Oligomers from the Ozonolyses of *cis*- and *trans*-3-Hexene and *cis*- and *trans*-2,5-Dimethyl-3-hexene

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Oligomers have been obtained by ozonolysis of the title olefins in a variety of solvents including *n*-butyraldehyde. The oligomers have structures which are basically polyozonides. Oligomer molecular weights, composition, and yields are solvent dependent. Aldehyde solvent gives the highest yields and lowest molecular weights. It is suggested that oligomers arise from nonconcerted addition of carbonyl and carbonyl oxide units.

As described in the previous paper,[1] in this series we have been conducting intensive investigations on the chemistry and physical properties of ozonolysis oligomers. Oligomers are the colorless, glassy, higher molecular weight materials which accompany ozonide formation in the ozonolysis of olefins. Our goal is to use the data collected on the these nonozonide ozonolysis products to gain additional insight into the mechanism of ozonolysis. These oligomer products have been recognized for some time.[2-11] They are difficult to characterize, but previous efforts have led to a variety of suggested structures including polycarbonyl oxides,[1,12-15] polyozonides,[7,16-22] and more random arrangements of ether and peroxide linkages including in one case[23] incorporation of a trioxide linkage.

To the best of our knowledge the most recent extensive investigations of oligomers are those of Greenwood and Rubinstein,[23] Razumovskii et al.,[19,20] and Fliszár and coworkers.[15,24-27] The work reported here is based on and represents, we believe, an extension of these important studies. Greenwood and Rubinstein[23] studied the oligomers obtained from 2-butene, 2-pentene, and 3-hexene. One of the most significant results of this work was the conclusion that the oligomers contained no carbon–carbon linkages. This conclusion was based on the fact that lithium aluminum hydride reduction of the oligomers did not yield α-diols. The authors also concluded that their elemental analysis data was not consistent with a polycarbonyl oxide structure. They concluded instead that their oligomers contained a variety of oxygen linkages and were not simply composed of alternating ether and peroxide linkages.

Razumovskii et al.[19,20] studied oligomers obtained from 2-butene, 2-pentene, 1-hexene, and 3-hexene. These authors concluded that their oligomers were composed of three to twelve monomer units and were made up of both aldehyde and carbonyl oxide units although not necessarily in a regular repeating pattern. Razumovskii et al.[19,20] also concluded that the oligomers had cyclic structures. They also investigated the oligomers obtained from the ozonolysis of cyclohexene in nonparticipating solvents. In this case the aldehyde and carbonyl oxide units are contained within the same molecule. This situation leads to the formation of a larger variety of oligomer structures including those whose structures were concluded to be polyozonides as well as cross-linked polyozonides.

Fliszár et al.[15,24-27] studied oligomers from phenyl-substituted ethylenes. They found that carbonyl oxides, which are not incorporated into ozonide, react to give oligomers. Aldo oligomers decomposed at room temperature while keto oligomers, i.e., those from tetrasubstitited olefins, were stable at room temperature. These workers also concluded that their oligomers were open-chain, polymeric peroxides in all cases as opposed to the cyclic structures proposed by Razumovskii et al.[19,20]

We report here studies on the oligomers obtained from ozonolysis of the stereoisomers of 3-hexene and 2,5-dimethyl-3-hexene. The oligomers were obtained under a variety of reaction conditions including the use of aldehyde as solvent. The latter conditions are particularly important to an understanding of the excess aldehyde effect[28-32] and perhaps also of the question of concertedness[32] in the ozonide-forming step of the overall ozonolysis process.

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Table I. Summary of Oligomer Experimental Data[a]

