qualitative, their yields should be equal, or only slightly higher, than the yields of the respective fluorohydrins.

Reaction of Diphenylacetylene (28) with 1. Compound **28** (180 mg, 1 mmol) was added to Freon containing 2.5 mmol of **1**. The IR spectrum of the crude product mixture showed a wide carbonyl absorption at 1800 cm^{-1}. Fast TLC indicated that there is neither benzil (**31**) nor α-fluoro-α-phenylacetophenone (**30**) in the crude reaction mixture. After column chromatography or high-pressure LC, however, 80 mg of **28** was first recovered, followed by **30** (30% yield based on converted starting material): mp 49 °C;[16] ^{1}H NMR δ 6.50 (CHF, 1 H, d, $J = 49$ Hz), 7.25–8.0 (m, 10 aromatic protons); ^{19}F NMR ϕ^* 176.3 (d, $J = 49$ Hz). The main fraction proved to be benzil (55% yield based on converted starting material) identical in all respects with an authentic sample.

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Registry No. 1, 359-46-6; **2**, 103-30-0; **3a**, 72301-32-7; **3b**, 72301-33-8; **6a**, 3451-35-2; **6b**, 3527-61-5; **7**, 645-49-8; **8**, 1149-18-4; **9a**, 72318-09-3; **9b**, 72318-10-6; **10a**, 72301-34-9; **10b**, 72301-35-0; **11**, 46925-32-0; **12**, 20488-42-0; **13a**, 72301-36-1; **14a**, 72301-37-2; **15**, 1657-50-7; **16a**, 72301-38-3; **17a**, 72301-39-4; **18a**, 72301-40-7; **19a**, 72301-41-8; **20**, 38453-72-4; **21a**, 72301-42-9; **21b**, 72301-43-0; **22a**, 72301-44-1; **22b**, 72301-45-2; **23**, 1694-19-5; **24a**, 72301-46-3; **24b**, 72301-47-4; **25a**, 72301-48-5; **25b**, 72301-49-6; **28**, 501-65-5; **30**, 720-43-4; **31**, 134-81-6; **32**, 72301-50-9; **34**, 1860-17-9; **35a**, 72301-51-0; **36a**, 72301-52-1; **36b**, 72301-53-2; **37a**, 72301-54-3; **38a**, 72301-55-4.

Ozonolysis. The Added Aldehyde Effect[1]

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The effect of increasing amounts of *n*-butyraldehyde on ozonide yield and stereochemistry in the ozonolysis of *cis*- and *trans*-2,5-dimethyl-3-hexenes has been studied. A similar study was carried out on *trans*-2,2,5,5-tetramethyl-3-hexene. The results are interpreted by using a mechanistic scheme involving syn and anti carbonyl oxide isomers as well as some contribution from nonconcerted ozonide formation.

Recent years have seen an accumulation of an enormous amount of data on the ozonolysis reaction along with continued efforts to provide a comprehensive mechanistic scheme for the reaction.[2] Theoretical chemists have also found the problem to be an interesting one and have made suggestions which both challenge longstanding views and provide stimulation for new experimental approaches.[3–6]

For some time now we have been involved in an approach to the ozonolysis mechanism problem in which the effects of a number of reaction variables on typical reaction parameters (yield, stereochemistry, etc.) are systematically studied.

One of the reaction variables which has received some attention by us and other workers is that of solvent.[7–17] In a small number of instances such studies have included the special case in which aldehyde is added to the reaction medium[11,16,18–21] or is the actual solvent.[22] Such studies present particularly challenging problems in interpretation because in theory aldehydes are capable of influencing the reaction in at least two general ways, i.e., by exercising a medium (polar) effect on the process occurring and/or by participating at one or more points in the overall chemistry.

One of the remarkable effects of aldehyde as ozonolysis solvent is a suppression, partial or complete, of formation of ozonide.[22] Inasmuch as all of the current mechanistic proposals retain a step in which aldehyde and carbonyl oxide combine to give ozonide, this observation is troublesome and requires further consideration.

Story et al.[22] explain their results by postulating a reductive ozonolysis, that is, a reaction in which aldehyde is oxidized to acid and an ozonolysis intermediate (they suggest the Staudinger[23] molozonide) is reduced. Bailey et al.[20] have observed a similar effect of added aldehyde on ozonide yield but suggest that the aldehyde is oxidized by some other intermediate, possibly a 1,2,3-trioxolane or carbonyl oxide.

In a study designed to determine more specifically the point in the overall reaction scheme where the aldehyde is exerting an influence or actually intervening, we recently reported[16] that adding aldehyde to the solid 1,2,3-trioxolane formed in the ozonolysis of *trans*-di-*tert*-butylethylene (**1**) leads to decreased and ultimately zero ozonide yield. The latter is obtained when the solid 1,2,3-trioxolane is allowed to warm up in 100% aldehyde. These results

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[1] Taken in part from the Ph.D. dissertation of Jang-Szu Su, UMSL.

