The mixture was cooled further to 5–10° and the reactor was carefully vented to release excess pressure. After settling, the catalyst was drained onto crushed ice, neutralized, and discarded. The alkylate layer was either quenched with ice and neutralized or placed in a monel still where all the HF and most of the benzene were removed under suction. The crude alkylbenzene was examined by glpc using a Barber–Coleman Mode 120 chromatograph equipped with a Sargent SR recorder with a coupled integrator. The stainless steel column was 150 ft × 0.02 in. and was coated with SE 30 silicon gum rubber. Another column of the same dimensions but coated with *m*-bis[*m*-(*m*-phenoxyphenoxy)phenoxy]-benzene[23] was also used. The crude product, except for that used for glpc analysis, was distilled in a glass apparatus and the fraction boiling at 128–134° (2 mm) ($n^{25}\text{D}$ 1.4805) was collected. The yield was 131.5 g or 90% of theoretical.

When alkylation was carried out in the presence of *n*-hexane, the hexane (800 cc) was charged to the reactor along with the benzene (2.5 moles) and hydrogen fluoride (10 moles). The olefin (0.6 moles) was diluted with 200 cc of *n*-hexane and pumped into the alkylator. The rest of the procedure was exactly as above. The yield of this reaction (89%) as well as all the subsequent alkylations was consistently high (87–92% of theoretical).

Alkylation by 1-Dodecene in the Absence of a Separate Catalyst Phase.—Anhydrous benzene (3.9 moles) and anhydrous hydrogen fluoride (2 moles) were charged to the reactor and heated to 55°. Agitation was started and the reactor was carefully vented to 30 psig at the same temperature.[24] A mixture of 0.6 moles of 1-dodecene in 1.3 moles of benzene was pumped into the reactor and the reaction was completed as above.

The same procedure was followed for alkylation in *n*-hexane solution except that the benzene (2.5 moles) and the dodecene (0.6 moles) were diluted with *n*-hexane (800 and 200 cc, respectively) before being charged to the reactor.

Alkylation with *trans*-6-Dodecene.—The same procedure was followed for alkylation of benzene with *trans*-6-dodecene, but the scale was only one-fifth that for 1-dodecene. When the reaction was run at 0°, stirring was continued for 30 min before the mixture was allowed to settle.

Check for Isomerization of the Phenylalkanes during Alkylation.—Two experiments were run in order to check for product isomerization under the prescribed alkylating conditions. In the first, a reaction was carried out in which benzene (1.3 moles) was alkylated at 55° in the presence of hydrogen fluoride (3 moles) with a mixture of 1-dodecene (0.2 moles) and 2-phenyldecane (0.03 mole). Analysis of the products by glpc failed to show any isomerization of the 2-phenyldecane.

In another experiment, the 2-phenyl isomer of the products from several alkylations was concentrated to 70% by distillation in a 15-plate column. The high 2-phenyl material was divided into equal parts. One was added to the olefin during alkylation and the other was added to an equal amount of a reaction mixture after alkylation was completed and the hydrogen fluoride had been completely removed. The products were analyzed by glpc and were found to contain the same isomer distribution.

Separation of the Phenyldodecane Isomers.—The product (0.65 mole) was fractionated through a 40-plate column between 128 and 135° (2 mm). Twelve different and approximately equal fractions were obtained. The first one contained 92% 5- and 6-phenyldodecanes and 8% 4-phenyldodecane. The latter was removed by passing through an F & M chromatograph, Model 720A, equipped with a 16 ft × 10 in. column coated with Chromosorb W (81%), Carbowax (18%), and silver nitrate (1%). The seventh fraction contained 60% 3-phenyldodecane and 40% 4-phenyldodecane. These were separated by the same preparatory glpc method. The last fraction of the distillate was pure 2-phenyldodecane. Nmr (CCl_4) of the individual isomers and the 5- and 6-phenyldodecanes mixture showed 2.35–2.65 (broad multiplet, 1 H, benzyllic) and 6.95–7.15 ppm (5 H, aromatic). Only the 2-phenyl isomer showed 1.18 ppm identified as the β-methyl group.[25]

Identification of 2-Methyl-2-Phenylundecane in the Product.—A solution of benzene (0.40 mole) in 1500 ml of *n*-hexane was alkylated with 1-dodecene (0.10 mole) in the presence of HF (3.0 moles) at 55° as described above. The organic layer was washed with water and NaOH as usual and then concentrated on a water bath to about 30 ml. Glpc analysis with the Carbowax–silver nitrate column or the polyphenyl ether (seven-ring) column showed a small band ($\approx 2\%$ of the product) between the 3- and the 2-phenyl isomers. This small band gave a single peak with an authentic sample of 2-methyl-2-phenylundecane. With the SE 30 silicon gum rubber column, the small band disappeared as did also the 2-methyl-2-phenylundecane band which overlapped with 3-phenyldodecane band.

Registry No.—Benzene, 71-43-2; 1-dodecene, 112-41-4; *trans*-6-dodecene, 7206-17-9; hydrogen fluoride, 7664-39-3.

---

[23] This compound is commonly known as poly-*m*-phenyl ether (seven ring) and was obtained from Monsanto Research Corp., Dayton, Ohio.

[24] In a number of previous runs it had been established that this procedure (in which excess HF is charged and then partially vented to a certain pressure) gives an amount of HF in the reactor which is reproducible enough to avoid any variation in the product distribution.

[25] M. M. Crutchfield, private communication. The spectra of 2-methyl-2-phenyldecane and 4-methyl-4-phenylundecane show the β-methyl groups at 1.25–1.30 ppm. The signal for the benzyllic proton is absent.