		anal. and mol wt										
		calcd[c]				found[d]						
olefin	solvent	C	H	O	mol wt	C	H	O	mol wt	TLC R_f	composition,[f] carbonyl oxide/carbonyl	wt. of oligomer, g
trans-2,5-dimethyl-3-hexene	$CH_3(CH_2)_4CH_3$	58.02	9.75	32.23	496	58.40	9.80	31.80	518	0.43	4:2	0.619
	$C_2H_5OC_2H_5$	57.49	9.63	32.88	584	57.23	9.50	33.27	578	0.37	5:2	0.389
	CH_2Cl_2	56.80	9.54	33.66	760	56.95	9.60	33.45	783	0.39	7:2	1.027
	$CH_3(CH_2)_2CHO$	61.17	10.26	28.57	392	59.12	10.22	30.63[e]	369	0.36	2:3	1.841
						60.21	9.64	30.07[b]	380	0.36	2:3	1.830
cis-2,5-dimethyl-3-hexene	$CH_3(CH_2)_4CH_3$	*g*				*g*				0.33	*g*	0.338
	$C_2H_5OC_2H_5$	*g*				*g*				0.28	*g*	0.258
	CH_2Cl_2	57.65	9.68	32.67	833	57.07	9.71	33.22	839	0.29	7:3	0.649
	$CH_3(CH_2)_2CHO$	57.49	9.63	32.88	584	56.43	8.99	34.58	556	0.27	5:2	1.019
trans-3-hexene	$CH_3(CH_2)_4CH_3$	55.57	9.34	35.09	1231	55.74	9.11	35.15	1223	0.23	8:11	0.607
	$C_2H_5OC_2H_5$	52.39	8.80	38.81	825	52.97	9.11	37.92	830	0.13	8:4	0.297
	CH_2Cl_2	52.21	8.77	39.02	1517	51.92	9.04	39.04	1497	0.12	15:7	0.79
	$CH_3(CH_2)_2CHO$	53.72	9.03	37.25	558	54.22	9.68	36.10	554	0.16	5.3[h]	1.44
cis-3-hexene	$CH_3(CH_2)_4CH_3$	*g*				*g*				0.25	*g*	0.192
	CH_2Cl_2	53.78	9.04	37.18	1807	53.17	9.36	37.47	1806	0.15	15:12	0.741

[a] Oligomers from ozonolysis of 0.5 M olefin at −78 °C using an O_3/O_2 stream. [b] Same as *a* except an O_3/N_2 stream was used. Analyzed for C, H, and O. [c] Calculated from molecular weight determinations and molecular weights of olefin-derived carbonyl oxide and carbonyl fragments. [d] C and H analyses carried out except for *b* and *e*. [e] Analyzed for C, H, and O. [f] Combinations shown are best fit for molecular weight and elemental analysis data and assume homogeneous materials. [g] Not determined. [h] $2CH_3CH_2CHO/1CH_3(CH_2)_2CHO$.

Results

The isomeric 2,5-dimethyl-3-hexenes and *trans*-3-hexene were each ozonized in hexane, diethyl ether, methylene chloride, and *n*-butyraldehyde. For *cis*-3-hexene only methylene chloride and hexane were used as ozonolysis solvents. In each case volatiles were removed from the reaction mixture via rotary evaporation and a vacuum pump and the glassy viscous residues purified further on preparative TLC plates. The samples of oligomer so obtained could be shown to be free of solvent, olefin, aldehyde, epoxide, and ozonide by GLC analysis. These oligomers were then subjected to a variety of analyses with results as shown as Table I.

Infrared and NMR Spectra. All of the oligomers have infrared absorptions in the 890–1300-cm^{-1} region. These absorptions are similar to those associated[33-41] with monomeric ozonides. In addition, all of the oligomers showed hydroxyl (ca. 3500 cm^{-1}) and carbonyl (ca. 1770 cm^{-1}) absorptions, the intensities of which were quite dependent on the solvent used to prepare the oligomer. In all cases these latter absorptions are very weak when hexane was used as the ozonolysis solvent. When the more polar solvents diethyl ether and methylene chloride were used, these absorptions increased in intensity by a factor of 2 or 3. When *n*-butyraldehyde was used as ozonolysis solvent, there was a dramatic increase in both hydroxyl and carbonyl absorptions in all of the oligomers. In the case of *trans*-2,5-dimethyl-3-hexene where both O_3/O_2 and O_3/N_2 ozonolysis procedures were used the intensities of the hydroxyl and carbonyl bands were approximately the same in the oligomers obtained from the two procedures.

The NMR spectra of all oligomers show absorption in the region of δ 4.87–5.38 which has been shown[40,42,43] to be associated with protons attached to the trioxolane ring in the cases of simple ozonides formed from nonterminal olefins. These absorptions in the cases of the oligomers are not well resolved, however, and perhaps reflect a nonregularity in the oligomer structures, rather than a uniform structure of alternating ether and peroxide linkages. When *n*-butyraldehyde was used as solvent, the oligomers obtained show an additional broad NMR absorption in the region of δ 6.0–6.5. This absorption has not been definitely assigned, but it could reflect the additional hydroxyl content signified by the corresponding infrared spectra. In the cases of the isomeric 2,5-dimethyl-3-hexenes the oligomers obtained in *n*-butyraldehyde solvent have methylene group absorptions in their spectra which is attributed to incorporation of butyraldehyde units into the oligomer structure.

