

## Studies in Ozonolysis. IV. Steric Effects in Determining the Existence of the Molozonide<sup>1</sup>

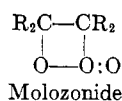
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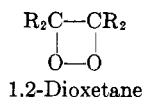
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Ozonation of alkenes in ether solution at  $-112^\circ$  followed by treatment with isopropyl Grignard reagent at this temperature gave propene, propane, and 2-propanol as reaction products. From various alkenes the following additional products were obtained: *trans*-2-pentene gave *threo*-pentane-2,3-diol and minor amounts of 3-methyl-2-butanol and 2-methyl-3-pentanol; *trans*-3-hexene gave *dl*-hexane-3,4-diol and a minor amount of 2-methyl-3-pentanol; 1-pentene gave pentane-1,2-diol, 2-methyl-1-propanol, and 2-methyl-3-hexanol; *cis*-2-pentene gave 3-methyl-2-butanol and 2-methyl-3-pentanol, but no  $\alpha$ -diol; *cis*-3-hexene gave 2-methyl-3-pentanol, but no  $\alpha$ -diol. The products from the *trans* alkenes and 1-pentene indicate that a stable molozonide, assumed to be a 1,2,3-trioxolane, resulting from the stereospecific *cis* addition of ozone to the carbon-carbon double bond was formed. Such a species would appear not to have been formed in the reaction of ozone with the *cis* alkenes. The various alcohols are assumed to have been formed by reaction of ozonide with the Grignard reagent. These data may be explained by the steric interaction between two *cis* alkyl groups and the lone pair orbitals on the oxygen atoms of the molozonide being so great as to prohibit a stable structure, whereas, when the two alkyl groups are *trans*, the steric interactions are markedly diminished and a stable molozonide may be formed.

From the fact that a monomeric ozonide could not be converted to the polymeric ozonide, Staudinger<sup>2</sup> concluded that these materials must be secondary reaction products which arise from a primary reaction product. This primary product was called a molozonide, and it was formulated as the following.



The reason for this formulation was simply that Staudinger also was interested in autoxidation of alkenes, and he was trying to correlate ozonation and autoxidation. There were many similarities between these two reactions; the initial product of autoxidation was believed to be a moloxide which was formulated as a 1,2-dioxetane; hence the molozonide was formu-



lated as indicated above. Staudinger postulated that this molozonide could rearrange to the ozonide, it could polymerize, it could revert to reactants, or it could fragment to carbonyl compounds, carboxylic acids, and ketone diperoxide.

In the years following Staudinger's postulation of a molozonide there were attempts to obtain evidence for this species. One of the more careful studies was that reported by Pummerer and Richtzenhain,<sup>3</sup> but they could find no evidence for an  $\alpha$ -diol, which would be the expected reduction product of the molozonide. It was not until 1960 that some firm evidence for the existence of the molozonide appeared. Criegee and Schröder<sup>4</sup> reported the results of some experiments with *cis*- and *trans*-di-*t*-butylethylene, and these results clearly showed that the *trans* alkene gave a molozonide which was stable at  $-75^\circ$  but which rearranged at a somewhat higher temperature to the ozonide. The *cis* alkene-ozone reaction gave no evidence of the formation

of a molozonide. It was stated that one could say nothing about why the molozonide could be isolated in the case of the *trans* alkene, and that similar experiments with related alkenes were unsuccessful in detecting the existence of a molozonide.

