removing the solvent, the residue was taken up in water. The aqueous solution was acidified with 3 $N$ sulfuric acid, and the resulting precipitate was dried and taken up in ether. The ether extract was dried over magnesium sulfate. Evaporation of the ether left 1.8 g. (72%) of 1,1,4,4-tetraphenylbutyne-1,4-dicarboxylic acid (IV), m.p. 198°. It was identical with IV in all respects.

**Diphenylfumaric Acid.**—Diphenylacetylene (1.78 g., 0.01 mole) was stirred, under nitrogen, with 1.2 g. of potassium in 100 ml. of THF. After 5 hr., the solution was poured over excess Dry Ice. Decolorization was immediate. The solution was evaporated and the residue was extracted with water. The aqueous layer was acidified to liberate the dicarboxylic acid which separated as a gummy solid. After several days the product crystallized. After thorough washing with carbon tetrachloride a 25% yield of diphenylfumaric acid was obtained, m.p. 266°,[18] neut. equiv. 134 (calcd. 134). The use of lithium in place of potassium gave slightly higher yields.

**Reaction of 5-Decyne with Sodium-Potassium Alloy.**—5-Decyne (10 g., 0.073 mole) in 250 ml. of DME was added to the alloy (4 g. of K to 0.5 g. of Na) under nitrogen, and the mixture was stirred for 10 hr. It was then poured over Dry Ice. The solvent was removed under reduced pressure, and the residue was extracted with water. The aqueous layer was acidified and extracted with ether. Evaporation of the ether gave 4.5 g. of oily product. Careful fractional distillation gave two fractions, 68–71° at 5 mm. and 108–111° at 5 mm. The lower boiling product proved to be valeric acid.

*Anal.* Calcd. for $C_5H_{10}O_2$: C, 58.82; H, 9.80; neut. equiv., 102. Found: C, 58.57; H, 9.98; neut. equiv., 101.

The higher fraction was shown to be 2-heptynoic acid.

*Anal.* Calcd. for $C_7H_{10}O_2$: C, 66.66; H, 7.94; neut. equiv., 126. Found: C, 66.57; H, 7.97; neut. equiv., 125.

Triple-bond absorption in the infrared occurred at 2240 cm.$^{-1}$, $\lambda_{max}^{C_2H_5OH}$ 207 mμ (ε 69,500).

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[18] S. Wawzonek and D. Wearring [*J. Am. Chem. Soc.*, **81**, 2067 (1959)] reported m.p. 263–265° for a sample prepared by a different method.

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# Ozonides from Asymmetrical Olefins. Reaction with Triphenylphosphine

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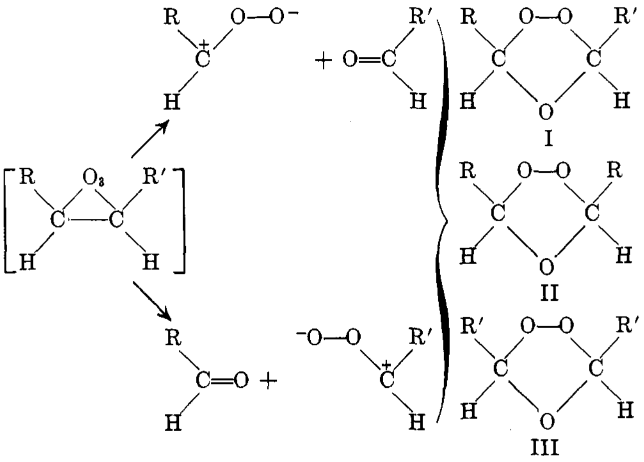
The ozonation of asymmetrical olefins, R—CH=CH—R′, has led to one asymmetrical or natural ozonide and two symmetrical or unnatural ozonides as predicted by the Criegee mechanism. The relative yields of the three ozonides were determined by gas chromatography. The investigation was carried out with 2-hexene, 4-methyl-2-pentene, 4-nonene, and 2,6-dimethyl-3-heptene at −78°. The ozonides were reduced quantitatively with triphenylphosphine to the corresponding carbonyl compounds. 2-Butene ozonide and 2,5-dimethyl-3-hexene ozonide could be separated into *cis* and *trans* isomers by g.l.c. technique. One of these isomers was more readily reducible by triphenylphosphine than the other which permitted the preparation of the less reactive isomer in pure form. The *cis–trans* ratio of the ozonides depended largely on the nature and steric configuration of the original olefin. This would indicate that some of the ozonides were formed by a stereospecific mechanism.

A previous investigation of the ozonation of 2,6-dimethyl-2,6-octadiene in the absence of a solvent showed that 2-butene ozonide was one of the reaction products.[2] To our knowledge this was the first reported example of the formation of an unnatural ozonide. This was considered as a further verification of the Criegee mechanism[3] since 2-butene ozonide was formed presumably by reaction of the zwitterion $H_3C—^+CH—O—O^-$ with acetaldehyde. Identification of other ozonides formed during the ozonation of 2,6-dimethyl-2,6-octadiene proved to be difficult since a variety of ozonides could be formed. It was decided, therefore, to investigate a number of simple asymmetrical olefins, R—CH=CHR′, which according to Criegee's mechanism may give rise to three different monomeric ozonides as shown below assuming a primary ozonide to be the initial product.[4] A necessary requirement for the formation of the natural ozonide I and the two symmetrical or unnatural ozonides II and III is a sufficient lifetime for the zwitterions to react statistically as well as the absence of a complete solvent cage which would prevent the formation of the unnatural ozonides. After our work had been completed, papers by Riezebos and co-workers[5] and Privett and Nickell[6] came to our attention in which it was shown that the ozonation of methyl oleate yielded the three possible ozonides.