Ozonolysis. IX. The Alkene Ozonation Oligomer

Fred L. Greenwood[1] and Harry Rubinstein[2]

Departments of Chemistry, Tufts University, Medford, Massachusetts, and Stanford University, Palo Alto, California

Received March 31, 1967

The ozonation products from the geometric isomers of 2-butene, 2-pentene, and 3-hexene have been determined. The *cis*-alkenes gave excellent yields of ozonide and minor amounts of aldehyde and oligomer. With the *trans*-alkenes oligomer was the major product; in *n*-pentane solvent little aldehyde and a minor amount of ozonide were formed. In methylene chloride solvent *trans*-3-hexene gave a markedly increased amount of aldehyde but the same yield of ozonide as in pentane solvent. However, in ether solvent this alkene gave about twice as much ozonide as in pentane or methylene chloride solvent. The ozonation temperature exerted a minor effect on the relative amounts of products. The evidence does not support any of the structures that have been suggested for the oligomer and a new structure is proposed.

From the time that the ozonation of alkenes has been a practical laboratory process, it has been recognized[3] that substances which were polymeric[4] could be formed in this reaction. Indeed, it was a study of these substances that led Staudinger[5] to postulate that a molozonide must be the first product of an alkene–ozone reaction. Although some peroxidic oligomer would appear to be formed in most, if not all, alkene ozonations, these substances have received little attention. Fre-

---

[1] During the latter stages of the work reported herein, F. G. is indebted to the Department of Chemistry, Stanford University, for its hospitality and to the Petroleum Research Fund of the American Chemical Society for partial financial support during sabbatical leave from Tufts University.

[2] Participant, summer 1965, NSF Research Participation for College Teachers Program.

[3] C. Harries and R. Seitz, *Ann.*, **410**, 21 (1915); C. Harries and H. Wagner, *ibid.*, **410**, 29 (1915).

[4] Actually, these substances should be designated as oligomers and not polymers, for they are of low molecular weight.

[5] H. Staudinger, *Ber.*, **58**, 1088 (1925).

TABLE I

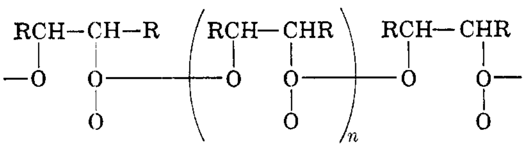
OZONATION PRODUCTS FROM ALKENE GEOMETRIC ISOMERS[a]

Alkene	Solvent	Reaction temp, °C	C in alkene, g	Aldehyde, mmoles	C in aldehyde, g	Oligomer, g	C in oligomer, g	Oligomer, mol wt	2-Butene ozonide, mmoles	2-Pentene ozonide, mmoles	3-Hexene ozonide, mmoles	C in ozonide, g
cis-2-Butene	n-C_5H_{12}	−30	2.40	4.72	0.11	0.52[b]	0.23	286				
	n-C_4H_{10}	−70	2.40			0.49			35.7			1.71
trans-2-Butene	n-C_5H_{12}	−30	2.40	9.51	0.23	2.10[b]	0.97	229				
	n-C_4H_{10}	−30	2.40			1.60			18.0			0.86
cis-2-Pentene	n-C_5H_{12}	−30	3.00	MeCHO, 2.70 EtCHO, 3.24	0.18	0.52[b]	0.25	370				
	n-C_4H_{10}	−30	3.00			0.32			1.83	35.8	3.70	2.50
trans-2-Pentene	n-C_5H_{12}	−30	3.00	MeCHO, 4.18 EtCHO, 7.14	0.36	2.61[b]	1.25	395				
	n-C_4H_{10}	−30	3.00			2.28			0.83	14.5	2.73	1.11
cis-3-Hexene	n-C_5H_{12}	−30	3.60	3.80	0.14	0.46	0.25	542			43.9	3.16
	n-C_5H_{12}	−70	3.60	3.17	0.11	0.42	0.23				40.4	2.91
	Et_2O	−110	3.60	3.10	0.11	0.18	0.10				40.1	2.89
trans-3-Hexene	n-C_5H_{12}	−30	3.60	8.81	0.32	3.77[b]	1.96	512			11.3	0.81
	n-C_5H_{12}	−70	3.60	8.34	0.30	4.56[c]	2.46	567			10.4	0.75
	CH_2Cl_2	−30	3.60	32.0	1.15	2.44	1.29	347			12.1	0.87
	CH_2Cl_2	−70	3.60	21.2	0.76	3.23	1.71				11.6	0.84
	Et_2O	−30	3.60	17.6	0.63	1.56	0.83	335			21.8	1.57
	Et_2O	−70	3.60	15.6	0.56	2.06	1.09	458			20.6	1.48
	Et_2O	−110	3.60	12.5	0.45	2.73[b]	1.45	726			17.7	1.27

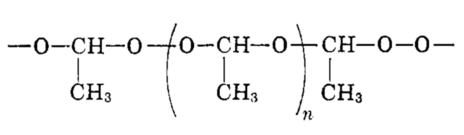
[a] All data are calculated on the basis of 50.0 mmoles of ozone reacting with excess alkene. [b] These oligomers were reduced with lithium aluminum hydride. [c] Designated as oligomer A in text.

quently, in considerations of the mechanism of the alkene–ozone reaction, they are completely ignored and this despite the fact that the oligomer may be the principal reaction product.