While another facet of the alkene-ozone reaction was pursued, it was decided to carry out ozonations at a temperature below  $-75^\circ$ , which, by and large, had been the lowest temperature employed to that time. At the conclusion of the ozonation of a relatively concentrated solution of 3-octene in *n*-pentane at  $-95^\circ$ , white crystals were present. These crystals exhibited the behavior observed earlier by Criegee and Schröder<sup>4</sup> for their molozonide; *i.e.*, on warming to  $-85^\circ$  the reaction mixture underwent a mild eruption, the crystals disappeared, and the temperature of the solution was  $-65^\circ$ . In a second ozonation of 3-octene in *n*-pentane at  $-95^\circ$  the ozonation mixture was treated at  $-95^\circ$  with isopropyl Grignard reagent. From this reaction mixture was obtained *n*-butylisopropylcarbinol, ethylisopropylcarbinol, and a high-boiling residue which gave a positive test for  $\alpha$ -diol with periodic acid. These results indicated that it might be advantageous to examine the ozonation at a low temperature of some simple alkenes, and Criegee and Schröder's results indicated it might be worthwhile to examine *cis* and *trans* alkenes.

Since the molozonide of simple alkenes would appear to be an unstable species, in experiments designed to detect it one should use as low a temperature as possible. The boiling point of ozone is reported as  $-112^\circ$ . It was considered injudicious to introduce liquid ozone into an alkene solution, hence a temperature of  $-112^\circ$  was used for the ozonations and the treatment of the ozonation mixture with isopropyl Grignard reagent. The ozonations were carried out in dilute ether solution to avoid separation of solid material on addition of the Grignard reagent. The reaction mixture was refluxed until the evolution of gas ceased. In every case this gas contained propene and propane. Hydrolysis of the reaction mixture was effected with aqueous ammonium chloride, and the mixture refluxed to obtain propane as a measure of the excess Grignard reagent. The liquid reaction products were separated by distillation into low-boiling and high-boiling (when present)

(1) Presented at the Southwest Regional Meeting, American Chemical Society, Houston, Texas, Dec. 5-7, 1963.

(2) H. Staudinger, *Ber.*, **58**, 1088 (1925).

(3) R. Pummerer and H. Richtzenhain, *Ann.*, **529**, 33 (1937).

(4) R. Criegee and G. Schröder, *Chem. Ber.*, **93**, 689 (1960).

materials. The low-boiling material was a mixture of alcohols, and the high-boiling material, when obtained, was primarily  $\alpha$ -diol. Considerable isopropyl alcohol was present in the low-boiling material from each experiment.

From *trans*-2-pentene was obtained a good yield of *threo*-*dl*-pentane-2,3-diol and smaller amounts of methylisopropylcarbinol and ethylisopropylcarbinol. Authentic *threo*- and *erythro*-pentane-2,3-diol were completely separated by vapor phase chromatography (v.p.c.) on a phenyldiethanolamine succinate (PDEAS) column. The diol from the alkene by v.p.c. gave a *threo*-diol peak which exhibited no evidence of a shoulder; hence this *threo*-diol would appear to be free of the *erythro* isomer. Identity of the *threo*-diol was verified by the preparation of a bis-3,5-dinitrobenzoate. The two carbinols are assumed to arise by reaction of the Grignard reagent with a small amount of the ozonide present in the ozonation mixture. *trans*-3-Hexene gave a respectable yield of *dl*-hexane-3,4-diol and a minor amount of ethylisopropylcarbinol. This carbinol supposedly arose from reaction of a small amount of ozonide with the Grignard reagent. Since the phenyldiethanolamine succinate column effectively separated *threo*- and *erythro*-pentane-2,3-diol, it was assumed that the column could separate *dl*- and *meso*-hexane-3,4-diol. The diol from the hexene by v.p.c. gave a *dl* peak which had no evidence of a shoulder; hence this *dl*-diol would appear to be free of the *meso* isomer. Verification of the *dl*-diol was made by the preparation of a bis-3,5-dinitrobenzoate. 1-Pentene gave rise to isobutyl alcohol and *n*-propylisopropylcarbinol, supposedly by interaction of the ozonide and the Grignard reagent, and pentane-1,2-diol. The identity of the diol was confirmed by the preparation of a bisphenylurethane.

