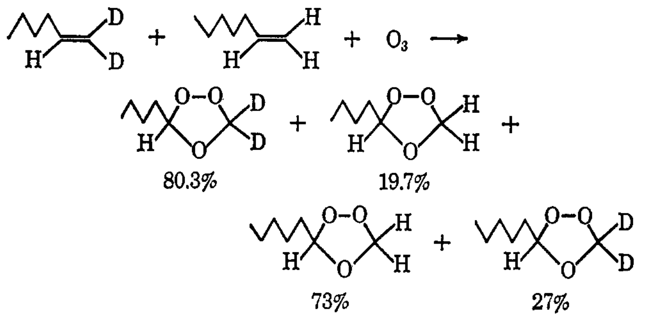


exchange. The hexene-1 ozonide consists of 80.3% dideuterated material and 19.7% undeuterated ozonide. The heptene-1 ozonide has a 73% undeuterated fraction and a 27% dideuterated fraction.



The combined observations of high yield, loss of stereochemistry, and relative inaccessibility of intermediate suggest a mechanism in which the molozonide is rather unstable and undergoes fairly rapid cleavage to the Criegee zwitterion and aldehyde fragments[17] and then recombination to ozonide. The entire process is not entirely intramolecular, however, since some exchange recombination occurs. At present it is not known whether these latter reactions involve a Criegee[17] zwitterion, or the molozonide, or some combination of both. What is certain is that this reaction is quite sensitive to the steric requirements of the aldehyde.[2]

Experimental Section

Procedures and Equipment.—The general procedure and equipment used in this study is the same as that described earlier.[2]

Bis(3-methyl-2-butyl)borane (Disiamylborane).—Into a three-necked flask was placed 2-methylbutene-2 (16.8 g, 0.24 mol) in 100 ml of dry ether. The flask was immersed in an ice bath and diborane, generated by the addition of boron trifluoride etherate (17 g, 0.12 mol) to lithium aluminum hydride (4.6 g, 0.12 mol) in 100 ml of dry ether, was introduced into the olefin solution. The resulting disiamylborane was used in the following preparations.

***trans*-d_1-Hexene-1.**—To disiamylborane at 0° was added dropwise 1-hexyne (8.2 g, 0.1 mol). After the reaction mixture had stood for 1 hr at 0°, d_1-acetic acid was added dropwise to the cold reaction solution. This solution was allowed to stand at room temperature overnight and 100 ml of ice water was added. The organic layer was washed first with a sodium carbonate solution, then water, and then dried ($MgSO_4$). Distillation through a spinning band column gave a mixture of 2-methylbutene-2, 1-hexyne, and product. The product was purified by glpc using a 20 ft, 20% cyanosilicone column. The yield was 4.1 g (48.2%). The nmr (neat) of the pure material had a multiplet at 4.2 (1 H) a doublet (J = 18 Hz) of triplets (J ~ 1.0 Hz) at 4.92 and 5.22 (1 H), and multiplets at 7.9 (2 H), 8.7 (4 H) and 9.1 (3 H). These absorptions are assigned to the 2-vinyl, 1-vinyl, 3-methylene, 4- and 5-methylene, and methyl protons of *trans*-d_1-1-hexene, respectively.

***cis*-d_1-Hexene-1.**—The procedure given for the *trans* compound was repeated except using d_1-hexyne-1 (8.2 g, 0.1 mol) and normal acetic acid. The yield after glpc purification was 3.8 g (44.6%). The nmr (neat) of the pure material had a multiplet at 4.25 (1 H), a doublet (J = 10 Hz) of triplets (J ~ 1.0 Hz) at 5.04 and 5.20 (1 H), and multiplets at 7.95 (2 H), 8.7 (4 H), and 9.1 (3 H). These absorptions are assigned to the 2-vinyl, 1-vinyl, 3-methylene, 4- and 5-methylene, and methyl protons of *cis*-d_1-hexene-1, respectively.

