Ozonolysis. Temperature Effects

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Ozonolysis of *cis*- and *trans*-diisopropylethylene over the temperature range −1 to −122° both alone and in the presence of propionaldehyde suggests that more than one mechanism may be responsible for ozonide formation, particularly at the lower temperatures. The cross ozonide cis/trans ratio is quite temperature dependent while normal ozonide cis/trans ratios show smaller effects.

As part of a comprehensive study of the ozonolysis reaction, we have been systematically studying a number of reaction variables. Some of the results of such studies emphasizing olefin stereochemistry[2] steric effects,[2] solvent,[3] concentration,[3] and use of ^{18}O labeling[4] have been reported.

We report here the results of a comprehensive study of the effect of temperature on a particular ozonolysis reaction. Very little attention has been paid to ozonolysis conditions where temperature is the sole variable. Some mention of temperature effects has been made in the literature[5,6] and recently Fliszár and Carles[7] have provided some more comprehensive data in this field.

The effect of temperature on the ozonolysis reaction is important from a mechanistic viewpoint.[8] We have suggested[2,9] that in some cases the ozonide cis/trans ratio produced may be affected by a reaction between the initial olefin–ozone adduct and aldehyde in addition to the usual Criegee[10] zwitterion contribution. This kind of contribution to the ozonide cis/trans ratio would be expected to be more important at lower temperatures where the initial adduct has greater stability.

We were prompted to suggest this complementary mechanism primarily on the basis of an increasing amount of data indicating that the ozonide cis/trans ratio can depend upon olefin geometry.[9] Criegee had explicitly postulated that the ozonide cis/trans ratios do not depend upon olefin geometry according to his mechanism.[11] Fliszár[7] and Bailey[5] have also suggested modifications to the Criegee mechanism.

Results and Discussion

Data on the effect of temperature on the ozonolysis of *cis*- and *trans*-diisopropylethylene were obtained in three main sets. In each set the olefin was present as a 0.2 *M* solution in pentane and was ozonized to 50% conversion. In set 1 no aldehyde was present. In set 2 the solutions contained propionaldehyde in 0.2 *M* concentration in addition to the olefin. In set 3 10 ml of 0.2 *M* propionaldehyde in pentane was added after ozonolysis of the olefin was completed. In addition, as a result of some surprising results obtained in preliminary experiments, the ozonized solutions were consistently warmed up by two different procedures prior to sampling. In the first of these procedures the reaction vessels were immediately immersed into water at room temperature after ozonolysis. In the second procedure the reaction vessels were left in the cooling baths and allowed to warm to room temperature slowly. This second procedure typically required several hours. For the sake of simplicity these procedures will subsequently be referred to as fast and slow warm-up, respectively.

Some data were also obtained on the effect of temperature on the ozonolysis of an unsymmetrical olefin by ozonizing 0.2 *M* solutions of *cis*- and *trans*-4-methyl-2-pentene at the temperature extremes.

In set 1 it was found that the isomeric olefins give a different but temperature-independent ozonide cis/trans ratio when a fast warm-up procedure is used. These ratios are *ca.* 56/44 and 39/61 for the cis and trans olefins, respectively. When a slow warm-up was used, the cis olefin shows a slight change in this ratio at temperatures below −100°, reaching 61/39 at −123°. For the trans olefin this effect is more pronounced and begins at −80° (Figure 1). The ozonide cis/trans ratio finally achieved under these conditions from the trans olefin is approximately the same as the constant ratio given by the cis olefin.

This striking effect of the warm-up procedure suggests that care will have to be taken in interpreting results when the rate of warm-up has not been specified. The large scatter in the data of Figure 1 is probably associated with the observed formation of varying amounts of explosive crystals in this case. In some experiments in this series, using the trans olefin at very low temperatures, mild explosions occurred during the warm-up procedure. While these solutions were sometimes inhomogeneous at low temperatures, the data was obtained only on the homogeneous room temperature solutions.

The ozonide yields were fairly temperature independent in this first set. For the cis olefin the yield varied from 60 to 70% from the highest to the lowest temperature, respectively. For the trans olefin the yield was fairly constant at approximately 43%. The yield data for the trans olefin did have a lot of scatter which may also be associated with the crystal formation described above.