*cis*-2-Pentene gave good yields of methylisopropylcarbinol and ethylisopropylcarbinol, and *cis*-3-hexene gave a good yield of ethylisopropylcarbinol. In neither case could any  $\alpha$ -diol be detected.

One would expect propene from the reaction of ozonized alkene and isopropyl Grignard reagent, for the reaction of di-*t*-butyl peroxide with Grignard reagents has been reported<sup>5</sup> to give an alkene from the Grignard reagent. Isopropyl alcohol and propane, also, would be expected reaction products, for *t*-butyl hydroperoxide on reaction with the Grignard reagent has been reported<sup>6</sup> to give an alkane and an alcohol corresponding to the Grignard reagent. In the present experiments it is difficult to understand the large amount of propane formed unless one assumes that the ozone was reacting to some extent with the ether to form an active hydrogen-containing compound. Indeed, ether cooled to  $-112^\circ$  did react avidly with ozone. That not all of the ozone introduced into the alkene-ether solution was reacting with the alkene is indicated by material balance calculations. In each experiment the identified products account for about 80% of the carbon in the reactants, whereas the products account for but 65-70% of the ozone introduced into the reaction mixture. One way of explaining this low oxygen balance would be for some of the ozone to

effect an oxidation of the ether and lose some oxygen in the process.

To rule out the possibility of any of the  $\alpha$ -diol found in the above-described experiments having been formed by the Grignard reagent effecting condensation of an aldehyde, propionaldehyde and isopropyl Grignard reagent were subjected to the same reaction conditions and work-up procedure as used in the ozonation experiments. A surprisingly large amount (0.72 g. from 3.73 g. of aldehyde) of high-boiling material was obtained, but this material gave a negative test for  $\alpha$ -diol with periodic acid.

The experiments with *trans*-2-pentene, *trans*-3-hexene, and 1-pentene indicate that there was a stable species which resulted from the stereospecific *cis* addition of ozone to the carbon-carbon double bond, and this species was stable at a temperature where it would react with the isopropyl Grignard reagent. In the case of *cis*-2-pentene and *cis*-3-hexene, it is clear that, if a species resulting from *cis* addition of ozone was formed, it was not stable at a temperature where it would react with the Grignard reagent. This *cis* addition species is the molozonide, and it is formulated as a 1,2,3-trioxolane. In such a structure the valence orbitals of each oxygen atom will assume a tetrahedral arrangement. This means that each oxygen atom will have an orbital containing a lone pair of electrons projecting above the trioxolane ring and such an orbital projecting below the plane of the ring. These orbitals will have some space requirement, and the question is "how much?"

Barton and Cookson<sup>7</sup> by analogy with some carbanion chemistry made the suggestion that piperidine should exist predominantly in that conformation with the hydrogen atom on the nitrogen atom in an axial position. Aroney and LeFèvre<sup>8</sup> concluded from dipole moment studies with piperidine that the space requirement for a lone pair orbital appeared to exceed that of a covalently bound hydrogen atom. Later, from some studies on N-methylpiperidine they<sup>9</sup> concluded that the lone pair orbital must have a space requirement approaching that of a methyl group. If one accepts the more modest space requirement for the lone pair orbital, one can simulate a model for a trioxolane by constructing a model for cyclopentane in which the hydrogen atoms on three contiguous carbon atoms represent the space requirement of the lone pair orbitals of the oxygen atoms in a trioxolane. If in such a model one places two ethyl groups or a methyl and an ethyl group in a *cis* configuration, one finds the alkyl groups can be fitted into the model but they are permitted almost no rotational freedom.

At present the working hypothesis is that a molozonide will not be stable if a methyl and an ethyl or any pair of larger alkyl groups are in a *cis* configuration; the steric interactions between the alkyl groups and the lone pair orbitals do not permit a stable molecule. In a molozonide of *trans* configuration the steric interactions are considerably diminished, and such a structure is stable. Hence, a *trans* alkene on ozonation will form a molozonide as an intermediate: if the temperature at which the ozonation is carried out is low enough, the molozonide will be stable; if the temperature is

(5) T. W. Campbell, W. Burney, and T. L. Jacobs, *J. Am. Chem. Soc.*, **72**, 2735 (1950).