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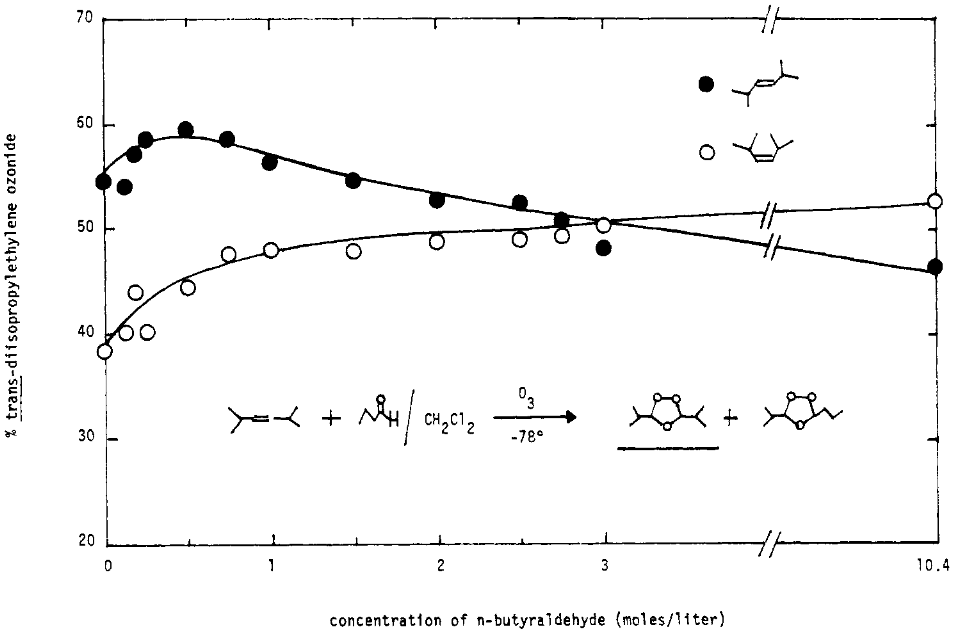

Figure 1. 1,2-Diisopropylethylene ozonide cis/trans ratio as a function of added *n*-butyraldehyde concentration in the ozonolysis of *cis*- and *trans*-1,2-diisopropylethylene at −78 °C.

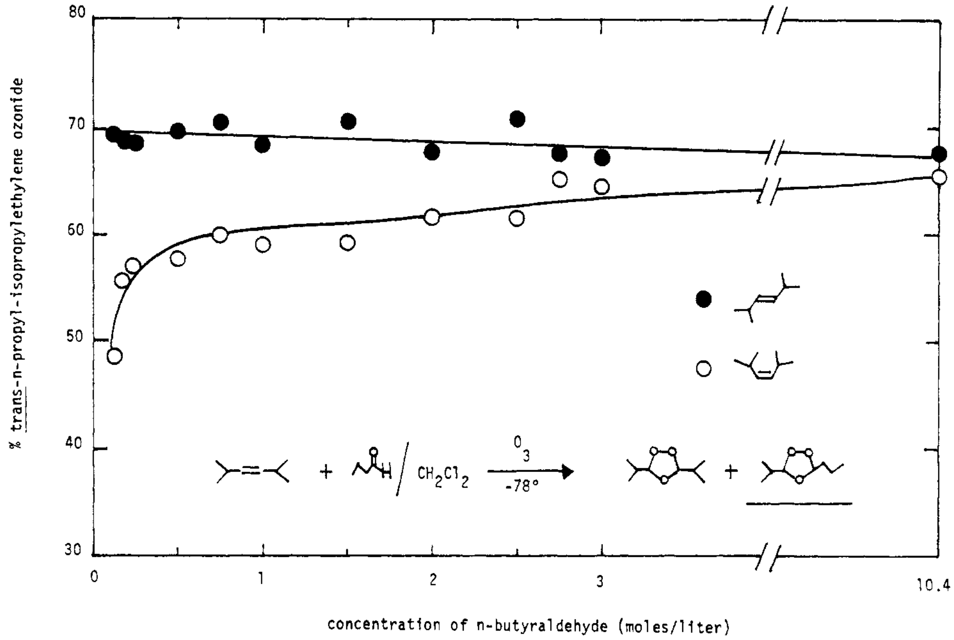

Figure 2. *n*-Propylisopropylethylene ozonide cis/trans ratio as a function of added *n*-butyraldehyde concentration in the ozonolysis of *cis*- and *trans*-1,2-diisopropylethylene at −78 °C.

suggest that the aldehyde is exerting an influence *after* the generally accepted first step in the process, namely, 1,2,3-trioxolane formation. Because there is some reason to believe that the olefin used, *trans*-di-*tert*-butylethylene, may be anomalous, this conclusion should probably not be considered a general one at this time.

In the present work we extend the studies of the ozonolysis of 1 to reaction media containing increasing amounts of aldehyde. We also report the results of similar studies on the stereoisomers of 1,2-diisopropylethylene. These most recent results, combined with the earlier ones[16] on 1 and the stereoisomers of 3-hexene,[19] permit us to speculate further on the origin of the added aldehyde effect.

Results and Discussion

The results of the −78 °C ozonolyses of *cis*- and *trans*-2,5-dimethyl-3-hexenes are shown in Figures 1–4. Increasing the concentration of added *n*-butyraldehyde has a small effect on the diisopropylethylene ozonide stereochemistry for both olefin isomers (Figure 1). In the case of the trans olefin the ozonide has a lower trans content in 100% aldehyde solvent as compared to CH_2Cl_2 solvent. An opposite effect is observed for the cis olefin where the trans ozonide content has increased in aldehyde solvent as compared to CH_2Cl_2. Indeed, in aldehyde solvent the cis olefin gives a higher percentage trans ozonide than the trans olefin. This is contrary to what is observed in most solvents where the trans olefin usually gives a higher trans ozonide content than the cis olefin.