The oligomer has been formulated in various ways. Staudinger[5] considered that an oxygen–oxygen bond of the molozonide underwent cleverage and that the resulting species polymerized to give a substance of the structure



Rieche, *et al.*,[6] have reported the most extensive study of the peroxidic oligomer and, while they recognized that the oligomer was sensitive to heat, they did not realize the full extent of this sensitivity. From a consideration of chemical behavior and molecular refraction, they concluded that their 2-butene ozonation oligomer consisted of ethylidene groups joined by alternating peroxidic and ether linkages. The mol-



ecular weight values were always in the range of four- to eightfold the unit $C_4H_8O_3$. The parachor value and comparison of the ultraviolet spectrum of the oligomer with that of various peroxides suggested that the oligmer may exist as a large ring, but they did not view the ring structure as firmly established. Criegee[7] envisaged the oligomer as resulting from polymerization of the dipolar ion $R\overset{+}{C}HO\overset{-}{O}$. Bailey and Mainthia[8] and Perry[9] reported some work on the oligomers from the ozonation of phenanthrene and norbornylene, respectively. They concluded that the best structure for the oligomer was one in which the hydrocarbon portions of the oligomer were joined through an ozonide ring.

The ozonation of the stereoisomers of the simpler, symmetrically substituted ethylenes has been studied and the results are recorded in Table I. The first striking fact is the influence of alkene geometry on the course of the ozonation reaction. The *cis*-alkenes gave excellent yields of ozonide and very little aldehyde and oligomer and the solvent had little effect on the course of the reaction. With the *trans*-alkenes, on the other hand, the oligomer was in nearly all cases the major product. Schröder[10] has also reported an nstance of the influence of alkene geometry on the yield of ozonide. In the *trans*-alkene ozonations there were some striking solvent effects and some minor temperature effects. For volatility reasons most of the ozonations with a *trans*-alkene were carried out with *trans*-3-hexene. In n-pentane and in methylene chloride, two solvents of markedly different polarity (n-pentane, $\mu < 0.05$ D.;[11] methylene chloride, μ 1.47 D.[12]), the same amount of ozonide was formed at a reaction temperature of −30 and −70°. However, the amount of aldehyde formed in the more polar solvent was much greater and less aldehyde was formed at −70° than was observed at −30°. A consequence of these latter facts was that more oligomer was formed at −70° than at −30°. Verification of the fact that during the ozonation of an alkene in n-pentane solvent more aldehyde was formed at higher reaction temperatures was obtained some years ago in our laboratory when solutions of 3-octene were ozonized and the infrared spectra of the reaction mixtures were recorded at −70°. With an ozonation temperature of −70° there was a very weak but a definite absorption peak at 1739 cm^{-1} which was attributable to aldehyde. With an ozonation temperature of −40° the absorption at 1739 cm^{-1} was still weak but clearly stronger than that observed when the ozonation temperature was −70°. In ether, a solvent

---

(6) A. Rieche, R. Meister, and H. Sauthoff, *Ann.*, **553**, 187 (1942).

(7) R. Criegee, *Record Chem. Progr.*, **18**, 111 (1957).

(8) P. S. Bailey and S. B. Mainthia, *J. Org. Chem.*, **23**, 1089 (1958).

(9) R. H. Perry, Jr., *ibid.*, **24**, 829 (1959).

(10) G. Schröder, *Chem. Ber.*, **95**, 733 (1962).

(11) J. H. La Rochelle, *Dissertation Abstr.*, **17**, 46 (1957).

(12) B. Krishna and K. K. Srivastava, *J. Chem. Phys.*, **32**, 663 (1960).

which is less polar (μ 1.18 D.[13]) than methylene chloride but which may function as a nucleophile, the yield of ozonide from *trans*-3-hexene was markedly enhanced over that found with methylene chloride as solvent and this increased ozonide yield meant a diminished yield of aldehyde and of oligomer. As the reaction temperature was lowered from −30 to −110°, there was a diminution in the yield of aldehyde and ozonide and a corresponding increase in the yield of oligomer.

In an endeavor to gain some knowledge of the structure of the oligomers, they were reduced with lithium aluminum hydride. The expected alcohols were obtained in good yield. The aqueous layer of the hydrolysis mixture was extracted exhaustively with ether and the minute amount of residue remaining after evaporation of the ether was tested with periodic acid for the presence α-diol. In only one instance was a firm positive test obtained and that was with the oligomer which was obtained from the ozonation of *trans*-2-butene at -55° without solvent, an experiment which is not reported in Table I. In all other cases the residue gave a weakly positive or negative test for α-diol. The minute amount of this residue enables one to dispense with the Staudinger structure for the oligomer, for an oligomer of such structure should give an excellent yield of α-diol. The evidence does indicate that there may be present in some oligomers a small amount of linkage of the type -OCH(R)CH(R)O-, but there can be very little, if any, of this in most oligomers.

From a symmetrical alkene the Criegee mechanism would demand an amount of carbon in the aldehyde equal to that occurring in the oligomer. The data for 2-butene and 3-hexene in Table I show that this is rarely the case. The carbon–hydrogen analyses of the oligomers were never so low as those required by the formula $RCHO_2$, for those oligomers which were obtained from ozonations which were carried out in *n*-pentane the carbon–hydrogen values were those required by the formula $R_2C_2H_2O_3$, and for the others the carbon-hydrogen values fell between those required by the two above-mentioned formulas. It is conceivable that under some ozonation conditions the resulting oligomer may have the structure suggested by Criegee, but in most instances it cannot.

To obtain some information relating to Rieche's oligomer structure, the lithium aluminum hydride reduction of oligomer A (*cf.* footnote *c*, Table I) was compared with that of 3-hexene ozonide, a compound with peroxidic and ether linkages attached to the same carbon atom. If one compares the stoichiometry of these two reactions which is reported in the Experimental Section, one is tempted to conclude that Rieche's structure with alternating peroxidic and ether linkages has some merit. However, the thermochemistry of these two reductions was markedly different. The oligomer reduction was very exothermic, whereas in the ozonide reduction no undue caution needed to be observed during the addition of the hydride. This difference would point to a rather fundamental structural difference between the oligomer and the ozonide.