The ozonation of four asymmetrical olefins, 2-hexene, 4-methyl-2-pentene, 4-nonene, and 2,6-dimethyl-3-heptene, as well as three symmetrical olefins, 2-butene, 3-hexene, and 2,5-dimethyl-3-hexene, was investigated. The ozonation was carried out at −78°, usually in a solvent such as $n$-pentane. The monomeric ozonides were separated from the total ozonation product, which usually contained much polymeric material, by distillation, and the yield was determined by weight. Gas chromatographic analysis showed that the symmetrical olefins formed only one ozonide, whereas the asymmetrical olefins gave three different

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[1] To whom communications should be sent.

[2] Presented before the Division of Rubber Chemistry, American Chemical Society, Cleveland, Ohio, Oct. 18, 1962; O. Lorenz and C. R. Parks, *Rubber Chem. Technol.*, **36**, 201 (1963).

[3] R. Criegee, *Ann.*, **583**, 1 (1953); R. Criegee, *et al.*, *Chem. Ber.*, **88**, 1878 (1955); for a summarizing discussion of ozonation, see P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

[4] R. Criegee and G. Schroeder, *Chem. Ber.*, **93**, 689 (1960).

[5] G. Riezebos, J. C. Grimmelikhuysen, and D. A. van Dorp, *Rec. trav. chim.*, **82**, 1234 (1963).

[6] O. S. Privett and E. C. Nickell, *J. Lipid Res.*, **4**, 208 (1963).

TABLE I

MONOMERIC OZONIDES FROM OLEFINS

| Olefin | Solvent | Volume ratio of solvent/olefin | Monomeric ozonides formed | Mole % of total ozonides | Molar ratio of ozonides | Yield, %[a] |
|---|---|---|---|---|---|---|
| 2-Butene | None | . . . | 2-Butene ozonide | 100 | . . . | 20 |
| 3-Hexene | *n*-Pentane | 3 | 3-Hexene ozonide | 100 | . . | 22 |
| 2,5-Dimethyl-*cis*-3-hexene | *n*-Pentane | 2 | 2,5-Dimethyl-3-hexene ozonide | 100 | . . . | 95 |
| 2,5-Dimethyl-*trans*-3-hexene | *n*-Pentane | 3 | 2,5-Dimethyl-3-hexene ozonide | 100 | . . . | 60 |
| 2-Hexene | *n*-Pentane | 3 | 2-Butene ozonide[b] | 20 | 0.30 | |
| | | | 2-Hexene ozonide[b] | 66 | 1.00 | 50 |
| | | | 4-Octene ozonide[b] | 14 | 0.21 | |
| 4-Methyl-2-pentene | *n*-Pentane | 2 | 2-Butene ozonide[b] | 7 | 0.09 | |
| | | | 4-Methyl-2-pentene ozonide[b] | 79 | 1.00 | 45 |
| | | | 2,5-Dimethyl-3-hexene ozonide[b] | 14 | 0.18 | |
| 4-Nonene | *n*-Pentane | 1 | 4-Octene ozonide[b] | 23 | 0.36 | |
| | | | 4-Nonene ozonide[b] | 63 | 1.00 | 67 |
| | | | 5-Decene ozonide[b] | 14 | 0.22 | |
| 2,6-Dimethyl-3-heptene | *n*-Pentane | 1 | 2,5-Dimethyl-3-hexene ozonide[b] | 20 | 0.28 | |
| | | | 2,6-Dimethyl-3-heptene ozonide[b] | 72 | 1.00 | 67 |
| | | | 2,7-Dimethyl-4-octene ozonide[c] | 8 | 0.11 | |
| 2-Butene | Propionaldehyde | 1 | 2-Butene ozonide[b] | 44 | 0.79 | 20 |
| | | | 2-Pentene ozonide[c] | 56 | 1.00 | |
| 3-Hexene | *n*-Butyraldehyde | 3 | 3-Hexene ozonide[b] | 17 | 0.20 | 40 |
| | | | 3-Heptene ozonide[b] | 83 | 1.00 | |
| 3-Hexene | Isobutyraldehyde | 3 | 3-Hexene ozonide[b] | 13 | 0.16 | 40 |
| | | | 2-Methyl-3-hexene ozonide[c] | 87 | 1.00 | |
| 2-Hexene | *n*-Butyraldehyde | 1 | 2-Butene ozonide[b] | 10 | 0.20 | |
| | | | 2-Hexene ozonide[b] | 50 | 1.00 | 53 |
| | | | 4-Octene ozonide[b] | 40 | 0.80 | |
| 4-Methyl-2-pentene | Isobutyraldehyde | 2 | 2-Butene ozonide[b] | 3 | 0.04 | |
| | | | 4-Methyl-2-pentene ozonide[b] | 75 | 1.00 | 44 |
| | | | 2,5-Dimethyl-3-hexene ozonide[b] | 22 | 0.29 | |
| 2,6-Dimethyl-3-heptene | Isobutyraldehyde | 1 | 2,5-Dimethyl-3-hexene ozonide[b] | 37 | 0.63 | |
| | | | 2,6-Dimethyl-3-heptene ozonide[b] | 59 | 1.00 | 68 |
| | | | 2,7-Dimethyl-4-octene ozonide[c] | 4 | 0.07 | |

[a] Mole of monomeric ozonide (× 100) per mole of olefin ozonized. [b] Could be separated in pure form, or identification was possible with an authentic sample. [c] Difficult to obtain from the reaction mixture in pure form by distillation.

ozonides. The relative amounts of the three different ozonides were determined by measuring the areas of the peaks in the chromatogram. Data are given in Table I. A typical chromatogram is shown in Figure 1 for ozonized 2-hexene. The yield of the three ozonides decreased in the order: 2-hexene ozonide > 2-butene ozonide > 4-octene ozonide which were formed in a molar ratio of 1.0:0.38:0.17. Acetaldehyde, *n*-butyraldehyde, and unreacted 2-hexene were also detected in the chromatogram in addition to *n*-pentane which was used as the solvent.