For the cross ozonide, *n*-propylisopropylethylene ozonide, the aldehyde concentration has little effect on the ozonide stereochemistry in the case of the trans olefin (Figure 2). In the case of the cis olefin, however, the effect is much greater, and, as with the diisopropylethylene ozonide from the same olefin, the percentage trans ozonide content increases with increasing aldehyde concentration and is considerably higher (65.8%) in 100% aldehyde than

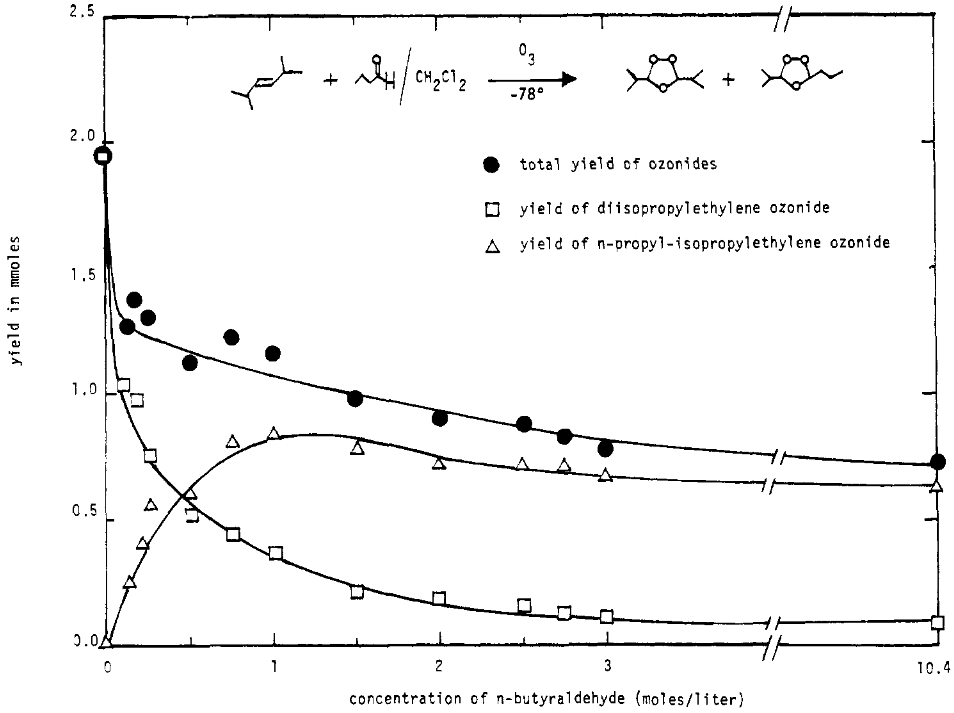

Figure 3. Variation of 1,2-diisopropylethylene, *n*-propylisopropylethylene, and total ozonide yields as a function of added *n*-butyraldehyde concentration in the ozonolysis of *trans*-1,2-diisopropylethylene at −78 °C.

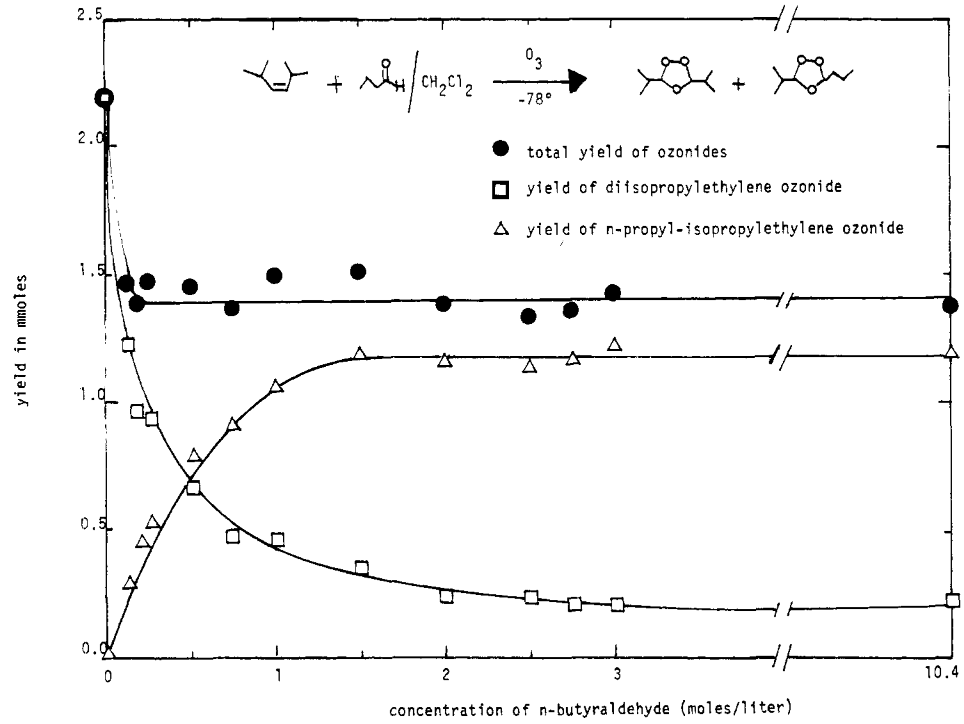

Figure 4. Variation of 1,2-diisopropylethylene, *n*-propylisopropylethylene, and total ozonide yields as a function of added *n*-butyraldehyde concentration in the ozonolysis of *cis*-1,2-diisopropylethylene at −78 °C.

in a CH_2Cl_2 solution containing 0.0625 M aldehyde (53.7%).