(6) S.-O. Lawesson and N. C. Yang, *ibid.*, **81**, 4230 (1959).

(7) D. H. R. Barton and R. C. Cookson, *Quart. Rev. (London)*, **10**, 44 (1956).

(8) M. Aroney and R. J. W. LeFèvre, *Proc. Chem. Soc.*, 82 (1958).

(9) M. Aroney and R. J. W. LeFèvre, *J. Chem. Soc.*, 3002 (1958).

too high, the molozonide will not be stable and will rearrange to the more stable ozonide. A *cis* alkene on ozonation will not form a molozonide, but will form the ozonide directly.

### Experimental

**Chemicals.**—*n*-Pentane (pure grade, Phillips Petroleum Co.) was treated with excess ozone at  $-40^{\circ}$ ; the pentane was entrained with a stream of nitrogen and extracted successively with aqueous potassium iodide, aqueous sodium thiosulfate, and water. Finally, it was filtered through a pad of phosphorus pentoxide.

**Ethyl ether** (analytical reagent, anhydrous, Mallinckrodt) was stored over sodium ribbon.

**Propionaldehyde** (Matheson Coleman and Bell) was distilled under a nitrogen atmosphere through a spinning-band column (7-mm. i.d.  $\times$  600 mm.), b.p.  $47.7^{\circ}$  (758 mm.),  $n_D^{25}$  1.3600.

**Isopropyl bromide** (Matheson Coleman and Bell) was distilled through a Fenske column (20-mm. i.d.  $\times$  760 mm.), b.p.  $60^{\circ}$  (759 mm.).

**3-Octene** was prepared by a Boord synthesis, b.p.  $122.8^{\circ}$  (748 mm.),  $n_D^{25}$  1.4112.

**1-Pentene** (research grade, Phillips Petroleum Co.) was distilled through a spinning-band column under a nitrogen atmosphere, b.p.  $29.8^{\circ}$  (757 mm.).

*cis*- and *trans*-2-pentene and *cis*- and *trans*-3-hexene were API standard samples (Carnegie Institute of Technology).

**1,2-Pentanediol** was prepared from 1-pentene by the method of Emmons, *et al.*,<sup>10</sup> b.p.  $70^{\circ}$  (0.7 mm.),  $n_D^{25}$  1.4372; lit.<sup>10</sup> b.p.  $78-80^{\circ}$  (0.3 mm.),  $n_D^{20}$  1.4400.

**erythro-dl-Pentane-2,3-diol** was prepared from *trans*-2-pentene by the method of Emmons, *et al.*,<sup>10</sup> b.p.  $52^{\circ}$  (1 mm.),  $n_D^{25}$  1.4406; lit.<sup>11</sup> b.p.  $93.5^{\circ}$  (13 mm.),  $n_D^{20}$  1.4431.

**threo-dl-Pentane-2,3-diol** was prepared from *cis*-2-pentene by the method of Emmons, *et al.*,<sup>10</sup> b.p.  $54^{\circ}$  (1 mm.),  $n_D^{25}$  1.4335; lit.<sup>11</sup> b.p.  $88.5^{\circ}$  (13 mm.),  $n_D^{20}$  1.4370.

**Ozonation Procedure.**—An ozonizer<sup>12</sup> operating at an oxygen flow rate of 13.0 l./hr. produced an ozone-oxygen solution containing 1.5–2.0 vol. % of ozone. The ozone concentration remained constant during each ozonation. The ozone-oxygen solution was bubbled into the alkene solution which was cooled to the appropriate temperature until the desired amount of ozone had been introduced.