Separation of the three ozonides formed from asymmetrical olefins was possible by fractional distillation as long as the boiling points of the different reaction products were not too close together. It was usually possible to separate ozonides which differed by at least two carbon atoms. The lowest boiling of the three ozonides was difficult to separate in pure form since it frequently contained large amounts of the higher boiling aldehyde and unreacted olefin. Identification of the ozonides was made from carbon, hydrogen, and Unterzacher oxygen analyses, active oxygen by reduction with triphenylphosphine, infrared spectra, and comparison of the retention times from gas chromatography with authentic samples obtained by the ozonation of symmetrical olefins.

The molar ratio of the three ozonides I, II, and III should approach a statistical value of 2:1:1 provided there is no preferred breakdown of the initial ozonide and no solvent cage. The experimentally determined values of the molar ratio of the three ozonides differed from the statistical value, the yield of the symmetrical or unnatural ozonides always being lower. This means that part of the reaction always occurs in a cage depending on the nature of the olefin, the nature and amount of the solvent, and on the temperature of ozonation. There is also a preference for the breakdown to a certain zwitterion and aldehyde since the two unnatural ozonides are not found in equimolar amounts. The situation is complicated, however,

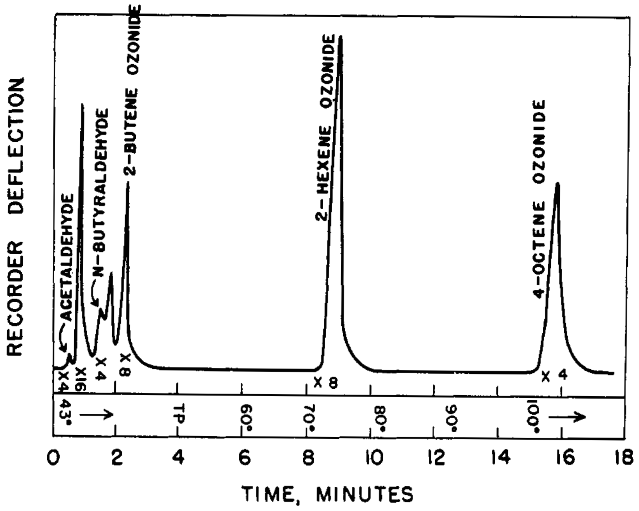


Figure 1.—Chromatogram of ozonized 2-hexene. Unlabeled peaks are *n*-pentane which was used as a solvent (left) and unreacted 2-hexene.

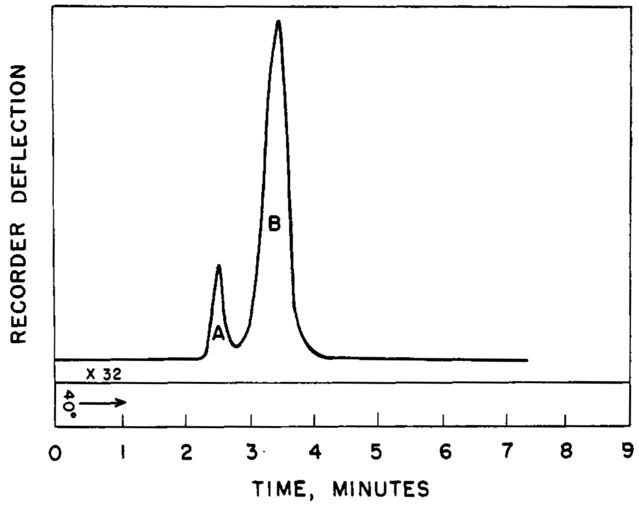
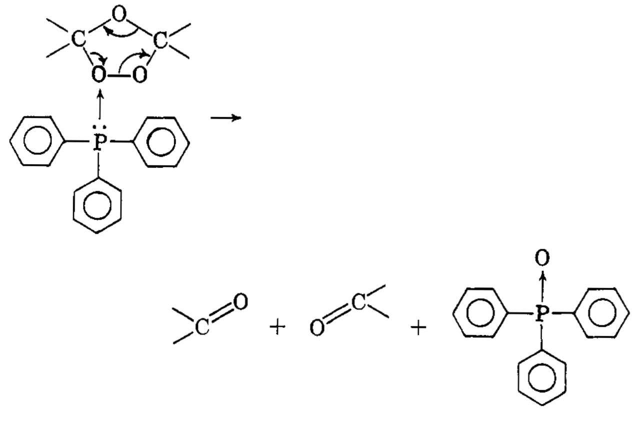


Figure 2.—Chromatogram of 2-butene ozonide prepared from the *trans* olefin.

because it is not known to what extent each zwitterion polymerizes rather than reacts with an aldehyde.

To obtain more information concerning the preferred formation of certain zwitterions, the ozonation of some asymmetrical olefins was carried out in the presence of an aldehyde. It is not surprising that the normal ozonide was always the main reaction product, as any reaction which occurs in the cage would always lead to the normal ozonide (see Table I). Further work using different aldehydes is required before a general conclusion can be drawn concerning the preferred breakdown of the initial product. Criegee and co-workers[7] have reported on the ozonation of olefins in the presence of aldehydes as a method for the preparation of ozonides. They obtained, *e.g.*, 1-pentene ozonide by the ozonation of 4-octene in the presence of formaldehyde. We have found that other aliphatic aldehydes such as acetaldehyde, propionaldehyde, *n*-butyraldehyde, and isobutyraldehyde react in the same way as formaldehyde. As an example, the ozonation of *trans*-3-hexene in the presence of *n*-butyraldehyde gave 3-heptene ozonide as the main reaction product, whereas the formation of 3-hexene ozonide was suppressed.