The effects of increasing concentrations of added aldehyde on ozonide yield are shown in Figure 3 and 4. In the case of the trans olefin (Figure 3), increasing concentrations of added aldehyde lead to decreasing amounts of normal ozonide formation and increasing amounts of cross ozonide formation, as expected. However, the added aldehyde conditions lead to a decrease in total ozonide yield, with the effect being most pronounced at the lower aldehyde concentrations. Ultimately, the total ozonide yield in butyraldehyde solvent is only ca. 37% of that obtained in methylene chloride solvent.

The yield results with the cis olefin (Figure 4) are, in general, similar to those found for the trans olefin. Thus, increasing aldehyde concentration leads to increasing cross ozonide formation and decreasing normal ozonide formation. Again, the added aldehyde tends to decrease total ozonide yield. There is a difference between the two olefins, however. The reduction in total ozonide yield is much less in the case of the cis olefin. In butyraldehyde solvent the cis olefin gives a total ozonide yield which is ca. 64% of that obtained in methylene chloride solvent, in contrast to the corresponding figure of ca. 37% for the

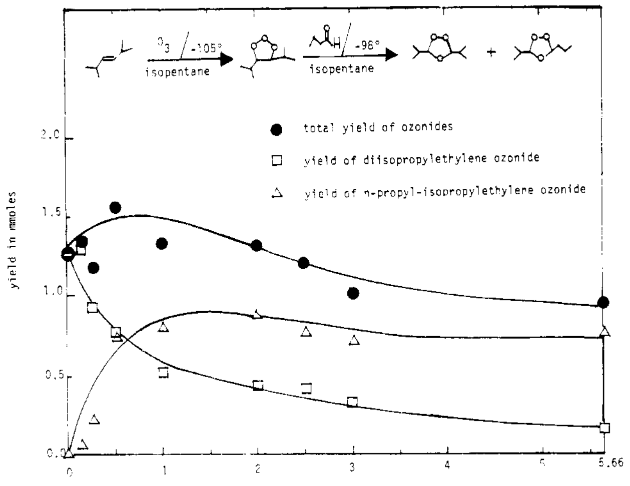

Figure 5. Variation of 1,2-diisopropylethylene, *n*-propylisopropylethylene, and total ozonide yields as a function of added *n*-butyraldehyde concentration. Aldehyde added after the ozonolysis of *trans*-1,2-diisopropylethylene at −105 °C.

trans olefin.

In a separate set of experiments *trans*-2,5-dimethyl-3-hexene was ozonized at a lower temperature (−105 °C), and then varying amounts of *n*-butyraldehyde were added after completion of ozonolysis and before slow warmup. Under these circumstances the aldehyde cannot be exercising a medium effect on the initial olefin–ozone reaction. The effect on ozonide yield is shown in Figure 5. Several points require comment. Although the yield of normal ozonide in methylene chloride solvent is lower at the lower temperature used here (−105 °C vs. −78 °C), the effect of varying amounts of added aldehyde on the rate of reduction of that yield is quite different in the two types of experiments. The same concentration of aldehyde present during the ozonolysis at −78 °C leads to a greater reduction in normal ozonide yield than it does when this aldehyde concentration is produced after ozonolysis at −105 °C and before warmup. At the same time, the aldehyde added after ozonolysis at −105 °C is somewhat more efficient at producing cross ozonide than it is when present in the corresponding concentration during ozonolysis at −78 °C. The net result of these two effects is to produce an optimal (low) concentration of added aldehyde with respect to total ozonide yield (Figure 5). The effect of added aldehyde on normal and cross ozonide stereochemistry in this set of experiments (not shown) is essentially negligible. The normal ozonide trans/cis ratio was ca. 55/45 in both methylene chloride solvent and the highest aldehyde concentration used (5.6 M). This is in slight contrast to the −78 °C experiments in which the normal ozonide ratio in methylene chloride is essentially the same as it is at the lower temperature, but increasing aldehyde concentration caused a small decrease in the ozonide trans/cis ratio.

Likewise, the varying concentrations of added aldehyde had little effect on the cross ozonide stereochemistry in the −105 °C experiment. The ozonide trans/cis ratio was ca. 60/40 throughout. Again, this contrasts slightly with the −78 °C experiments in which the cross ozonide trans/cis ratio was essentially invariant at various aldehyde concentrations but at the higher trans/cis ratio of ca. 68/32.

The results obtained from ozonolysis of 1 at −78 °C in various solvents ranging from 100% hexane to 100% *n*-butyraldehyde are shown in Figure 6. The plots indicate the effect of increasing amounts of *n*-butyraldehyde on ozonide yield (in percent and millimoles produced). There is a smooth and pronounced decrease in ozonide yield with increasing amounts of butyraldehyde in the reaction solvent until the amount obtained (1.9%) in aldehyde solvent is negligible. These results are similar to those obtained[16] when increasing concentrations of aldehyde are added to the solid 1,2,3-trioxolane obtained from the ozonolysis of 1. They also are consistent with those obtained by Story et al.,[22] who found that addition of propionaldehyde to the white solid obtained upon ozonolysis of 1 gave a reduced yield (<10%) of normal ozonide and no cross ozonide.