The differences observed between the fast and slow warm-up procedures at very low temperatures is almost certainly associated with the presence of the initial ozonide. A lower temperature is required for these ef-

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(1) Ciba Photochemical, Ltd., Fribourg, Switzerland. The work was carried out at Bell Telephone Laboratories, Murray Hill, N. J.

(2) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Amer. Chem. Soc.*, **88**, 3143 (1966).

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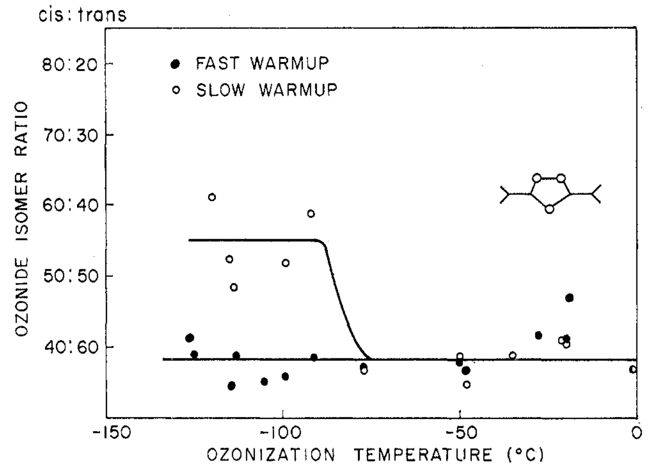


Figure 1.—Dependence of the ozonide cis/trans ratio on the ozonolysis temperature of *trans*-diisopropylethylene.

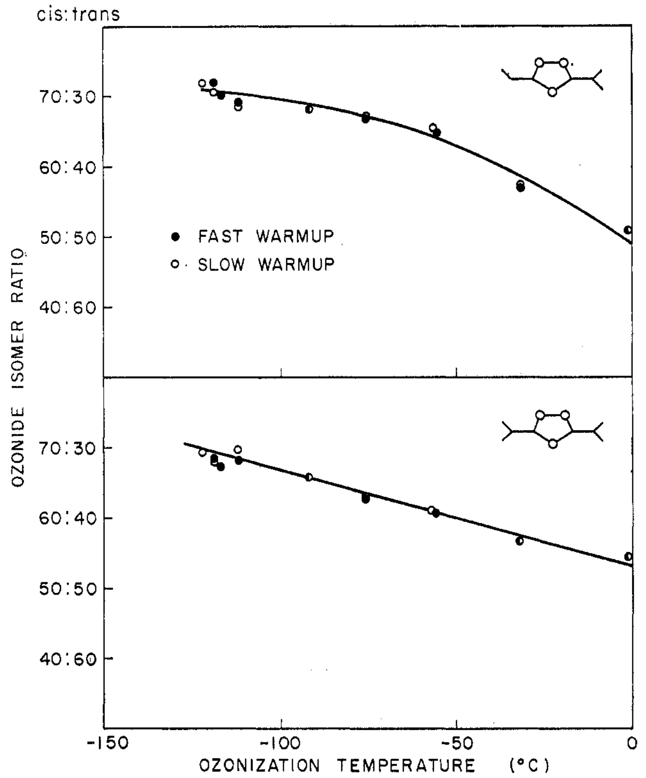


Figure 2.—Dependence of the ozonide cis/trans ratio on the ozonolysis temperature of *cis*-diisopropylethylene with propionaldehyde present during the ozonolysis.

fects to be noticeable in the cis olefin in keeping with the expected[12-18] greater instability of the initial adduct for cis olefins. The effect on the ozonide cis/trans ratio for the trans olefin below −80° and the cis olefin below −100° suggests that another mechanism may be competing with the zwitterion–aldehyde mechanism under these conditions. A number of possibilities could explain these results. We suggest as one possibility that the initial ozone–olefin adduct, **1**, has two possible modes of decomposition. Decomposition in a concerted manner to give the Criegee zwitterion and a carbonyl compound leads to an ozonide isomer ratio which is usually dominant. At the lower temperatures this process also predominates provided that a fast warm-up procedure is used. Under low temperature conditions where an appreciable amount of the initial adduct can accumulate the slow warm-up procedure could lead to a significant contribution of a one-bond breaking process to give **2**, which than can allow for other ozonide-forming reactions to occur, which processes may give a different ozonide cis/trans ratio.