Peroxy compounds are usually determined by an iodometric method. Ozonides will oxidize iodide ions quantitatively to iodine but only if the ozonides yield ketones upon reduction. With ozonides that give aldehydes, low values are obtained.[8] An investigation of the reduction of ozonides with triphenylphosphine indicated that this reaction proceeded quantitatively when aldehydes, as well as ketones, are formed on reduction. If an excess of triphenylphosphine is used, the unreacted triphenylphosphine can be determined by titration with iodine. The reaction was generally carried out at room temperature and in the absence of oxygen. A polar solvent, usually ethyl alcohol, was used since the reaction proceeded slowly in a nonpolar medium. Details are given elsewhere.[9] The effect of polar solvents on the reaction rate is indicative of a mechanism involving polar transition states. A nucleophilic attack of triphenylphosphine may initiate the reduction of ozonides. This is similar to the mechanism proposed for the reaction of triphenylphosphine with sulfur.[10] The reduction of ozonides by triphenylphosphine was found to be a valuable tool for the determination of the structure of ozonides. The carbonyl compounds formed could be readily identified by gas chromatographic analysis.



*cis* and *trans* isomers of an ozonide may be expected when each of the two carbon atoms of the five-membered ring contain two different substituents, *e.g.*, hydrogen and alkyl. According to the Criegee mechanism there is a splitting of the primary ozonide and, therefore, the same relative amounts of the two isomeric ozonides should be expected regardless whether one starts with the *cis* or the *trans* olefin. These amounts would depend on the relative stabilities of the final products and need not necessarily be in a 1:1 ratio. Schroeder[11] was able to detect the *cis* and *trans* isomers of di-*t*-butylethylene ozonide by means of gas chromatography. The results were surprising, however, as the *trans* olefin formed the *trans* ozonide exclusively, while the *cis* olefin yielded the *cis* and *trans* ozonides in a 70:30 ratio. These two isomers showed different reaction rates when reduced with lithium aluminum hydride. Steric considerations suggested that the more easily reducible isomer had the *cis* configuration. The three pairs of *cis* and *trans* isomers of the ozonides which can

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(7) R. Criegee, G. Blust, and H. Zinke, *Chem. Ber.*, **87**, 766 (1954).

(8) R. Criegee, A. Kerckow, and H. Zinke, *ibid.*, **88**, 1878 (1955).

(9) O. Lorenz, *Anal. Chem.*, **37**, 101 (1965).

(10) P. D. Bartlett and G. Meguerian, *J. Am. Chem. Soc.*, **78**, 3710 (1956).

(11) G. Schroeder, *Chem. Ber.*, **95**, 733 (1962).

be formed from methyl oleate have also been reported.[5,6] Their separation has been accomplished by thin layer and elution chromatography. Recently the ozonation of 2-pentene has been investigated in detail by Loan, Murray, and Story.[12] Each of the three ozonides was shown to exist as a *cis–trans* pair by n.m.r. spectra.

The chromatogram of the two butene ozonides which were prepared from *trans*-2-butene is shown in Figure 2. The two isomers were present in a ratio of *ca.* 1:8 with isomer A having the lower boiling point. Figure 3 shows the chromatogram of partially reduced 2-butene ozonide dissolved in 2,6-dimethyloctadiene using triphenylphosphine as the reducing agent. Acetaldehyde was the only reaction product indicating that A and B are geometric isomers. A comparison of this chromatogram with that of Figure 2 shows that A reacted more readily than B; 90% of the original amount of A had reacted compared with 17% of B. This difference in reaction rates permitted the preparation of isomer B in the pure form by partial reduction with triphenylphosphine whereby component A was completely removed. When *cis*-2-butene was ozonized, the lower boiling isomer A was obtained in much smaller yield, about 2% of the total monomeric ozonide. 2-Butene ozonide formed from 4-methyl-*trans*-2-pentene contained only traces of A, whereas the ozonation of 2,6-dimethyl-2-*trans*-6-octadiene gave almost as much A as B.

Ozonation of 2,5-dimethyl-*cis*-3-hexene gave a remarkably high yield of the monomeric ozonide (95% of theory) which contained the two isomers in a ratio of about 1:1. The *trans* olefin formed the isomeric ozonide having the shorter retention time in a larger concentration, a ratio of about 3:1 as shown in Figure 4. Ozonation of 4-methyl-*trans*-2-pentene in isobutyraldehyde gave 2,5-dimethyl-3-hexene ozonide with *cis* and *trans* isomers having a composition similar to that obtained from 2,5-dimethyl-*trans*-3-hexene. Reduction with triphenylphosphine again showed that the two compounds were geometric isomers, isobutyraldehyde being the only reaction product. With this ozonide, the isomer with the longer retention time was the more easily reducible. Schroeder[11] has assigned the *cis* configuration to the more readily reducible di-*t*-butylethylene ozonide since it offered less steric hindrance to the attack of lithium aluminum hydride. The *cis* isomer had the longer retention time. The situation is very similar with 2,5-dimethyl-3-hexene ozonide in that the steric effect of the fairly bulky isopropyl group should be similar to that of the *t*-butyl group. Likewise, the *cis* ozonide which is the more readily reducible showed the longer retention time.