In no case, including 100% aldehyde solvent, were we able to detect formation of any cross ozonide incorporating butyraldehyde in these experiments. The stereochemistry of the normal ozonide obtained under all solvent conditions was 100% trans.

It is clear that the presence of butyraldehyde in the reaction medium leads to a reduction, sometimes drastic, in ozonide yield. The question of whether this is a medium (polar) effect alone or is due to participation of aldehyde in nonozonide-forming pathways is not readily answered. One has to be cautious when making comparisons with previously reported[24] effects of solvent polarity on ozonide

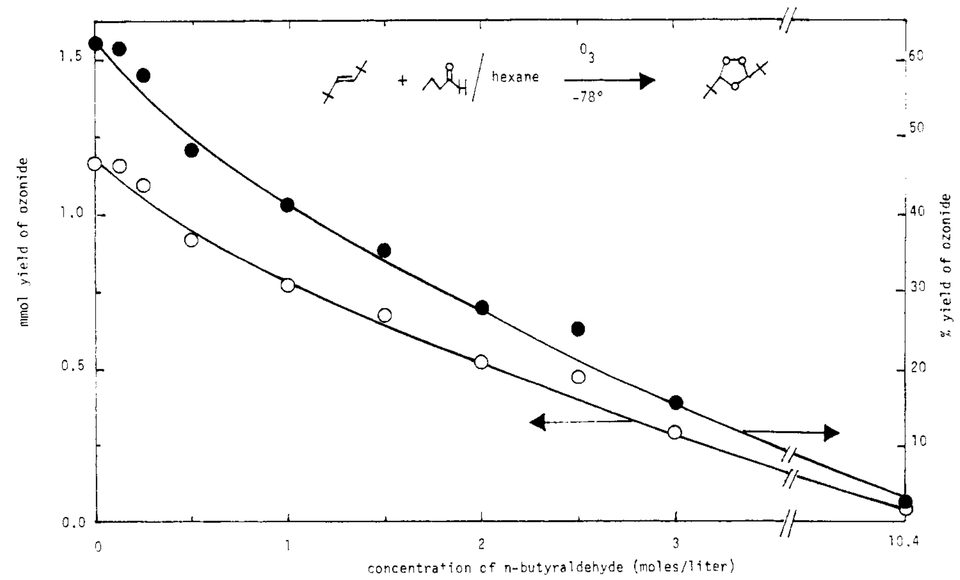

Figure 6. Ozonide yield as a function of added *n*-butyraldehyde in the ozonolysis of *trans*-1,2-di-*tert*-butylethylene at −78 °C.

yield, since these previous results may not have been obtained under reaction conditions (e.g., temperature, concentration, etc.) which are in fact comparable. It is now well established[2] that many reaction variables, including temperature and olefin concentration, can also affect ozonide yield.

Story et al.[22] reported that ozonolysis of *trans*-diisopropylethylene in acetone solvent gave a "good yield" of normal ozonide in contrast to the results they obtained (0% ozonide) when using propionaldehyde solvent. These workers argue that these results eliminate solvent polarity as being responsible for the great drop in yield in aldehyde solvent.

A possible explanation for the effect of added aldehyde on yield and ozonide stereochemistry includes consideration of carbonyl oxide syn/anti distribution and the effect of an increasingly polar medium on this distribution, as well as considerations of the susceptibility of carbonyl oxide–aldehyde adducts to non-ozonide-producing pathways. Included in the latter group are pathways promoted by, and incorporating, added aldehyde.

We earlier[25] speculated about carbonyl oxide syn/anti equilibration effects on ozonide stereochemistry. Mile and Morris[26] have also used this concept in interpreting the effects of reaction mixture warm-up times on final ozonide stereochemistry in the ozonolysis of *cis*- and *trans*-diisopropylethylene.

A major difficult in using this approach is the present disagreement on the thermodynamic stability of the carbonyl oxide stereoisomers. Using MINDO/3, Hull[27] has concluded that the syn configuration is the more stable one in the case of methyl-substituted carbonyl oxide. On the basis of CNDO/2 calculations, Rouse[28] concluded that the syn configuration is the more stable for both methyl- and *tert*-butyl-substituted carbonyl oxides. On the other hand Harding and Goddard,[5] using generalized valence bond calculations (GVB), have concluded that the anti configuration is more stable than the syn isomer by 1–2 kcal, apparently for all carbonyl oxides. In applying the syn/anti equilibration scheme, Mile and Morris[26] assumed that the anti form is the more stable one.

A rationalization of our present and previous[16,19] results on ozonide yield and stereochemistry is made possible if the assumption of a greater stability for the syn carbonyl oxide is made. This is particularly the case if one incorporates the recent ideas of Harding and Goddard[5] on the relative susceptibility of carbonyl oxide–aldehyde adducts to nonozonide pathways. The assumption of a greater stability for the syn carbonyl oxide stereoisomer is not entirely arbitrary. Experimental evidence has been presented[29-37] which indicates a greater thermodynamic stability for the syn isomer in a number of systems which are isoelectronic with carbonyl oxides. Included in these studies are the lithiated derivatives of nitrosamines,[29-31] dimethylamides,[31-32] oximes,[33,34] hydrazones,[35,36] and aldimines.[37] Also related are the many reported instances[38] of greater cis thermodynamic stability in a variety of allyl organometallics. Of particular importance to the present work is the reported[38] reversal of stability observed when isomers of 1-methylallyl anion are examined in the gas phase (the cis isomer is less stable in the gas phase). As pointed out by the authors,[38] this latter work suggests a major role for the solvent in determining thermodynamic stability in these systems.