**Ozonation of 3-Octene.**—Ozone (18.0 mmoles) was introduced into a solution of 2.24 g. (20.0 mmoles) of 3-octene in 40 ml. of *n*-pentane which was cooled to  $-95^{\circ}$  (frozen acetone bath). At the conclusion of the ozonation white crystals were present. A thermometer was placed directly into the reaction mixture and it was allowed to warm. At a temperature of  $-85^{\circ}$  the reaction mixture underwent a mild eruption; after the eruption the solution temperature was  $-65^{\circ}$  and the crystals had disappeared. The crystals would appear to be molozonide, and their behavior paralleled that observed by Criegee and Schröder<sup>4</sup> in an experiment with *trans*-di-*t*-butylethylene.

**Reaction of Ozonized 3-Octene with Isopropyl Grignard Reagent.**—At the conclusion of the addition of 38.0 mmoles of ozone to a solution of 4.48 g. (40.0 mmoles) of 3-octene in 100 ml. of *n*-pentane which was cooled to  $-95^{\circ}$ , no crystals were present. The reaction mixture was purged with nitrogen for 0.75 hr. The reaction flask was fitted with a stirrer, dropping funnel, and thermometer well. During the dropwise addition of 200 ml. of 2.2 *M* isopropylmagnesium bromide the temperature of the reaction mixture was not permitted to rise above  $-90^{\circ}$ . At the conclusion of the addition considerable solid material had separated. After standing overnight the reaction mixture was refluxed for 0.5 hr. Gas (presumably propene) which decolorized bromine-water was evolved during the reflux period. After hydrolysis of the reaction mixture with aqueous sulfuric acid and ether extraction of the aqueous layer, the combined extracts and organic layer was dried over sodium sulfate.

After removal of the ether and pentane through the Fenske column the residue was distilled through a spinning-band column at 1 mm. to effect a separation of the more volatile from the less

volatile material. The residue (0.86 g.) gave a positive test for  $\alpha$ -glycol with periodic acid. The more volatile material was distilled through the spinning-band column to give 1.54 g. (15.1 mmoles) of 2-methyl-3-pentanol, b.p.  $52^{\circ}$  (29 mm.),  $n_D^{25}$  1.4148 [authentic alcohol,<sup>13</sup> b.p.  $52^{\circ}$  (31 mm.),  $n_D^{25}$  1.4148, 3,5-dinitrobenzoate m.p.  $89.4-90.2^{\circ}$ ], 2.25 g. (17.3 mmoles) of 2-methyl-3-heptanol, b.p.  $83^{\circ}$  (29 mm.),  $n_D^{25}$  1.4240 [lit.<sup>14</sup> b.p.  $76^{\circ}$  (20 mm.),  $n_D^{25}$  1.4246], and various intermediate fractions.

**Reaction of Ozonized *trans*-3-Hexene with Isopropyl Grignard Reagent.**—A solution of 3.20 g. (38.0 mmoles) of *trans*-3-hexene in 400 ml. of ether was cooled to  $-112^{\circ}$  (frozen ether bath) and 1.73 g. (36.1 mmoles) of ozone was added. Nitrogen was passed through the reaction mixture for 1 hr. to purge it of oxygen. The reaction flask was fitted with a stirrer, dropping funnel, and thermometer well. During the addition of 300 ml. of 1.14 *M* (342 mmoles) isopropylmagnesium bromide the temperature of the reaction mixture did not rise above  $-110^{\circ}$ . After standing overnight, the reaction mixture was refluxed for 15 min. During reflux gas that decolorized bromine-water was evolved. The reaction flask was cooled and the mixture was hydrolyzed with aqueous sulfuric acid. The aqueous layer was extracted in a continuous extractor with alcohol-free ether, the combined ether solutions were dried over sodium sulfate, and the ether was removed through the Fenske column. The residue was distilled through a spinning-band column to give a forerun containing an uncertain amount of isopropyl alcohol. That this forerun contained isopropyl alcohol was verified by the preparation from it of isopropyl 3,5-dinitrobenzoate, m.p. and m.m.p.  $121.8-122.2^{\circ}$ . Also obtained were 1.25 g. (12.2 mmoles) of 2-methyl-3-pentanol, b.p.  $56^{\circ}$  (31 mm.),  $n_D^{25}$  1.4138–1.4148, 3,5-dinitrobenzoate m.p. and m.m.p.  $87.2-88.6^{\circ}$  (lit.<sup>13</sup> *vide supra*); and 2.05 g. (17.3 mmoles) of *dl*-hexane-3,4-diol, b.p.  $69-72^{\circ}$  (3 mm.),  $n_D^{25}$  1.4275–1.4415, bis-3,5-dinitrobenzoate m.p.  $166.2-167.4^{\circ}$  (lit.  $n_D^{25}$  1.4412,<sup>15</sup> bis-3,5-dinitrobenzoate<sup>16</sup> m.p.  $167-168^{\circ}$ ).