The assignment of the steric configurations for the 2-butene ozonides is more difficult. Steric effects do not seem to be of importance in explaining the different rates of reduction by triphenylphosphine. *cis*-2-Butene yielded more isomer B (98%) with the longer retention time than *trans*-2-butene (89%). This suggests assigning the *cis* configuration to isomer B with the longer retention time although it reacted more slowly with triphenylphosphine than isomer A. If the assignments are correct in all three of these examples, the *cis* isomer always has the longer retention time. All assignments, however, should be considered as tentative.

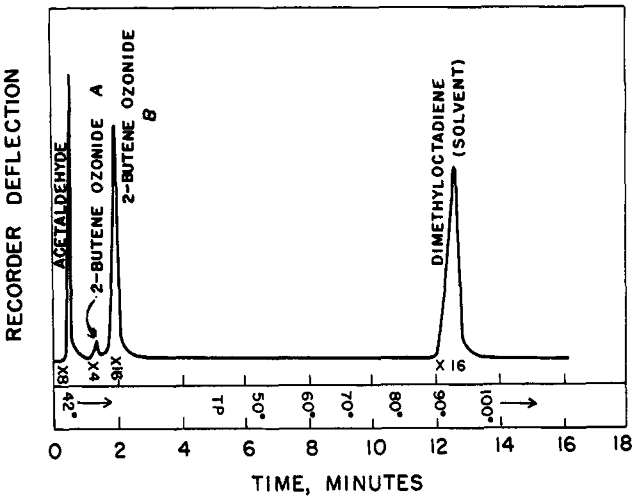

Figure 3.—Chromatogram of 2-butene ozonide partially reduced with triphenylphosphine.

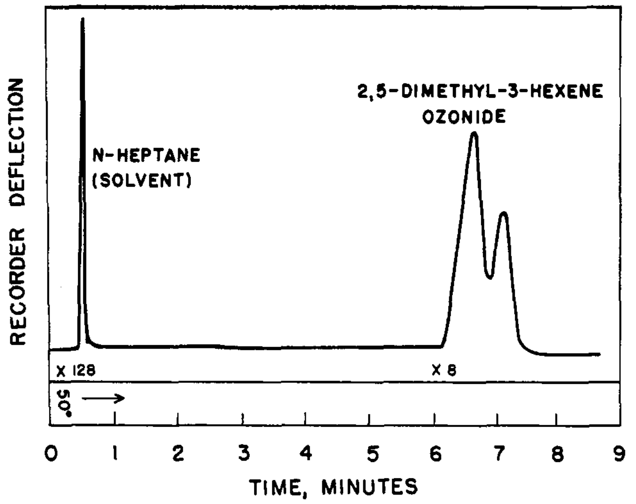

Figure 4.—Chromatogram of 2,5-dimethyl-3-hexene ozonide prepared from the *trans* olefin.

The dependence of the *cis–trans* ratio of the ozonides upon the geometry of the original olefin strongly suggests the possibility that the formation of ozonides occurs in part by a stereospecific mechanism in which there may not be a complete cleavage or breakdown of the primary ozonide. Additional evidence has recently been advanced by Greenwood[13] who postulated that only *trans* olefins can form a primary ozonide[4] as an intermediate. Olefins with a methyl and ethyl or any pair of larger groups in the *cis* configuration will not form a primary ozonide due to steric effects but will form the ozonide directly. As was pointed out above, steric considerations did not seem to be of importance in explaining the different rates of reduction of the *cis*- and *trans*-2-butene ozonides by triphenylphosphine. This would still be consistent with Greenwood's postulation as 2-butene contains only two methyl groups.

## Experimental

**Ozonation of Olefins.**—The olefins were obtained from Chemical Samples Co., Columbus, Ohio, except the samples of

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[12] L. D. Loan, R. W. Murray, and P. R. Story, *J. Am. Chem. Soc.*, **87**, 737 (1965).

[13] F. L. Greenwood, *J. Org. Chem.*, **29**, 1321 (1964).

2-butene which came from Phillips Petroleum Co. Ozonation of the olefins was carried out with a Welsbach T-23 laboratory ozonator which was adjusted to produce 4 g. of ozone/hr. at a flow rate of 700 ml./min. The ozone-containing oxygen stream was precooled by passing through a glass spiral kept at −78° (using a Dry Ice–acetone cooling mixture) before it entered the reaction vessel which was also kept at −78°. The olefins used were peroxide-free. If peroxides were present as indicated by the iodine test, they were removed by shaking with ferrous sulfate and sulfuric acid solution. The olefin was dried over magnesium perchlorate and distilled. 2-Butene and 2-hexene could be ozonized in the absence of a solvent at −78°. Using *trans*-3-hexene and 4-methyl-*trans*-2-pentene without a solvent, explosions occurred shortly after the addition of ozone was begun. The ozonation of 4-nonene, 2,5-dimethyl-3-hexene, and 2,6-dimethyl-3-heptene was not investigated in the absence of a solvent. For reasons of safety, most of the experiments were carried out in the presence of a solvent, *n*-pentane and various aldehydes being used.

The monomeric ozonides were separated from the total ozonation product by distillation and the yield was determined by weight. Infrared spectra showed a characteristic absorption at 1100 cm.$^{-1}$. If a carbonyl band appeared in the spectrum, the ozonide was dissolved in ether and washed with sodium bicarbonate solution. This was necessary especially when the ozonation was carried out in the presence of an aldehyde, as the product contained appreciable amounts of acids. After drying the ether solution over magnesium perchlorate, the product was redistilled. The purity of the ozonides was determined by gas chromatography and by reaction with triphenylphosphine for active oxygen.