It is reasonable to expect, therefore, that solvent will play a major role in determining syn/anti carbonyl oxide isomer ratios as well as the rate of isomerization of the isomers. Such solvent effects should be translated into ozonide stereochemistry effects.

Application of this approach is first made to the yield results (Figures 3, 4 and 6). First, it is clear that *trans*-diisopropylethylene suffers a greater reduction in ozonide yield with increasing added aldehyde concentration than the cis isomer. Likewise, increasing the substituent size (*trans*-di-*tert*-butylethylene vs. *trans*-diisopropylethylene) causes a further increase in the susceptibility to ozonide yield decrease brought about by added aldehyde. Both the Bailey–Bauld[7] and Kuczkowski[39] mechanism schemes predict that cis olefins will give predominantly anti carbonyl oxides and that the corresponding trans olefin isomers will give predominantly syn carbonyl oxides. Also, increasing the size of the olefin substituent is predicted to increase the amount of the dominant carbonyl oxide isomer. Interestingly enough, Harding and Goddard have predicted[5] that syn carbonyl oxides with bulky substituents will add to the aldehyde carbonyl group to produce an intermediate (written as a diradical in their scheme) which is "expected to lead to an increase in radical reactions (polymeric products) and a decrease in ozonide yield".

Thus, trans olefins with bulky substituents should give more syn carbonyl oxide, and consequently lower ozonide yields, as is generally observed. If it is assumed that one effect of increasing added aldehyde concentration is to increase the polarity of the medium and thus to permit shifting of the syn/anti distribution toward the thermodynamic distribution (i.e., more syn under the present assumption), then the effect of increasing concentration of added aldehyde on ozonide yield is also understandable. Higher concentrations of added aldehyde should lead to greater reductions in ozonide yield, as observed (Figures 4 and 5). Furthermore, the greater reduction in yield in the case of *trans*-di-*tert*-butylethylene is presumably due to an even greater proportion of syn carbonyl oxides brought about by the presence of a larger substituent.

Although the added aldehyde can be expected to exert a medium effect on the syn/anti distribution as described above, it may also play a role in diverting the carbonyl oxide–aldehyde adducts to nonozonide products. Such a role could be exercised a priori in at least two different manners. The intermediate **2** could add one or more aldehyde molecules before terminating, as suggested earlier

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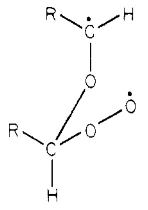
(40) Note added in proof: Block et al. have recently shown that the syn isomer is the major component in a series of sulfine stereoisomeric mixtures. Sulfines are the monothio analogues of the carbonyl oxides (Block, E.; Revelle, L. K.; Bazzi, A. B.; *Tetrahedron Lett.*, in press).



2

by us.[16] Another possibility which should at least be considered is that the aldehyde molecules may undergo hydrogen atom transfer reactions to the intermediate and thus prevent ozonide formation. These roles of the added aldehyde depend upon the existence of an intermediate such as **2** and thus upon a nonconcerted ozonide-forming process as suggested earlier by us[16] and now examined in greater detail by Harding and Goddard.[5]

Experimental evidence for such reactions of the added aldehyde may become available by studying in more detail the polymeric products, i.e., oligomers, of the ozonolysis reaction. Such studies are now under way in our laboratory.

Application of the assumption of a greater thermodynamic stability for the syn carbonyl oxide to the stereochemical results is now considered. In the case of *cis*-diisopropylethylene, the assumption of a shift in the syn/anti carbonyl oxide distribution toward the syn isomer would predict a greater percentage of trans ozonide as the added aldehyde concentration is increased. This is indeed the case for both the normal and cross ozonides produced (Figures 1 and 2). In the case of the trans olefin isomer, increasing aldehyde concentration has the same effect on ozonide stereochemistry except in the normal ozonide. Here, increasing concentrations of added aldehyde cause a shift to a lower trans normal ozonide content. This shift would seem to be in conflict with the assumption of a movement to a higher syn carbonyl oxide content. Two points need to be added, however. First, the ozonide stereochemical change in the trans olefin case is less than that observed with the cis olefin. This is consistent with what was observed earlier[18] in the case of the stereoisomers of 3-hexene with added butyraldehyde. Second, a complex combination of kinetic factors could combine to bring about the observed stereochemical result in the case of the trans olefin. These factors include: rate of decomposition of the initial ozonide (known to be slower for the trans isomer), rate of syn–anti interconversion, rate of addition of carbonyl oxide stereoisomers to aldehyde, and, in the case of nonconcerted addition, rate of conversion of carbonyl oxide–aldehyde intermediates to ozonide.

The latter factor may be particularly important in the present work. Harding and Goddard have suggested[5] that an additional consequence of increasing the solvent polarity could be an increased lifetime for intermediates such as **2**. Such an increased lifetime would lead to a loss in stereoselectivity in the ozonide, which is what is observed for both olefin isomers as seen in Figures 1 and 2 (i.e., the olefin isomers give more similar ozonide stereochemical distributions in aldehyde than in methylene chloride solvent).