**Reaction of Ozonized *cis*-3-Hexene with Isopropyl Grignard Reagent.**—An experiment with 3.09 g. (36.7 mmoles) of *cis*-3-hexene, 1.67 g. (34.8 mmoles) of ozone, and 300 ml. of 1.13 *M* (339 mmoles) isopropylmagnesium bromide was carried out as described above. After removal of ether the residue gave a negative test for  $\alpha$ -glycol with periodic acid. Distillation of the residue through the spinning-band column gave 1.31 g. (21.8 mmoles) of isopropyl alcohol, b.p.  $71-81^{\circ}$  (759 mm.),  $n_D^{25}$  1.3750–1.3755, 3,5-dinitrobenzoate m.p. and m.m.p.  $122.6-123.2^{\circ}$ ; and 4.80 g. (47.0 mmoles) of 2-methyl-3-pentanol, b.p.  $52.0-52.2^{\circ}$  (31 mm.),  $n_D^{25}$  1.4130–1.4138, 3,5-dinitrobenzoate m.p. and m.m.p.  $86.3-87.7^{\circ}$  (lit.<sup>13</sup> *vide supra*). The 0.44 g. of distillation residue gave a negative test for  $\alpha$ -glycol.

**General Procedure for Reaction of Ozonized Alkenes with Isopropyl Grignard Reagent.**—A solution of the alkene (*ca.* 40 mmoles) in 400 ml. of ether was cooled to  $-112^{\circ}$  and 95% of the theoretical amount of ozone was added. After standing for 30 min. while the oxygen of the ozonizer was displaced with nitrogen, the reaction mixture was purged of oxygen by bubbling nitrogen through it for 1 hr. The reaction flask was fitted with a stirrer, dropping funnel, thermometer well, and outlet tube which was connected to a Dry Ice-alcohol-cooled trap which was protected with a mercury trap. During the dropwise addition of a known amount of Grignard reagent the temperature of the reaction mixture did not rise above  $-110^{\circ}$ . During a 2-day period the reaction mixture warmed to  $10^{\circ}$ , and nothing had condensed in the Dry Ice-alcohol-cooled trap. The dropping funnel was replaced by a reflux condenser which was connected to a gas-collecting bottle containing saturated salt solution. The outlet tube was sealed and the reaction mixture refluxed until no more gas was evolved (1 hr.). This gas was analyzed by v.p.c. (Wilkens Aerograph Model A-110-C, 20-ft. dimethylsulfolane column) and by mass spectrometry.<sup>17</sup> The reaction mixture was cooled to  $-15^{\circ}$  with a salt-ice bath. It is necessary to keep a record of the nitrogen dissolved by the reaction mixture during this cooling. After hydrolysis by the addition of saturated, aqueous ammonium chloride, the reaction mixture was refluxed until the evolution of

(13) Prepared from propionaldehyde and isopropyl Grignard reagent.