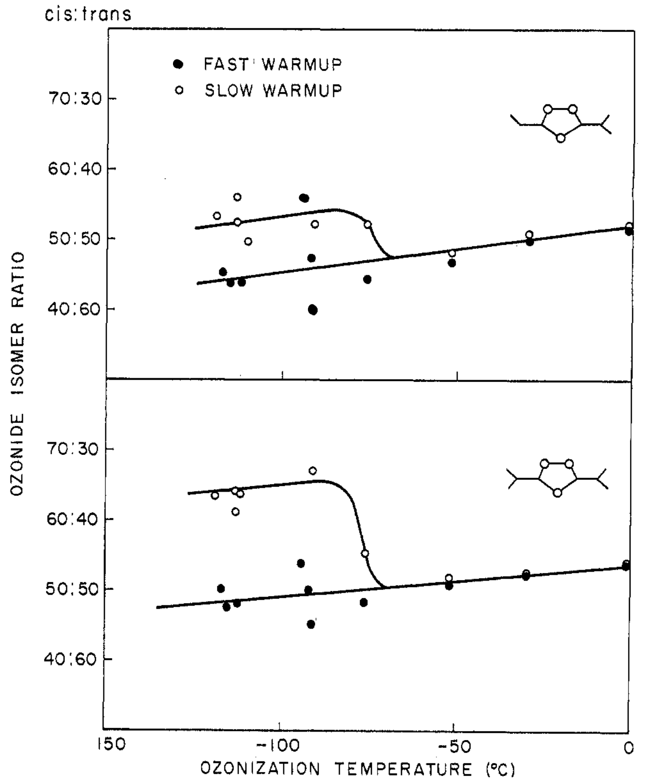
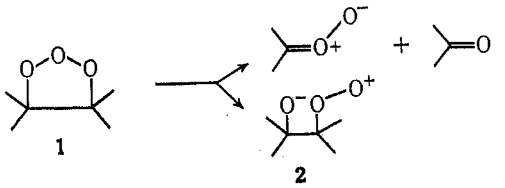


Figure 3.—Dependence of the ozonide cis/trans ratio on the ozonolysis temperature of *trans*-diisopropylethylene with propionaldehyde present during the ozonolysis.



The most pertinent data for set 2 with propionaldehyde present during the ozonolysis are given in Figures 2–4. For the cis olefin (Figure 2) the different warm-up procedures do not affect the cis/trans data. The ozonide cis/trans ratios for both the normal (diisopropyl ozonide) and the cross ozonide (ethyl isopropyl ozonide) do show a strong temperature dependence, however. For both ozonides, lower temperatures give more cis ozonide. The normal ozonide cis/trans ratio actually is higher at lower temperatures in the presence of added aldehyde (Figure 2) than in the absence of added aldehyde. If the syn/anti zwitterion explanation[5] were dominant and these zwitterions reacted with aldehyde to affect the ozonide cis/trans ratio as postulated by Bailey, *et al.*, then this would mean that the added propionaldehyde was preferentially diverting syn zwit-

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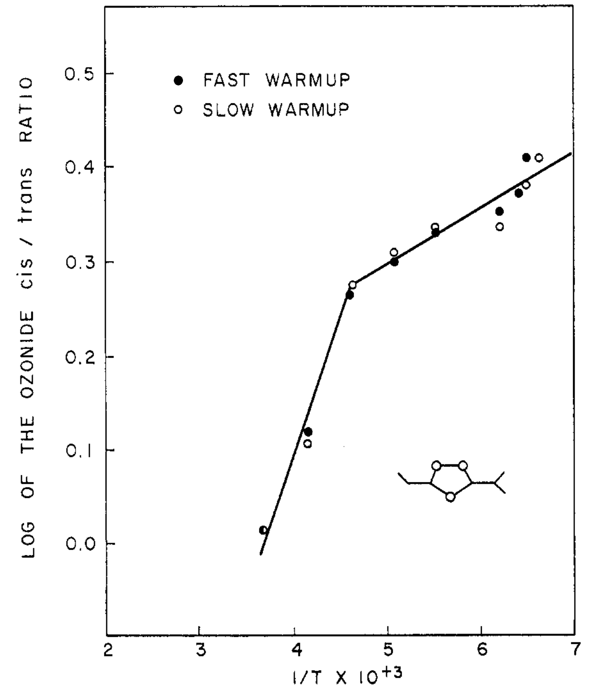


Figure 4.—A plot of the logarithms of the 2-methyl-3-hexene ozonide cis/trans ratios *vs.* reciprocal temperature for ozonolysis of *cis*-diisopropylethylene in the presence of propionaldehyde.

terions, whereas intuitively one might expect the anti zwitterions to be more easily diverted by added aldehyde. The general concept of syn and anti zwitterions is consistent with the temperature data, however. Thus the temperature dependence of the ozonide cis/trans ratio could be due to a constantly changing equilibrium between syn and anti zwitterions.