We emphasize again that the foregoing discussion is based on the assumption of the syn carbonyl oxide being more stable in this case. In our judgment such an assumption leads to a greater fit between experiment and theory than that given by assuming the anti carbonyl oxide to be more stable.

What is really needed is better agreement among theoreticians regarding the stabilities of the carbonyl oxides or, preferably, an experimental determination of their relative stabilities. Efforts directed toward the latter goal are under way in this laboratory.

It seems to us that the present results, as well as many of those obtained previously,[2] give further support to a mechanistic scheme involving at least some contribution from nonconcerted ozonide formation.

Experimental Section

Safety. Some efforts to isolate the 1,2,3-trioxolane in the case of *trans*-diisopropylethylene resulted in severe detonations. The detonations occurred in approximately one-third of the attempts and under conditions which differed in no readily apparent way from those in which no detonations occurred. **Extreme caution** should always be exercised when handling these unstable ozonolysis intermediates. In particular, all reactions and warm-ups should take place behind safety shields. The results presented herein contain no data from experiments in which observable detonations occurred.

Instrumentation. NMR spectra were recorded with a Varian T-60 NMR spectrometer. Mass spectra were obtained using as Associated Electronics Industries Model MS-12 mass spectrometer. Infrared spectra were recorded with Perkin-Elmer Models 137 or 337 infrared spectrophotometers. Analytical and preparative GLPC work was carried out on Varian HY-FI Model 600-D and Varian-Aerograph Model A-705 gas chromatographs. The following GLPC columns were employed: column A, 0.25 in. × 6 ft, 7% β,β′-oxydipropionitrile on 60/80 Chromosorb G, DMCS; column B, 0.125 in. × 15 ft, 7% β,β′-oxydipropionitrile on 60/80 Chromosorb G, DMCS; column C, 0.375 in. × 12 ft, 7% β,β′-oxydipropionitrile, on 45/60 Chromosorb G-AW, DMCS.

Materials. The olefins used were from Chemical Samples Co., Columbus, OH. The stated purity was 98 or 99% and was checked by GLPC analysis before use. In the case of *trans*-2,5-dimethyl-3-hexene, it was necessary to pass the olefin through neutral silica gel twice before obtaining material of 98% (GLPC) purity. Butyraldehyde was purified by distillation under argon immediately before use. Isopentane was purified by distillation under argon, with the fraction boiling at 29 °C being collected for use. Methylene chloride was purified by overnight stirring with concentrated sulfuric acid, washing, drying with calcium chloride, and finally distilling under argon from calcium hydride. Hexane was Fisher Certified Grade (99%) and was checked by GLPC before use.

General Ozonolysis Procedure. 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^{-1}. The ozonolysis solutions were purged with argon for 10 min before and after passing the ozone/oxygen 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 completion of ozonolysis, the reaction mixtures were subjected to a "slow warm-up procedure" as follows. The reaction solutions were allowed to stand in the cooling bath until room temperature was reached (ca. 40 h).

Ozonolysis of *cis*- and *trans*-2,5-Dimethyl-3-hexene. The general ozonolysis procedure was used with the reaction solution cooled to ca. −78 °C in a dry ice–methanol bath. In all cases ozonolyses were carried out on a total reaction volume of 10 mL which contained 5 mmol (0.5 M) of the olefin. The solutions were brought to the 10 mL total with methylene chloride, methylene chloride containing varying amounts of *n*-butyraldehyde, or 100% *n*-butyraldehyde (see Figures 1–4). Ozonolysis was continued to 75% of the theoretical amount required.

Upon completion of the ozonolysis and use of the slow warm-up procedure the reaction solutions were then subjected to GLPC analysis using column A (column temperature, 50 °C). Preparative GLPC was used to isolate the isomeric 2,5-dimethyl-3-hexene and *n*-propylisopropylethylene ozonides, the latter being the cross ozonide formed by reaction with *n*-butyraldehyde. The ozonides were identified on the basis of GLPC, NMR, and IR data. The isolated ozonides were used to make up standard solutions for GLPC analysis to obtain ozonide yield and stereoisomer ratio data.

Ozonide isomer ratios were determined from xerographic copies of the GLPC recorder traces using the cut-and-weigh method.

Thermal conductivities of ozonide stereoisomers were assumed to be equal. Ozonide ratio peak areas used were based on at least three successive determinations on each of three separate injections. The determinations have a maximum variation of ±0.5%. Ozonide yields were determined in a similar manner using standard solutions to calibrate peak areas. Yield data were determined with a precision of ±0.5%. Results of the analyses are shown in Figures 3 and 4.

The GLPC chromatograms were also used to check for actual olefin consumption. In particular, the olefin consumptions were checked for the ozonolysis of *trans*-2,5-dimethyl-3-hexene in methylene chloride and *n*-butyraldehyde solvents. The total ozonide yield in these two solvents differs greatly (CH_2Cl_2, 1.96 mmol; *n*-butyraldehyde, 0.72 mmol). Yet the olefin consumption in these cases differs only slightly (CH_2Cl_2, 3.72 mmol; *n*-butyraldehyde, 3.59 mmol). The difference in ozonide yield is, therefore, not due to a reduced olefin consumption in the aldehyde solvent.