If the oligomer had Rieche's structure, one might expect that in its nmr spectrum the methine proton absorption should show considerable structure, for each such proton is attached to a carbon atom which carries the same alkyl group and both a peroxidic and an ether linkage. In fact, the methine proton absorption of oligomer A was a broad, structureless peak (5.70–4.86 ppm) which was centered at 5.28 ppm. The position of the methine proton absorption is influenced by the number of oxygen atoms attached to the methine carbon atom. Thus, the nmr absorption of such a methine proton in the following compounds[14] is centered at the position indicated: 2-butanol, 3.87 ppm; *sec*-butyl hydroperoxide, 3.94; di-*sec*-butyl peroxide, 3.87; diethyl acetal, 4.72; α-hydroxyisobutyl isobutyl peroxide, 4.86; 2-butene ozonide, 5.47. A possible explanation of the broad, structureless, methine proton peak of oligomer A is that the methine carbon atoms have attached to them a variety of types of oxygen linkages. These would give rise to absorption at somewhat varied positions which when superimposed would lead to a broad, structureless peak.

Infrared absorption spectra indicated the presence in oligomer A of some type of very labile linkage. The oligomer was stored at a low temperature and the spectrum of a sample which was determined as rapidly as possible showed a bare suggestion of hydroxyl and carbonyl absorption at 3425 and 1748 cm^{-1}, respectively. The peroxide absorption was a broad band with a single peak at 1079 cm^{-1} (strong) which had a shoulder at 1142 cm^{-1}. A sample of the oligomer decreased markedly in viscosity on standing for 3 days at room temperature. Absorption at 1724 cm^{-1} (m) in the infrared spectrum of this material indicated[15a] the presence of carboxyl groups. The hydroxyl peak at 3425 cm^{-1} (w) was now quite marked. A shoulder at 1739 cm^{-1} on the 1724-cm^{-1} peak in conjunction with a peak at 2725 cm^{-1} (w) suggested[15b] the presence of an aldehyde function. The peroxide absorption was now a broad peak with a doublet at 1100 and 1079 cm^{-1} (s) with a shoulder at 1142 cm^{-1}. Clearly, room temperature is sufficient to effect fundamental changes in the structure of the oligomer.

The data indicate that the alkene ozonation oligomer does not have any specific structure. It would appear that its structure will depend on the ozonation conditions. Both the dipolar ion fragment and the aldehyde fragment are incorporated into the oligomer in varying ratios and this reaches a value of 1:1 when *n*-pentane is the solvent. These fragments would appear to be linked by a variety of types of oxygen linkages which do not occur in any regular sequence. It is clear, also, that in the oligomer one will rarely have carbon–carbon bonding between carbon atoms which were linked by the double bond in the alkene.

The nmr spectrum of oligomer A may be interpreted to indicate a variety of oxygen linkages between the hydrocarbon portions of the oligomer (*vide supra*) and the infrared absorption studies (*vide supra*) indicate a very labile oxygen linkage. This labile oxygen linkage would not appear to be a carbon atom

---

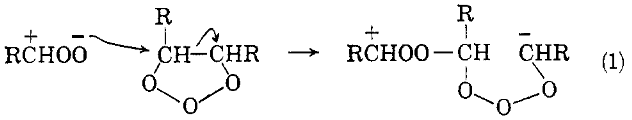
[13] L. Sobczyk and J. K. Syrkin, *Roczniki Chem.*, **31**, 1245 (1957); *Chem. Abstr.*, **52**, 7798*i* (1958).

[14] For samples and nmr spectra of some of the compounds we are indebted to Dr. H. S. Mosher, Stanford University, and to Dr. T. Mill, Stanford Research Institute.

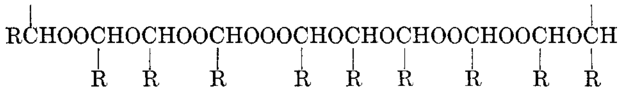
[15] (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 167; (b) *ibid.*, p 157.

carrying two peroxidic linkages, for such structures are quite stable.[16] Also, it would not appear to be a carbon atom carrying both a peroxidic linkage and another oxygen atom, for ozonides, α-hydroxy dialkyl peroxides, and α-hydroperoxy ethers are stable. It is suggested that this labile linkage in oligomer A is one with three contiguous oxygen atoms. There is one report in the literature[17] of a stable compound with three contiguous oxygen atoms and that is the compound CF_3OOOCF_3, bp −13.5°. A "trioxide" has been postulated by Bartlett and Günther[18] as an intermediate in the reaction of *t*-butyl hydroperoxide with lead tetraacetate and of *t*-butyl hydroperoxide with ozone. Such a linkage is rather well established in the molozonide.[19a–c] Here, however, it is in a ring and constitutes an unstable, high-energy system. In an open-chain system three contiguous oxygen atoms should be able to get into a much more favorable conformation which would be considerably more stable than the molozonide structure.