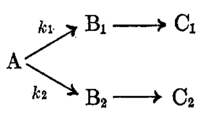
For the cis olefin the yield of the cross ozonide decreases slightly from 18.7% at −1° to 14% at *ca.* −100° after which it again increases slightly to 18%. Again this could indicate the contribution of an additional mechanism at very low temperatures where the concentration of initial adduct is expected to be higher. The yield of normal ozonide is constant and lower (21%) at all temperatures in the presence of added aldehyde as expected.

For the trans olefin a similar but less-pronounced dependence of ozonide cis/trans ratio on temperature is found (Figure 3). In this case a slightly lower ratio is obtained at lower temperatures. The warm-up procedure again has a pronounced effect on the results below −80°. The slow warm-up procedure gives a considerably higher percentage of cis ozonide in both normal and cross ozonide. As with the cis olefin the cis/trans ratio attained in the trans olefin at low temperature with fast warm-up is higher than that obtained without added aldehyde. This again suggests that the added aldehyde may be preferentially intercepting trans ozonide precursors. In this case, the required preference for reaction with syn zwitterions could be due to the smaller size of the propionaldehyde.

The yield data for the trans olefin show only a slight temperature dependence. The different warm-up procedures do affect the yields of both ozonides at low temperatures. For example the normal ozonide yield with fast warm-up is 12% as compared to 22% with slow warm-up. The added aldehyde is more efficient at trapping ozonide precursors under fast warm-up conditions where the cross ozonide is obtained in 18% yield as compared to 10% with slow warm-up.

The possibility of a mechanism change with temperature is examined further in Figure 4. Here the logarithms of the cis/trans ratios of ethyl isopropyl ozonide obtained from the ozonolysis of *cis*-diisopropylethylene in the presence of propionaldehyde are plotted against the reciprocals of the absolute temperatures used. For a general system such as that given in Scheme I one would obtain a product ratio, $C_1/C_2 = k_1/k_2$. Assuming

SCHEME I



an Arrhenius relation, $k = A \exp(-E/RT)$, for the rate constants, k_1 and k_2, then one would expect a single mechanism to give a straight line in Figure 4. Exactly such a linear plot was recently obtained by Fliszár and Carles[7] in their studies of the temperature dependence of ozonolysis of selected phenylethylenes over a smaller temperature range. The lowest temperature used in their studies was −15°, however.

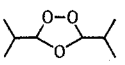
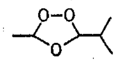
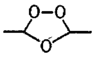
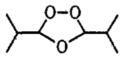
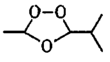
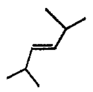
The data in Figure 4 are best accommodated by two intercepting straight lines and suggest that there may be two mechanisms operative with a different mechanism dominant above and below about −60°. Such an explanation might also be consistent with the yield data. The plot in Figure 4 could also be explained by a more complex scheme based on the syn/anti zwitterion concept.

The data for the set of experiments in which propionaldehyde was added to the reaction mixture after ozonolysis was complete are given in Figures 5 and 6. Here it is found that substantial amounts of the added aldehyde are incorporated into ozonide below −50° in the case of the trans olefin and below −100° in the case of the cis olefin. Obviously below these temperatures there must be an intermediate which can be converted into ozonide and which has a lifetime which is long enough so that aldehyde added after the ozonolysis can interfere with its normal fate. Again, these observations are consistent with the known relative stabilities[12–18] of the initial adduct so that the species being trapped with the added aldehyde most likely is the initial adduct or a transformation product of it. The latter species includes one-bond cleavage intermediates such as **2** and concerted decomposition intermediates such as the zwitterion.