Oligomer Molecular Weight, Yield, and Composition. Data on molecular weights and yield (weight) of oligomers obtained are given in Table I. The oligomer composition data given are based on a best fit approach using cryoscopic molecular weight and elemental analysis data and assuming that the oligomers are homogeneous and consist of aldehyde and carbonyl oxide units only. This approach is only an approximation since the spectroscopic data indicate the presence of small amounts of other structures in the oligomers. Also, it is unlikely, despite their apparent homogeneous behavior in TLC analysis, that the oligomers are actually homogeneous.[44] The molecular weight and composition data indicate that the oligomers contain between 5 and 27 monomer units with an average of approximately 12. This is generally consistent with that observed by earlier workers.[45] In cases where comparable data are available for the 3-hex-

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(44) In a preliminary experiment using HPLC analysis we have shown that the oligomer from *trans*-2,5-dimethyl-3-hexene ozonized in *n*-butyraldehyde solvent consists of at least three compounds. It is likely that these materials are similar in structure so that the composition data gven probably represent a composite for the oligomer fraction.

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Table II. Chemical Characteristics of Oligomers[a,b]

oligomer obtained from ozonolysis of	solvent stored in	product[c]		
		epoxide		*n*-butyric acid
		cis	trans	
t-$(CH_3)_2CHCH=CHCH(CH_3)_2$ in CH_2Cl_2	$CH_3(CH_2)_2CHO$	no	no	yes
	t-$(CH_3)_2CHCH=CHCH(CH_3)_2$	no	yes	no
	c-$(CH_3)_2CHCH=CHCH(CH_3)_2$	yes (54)	yes (46)	no
t-$(CH_3)_2CHCH=CHCH(CH_3)_2$ in $C_2H_5OC_2H_5$	$CH_3(CH_2)_2CHO$	no	no	yes
	t-$(CH_3)_2CHCH=CHCH(CH_3)_2$	no	yes	no
	c-$(CH_3)_2CHCH=CHCH(CH_3)_2$	yes (58)	yes (42)	no
t-$(CH_3)_2CHCH=CHCH(CH_3)_2$ in $CH_3CH_2CH_2CHO$	$CH(CH_2)_2CHO$	no	no	yes
	t-$(CH_3)_2CHCH=CHCH(CH_3)_2$	no	yes	no
	c-$(CH_3)_2CHCH=CH(CH_3)_2$	yes (62)	yes (38)	no
t-$(CH_3)_2CHCH=CHCH(CH_3)_2$ in $CH_3(CH_2)_4CH_3$	$CH_3(CH_2)_2CHO$	no	no	yes
	t-$(CH_3)_2CHCH=CHCH(CH_3)_2$	no	yes	no
	c-$(CH_3)_2CHCH=CHCH(CH_3)_2$	yes (55)	yes (45)	no
c-$(CH_3)_2CHCH=CHCH(CH_3)_2$ in CH_2Cl_2	$CH_3(CH_2)_2CHO$	no	no	yes
	t-$(CH_3)_2CHCH=CHCH(CH_3)_2$	no	yes	no
	c-$(CH_3)_2CHCH=CHCH(CH_3)_2$	yes (59)	yes (41)	no
c-$(CH_3)_2CHCH=CHCH(CH_3)_2$ in $CH_3CH_2CH_2CHO$	$CH_3(CH_2)_2CHO$	no	no	yes
	t-$(CH_3)_2CHCH=CHCH(CH_3)_2$	no	yes	no
	c-$(CH_3)_2CHCH=CHCH(CH_3)_2$	yes (67)	yes (33)	no
t-$CH_3CH_2CH=CHCH_2CH_3$ in CH_2Cl_2	$CH_3(CH_2)_2CHO$	no	no	yes
	t-$CH_3CH_2CH=CHCH_2CH_3$	no	yes	no
	c-$CH_3CH_2CH=CHCH_2CH_3$	yes (58)	yes (42)	no
t-$CH_3CH_2CH=CHCH_2CH_3$ in $C_2H_5OC_2H_5$	$CH_3(CH_2)_2CHO$	no	no	yes
	t-$CH_3CH_2CH=CHCH_2CH_3$	no	yes	no
	c-$CH_3CH_2CH=CHCH_2CH_3$	yes (60)	yes (40)	no
t-$CH_3CH_2CH=CHCH_2CH_3$ in $CH_3CH_2CH_2CHO$	$CH_3(CH_2)_2CHO$	no	no	yes
	t-$CH_3CH_2CH=CHCH_2CH_3$	no	yes	no
	c-$CH_3CH_2CH=CHCH_2CH_3$	yes (61)	yes (39)	no
t-$CH_3CH_2CH=CHCH_2CH_3$ in $CH_3(CH_2)_4CH_3$	$CH_3(CH_2)_2CHO$	no	no	yes
	t-$CH_3CH_2CH=CHCH_2CH_3$	no	yes	no
	c-$CH_3CH_2CH=CHCH_2CH_3$	yes (60)	yes (40)	no
c-$CH_3CH_2CH=CHCH_2CH_3$ in CH_2Cl_2	$CH_3(CH_2)_2CHO$	no	no	yes
	t-$CH_3CH_2CH=CHCH_2CH_3$	no	yes	no
	c-$CH_3CH_2CH=CHCH_2CH_3$	yes (64)	yes (36)	no