The data of Table I may be explained qualitatively by the relative stability of *cis*- and *trans*-molozonides and the conversion of the molozonide to ozonolysis products by a polar process. Published data[19b] indicate that the *cis*-molozonide is an extremely unstable species and subsequent work[19d] has substantiated this instability. The *trans*-molozonide, on the other hand, is sufficiently stable to have been observed as a solid[19a,b] and in solution.[19c] The alkene–ozone reaction would appear to be a stereospecific one;[19a–c] thus, in a *trans*-alkene–ozone reaction at any instant of time one would expect the molozonide concentration to be markedly greater than in a *cis*-alkene–ozone reaction. If one accepts the Criegee cleavage of the molozonide to aldehyde and dipolar ion fragments, then in an ozonation reaction mixture one may consider that there are three reactive fragments—the two cleavage fragments and the molozonide. There is evidence[19c] that the molozonide may undergo attack at a ring carbon atom by a nucleophilic oxygen atom. One would not expect an aldehyde to give this type of attack, but the dipolar ion may well react in such fashion. Thus, in an ozonation reaction mixture one may consider that there are two competing, principal reactions: (1) reaction of dipolar ion with aldehyde to produce ozonide and (2) reaction of dipolar ion with molozonide to initiate the formation of oligomer. In a *cis*-alkene–ozone reaction, (1) would be expected to predominate and in this way one may explain the excellent yields of ozonide and the minor amounts of aldehyde and oligomer that are obtained from *cis*-alkenes.


(1)

In a *trans*-alkene–ozone reaction the dipolar ion–molozonide reaction becomes important and one may view the reaction as given in eq 1. The resulting species may be viewed as proceeding to oligomer in a variety of ways: it could react with cleavage fragments, it could react with more molozonide, and it could lose aldehyde and the remaining fragment could react with more molozonide or cleavage fragments. There is the possibility, of course, that some oligomer may arise by combination of cleavage fragments. With the above-described processes one would expect that the structure of the oligomer will vary with experimental conditions. One possible structure that one could write would be



$$\text{R}\overset{|}{\text{C}}\text{HOO}\underset{\substack{|\\ \text{R}}}{\text{C}}\text{HO}\underset{\substack{|\\ \text{R}}}{\text{C}}\text{HOO}\underset{\substack{|\\ \text{R}}}{\text{C}}\text{HOOO}\underset{\substack{|\\ \text{R}}}{\text{C}}\text{HO}\underset{\substack{|\\ \text{R}}}{\text{C}}\text{HO}\underset{\substack{|\\ \text{R}}}{\text{C}}\text{HOO}\underset{\substack{|\\ \text{R}}}{\text{C}}\text{HOO}\underset{\substack{|\\ \text{R}}}{\text{C}}\text{HO}\overset{|}{\underset{\substack{|\\ \text{R}}}{\text{C}}}\text{H}$$

The presence of such a material in oligomer A could explain the nmr spectrum and the lability of this oligomer and also the large amount of heat evolved when this oligomer was reacted with hydride.

One would expect that in a polar solvent more aldehyde would be formed. Also, if the above-described process is the source of the oligomer, then the lower the ozonation temperature for a *trans*-alkene the more oligomer one should find. The data show these trends.

In several of the recent studies on the ozonation reaction, gas chromatography has been used. Temperatures which would seem to be rather high for peroxidic compounds have been employed and in some instances crude ozonation reaction mixtures have been subjected to gas chromatography. Having samples of ozonide and oligomer at hand, a few experiments were carried out on the heat stability of these substances. With a silicone SF96 column at 65°, 3-hexene ozonide gave but a single peak. At 80° peaks due to decomposition products appeared before the main ozonide peak and at 100° these decomposition peaks were more pronounced. Not surprisingly, oligomer A was found to contain a small amount of ozonide, and at 65° no other peak was observed for 40 min after elution of the ozonide. At 80 and at 100° the ozonide in the oligomer gave the decomposition pattern which was observed with the ozonide itself; of more importance was the fact that before the ozonide elution was complete either the oligomer or its pyrolysis products began to be eluted and this elution continued for a long period of time (40–60 min). The facts would suggest that one must exercise caution with the temperature employed during the gas chromatography of ozonides, and, since it would appear to be impossible to avoid some oligomer formation during ozonation, the practice of subjecting crude ozonation reaction mixtures to gas chromatography is a questionable one.

Experimental Section

n-**Butane** (Matheson Scientific, Inc., instrument grade) was led through concentrated sulfuric acid, glass wool, a tube (60 cm × 30 mm) which was filled with sodium ribbon, and then condensed in the reaction flask. *n*-Pentane was from the same source and was purified as described previously.[20] Anhydrous

---

[16] F. H. Dickey, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **71**, 1432 (1949).

[17] V. A. Ginsburg, E. S. Vlasova, N. M. Vasil'eva, N. S. Mirzabekova, S. P. Makarov, A. I. Shchekotikhin, and A. Y. Yakubovich, *Dokl. Akad. Nauk SSSR*, **149**, 97 (1963).

[18] P. D. Bartlett and P. Günther, *J. Am. Chem. Soc.*, **88**, 3288 (1966).

[19] (a) R. Criegee and G. Schröder, *Chem. Ber.*, **93**, 689 (1960); (b) F. L. Greenwood, *J. Org. Chem.*, **30**, 3108 (1965); (c) P. S. Bailey, J. A. Thompson, and B. A. Shoulders, *J. Am. Chem. Soc.*, **88**, 4098 (1966); (d) F. L. Greenwood, unpublished results.

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

ether (Mallinckrodt Chemical Co.) was stored over sodium ribbon. Methylene chloride (Matheson Scientific, Inc., Spectroquality) was used as received. *cis-* and *trans*-2-butene were research grade materials (Phillips Petroleum Co.). *cis-* and *trans*-2-pentene were API standard samples (Carnegie Institute of Technology). *cis*-3-hexene and some of the *trans* isomer were API standard samples. Some of the *trans*-3-hexene (Chemical Samples Co.) was material which had been distilled from hydroquinone under a nitrogen atmosphere through a spinning-band column: bp 72.0° (761 mm); $n^{25}\text{D}$ 1.3913.