At higher temperatures, where the added aldehyde cannot intercept an intermediate, the ozonide cis/trans ratio for the normal ozonide is the same for both the cis and trans olefin as that found in the experiments where no aldehyde is added. At lower temperatures this ratio is quite temperature dependent for both the cis and trans olefins. In both cases more cis ozonide is obtained below the expected decomposition temperature of the initial adduct. For the cis olefin the cis/trans ratio reaches 67/33. For the trans olefin it reaches 50/50 for fast warm-up. In the case of the trans olefin the two warm-up procedures again give different results below −70° (Figure 6). The slow warm-up procedure gives a higher ozonide cis/trans ratio for both the nor-

TABLE I

OZONIDE CIS/TRANS RATIOS AND OZONIDE YIELDS IN OZONOLYSIS OF *cis*- AND *trans*-4-METHYL-2-PENTENE

			Ozonide stereoisomer distributions, %				Ozonide yields, % (based on ozone introduced)		
									
Olefin	Ozonization temp, °C	Warm-up	Cis	Trans	Cis	Trans			
	−122	Fast	45	55	25	75	4.8	32.4	5.2
	−113		46	54	29	71	4.1	33.1	4.2
	−1		49	51	47	53	4.7	26.3	5.2
	−124	Slow	42	58	35	65	2.4	40.1	3.1
	−1		49	51	45	55	5.8	27.2	5.0
	−119	Fast	42	58	63	37	5.3	74.7	3.5
	−1		44	56	55	45	9.7	52.1	12.5
	−119	Slow	57	43	75	25	3.5	80.2	2.4
	−1		44	56	55	45	10.4	55.3	11.8

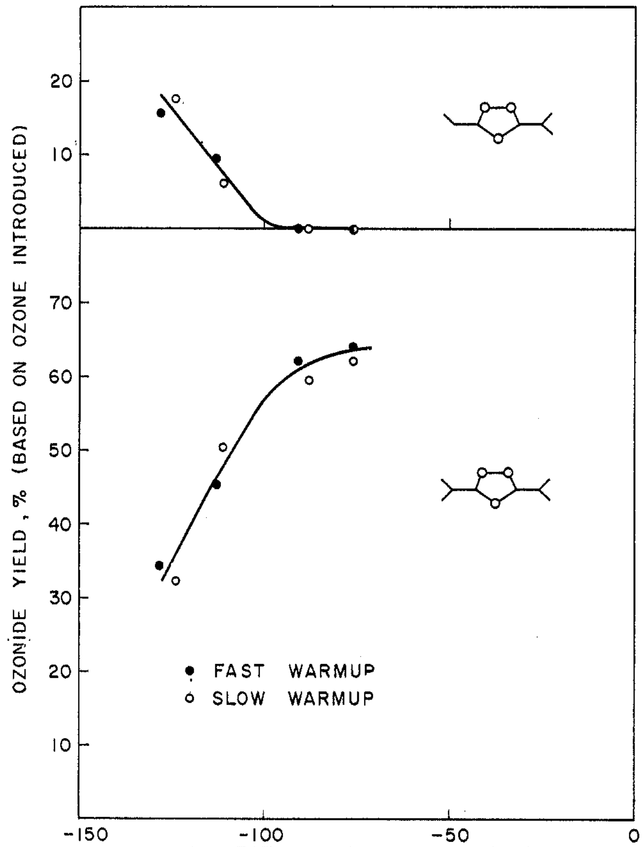


Figure 5.—Dependence of the ozonide yield on the ozonolysis temperature of *cis*-diisopropylethylene with propionaldehyde added after the ozonolysis.