[a] The numbers in parentheses indicate the distribution of epoxide obtained. [b] All oligomers were obtained from ozonolyses in an ozone–oxygen stream. [c] No ozonide was found in any case.

anes, our molecular weights are generally higher than those reported by Greenwood and Rubinstein.[23] This presumably reflects the higher olefin concentrations used in our work.

There is a solvent effect on oligomer molecular weight. Perhaps the most noticeable influence is that of an aldehyde as the ozonolysis solvent. In every case examined such ozonolyses gave oligomer of the lowest molecular weight. In some cases the effect was dramatic. Thus, *trans*-3-hexene gives oligomer of molecular weight 1223 in hexane while the oligomer obtained in *n*-butyraldehyde has a molecular weight of only 554. This influence of aldehyde solvent carries over into the weight of oligomer-obtained data. In all cases, aldehyde solvent leads to the formation of more oligomer. This effect is presumably related to the excess aldehyde effect[28-32] in which it has been found that increasing amounts of aldehyde lead to decreasing amounts of ozonide with the effect being most pronounced for trans olefins with large substituents. The stereochemical influence is also reflected in the current data where *trans*-2,5-dimethyl-3-hexane undergoes an 82% increase in oligomer product in going from methylene chloride to aldehyde solvent whereas the cis isomer shows a 58% increase in oligomer weight for the same solvent change. The use of aldehyde solvent also generally leads to an increase in the proportion of carbonyl as opposed to carbonyl oxide units in the oligomers. For a given olefin the use of diethyl ether solvent leads to the formation of less oligomer than obtained in hexane or methylene chloride solvent. This also is consistent with the general observation[45] that diethyl ether solvent leads to higher ozonide yields.

There is no obvious relationship between TLC R_f values and oligomer molecular weight or polarity. These data do indicate the clean manner in which oligomers can be handled by this analytical technique, however. What is required next is further examination of these oligomers by HPLC analysis in order to answer the question of fraction homogeneity.[44]

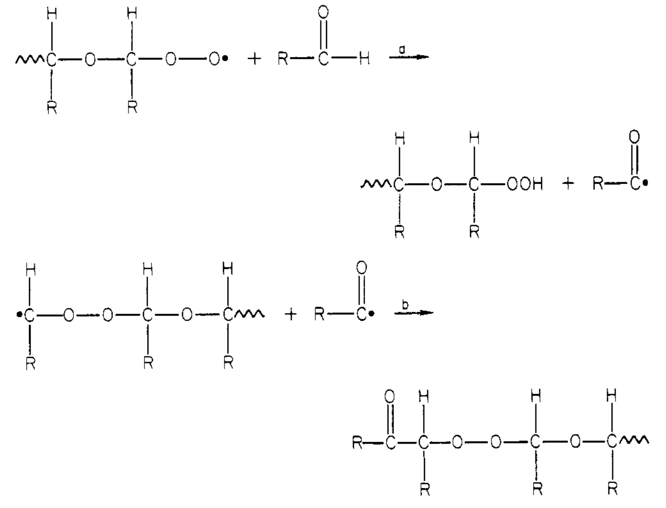
Chemical Properties of Oligomers. Samples of the oligomers were stored in a variety of solvents (Table II) for 5 weeks at room temperature. In separate experiments it was shown that similar storage of the isolated oligomers obtained from ozonolyses in hexene, methylene chloride, or diethyl ether in the ozonolysis solvent did not lead to the formation or release of epoxide, ozonide, or butyric acid. Similar results were obtained when the oligomers produced in aldehyde solvent were stored in hexane.