Ozonolysis of *trans*-2,2,5,5-Tetramethyl-3-hexene. The general ozonolysis procedure was used with the reaction solutions cooled to ca. -78 °C in a dry ice–methanol bath. The ozonolysis solutions were 5 mL of an 0.5 M solution of *trans*-2,2,5,5-tetramethyl-3-hexene in *n*-hexane, mixtures of *n*-hexane–*n*-butyraldehyde, or 100% *n*-butyraldehyde. Ozonolysis was continued to 75% of the theoretical amount required. Ozonide isomer distributions and yields were determined as described above, using column B for analytical GLPC (column temperature, 50 °C) and column C for preparative GLPC (column temperature, 65 °C). The results are shown in Figure 6.

Low-Temperature Ozonolysis of *trans*-2,5-Dimethyl-3-hexene. The general ozonolysis procedure was used with the reaction solutions cooled to -105 °C in a liquid N_2–isopentane bath. The ozonolysis solutions contained 2.5 mmol of *trans*-2,5-dimethyl-3-hexene in 5 mL of isopentane. Ozonolysis was continued until ozone was present in excess as evidenced by the appearance of a blue color (ca. 30 min). The reaction solutions were then purged with argon until the blue color was removed. At this point the reaction mixtures contained a white precipitate. The reaction mixtures were then warmed up to -98 °C, and solutions containing various amounts of *n*-butyraldehyde in isopentane (total volume of 5 mL) were added. The reaction mixtures were purged with argon continuously during addition of the aldehyde solutions. After addition of the aldehyde solutions, the reaction mixtures were allowed to warm up using the slow warmup conditions. During some of these warmups small explosions occurred which were contained within the reaction vessel. These were presumably due to rapid decomposition of the unstable trioxolane.

The reaction mixtures were analyzed by GLPC using column A (column temperature, 50 °C) to determine ozonide yields and isomer distributions. The GLPC chromatograms indicated that all of the olefin had reacted. Results of these analyses are shown in Figure 5.

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Registry No. *cis*-2,5-Dimethyl-3-hexene, 10557-44-5; *trans*-2,5-dimethyl-3-hexene, 692-70-6; *trans*-2,2,5,5-tetramethyl-3-hexene, 692-48-8; *n*-butyraldehyde, 123-72-8; *cis*-2,5-dimethyl-3-hexene ozonide, 13126-94-8; *trans*-2,5-dimethyl-3-hexene ozonide, 13126-95-9; *cis*-*n*-propylisopropylethylene ozonide, 72444-59-8; *trans*-*n*-propylisopropylethylene ozonide, 72444-60-1; *cis*-2,2,5,5-tetramethyl-3-hexene ozonide, 16187-12-5; *trans*-2,2,5,5-tetramethyl-3-hexene ozonide, 16187-11-4.

Hydroformylation of Methyl Methacrylate Catalyzed by Homogeneous and Polymer-Attached Rhodium Complexes

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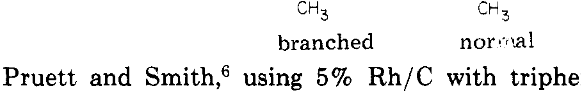
The hydroformylation of methyl methacrylate has been studied in the presence of $RhH(CO)(PPh_3)_3$ or its polymer-anchored analogue as the catalyst. The branched/normal product ratio was exceptionally sensitive to conditions, increasing as (1) [P]/[Rh] increased, (2) the pressure increased, (3) PPh_3 was replaced by $Ph_2P(CH_2)_2P(Ph)(CH_2)_2PPh_2$, and (4) the polymer-supported phosphines replaced PPh_3 at equivalent P/Rh ratios. The branched/normal selectivity decreased as (1) $[H_2]/[CO]$ increased and (2) the temperature increased. Changing the solvent from benzene to THF or adding Et_3N had only minor effects on selectivity. The results are interpreted in terms of Wilkinson's mechanism where electronic effects control double-bond insertion into the rhodium–hydride bonds but isomerization equilibria of alkyl or acyl intermediates become more important at higher temperatures.

The hydroformylation of α,β-unsaturated esters, and in particular acrylates and methacrylates, has received much attention as a route to 1,3- and 1,4-difunctional compounds.[1-6] The product distribution in the hydroformylation of ethyl acrylate has been studied with cobalt[1,2] and rhodium[3,4] catalyst systems. The rhodium-catalyzed hydroformylation of methyl methacrylate (MMA) has been studied and the normal/branched selectivity has been found to be highly dependent on reaction conditions.[4-6] For example, Falbe[5] found the branched product (eq 1) was favored at low temperatures while the normal product dominated at high temperatures when a Rh_2O_3 catalyst was used. At 1000 atm (1:1 H_2/CO) the branched isomer accounted for ca. 85% of the product at 80 °C vs. only 13% at 150 °C. Higher pressures favored formation of the branched isomer as did the addition of phosphine ligands.



$$CH_2{=}C(CO_2CH_3)CH_3 \xrightarrow[H_2/CO]{RhL_x} HC(=O)C(CH_3)_2CO_2CH_3 + HC(=O)CH_2CH(CH_3)CO_2CH_3 \quad (1)$$

Pruett and Smith,[6] using 5% Rh/C with triphenyl phosphite ([P]/[Rh] = 6.1), found that the yield of the

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