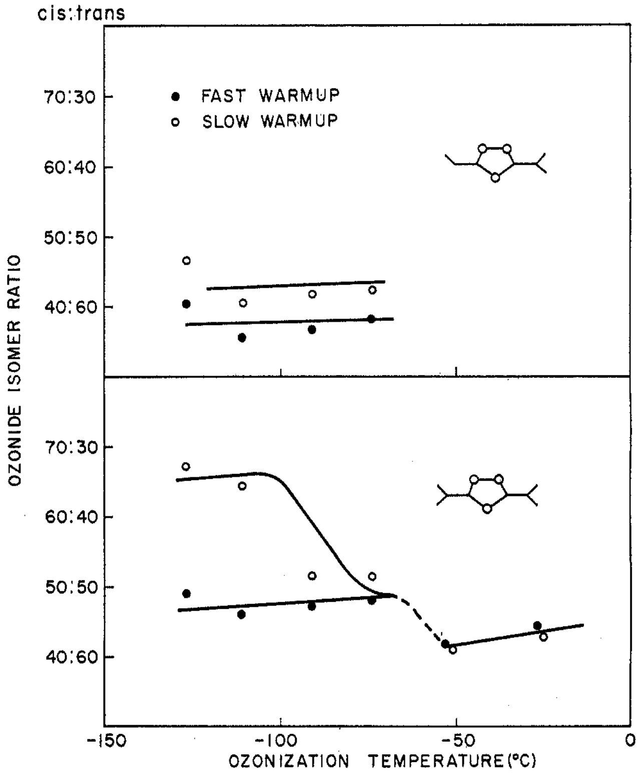


Figure 6.—Dependence of the ozonide cis/trans ratio on the ozonolysis temperature of *trans*-diisopropylethylene with propionaldehyde added after the ozonolysis.

mal ozonide and cross ozonide. The normal ozonide ratio obtained by either procedure is approximately the same as that obtained earlier with aldehyde present during the ozonolysis (Figure 3). The effect on the ozonide yield from the trans olefin is also consistent with the results obtained with aldehyde present throughout, namely that slow warm-up give a higher yield of normal ozonide and a lower yield of cross ozonide.

The results obtained with the unsymmetrical olefins, *cis*- and *trans*-4-methyl-2-pentene, are given in Table I. With respect to yield, the results show that solutions ozonized at low temperature and warmed up slowly give rise to only about half as much cross ozonide as solutions ozonized at high temperatures. This is the same effect observed for the ozonolysis of *trans*-diisopropylethylene in the presence of propionaldehyde. Furthermore, the results in Table I indicate that *trans*-4-methyl-2-pentene always gives about the same amount of cross ozonide upon fast warm-up regardless of the reaction temperature. These results would seem to eliminate further consideration of a bimolecular reaction between two initial adducts.

The effects on the ozonide cis/trans ratios given in Table I are also interesting. As reported recently by Fliszár and Carles[7] we find that the normal ozonide (4-methyl-2-pentene) cis/trans ratio is relatively independent of temperature and of olefin geometry. The one major exception is found for the cis isomer ozonized at −119° and warmed slowly. For the cross ozonide (diisopropyl ozonide), a pronounced dependence of the ozonide cis/trans ratio on both temperature and olefin geometry was found. These results are also consistent with those reported by Fliszár and Carles.[7]

Summary and Conclusions

The results reported here serve to emphasize again the recent observations by ourselves and others that the ozonolysis reaction probably proceeds by several different pathways depending upon a number of reaction conditions.

It has been shown here that ozonolysis temperature can affect both ozonide yield and ozonide isomer ratio. These effects are more pronounced in cross ozonides obtained either by ozonolysis of an unsymmetrical olefin or by adding a foreign aldehyde to the ozonolysis of a symmetrical olefin. The rate at which an ozonolysis reaction mixture is warmed to room temperature also affects ozonide yield and isomer ratio. Both of these effects are more pronounced at lower temperatures suggesting that they are related to the concentration of the initial olefin–ozone adduct.

These results coupled with the recently obtained[19] ^{18}O-labeling data under variable temperature conditions provide additional support for our earlier suggestion[2,9] for an additional ozonolysis pathway. Such a pathway appears to be important only at lower temperatures as expected.

Ozonolysis temperatures and rate of warm-up have not usually been sufficiently specified in earlier papers dealing with the ozonolysis mechanism. The results given here indicate that some care should be taken in the interpretation of some of the earlier results.

Experimental Section

Safety.—Although no accidents occurred during the work described here, it should be kept in mind that some of the ozonolysis products, particularly those found at low temperatures, are potentially quite explosive. Safety shields were used during all handling of the solutions at low temperatures and the risk was further reduced by handling only relatively small amounts of ozonolysis products at one time.

Materials.—Research grade *n*-pentane (Phillips Petroleum Co.) was used as solvent. The olefins, *cis*- and *trans*-2,5-dimethyl-3-hexene (Chemical Samples Co.) and *cis*- and *trans*-4-methyl-2-pentene (Phillips Petroleum Co.), and, the aldehydes, propionaldehyde and isobutyraldehyde (Matheson Coleman and Bell), were also of high purity. All olefins and aldehydes were distilled immediately before use.