As shown in Table II the oligomers are capable of epoxidizing olefins and converting *n*-butyraldehyde to *n*-butyric acid. In the epoxidation reaction trans olefins give trans epoxides and cis olefins give a mixture of cis and trans epoxides, with the cis being favored.

Discussion

The data are most consistent with a modified polyozonide structure assignment for the oligomers. The major modification is a nonregular pattern of carbonyl oxide and carbonyl units. A second modification is the incorporation of some carbonyl- and hydroxyl-containing units. The dependence of the latter modification on solvent polarity and particularly the increase in the contribution of these structural units observed in aldehyde solvent suggest that these units originate largely in aldehyde, either present as

Scheme I



an ozonolysis product or, especially, when used as a solvent.

While the mechanism by which units become incorporated into the oligomer structure is not known, a number of factors suggest that free radical processes may be involved. There are a growing number of reports in the literature suggesting a role for free radicals in the overall reaction(s) between ozone and organic materials, especially unsaturated organic materials.[46-58] Pryor has described[59] some particularly elegant work in which spin traps are used to disclose the presence of free radicals in the reaction between olefins and ozone. A possible sequence of events for oligomer modification is shown in Scheme I. A radical at the end of the growing oligomer, most likely an alkoxy or peroxy radical (reaction a) is postulated as abstracting the very labile [60-62]acyl hydrogen from an aldehyde molecule. The acyl radical produced in this step is then available to add to the growing oligomer at a terminal radical. There are a number of possibilities for the latter step one of which is shown (reaction b).

A number of experimental observations add to the attractiveness of this suggested sequence of events. First, additional aldehyde, as, for example, when aldehyde is used as the solvent, leads to the presence of more hydroxyl and carbonyl units in the oligomer. Second, aldehyde solvent decreases the molecular weight of oligomer obtained while at the same time increasing the total amount of oligomer produced. If the events of Scheme I are taking place then aldehyde is serving the role of a chain-stopping agent leading to lower molecular weights in the oligomer. The influence of aldehyde concentration on oligomer weight presumably arises because of the nature of the oligomer-forming process.

The fact that the oligomers contain both aldehyde and carbonyl oxide units suggests to us that it must be possible for these units to react in a nonconcerted manner as proposed[28,32] earlier by us and by Harding and Goddard.[63] Indeed, the incorporation of an added, foreign aldehyde into the oligomer structure as observed here adds strength to this view. The effect of aldehyde as the solvent observed here suggests that increasing amounts of aldehyde can also encourage such nonconcerted processes, thus increasing the yield of oligomer. We had earlier suggested[28,32] this idea to explain the added aldehye effect on ozonide yield. According to that suggestion, added aldehyde reduces ozonide yield by diverting intermediates, produced by nonconcerted addition of carbonyl and carbonyl oxide to nonozonide, i.e., oligomer, products. The preceding paper in this series suggests that this role of aldehyde is not operative for the case of *trans*-di-*tert*-butylethylene for a variety of reasions, including the steric bulk associated with the *tert*-butyl group.

The present results strengthen the view that carbonyl and carbonyl oxide fragments can undergo nonconcerted addition. Indeed, some of these results would seem to require such a process. The question of the relationship of this conclusion to the ozonide-forming reaction as well as the whole question of the mechanism of ozonolysis is an important one.

There are at least two ways of reconciling these results with current views[48] of the mechanism which incorporate a concerted addition of the reaction fragments in a very critical way. First, one may suggest that there are two reaction modes for the recombination of aldehyde and carbonyl oxide fragments. One of these is concerted and leads to ozonide, simultaneously providing a framework for understanding the great complexity of the ozonolysis process. The second reaction mode is nonconcerted and leads, for example, to oligomers. According to this view both reaction modes are possible.