**Gas Chromatography.**—The structure and purity of the olefins were determined by gas chromatography using a Perkin-Elmer Model 154 chromatograph with a 50-ft. packed column containing 20% $\beta,\beta'$-oxydipropionitrile as the substrate or a 150-ft. capillary column coated with squalane. It has been found by Hively[14] that for dialkylethylenes the retention time of the *cis* form relative to that of the *trans* isomer on a highly polar substrate was always greater than this ratio on a nonpolar column. This enables one to assign *cis* and *trans* configurations to a mixture of a particular olefin.

An Aerograph, Model A350, with temperature programmer, was used to analyze the ozonation products of the olefins and the monomeric ozonides. Columns 5 ft. × 0.25 in. were used containing 5% silicone SE-30 on Gas-chrom Z, 60–80 mesh, except for the separation of the *cis* and *trans* isomers of 2,5-dimethyl-3-hexene ozonide where 5% Carbowax 20,000 was used as the substrate. A separation could not be made using silicone. The temperature of the columns is given in the figures, both column and injector being kept below 80° wherever possible. The addition of a solvent such as *n*-pentane or dimethyloctadiene helped to prevent decomposition of the ozonides in the chromatograph. The purity of the ozonides obtained by distillation could be readily checked by gas chromatographic analysis. In addition, a chromatogram was run on the total ozonation mixture obtained from each ozonized olefin to determine the relative amounts of the different ozonides. A comparison was made of the retention times with known samples of each ozonide involved.

**Ozonation of 2-Hexene.**—The 2-hexene consisted of 85% *cis* and 13% *trans* with 2% 2-methyl-2-pentene and 1-hexene as impurities. 2-Hexene (40 ml., 27.2 g., 0.324 mole) in 120 ml. of *n*-pentane was ozonized for 216 min. with 14.4 g. (0.30 mole) of ozone corresponding to 93% completion. *n*-Pentene was removed by distillation at 20° (150 mm.). Acetaldehyde as well as portions of *n*-butyraldehyde, unreacted 2-hexene, and 2-butene ozonide were also removed as indicated by g.l.c. analysis of the distillate. The pressure was lowered to 20 mm. and a fraction A of 15.2 g. boiling at 20–50° was collected. Fraction A consisted mainly of 2-hexene ozonide and a small amount of *n*-butyraldehyde. Another fraction B of 4.6 g. was collected, b.p. 30–50° at 0.8 mm., containing 4-octene ozonide and some 2-hexene ozonide. A viscous liquid, 18 g., remained. Fraction A was twice distilled. The portion boiling at 41.0–41.5° at 18 mm. was 2-hexene ozonide, $n^{25}\text{D}$ 1.4016, $d^{20}{}_4$ 0.9734.

*Anal.* Calcd. for $C_6H_{12}O_3$: C, 54.50; H, 9.15; O, 36.35; active O, 12.12. Found: C, 54.2; H, 9.0; O, 36.5; active O (by TPP), 11.85.

It was not possible to separate 2-butene ozonide in pure form from the lower boiling part of fraction A by distillation as it always contained large amounts of *n*-butyraldehyde and 2-hexene ozonide.

Fraction B was distilled three times and the fraction boiling at 32–34° at 0.7 mm. was collected. This material was 4-octene ozonide, $n^{25}\text{D}$ 1.4137, $d^{20}{}_4$ 0.9479.

*Anal.* Calcd. for $C_8H_{16}O_3$: C, 59.96; H, 10.07; O, 29.97; active O, 9.99. Found: C, 60.0; H, 10.1; O, 29.9; active O, 9.75.

Gas chromatography of the original reaction product was used to determine the relative yields of the three ozonides: 2-hexene ozonide, 2-butene ozonide, and 4-octene ozonide. It was assumed that a linear relationship exists between the areas and weights, this relationship being the same for the three ozonides.

**Ozonation of 4-Methyl-2-pentene.**—The 4-methyl-2-pentene consisted of 99.6% *trans* and 0.1% *cis*. This olefin could not be ozonized in the absence of a solvent. A spark was observed immediately after the reaction vessel was connected with the ozone stream. A white precipitate was formed which disappeared when the solution was allowed to warm. The precipitate did not reappear when the solution was again cooled to −78°. When one or more volumes of *n*-pentane was used as a solvent, the reaction could be carried out to completion. 4-Methyl-2-pentene (50 ml., 33.5 g., 0.40 mole) in 100 ml. of *n*-pentane was treated with 19.0 g. (0.40 mole) of ozone. The product was twice distilled. 4-Methyl-2-pentene ozonide (15.4 g.) was obtained containing a small amount of 2,5-dimethyl-3-hexene ozonide, b.p. 38.5° at 22 mm., $n^{25}\text{D}$ 1.3998, $d^{20}{}_4$ 0.9767.

*Anal.* Calcd. for $C_6H_{12}O_3$: C, 54.50; H, 9.15; O, 36.35; active O, 12.12. Found: C, 55.4; H, 9.5; O, 35.3; active O, 11.9.

2,5-Dimethyl-3-hexene ozonide (1.3 g.) was obtained, b.p. 48–49° at 12 mm. The polymeric residue weighed 20 g.

**Ozonation of 4-Nonene.**—The 4-nonene consisted of 84% *trans* and 13% *cis* with 3% of four unknown impurities. 4-Nonene (75 ml.; 54.8 g., 0.435 mole) in 75 ml. of *n*-pentane was treated with 19 g. (0.40 mole) of ozone. Total ozonides obtained were 46.5 g.; the polymeric residue weighed 23 g. Distillation and analysis of the fractions by gas chromatography indicated that separation of the three ozonides was difficult. The fraction boiling at 37–39° at 0.2 mm. gave 4-nonene ozonide containing some 4-octene and 5-decene ozonide, $n^{25}\text{D}$ 1.4190, $d^{20}{}_4$ 0.9372.