(14) G. L. Dorrough, H. B. Glass, T. L. Gresham, G. B. Malone, and E. E. Reid, *J. Am. Chem. Soc.*, **63**, 3100 (1941).

(15) E. von Rudloff, D. E. Stuetz, and H. F. Bauer, *Can. J. Chem.*, **35**, 315 (1957).

(16) W. G. Young, S. J. Cristol, and F. T. Weiss, *J. Am. Chem. Soc.*, **65**, 1245 (1943).

(17) The author indebted to the Texas Research Laboratories, Beacons, N. Y., for the mass spectrometric analyses.

(10) W. D. Emmons, A. S. Pagano, and J. P. Freeman, *J. Am. Chem. Soc.*, **76**, 3472 (1954).

(11) H. van Risseghem, *Bull. soc. chim. France*, 1661 (1959).

(12) F. L. Greenwood, *Ind. Eng. Chem., Anal. Ed.*, **17**, 446 (1945).

gas ceased (0.75 hr.). This gas was twice led through concentrated sulfuric acid to remove the ether, and the amount of the residual gas was a measure of the excess Grignard reagent. The addition of a small amount of sulfuric acid to the reaction mixture was necessary to break the emulsion. The aqueous layer was placed in a continuous extractor with alcohol-free ether. The combined ether solutions were dried over sodium sulfate, and the ether was removed through the Fenske column.

The residue was distilled *in vacuo* from a Claisen flask with a Vigreux distilling arm, first at 5 mm. to obtain the more volatile material and then at 0.1 mm. to obtain the high-boiling material. The more volatile material was a mixture of alcohols which was analyzed by v.p.c. (5% cyanosilicone on hexamethyldisilazane-treated Chromosorb W column). The composition (wt. %) of the mixture was calculated from the relative peak areas. The composition of known mixtures of isopropyl alcohol and 2-methyl-3-pentanol which was determined in this manner agreed within 2-3% of the known concentrations. This more volatile material was distilled through a small spinning-band column (7-mm. i.d.  $\times$  200 mm.); each fraction was subjected to v.p.c.; and the various alcohols were verified by comparison of their infrared spectra<sup>18</sup> with those of authentic alcohols. The high-boiling material was subjected to v.p.c. (30% phenyldiethanolamine succinate on hemamethyldisilazane-treated Chromosorb W column) to identify the diol, and the composition (wt. %) of the material calculated from the relative peak areas. The identity of the diol was verified by the preparation of a derivative.

**trans-2-Pentene.**—Alkene used was 3.08 g. (43.9 mmoles); ozone introduced, 41.7 mmoles; and Grignard reagent reacted, 155 mmoles. Refluxing the ozonation mixture gave 28.9 mmoles of propene and 54.7 mmoles of propane. The more volatile material (3.01 g.) contained isopropyl alcohol, 30.1 mmoles; 3-methyl-2-butanol, 8.2 mmoles; and 2-methyl-3-pentanol, 5.4 mmoles. The high-boiling material (2.68 g.) contained 23.2 mmoles of *threo-dl*-pentane-2,3-diol and 10 wt. % of unidentified material. The phenyldiethanolamine succinate column effected a complete separation of authentic *threo*- (smaller retention time) and *erythro*-pentane-2,3-diol. Since the *threo*-diol peak of the v.p.c. curve of the high-boiling material did not have a shoulder, one may conclude that little, if any, *erythro*-diol was in the reaction mixture. The high-boiling material gave the bis-3,5-dinitrobenzoate of *threo-dl*-pentane-2,3-diol, m.p. and m.m.p. 159.5-161.4°; lit.<sup>19</sup> m.p. 160.5°. After distillation of the high-boiling material a residue of 0.23 g. remained.