A second approach is to view the reaction of carbonyl and carbonyl oxide fragments as occurring via a single basic reaction mode but one which is susceptible, in a profound way, to changes, slight or major, in any one of a number of reaction characteristics. Included in this group are reaction solvent, temperature, olefin concentration, steric and stereochemical factors, etc. Thus, at one extreme is the joining of the reaction fragments in a manner which is basically nonconcerted but in which the rate of second bond closure is so rapid that the reaction approaches concertedness. At the other extreme is the case where the reacting fragments produce an intermediate after one bond formation, which intermediate may be diverted to other products, including oligomer, depending upon a number of reaction variables. In general, ozonolysis of a simple olefin in a hydrocarbon solvent would represent an example of one of these extremes, while examples from the present work in which aldehyde was used as solvent lie at the other extreme.

The results obtained by storing the oligomers in a variety of solvents (Table II) indicate that these materials are somewhat unstable as reported previously[45] for a variety of other oligomers. Several chemical characteristics of the

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decomposition products have been determined. These materials are able to convert aldehydes to acids and epoxidize olefins but are not trapped by aldehydes to give ozonides. The latter observation plus the stereochemistry of the epoxidation reaction would seem to argue against the release of free carbonyl oxides from the oligomers. We had earlier[64] shown that carbonyl oxides epoxidize olefin in a stereoselective manner. Thus trans olefins are converted to trans epoxides while cis olefins give mostly, but not completely, cis epoxides. This is generally the same stereochemical results reported by Hamilton and Keay[65,66] when the epoxidations are carried out by carbonyl oxides derived from oxonization of alkynes.

The epoxidation stereochemical results described here are similar to those obtained[1] with the oligomer produced by ozonolysis of *trans*-di-*tert*-butylethylene. In both of these cases trans olefins give trans epoxides and cis olefins give mostly cis epoxides. The difference is that the epoxide distribution obtained from cis olefins with the oligomers varies from slightly greater than 1:1 (cis/trans) to approximately 2:1 (cis/trans), whereas the carbonyl oxides tend to give a higher (ca. 80–90%) amount of cis ozonide. We suggest that the failure to trap carbonyl oxides with aldehydes in the present results indicates that the epoxidation stereochemistry differences are real and that the oxidant in the cases of oligomers is not a free carbonyl oxide.

It is possible that the slow decomposition of the oligomer generates an alkoxy or peroxy radical at the end of an oligomer chain. Such a species would be capable of epoxidizing olefins with the presence of the large oligomer chain leading to a different stereochemical result than that obtained with free carbonyl oxides. These radicals would also presumably oxidize aldehyde to acid as observed.

Experimental Section[67]

Instrumentation. NMR spectra were recorded on a Varian T-60 NMR spectrometer with deuteriochloroform as the solvent and tetramethylsilane as the internal standard. Mass spectra were obtained by using an Associated Electronics Industries Model MS-1201 B mass spectrometer at a 70-eV ionizing voltage. Infrared spectra were recorded with Perkin-Elmer Model 137 or Model 337 infrared spectrophotometer by using neat samples, and the spectra were calibrated with the 1601-cm^{-1} band of polystyrene film. Analytical and preparative GLC work was carried out on Varian Hy-Fi Model 600-D and Varian-Aerograph Model A-705 gas chromatographs. The following GLC columns were employed: column A, 0.25 in. × 6 ft, 7% β,β'-oxydipropionitrile on 60/80 Chromosorb G, DMCS treated; column B, 0.125 in. × 15 ft, 7% β,β'-oxydipropionitrile on 60/80 Chromosorb G, DMCS treated; column C, 0.375 in. × 12 ft; 7% β,β'-oxydipropionitrile on 45/60 Chromosorb G-AW, DMCS treated. Elemental analyses and cryoscopic molecular weight determinations were carried out by Galbraith Laboratories, Inc., Knoxville, TN.

Materials. The olefins were obtained from Chemical Samples Co., Columbus, OH. Both *cis*-2,5-dimethyl-3-hexene (99%) and *trans*-3-hexene (99%) were analyzed by GLC before use and were found to be of the stated purity. In the cases of *trans*-2,5-dimethyl-3-hexene and *cis*-3-hexene it was necessary to pass the olefins through neutral silica gel twice before obtaining material of suitable GLC purity (98%). Hexane (certified grade, 99 mol % pure) and anhydrous diethyl ether (ACS reagent grade) were obtained from Fisher Scientific Co., Fair Lawn, NJ. These solvents were also analyzed for purity by gas chromatography before use. Methylene chloride was purified by stirring overnight with concentrated sulfuric acid, washing, drying with $CaCl_2$, and finally distilling under argon from calcium hydride. Both *n*-butyraldehyde (99%; bp 75 °C) and isobutyraldehyde (98%; bp 63 °C) were obtained from Aldrich Chemical Co., Inc., Milwaukee, WI, and were purified by fractional distillation under argon immediately before use.