*Anal.* Calcd. for $C_9H_{18}O_3$: C, 62.04; H, 10.40; active O, 9.19. Found: C, 61.5; H, 10.0; active O, 9.00.

**Ozonation of 2,6-Dimethyl-3-heptene.**—The 2,6-dimethyl-3-heptene consisted of 94% *trans* and 4% *cis* with 2% of two unknown impurities. 2,6-Dimethyl-3-heptene (40 ml., 29.4 g., 0.233 mole) in 40 ml. of *n*-pentane was reacted with 11.0 g. (0.23 mole) of ozone. Total ozonides obtained were 27 g. The polymeric residue weighed 10 g. A 5-g. fraction was collected, b.p. 25–26° at 0.6 mm., which contained a mixture of 2,5-dimethyl-3-hexene ozonide and 2,6-dimethyl-3-heptene ozonide. A second fraction, 18 g., was twice distilled, b.p. 33–35° at 0.8 mm. This was 2,6-dimethyl-3-heptene ozonide, $n^{25}\text{D}$ 1.4159, $d^{20}{}_4$ 0.9318.

*Anal.* Calcd.: active O, 9.19. Found: active O, 8.95.

**Ozonation of 2-Butene.**—Commercial 2-butene was vaporized from a pressure cylinder and dried by passing through phosphorus pentoxide before being condensed into the reaction vessel. 2-Butene (50 ml., 31.7 g., 0.565 mole) was ozonized in the absence of a solvent. Ozone (13.5 g., 0.28 mole) was added which corresponded to approximately 50% completion. A preliminary distillation, 40° at 60 mm., gave 15 g. of product which contained a considerable amount of acetaldehyde. A second distillation gave 5.0 g. of 2-butene ozonide, b.p. 45–46° at 170 mm., $n^{25}\text{D}$ 1.3821, $d^{20}{}_4$ 1.0308.

*Anal.* Calcd.: active O, 15.37. Found: active O, 15.05.

A polymeric residue (15 g.) was obtained with a very high oxygen content.

*Anal.* Calcd. for $C_2H_5O_2$: C, 40.00; H, 6.67; O, 53.33. Found: C, 42.6; H, 7.5; O, 50.3.

To 5 ml. (3.11 g., 0.0556 mole) of 2-butene, 97.9% *cis* and 0.7% *trans* with 1.4% butane and propene as impurities, in 3 ml. of *n*-pentane was added 1.4 g. (0.029 mole) of ozone corresponding to approximately 50% completion. The product was isolated as above and analyzed by gas chromatography for *cis* and *trans* isomers.

To 5 ml. (3.02 g., 0.0538 mole) of 2-butene, 94.1% *trans* and 5.4% *cis* with 0.5% *n*-butane as impurity, in 3 ml. of *n*-pentane was added 1.4 g. (0.029 mole) of ozone. A two-phase system

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(14) R. A. Hively, *Anal. Chem.*, **35**, 1921 (1963).

formed during the ozonation. The product was isolated as above and analyzed by gas chromatography for *cis* and *trans* isomers.

**Ozonation of *trans*-3-Hexene.**—The addition of ozone to *trans*-3-hexene, 99.95% *trans*, in the absence of a solvent resulted in a violent explosion shortly after the ozonation was started whereby a dark-colored precipitate formed. When 3 vol. of *n*-pentane per volume of *trans*-3-hexene was used, the ozonation could be carried out to completion. To 20 ml. (13.6 g., 0.0162 mole) of *trans*-3-hexene in 60 ml. of hexane was added 7.6 g. (0.16 mole) of ozone. Distillation gave 4.7 g. of *trans*-3-hexene ozonide, b.p. 39.5° at 18 mm. A high yield of polymeric material was obtained, 13.7 g. The crude product was dissolved in ether and shaken with sodium bicarbonate solution to remove any propionic acid. After drying over magnesium perchlorate and removing the ether, the ozonide was distilled; b.p. 38.5° at 22 mm., $n^{25}\text{D}$ 1.4023, $d^{20}_4$ 0.9781.

*Anal.* Calcd.: active O, 12.10. Found: active O, 11.95.

**Ozonation of 2,5-Dimethyl-3-hexene.**—To 20 ml. (14.2 g., 0.127 mole) of 2,5-dimethyl-3-hexene, 99.8% *cis*, in 40 ml. of *n*-pentane was added 6.0 g. (0.125 mole) of ozone to completion. The product was twice distilled, b.p. 66° at 23 mm. 2,5-Dimethyl-3-hexene ozonide (19 g.) was obtained in high yield (95%); $n^{25}\text{D}$ 1.4115, $d^{20}_4$ 1.0398. There was almost no polymeric material.

To 15 ml. (10.7 g., 0.095 mole) of 2.5-dimethyl-3-hexene, 99.9% *trans*, in 45 ml. of *n*-pentane was added 4.7 g. (0.098 mole) of ozone to completion. The product was twice distilled and 9.6 g. of 2,5-dimethyl-3-hexene ozonide was obtained; b.p. 63–64° at 22 mm., $n^{25}\text{D}$ 1.4103, $d^{20}_4$ 1.0376. The polymeric product weighed 5.5 g.