3-Octene was prepared by a Boord synthesis. Distillation under a nitrogen atmosphere through a spinning-band column gave material of bp 122.8° (748 mm), $n^{25}\text{D}$ 1.4112.

2-Butene ozonide was prepared from 51.0 mmoles of the *cis*-alkene and 48.4 mmoles of ozone in 200 ml of *n*-butane at −70°. The solvent was removed on a rotary evaporator with the reaction flask in a Dry Ice–alcohol bath. The ozonide was collected on the rotary evaporator by permitting the reaction flask to warm to room temperature. On distillation there was collected as ozonide 3.61 g, 72% yield, of material: bp 43.8–44.0° (145 mm), $n^{25}\text{D}$ 1.3810.

Anal.[21] Calcd for $C_4H_8O_3$: C, 46.2; H, 7.7; mol wt, 104. Found: C, 46.3; H, 7.9; mol wt, 106 (cryoscopic, benzene).

The infrared spectrum of the ozonide showed no absorption in the hydroxyl or carbonyl regions. The strongest band of the spectrum was one at 1111 cm^{-1} with a shoulder at 1131 cm^{-1}. It is questionable whether this peak is diagnostic for ozonides as some authors have stated, for all peroxides have strong absorption in this region.[22]

The nmr spectrum[23] (60 Mc, neat, Me_4Si external standard) of the ozonide consisted of a doublet centered at 1.53 ppm and two overlapping quadruplets, one of which was centered at 5.44 ppm and the other at 5.48 ppm. The integrated areas of these two peaks were in the ratio 3.10:1.00. Both methine quadruplets had J = 5.0 cps.

3-Hexene ozonide was prepared from 34.7 mmoles of the *cis*-alkene and 33.0 mmoles of ozone in 250 ml of *n*-pentane at −30°. The solvent was removed on a rotary evaporator with the reaction flask in a bath which was cooled to −50°. The ozonide was collected on the rotary evaporator by permitting the reaction flask to warm to room temperature. On distillation there was collected as ozonide 3.82 g, 88% yield, of material: bp 43.5–44.0° (20 mm); $n^{25}\text{D}$ 1.4010.

Anal. Calcd for $C_6H_{12}O_3$: C, 54.5; H, 9.1; mol wt, 132. Found: C, 54.7; H, 9.3; mol wt, 126 (cryoscopic, benzene).

The infrared spectrum of the ozonide showed no absorption in the hydroxyl or carbonyl regions. The strongest band of the spectrum was a broad one which consisted of a doublet at 1117 and 1096 cm^{-1}. Its nmr spectrum has been reported earlier.[24]

Low-Temperature Infrared Studies.—Solutions of 2.24 g of 3-octene in 40 ml of *n*-pentane were treated at −40 and at −70° with 95% of the theoretical amount of ozone. Without permitting the reaction mixture to warm, it was transferred to a low-temperature infrared cell[25] and the spectrum recorded at −70°. Weak absorption at 1739 cm^{-1} was always observed, with the absorption being stronger with the reaction mixture which was prepared at −40° than with the one prepared at −70°. The other important feature of the spectra was a broad, intense peak which consisted of a doublet at 1117 and 1101 cm^{-1}.

Ozonation Reactions.—The ozonations reported in Table I were carried out by dissolving about 40.0 mmoles of the alkene in 250 ml of solvent, cooling the solution to the desired temperature, and adding 95% of the theoretical amount of ozone at a rate of some 500 mg/hr. Without permitting it to warm, the reaction flask was transferred to a rotary evaporator and the flask immersed in a cold bath. The temperature of this bath with the various solvents was, *n*-butane, −75°; *n*-pentane and ether, −50°; methylene chloride, −40°. The solvent was condensed in a liquid nitrogen cooled trap; after warming to room temperature the weight and volume (*ca.* 240 ml) of the solvent were determined. The reaction flask was allowed to warm to room temperature and the ozonide was collected in a different liquid nitrogen cooled trap. The yield of ozonide was obtained by direct weighing of the appropriate fraction of distillate which was collected from a vacuum distillation. The viscous, colorless oligomer remaining in the reaction flask was transferred to a small, tared flask with *n*-pentane washings in the case of the oligomers from 3-hexene and with anhydrous ether washings in the case of the ologomers from the other alkenes. The oxygen–carbon ratio in the oligomers from 2-butene and 2-pentene was high enough that these materials were only slightly soluble in *n*-pentane. The solvent was removed *in vacuo* and the amount of oligomer was obtained by direct weighing. The oligomer was stored in the freezing compartment of the refrigerator. These oligomers were sensitive to shock, but only with the one from 2-butene was caution necessary. In one instance some of this oligomer wetted a glass stopper and on removal of the stopper the neck of the flask was shattered. However, the oligomer in the flask did not explode.

Aldehyde Yields.—The amount of aldehyde in the solvent which was condensed in the liquid nitrogen cooled trap was obtained by gas chromatographic analysis. Because of operative difficulties this analysis was not done where *n*-butane was the solvent. The chromatographic instrument was an Aerograph Model A-90-P3. The chromatographic columns used for the various analyses follow: *n*-pentane and ether, 0.25 in. × 10 ft diethyleneglycol succinate; methylene chloride, 0.25 in. × 10 ft 30% Carbowax 400. Solutions of known concentration were prepared in order to obtain the appropriate correction factors.