Precoated thin-layer chromatography plates were obtained from Brinkmann Instruments, Inc., Westbury, NY, and were 20 cm × 20 cm × 1.0 mm silica gel with fluorescent indicator UV_{254}. Analytical thin-layer chromatography plates were obtained from Eastman Kodak Co., Rochester, NY, and were 2.5 cm × 8 cm silica gel with fluorescent indicator.

General Ozonolysis Procedure (Ozone–Oxygen). Ozone was produced in a Welsbach Model T-408 ozone generator and was delivered as an ozone/oxygen stream at a rate of 0.14–0.15 mmol of O_3/min. The oxonolysis solutions were purged with argon for 10 min before and after passing the O_3/O_2 stream. The ozone flow rate was determined iodometrically immediately prior to each ozonolysis. Actual ozone uptake was determined on the basis of this determination together with iodometry of the effluent gases from the reaction mixture. After ozonolysis was completed, the reaction mixtures were subjected to a "slow" warm-up procedure by allowing the reaction solutins to stand in the cooling bath until room temperature was reached (about 40 h).

General Ozonolysis Procedure (Ozone–Nitrogen). This procedure was used in those cases where oxygen-free ozone was desired. The O_3/O_2 stream with a flow rate of 0.14–0.15 mmol of O_3/min was carried into a U-shaped glass tube containing about 43 g of predried and cold (−78 °C) silica gel (Davidson Chemical, grade 40, mesh size 6–12) until the silica gel became a deep blue color. Generally it took about 4 h to reach this point. The silica gel containing tube was then purged with nitrogen at a slow rate for 20 min to remove any residual oxygen. The ozone was desorbed with nitrogen while the absorption tube was at -73 to -75 °C. All of the bound O_3 was delivered to the reaction vessel. The O_3/N_2 output was determined iodometrically in a separate experiment prior to each run. It was found that the total O_3 absorbed and delivered from the tube was reasonably constant. Complete delivery of the absorbed O_3 required approximately 10 h of N_2 flow.

Oligomers from Ozonolyses of the Isomeric 2,5-Dimethyl-3-hexenes and 3-Hexenes. The general ozonolysis procedure (O_3/O_2 or O_3/N_2 as desired; see Table I) was used with the reaction solution cooled to about −78 °C in a dry ice/methanol bath. In all cases ozonolyses were carried out on a total reaction volume of 50 mL which contained 25 mmol (0.5 M) of each olefin. Each solution was brought to the 50-mL total with methylene chloride, diethyl ether, *n*-hexane, or *n*-butyraldehyde except in the case of *cis*-3-hexene which was ozonized in methylene chloride and hexane only (see Table I).

After ozonolysis the volatiles were removed by using the rotary evaporator. The crude, highly viscous residue was then subjected to a vacuum (ca. 0.75 mmHg) for a 4-h period in order to remove trace amounts of volatiles. Each of the glassy residues so obtained was chromatographed on 20 cm × 20 cm, 1-mm thick precoated thin-layer chromatography plates (four plates required) with hexane–diethyl ether (80:20) as a developing solvent. The major (broad) band on each TLC plate was collected by several extractions with diethyl ether. Each of the purified glassy residues was then dissolved in diethyl ether for further determinations of R_f values and for GLC analysis. The R_f values of each oligomer were obtained by using at least three determinations on 3 cm × 15 cm Eastman Chromogram silica gel with fluorescent indicator with hexane–diethyl ether (80:20) as a developing system. Results of these analyses are given in Table I. The GLC analysis of each of these ether solutions of oligomer showed the absence of olefin, aldehyde, epoxide, and ozonide.

The ether solutions were evaporated to give the colorless, glassy oligomers (except in the cases of the isomeric 3-hexenes with CH_2Cl_2 as the solvent, where the oligomers were off-white). Each purified oligomer was then analyzed by NMR, IR, and mass spectral and TLC methods. Elemental analyses and cryoscopic molecular weight determinations were also obtained on the oligomer samples (see Table I).