**Ozonation of *trans*-3-Hexene in *n*-Butyraldehyde.**—To 60 ml. (40.6 g., 0.485 mole) of 3-hexene, 99.95% *trans*, in 180 ml. (147 g.) of *n*-butyraldehyde was added 23.0 g. (0.48 mole) of ozone. Distillation gave 28 g. of monomeric ozonides and 46 g. of residue. The ozonides were dissolved in an equal volume of ether and shaken with sodium bicarbonate solution. After drying over magnesium perchlorate and removing the ether, the product was redistilled. The fraction boiling at 48–49° at 7 mm. was 3-heptene ozonide, $n^{25}\text{D}$ 1.4059, $d^{20}_4$ 0.9619.

*Anal.* Calcd. for $C_7H_{14}O_3$: C, 57.45; H, 9.60; O, 32.83; active O, 10.94. Found: C, 57.5; H, 9.75; O, 33.0; active O, 10.85.

**Identification of Ozonides by Reduction with Triphenylphosphine.**—3-Hexene ozonide was reduced as follows. 3-Hexene (0.4 g., 3.03 mmoles) ozonide was mixed with 1.2 ml. of *n*-heptane and 1.2 g. (4.58 mmoles) of triphenylphosphine was added. The mixture was heated in a sealed tube for 60 min. in boiling water which completely reduced the ozonide. The tube was cooled in cold water which caused crystallization of triphenylphosphine oxide. The supernatant liquid was analyzed by gas chromatography. Two peaks were observed, corresponding to *n*-heptane (solvent) and propionaldehyde. The latter was identified by comparison of the retention time with an authentic sample of propionaldehyde and the addition of propionaldehyde to the reaction mixture and repeated chromatographic analysis. Similar experiments were made with the other ozonides. After it has been established that the reduction of ozonides by triphenylphosphine led exclusively to the corresponding carbonyl compounds, the unnatural ozonides could be identified in the same manner.

**Preparation of 2-Butene Ozonide (Isomer B).**—Triphenylphosphine (4.37 g., 0.0167 mole) was added to 25 ml. of *n*-pentane. After solid carbon dioxide was added to remove the air, the flask was connected to an effective reflux condenser and a slow stream of nitrogen was bubbled over the solution. Butene ozonide (5.2 g., 0.050 mole) was added. The ozonide was obtained by the ozonation of 2-butene (94% *trans*, 5% *cis*) and contained 13% of isomer A and 87% of isomer B. The triphenylphosphine dissolved upon shaking and triphenylphosphine oxide started to precipitate after a few minutes, whereupon acetaldehyde began to boil. After standing for 16 hr. at room temperature, the triphenylphosphine oxide was filtered off and the solution was distilled through a short column. After removal of the 2-pentane, 2.0 g. of 2-butene ozonide was obtained, b.p. 48° at 58 mm. G.l.c. analysis indicated that the product was free of component A; $n^{25}\text{D}$ 1.3815.

**Preparation of 2,5-Dimethyl-3-hexene Ozonide (Isomer A).**—2,5-Dimethyl-3-hexene ozonide (4.4 g., 0.0275 mole) prepared from the *trans* olefin (99.9% *trans*) was added to 25 ml. of *n*-pentane and treated with 4.32 g. (0.0165 mole) of triphenylphosphine. The mixture was heated for 5–10 min. in a water bath to achieve complete solution, whereupon triphenylphosphine began to precipitate. The mixture was allowed to stand for 16 hr. at room temperature and the triphenylphosphine oxide was filtered off. After removing the *n*-pentane, the remaining ozonide was distilled; 2.4 g., b.p. 61° at 21 mm., $n^{25}\text{D}$ 1.4100, $d^{20}_4$ 1.0370. Gas chromatography indicated that the more readily reducible form was removed.

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# Synthesis and Spectra of Di- and Polyphenylanthracenes

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Three diphenylanthracenes (1,9, 1,10, and 2,10) and 1,9,10-triphenylanthracene have been prepared and an improved synthesis of 1,4,9,10-tetraphenylanthracene is reported. N.m.r. spectra confirm the presence of face-to-face arrangements of the benzene rings in three of these compounds. Ultraviolet spectra of phenylanthracenes (9, 1, and 2), diphenylanthracenes (1,9, 1,10, 2,10, 2,9, 1,4, and 9,10), 1,9,10-triphenylanthracene, and 1,4,9,10-tetraphenylanthracene have been measured in methylene chloride. The red shifts in the long wave-length bands associated with di- and polyphenyl substitution are essentially additive for the entire series including those derivatives which possess parallel benzene rings. Gas–liquid chromatography of the six diphenylanthracenes has been investigated and retention times are reported.

In connection with problems arising from studies of homolytic arylation of anthracene we required authentic samples of the five diphenylanthracenes that have in common a 9-phenyl group. The 9,10 and 2,9 isomers were known but the 1,9-, 1,10-, and 2,10-diphenylanthracenes had not been described. Recent interest (*vide infra*) in the physical properties, particularly ultraviolet spectra, of systems containing perpendicular $\pi$-electron systems suggested inclusion of the polyphenylanthracenes.

A general route to diphenylanthracenes involves the preparation of the appropriate phenylanthrone followed by addition of phenylmagnesium bromide or phenyllithium. For example, 2,9-diphenylanthracene (**2**) has been prepared from biphenyl and phthalic anhydride by the sequence of reactions given in Scheme I.[1,2] Similar methods afforded 1,10- and 2,10-diphenylanthracenes (**6** and **10**) and are illustrated

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(1) R. Scholl and W. Neovius, *Ber.*, **44**, 1075 (1911).

(2) Y. Hirshberg and L. Haskelberg, *Trans. Faraday Soc.*, **39**, 45 (1943).