Ozonide Yields.—It was impossible to obtain reliable ozonide yields from 2-butene and 2-pentene with *n*-pentane solvent because much of the ozonide was entrained with the solvent. The total yield of ozonide in each experiment was obtained by direct weighing of the distilled ozonide. The amounts of C_4, C_5, C_6 ozonide which were obtained from 2-pentene were determined by gas chromatography of a *n*-pentane solution of the ozonide on a 0.25 in. × 5 ft SF 96 silicone column. It is important that the injection port and column temperature do not exceed *ca.* 65°. The 2-butene ozonide and 3-hexene ozonide in the ozonide from 2-pentene were verified by authentic samples. The central peak was assumed to be 2-pentene ozonide. Here the relative peak areas were assumed to be proportional to the weight per cent of each ozonide.

Oligomers.—The various oligomers gave the following analyses: from 2-butene, C, 46.2; H, 7.8; from 2-pentene, C, 48.8; H, 8.5; from 3-hexene in *n*-pentane solvent, C, 54.1; H, 9.2; from 3-hexene in other solvents, C, 52; H, 8.8. The oligomers were unstable at room temperature and the details of infrared spectra (CCl_4 solution) proving this are outlined in the Discussion. The nmr spectrum (60 Mc, CCl_4 solution, Me_4Si internal standard) of oligomer A was determined at −10°. The spectrum consisted of a structureless peak centered at 5.28, a second structureless peak centered at 1.70, and a distorted triplet centered at 0.95 ppm. The latter two peaks overlapped slightly. The integrated areas of these peaks were in the ratio 1.00:2.27: 3.15.

Thermal Stability of Ozonide and Oligomer during Gas Chromatography.—In order to check the stability of 3-hexene ozonide and of oligomer A during gas chromatography, *n*-pentane solutions of these two materials were chromatographed at injection port and column temperatures of 65, 80, and 100°. A 0.25 × 78 in. silicone SF 96 column and a helium flow of 75 ml/min were used. At 65° the ozonide had a retention time of 16 min and showed no evidence of decomposition. The oligomer contained a small amount of ozonide, but there was no elution of oligomer or its decomposition products during a period of 60 min. On injection of the ozonide at 80°, peaks due to pyrolysis products appeared before the main ozonide peak. The oligomer gave approximately the same pattern as the ozonide, but in addition and of importance there was a slow elution of oligomer or its pyrolysis products for some 40 min after the main ozonide peak. At 100° both the ozonide and oligomer gave the same behavior as at 80° except that the decomposition was more extensive.

Reduction of Oligomers.—In a three-necked flask which was fitted with a stirrer, reflux condenser, dropping funnel, and thermometer which reached into the reaction mixture was placed 0.80 g of lithium aluminum hydride and 50 ml of anhydrous ether. The mixture was refluxed for 30 min, cooled to −10°, and a solution of 1.00 g of oligomer in 25 ml of dry ether was

---

(21) Analyses were by Schwartzkopf Microanalytical Laboratory, Woodside, N. Y.

(22) F. Welch, H. R. Williams, and H. S. Mosher, *J. Am. Chem. Soc.*, **77**, 551 (1955); H. R. Williams and H. S. Mosher, *Anal. Chem.*, **27**, 517 (1955).

(23) For the nmr spectra we are indebted to Dr. Lois Durham, Stanford University.

(24) F. L. Greenwood and B. J. Haske, *Tetrahedron Letters*, No. 11, 631 (1965).

(25) The cells were essentially the same as that described by R. C. Lord, R. S. McDonald, and F. A. Miller, *J. Opt. Soc. Am.*, **42**, 149 (1952). A low-temperature cell filled with solvent was placed in the reference beam.

added at such a rate that the temperature of the reaction mixture did not rise above −5°. The reaction mixture was refluxed for 30 min and cooled to −10°, a solution of 4.13 g of concentrated sulfuric acid in 50 ml of water was added dropwise, and again the mixture was refluxed. The layers of the reaction mixture were separated and the ether layer was extracted with two 25-ml portions of water which were combined with the aqueous layer. The aqueous solution was shaken for a short time under vacuum to remove ether and the solution was distilled to give four 15-g portions of distillate. This distillate was gas chromatographed on a 0.25 in. × 10 ft 10% Ethofat on Fluoropak column. In the aqueous distillates from the various reductions the following alcohols were found: oligomer from 2-butene, ethanol; oligomer from 2-pentene, ethanol and 1-propanol; oligomer from 3-hexene, 1-propanol.

The aqueous residue remaining after the distillation and the ether layer were placed in a continuous ether extractor. After 4 days of operation the ether was removed through a helix-packed column. The small amount of ether remaining in the flask was removed with a stream of nitrogen. The minute amount of water-insoluble residue was worked with 0.5 ml of water and this water extract was tested with periodic acid. In every instance the test for α-diol was weakly positive or negative. A firm positive test was never obtained.

Oligomer A Reduction, Quantitative Study.—The apparatus was the same as that described for the other reductions. The apparatus was flushed with nitrogen and connected to a gas collection system which was filled with saturated, aqueous salt. The oligomer (2.04 g) was dissolved in 75 ml of dry ether and the solution was placed in the reaction flask and cooled to −15°. In the dropping funnel was placed 50 ml (pipet) of a water white, ethereal solution of lithium aluminum hydride which by standardization[26] was found to contain 37.8 mmoles of hydride. The addition of the hydride was at such a rate that the temperature of the reaction mixture did not rise above −10° and required 55 min. The reaction was very exothermic and the hydride had to be added cautiously. That an excess of hydride was used was indicated by a rapid drop in the temperature of the reaction mixture before all of the hydride had been added. The reaction mixture was refluxed for 30 min. The gas evolved during the reaction was bubbled through concentrated sulfuric acid and had a volume of 709 ml (STP), 31.6 mmoles. This gas burned with a pale blue flame and it was assumed to be hydrogen.