Chemical Properties of Oligomers. Samples (200 mg) of each of the purified oligomers, obtained as described above, were

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stored in 5 mL of each of the following: hexane, diethyl ether, methylene chloride, *n*-butyraldehyde, and parent olefin. The solutions were stored at room temperature for 5 weeks and then analyzed. Results of the analyses are given in Table II. The epoxides were analyzed by GLC using column A for analytical work and column C for preparative work. They were identified by comparing their GLC retention times and infrared and NMR spectra with those of the appropriate authentic compound. The authentic epoxides were synthesized by treating the corresponding olefin with *m*-chloroperbenzoic acid. Butyric acid was identified by comparing GLC, IR, and NMR data with those of commercially available authentic compound.

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Registry No. *trans*-2,5-Dimethyl-3-hexene, 692-70-6; *cis*-2,5-dimethyl-3-hexene, 10557-44-5; *trans*-3-hexene, 13269-52-8; *cis*-3-hexene, 7642-09-3; hexane, 110-54-3; diethyl ether, 60-29-7; dichloromethane, 75-09-2; butanal, 123-72-8.

Reactions of Azodiones with Electron-Rich Alkenes. 1,2,4-Triazoline-3,5-diones and Vinyl Ethers

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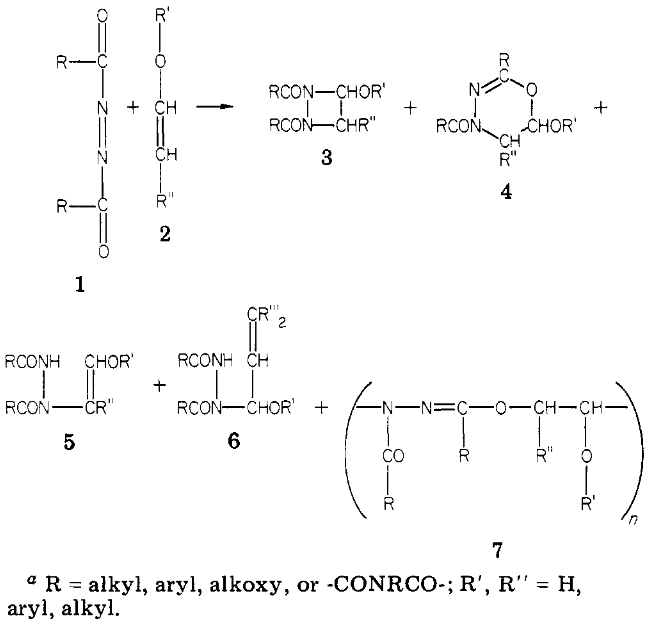
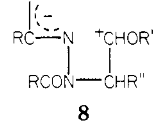
4-Substituted-1,2,4-triazoline-3,5-diones (R-TAD) react with vinyl ethers to give mixtures of 1,2-diazetidines and polymers. The ratio of diazetidine to polymer is very dependent on the nature of the alkoxy substituent of the vinyl ether. For example, ethyl vinyl ether gives only polymer, but 2-chloroethyl vinyl ether gives only 1,2-diazetidine. The rate of reaction is very dependent on the vinyl ether structure, decreasing in the order $CH_3CH_2OCH{=}CH_2 > ClCH_2CH_2OCH{=}CH_2 > C_6H_5OCH{=}CH_2$, but is not very sensitive to the nature of the 4-substituent in the triazolinedione. The involvement of a 1,4-dipole in 1,2-diazetidine formation was proven by trapping the intermediate in the reaction of 2-chloroethyl vinyl ether and C_6H_5-TAD with acetone. However, the rate of the reaction is insensitive to the polarity of the solvent. In order to reconcile these facts, the initial formation of a charge-transfer complex is postulated, which in turn collapses to a 1,4-dipole.

The thermal reaction of conjugated azodiones (**1**) with electron-rich alkenes such as vinyl ethers (**2**) gives rise to a variety of products (Scheme I) including 2 + 2 cycloadducts (**3**), 2 + 4 cycloadducts (**4**), proton abstraction products (**5**), products of the ene reaction (**6**), and polymers (**7**).[1-21] The 2 + 4 cycloadduct (**4**) is usually the major product unless the alkene has allylic hydrogens; then ene product **6** formation becomes competitive with cyclization. However, in a few cases[12] 2 + 2 cycloaddition competes successfully with 2 + 4 cycloaddition. It has been postulated[3-6,13-20] that products **3**, **5**, and **7** arise from dipolar intermediates (**8**). The ene product cannot involve **8** and

Scheme I[a]



[a] R = alkyl, aryl, alkoxy, or -CONRCO-; R', R'' = H, aryl, alkyl.



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