1,1-Dideuteriohexene-1.—The procedure given for *trans*-d_1-hexene-1 was repeated except that now both d_1-hexyne-1 and deuterioacetic acid were used. The yield of glpc purified product was 3.9 g (45.8%). The nmr spectrum had a multiplet at 4.25 (1 H), a weak doublet (J = 10 Hz) at 5.0 and 5.17, and multiplets at 7.9 (2 H), 8.7 (4 H) and 9.1 (3 H). These absorptions can be assigned to the 3-vinyl, residual 1-vinyl, 3-methylene, 4- and 5-methylene, and methyl protons of 1,1-dideuteriohexene-1, respectively. The weak doublet is due to residual 1-vinyl hydrogen which is estimated to be 8% of the initial value and must be *cis* because of the coupling (J = 10 Hz) observed.

Ozonolysis of 1-Deuterio Olefins.—The olefins were ozonized in various concentrations and to various conversions in pentane at −70°, and the resulting *cis–trans* distribution determined from the nmr spectra. In all cases this ratio was 50/50. The *cis*-d_1-hexene-1 was ozonized to 75% conversion and at concentrations of 0.5 and 0.25 *M*. *trans*-d_1-Hexene-1 was ozonized to 15, 50, and 75% conversion and at concentrations of 0.25 and 0.125 *M*. The nmr spectra of the recovered olefins indicated that no isomerization had occurred. The nmr spectrum of the ozonide mixture had a triplet (J = 5 Hz) at 4.97 (1 H), a singlet at 5.14 (0.5 H), a singlet at 5.25 (0.5 H), and a complex envelope between 8.2 and 9.3 (9 H). Average yield of ozonide was 80%.

Ozonolysis of 1,1-Dideuteriohexene-1 with Added Formaldehyde.—To the olefin (0.54 g, 6.25 mmol) in pentane (0.25 *M*) was added formaldehyde from the decomposition of 0.5 g (17.9 mmol) of paraformaldehyde. The reaction solution was ozonized to 75% conversion at −70°. The nmr spectrum of the ozonide produced showed a 37% incorporation of formaldehyde. When the same reaction was carried out using 0.9 g (32.1 mmol) of paraformaldehyde, the recovered ozonide showed a 39% incorporation of formaldehyde.

Ozonolysis of *cis*- and *trans*-Hexene-3 with Added Butyraldehyde.—These experiments were described earlier.[16] The ozonolyses were carried out on solutions of the olefins in pentane. The olefins were present at 0.5 *M* concentration and the butyraldehyde at 3.0 *M* concentration. The ozonolyses were continued to 75% conversion at −70°.

1-Deuteriohexyne-1.—To magnesium (8.5 g, 0.354 mol) in 250 ml of dry ether was added dropwise 44.3 g (0.31 mol) of methyl iodide. The reaction mixture was stirred for 2 hr and then 20.5 g (0.25 mol) of hexyne-1 was added dropwise. The reaction mixture was refluxed for 0.5 hr and then allowed to cool to room temperature. To the cooled solution was added with stirring 6.6 g (0.33 mol) of deuterium oxide. The reaction mixture was stirred for 0.5 hr and the product distilled out. After drying ($MgSO_4$) the product was redistilled to give 18.4 g (89%) with bp 72–73°. The nmr spectrum showed no acetylenic proton absorption.

Ozonolysis of 1,1-Dideuteriohexene-1 and Heptene-1.—A pentane solution which was 0.5 *M* in both 1,1-dideuteriohexene-1 and heptene-1 was ozonized at −70° to 75% conversion. The ozonides were collected by glpc and their deuterium content determined from the nmr spectra. The hexene-1 ozonide consisted of 80.3% dideuterated material and 19.7% undeuterated ozonide. The heptene-1 ozonide contained a 73% undeuterated fraction and a 27% dideuterated fraction.

Registry No.—**3**, 18963-98-9; ozonide of **3**, 18963-13-8; **4**, 18963-99-0; ozonide of **4**, 18963-12-7; 1,1-dideuteriohexene-1, 18963-11-6; 1-hexene, 592-41-6; ozonide of 1-hexene, 767-09-9.

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