For hydrolysis the reaction mixture was cooled to −15°, a solution of 7.8 g of concentrated sulfuric acid in 100 ml of water was added dropwise, and the mixture was refluxed for 15 min. The gas evolved was bubbled through concentrated sulfuric acid and had a volume of 1984 ml (STP), 88.6 mmoles. This gas was assumed to be hydrogen and it indicated that hydride equivalent to 15.6 mmoles of lithium aluminum hydride had reacted with the oligomer.

The layers of the reaction mixture were separated and the ether layer was extracted with four 25-ml portions of water which were combined with the aqueous layer. This aqueous solution was distilled to give four fractions (total wt, 75.8 g) which were found by gas chromatography (0.25 in × 5 ft Porapak Q column) to contain 1.46 g of 1-propanol. By gas chromatography (0.25 × 78 in. 20% Carbowax 20 M column) the ether layer was found to contain 0.36 g of 1-propanol. The total 1-propanol obtained was 1.82 g which contained 1.09 g of carbon. The oligomer used contained 1.10 g of carbon.

The aqueous residue from the distillation and the ether layer were placed in a continuous ether extractor. After 1 week of operation the ether was removed through a helix-packed column to leave a minute amount of water-insoluble oil. This was worked with a small amount of water and this aqueous extract gave a negative test for α-diol with periodic acid.

3-Hexene Ozonide Reduction.—The reaction was carried out as described immediately above for the oligomer A reduction. Lithium aluminum hydride (37.6 mmoles) and ozonide (2.04 g, 15.5 mmoles) were used. This reaction was not nearly so exothermic as the oligomer reduction; the hydride–ether solution could be added quite rapidly with the reaction flask being cooled with an ice–water bath. During the ozonide–hydride reaction, 931 ml (STP), 28.7 mmoles, of gas was evolved. By mass spectrometry[27] hydrogen was found to be the only gas evolved during the reaction. Hydrolysis of the reaction mixture gave 2127 ml (STP), 94.9 mmoles of gas. Thus, hydride equivalent to 13.9 mmoles of lithium aluminum hydride reacted with the ozonide. The aqueous distillate was found to contain 1.46 g of 1-propanol and the ether layer contained 0.42 g, making a total yield of 1.88 g. The theoretical yield of 1-propanol was 1.86 g.

Registry No.—*cis*-2-Butene, 590-18-1; *trans*-2-butene, 624-64-6; *cis*-2-pentene, 627-20-3; *trans*-2-pentene, 646-04-8; *cis*-3-hexene, 7642-09-3; *trans*-3-hexene, 13269-520-8; 2-butene ozonide, 13943-08-3; 3-hexene ozonide, 13943-09-4.

---

[26] H. Felkin, *Bull. Soc. Chim. France*, 347 (1951); E. Wiberg and R. U. Lacal, *Rev. Acad. Cienc. Exact. Fis. Quim. Nat. Zaragoza*, **10**, 97 (1955); *Chem. Abstr.*, **51**, 15319*d* (1957).

[27] We are indebted to Stanford Research Institute for this analysis.

Some 9,10-Disubstituted Derivatives of *cis*-Decalin, *cis*-Δ^2-Octalin, and *cis*-$\Delta^{2,6}$-Hexalin

William Bruce Scott and Richard E. Pincock

Department of Chemistry, University of British Columbia, Vancouver 8, Canada

Received April 14, 1967

The synthesis of several *cis*-decalin, *cis*-Δ^2-octalin, and *cis*-$\Delta^{2,6}$-hexalin derivatives with substituents in the 9,10-bridgehead positions is reported. Beginning with 9,10-bis(hydroxymethyl)-$\Delta^{2,6}$-hexalin (I, X = OH), displacement on its dimesyloxy derivative by cyanide ion gave the dinitrile I (X = CN) and a cyclic aminonitrile (IV). Hydrolysis of the dinitrile followed by $LiAlH_4$ reduction produced the extended diol, 9,10-bis(2-hydroxyethyl)-$\Delta^{2,6}$-hexalin (V, X = OH). This was converted in turn to the dimesylate, dibromide, and diiodide compounds. The diiodide, *cis*-9,10-bis(2-iodoethyl)-$\Delta^{2,6}$-hexalin, by several attempted cyclization reactions, gave predominately *cis*-9-ethyl-10-vinyl-$\Delta^{2,6}$-hexalin through an intramolecular hydrogen transfer. The *cis*-9,10-dimethyl decalin, octalin, and hexalin compounds were also prepared. The nmr spectra of several of the 9,10-bis-($-CH_2X$)-Δ^2-octalins (for X = OAc, O_3SCH_3, I, and the cyclic ether X = –O–) showed AB quartets for the 9,10-methylene protons. The magnetic nonequivalence of these two protons arises from the asymmetry produced by the presence of a double bond in one ring of this otherwise symmetrical bicyclic system.

In order to dampen the rates of conformational changes (such as the chair–chair inversion of cyclohexanes), a simple intuitive approach is to build up the number and size of groups which must be eclipsed at some time during the transformation. Although the rates of bond rotations of some ethane derivatives, and correspondingly of cyclohexyl derivatives, do not seem to depend primarily on the size of substituents,[1] it is still true that *massive* substitution can slow rates of rotation. For example, the activation energy for bond rotation in ethane, 2.8 kcal,[2] is increased to 10.8 kcal in

---

[1] E. B. Wilson, Jr., *Advan. Chem. Phys.*, **2**, 367 (1959).

[2] K. S. Pitzer, *Discussions Faraday Soc.*, **10**, 66 (1951).