**cis-2-Pentene.**—Alkene used was 3.04 g. (43.4 mmoles); ozone introduced, 41.2 mmoles; and Grignard reagent reacted, 157 mmoles. Refluxing the ozonation mixture gave 22.2 mmoles of propene and 43.2 mmoles of propane. The more volatile material (6.36 g.) contained isopropyl alcohol, 25.1 mmoles; 3-methyl-2-butanol, 27.5 mmoles; and 2-methyl-3-pentanol, 23.1 mmoles. High-boiling material (0.57 g.) was obtained, but it gave a negative  $\alpha$ -glycol test and v.p.c. showed it to contain no pentane-

2,3-diol. Hence, no diol was formed in this reaction. A residue of 0.18 g. remained after the high-boiling material was collected.

**trans-3-Hexene.**—Alkene used was 3.36 g. (39.9 mmoles); ozone introduced, 37.9 mmoles; and Grignard reagent reacted, 133 mmoles. Refluxing the ozonation mixture gave 28.2 mmoles of propene and 48.4 mmoles of propane. The more volatile material (2.80 g.) contained isopropyl alcohol, 32.9 mmoles; and 2-methyl-3-pentanol, 7.5 mmoles. The high-boiling material (2.99 g.) contained 16.4 mmoles of *dl*-hexane-3,4-diol and 35% of unidentified material. Since the phenyldiethanolamine succinate column separated *threo*- and *erythro*-pentane-2,3-diol, it was assumed that it would separate *dl*- and *meso*-hexane-3,4-diol. The diol peak in the v.p.c. curve of the high-boiling material had no indication of a shoulder; hence *meso*-diol is assumed to be absent. A residue of 0.67 g. remained after the high-boiling material was collected.

**cis-3-Hexene.**—Alkene used was 3.24 g. (38.5 mmoles); ozone introduced, 36.6 mmoles; and Grignard reagent reacted, 130 mmoles. Refluxing the ozonation mixture gave 16.2 mmoles of propene and 24.3 mmoles of propane. The more volatile material (6.65 g.) contained isopropyl alcohol, 26.0 mmoles; and 2-methyl-3-pentanol, 49.5 mmoles. No high-boiling material could be obtained, and a distillation residue of 0.37 g. remained. All of the products gave a negative  $\alpha$ -glycol test; hence no diol was formed in this reaction.

**1-Pentene.**—Alkene used was 3.02 g. (43.1 mmoles); ozone introduced, 40.9 mmoles; and Grignard reagent reacted, 148 mmoles. Refluxing the ozonation mixture gave 23.4 mmoles of propene and 50.3 mmoles of propane. The low-boiling material (4.56 g.) contained isopropyl alcohol, 19.9 mmoles; isobutyl alcohol, 15.1 mmoles; and 2-methyl-3-hexanol, 18.2 mmoles. The high-boiling material (1.38 g.) contained 29% of unidentified material and 9.4 mmoles of pentane-1,2-diol. This material gave the bisphenylurethane of pentane-1,2-diol, m.p. and m.m.p. 106.4-108.8°; lit.<sup>20</sup> m.p. 108-110°. A distillation residue of 0.23 g. remained.

An experiment in which isobutylmagnesium bromide was used gave similar results, *mutatis mutandis*.

#### Reaction of Propionaldehyde with Isopropyl Grignard Reagent.

—To rule out the possibility of any of the diol found in the above-described experiments having been formed by condensation of an aldehyde, 3.73 g. (64.2 mmoles) of propionaldehyde in 400 ml. of ether was treated with 90.0 mmoles of Grignard reagent under the same conditions as those used for the reaction of the ozonized alkenes with the Grignard reagent. There were obtained 52.4 mmoles of 2-methyl-3-pentanol and 0.72 g. of distillation residue. Neither of these materials gave a positive test for  $\alpha$ -glycol.

**Reaction of Ether with Ozone.**—Ether (50 ml.) was cooled to  $-112^\circ$  and ozonized. After 30 min. the ether was retaining 75% of the ozone passed into it.

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(18) Infrared spectra were obtained with a Perkin-Elmer Model 21 infrared spectrophotometer.

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