Ozonolysis Procedure.—A Welsbach Model T-23 ozonator was used as the ozone source. It was charged with tank oxygen of about 9-psi inlet pressure and yielded about 1 mol % of ozone in the exit stream at 115 V. The sample stream, which yielded 0.42 mmol of O_3 per minute was led into the reaction vessels (22-mm inner diameter, 20-cm high) through a glass tubing with the exit hole (3 mm in diameter) about 5 mm above the bottom of the reaction flask. The reaction vessels were always charged with 10 ml of reaction solution and the olefins were ozonized to 50% conversion based on the amount of ozone introduced.

Three different sets of experiments were carried out. In all of them the concentration of the olefin was 0.2 *M*. In the first set no aldehyde was present. In the second set the solutions were 0.2 *M* in propionaldehyde and in the third set 10 ml of an 0.2 *M* precooled (to the bath temperature) solution of propionaldehyde in *n*-pentane was added to the ozonized solutions about 25 sec after stopping the introduction of ozone.

The unsymmetrical olefins, *cis*- and *trans*-4-methyl-2-pentene, were ozonized at high ($-1°$) and low ($-122°$) temperatures (0.2 *M* olefin concentration, 50% conversion, pentane solvent).

In some separate experiments solutions of ozonized *trans*-diisopropylethylene were warmed up by a combination of slow and fast warm-up. Ozonized solutions which had stood at *ca.* $-90°$ for several hours gave rise to several mild explosions when they were warmed rapidly. This contrasts to freshly ozonized solutions at the same temperature which gave no evidence of explosions upon warm-up. The explosions may be due to the rapid decomposition of a precipitate which was observed to be present in such runs. These runs also gave low yields of ozonide presumably because an ozonide precursor, probably the 1,2,3-trioxalane, gave other products upon rapid decomposition. The mild explosion behavior is presumably also responsible for the scatter in yield and cis/trans data sometimes obtained for the trans olefin.

Ozonolysis temperature was measured using a copper constantan thermocouple in conjunction with a millivolt potentiometer (Leeds and Northrup Co.). The thermocouple reached into the reaction solution inside a closed thermowell which was partially filled with pentane. The temperature generally rose during the introduction of ozone sometimes reaching a temperature which was 6° higher than the initial temperature. The ozonolysis temperatures quoted are average temperatures. Their accuracy is estimated to be $\pm 2°$.

Gpc Analysis.—The ozonide yields and cis/trans ratios were determined by gpc using an Aerograph HY-FI Model 600 D gas chromatograph in conjunction with an Aerograph Model 471 digital integrator. A 10 ft by $^1/_{16}$ in. Micropak column containing 5% cyanosilicone fluid (XF-1150) on Chromosorb G of mesh size 100–120, operated at 45° and a nitrogen flow rate of 10 ml/min, achieved a sufficient separation for analysis. The sensitivity of the flame ionization detector (H_2 flow rate 20 ml/min) was determined using authentic samples and *n*-decane or *trans*-decalin as reference. The ozonolysis solutions contained the internal standard in *ca.* 5×10^{-3} *M* concentration. The structure and cis and trans isomer assignment was made on the basis of gpc and nmr data, and the correlation of these with the unequivocal stereoisomer assignment was made on the basis of partial resolution of the trans-*dl* pair for diisopropylethylene ozonide.[20] The cis ozonide has the longer retention time and the methine protons for the cis ozonide are at lower field in the nmr spectrum than the trans. For each experiment at least three integrations were made. The cis/trans ratios were generally within 1%. Under the conditions used no ozonide decomposition on the column could be detected. The ozonide yields and cis/trans ratios did not change after the solutions had stood at room temperature for several days.

The preparative separation of *cis*- and *trans*-diisopropylethylene ozonides was performed on a 30 ft by $^3/_8$ in. column containing 5% cyanosilicone fluid (XF-1150) on 45–60 mesh Chromosorb G. The He flow rate was 10 ml/sec and the column temperature was 57°.

Registry No.—*cis*-Diisopropylethylene, 10557-44-5; *trans*-diisopropylethylene, 692-70-6; propionaldehyde, 123-38-6.

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