Stereochemistry of Ozonide Formation. Effects of Complexing Agents and Rate of Warm-up[1]

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Abstract: Data concerning differences in cis–trans ozonide ratios, depending on (1) the presence or absence of complexing agents and (2) a fast or slow warm-up of the ozonolysis reaction mixture, are presented for five different cis–trans olefin pairs. Evidence is discussed which indicates that the carbonyl oxide intermediate is complexed at low temperatures and this either prevents equilibration of syn and anti carbonyl oxide stereoisomers or selectively favors the anti isomer through stronger complexation. The effects are greater the larger the olefinic double bond substituents. *trans*-1,2-Diisopropylethylene gives cis–trans ozonide ratios of greater than unity under slow warm-up conditions, which is contrary to predictions based on existing stereochemical mechanisms.

The first observation of complexes of ozone with carbon π systems was reported from this laboratory in 1971.[2,3] These complexes involved either aryl substituted ethylenes[2,3] or purely aromatic compounds.[4] Following our first communication,[2] similar complexes were claimed for certain aliphatic systems,[5,6] although doubt was cast upon the conclusions of Hull et al.[5] by the data reported by Alcock and Mile.[6]

In our 1974 paper,[4] we made the tentative observation that ozonolyses of cis and trans olefins with complexed ozone afforded cis–trans ozonide ratios which differed from those obtained with "free" ozone. This was confirmed in our most recent communication on the subject,[7] where improved technique and consistent results, using a slow warm-up procedure, were reported. Differences in results with slow and fast warm-ups were first observed by Murray and Hagen.[8]

The purpose of the present paper is to describe the experimental details of the findings presented in our 1976 communication,[7] as well as of some other recent work, and to discuss in greater detail the theoretical implications. Included in this paper are studies with the cis and trans isomers of 2,5-dimethyl-3-hexene (diisopropylethylene), 2,2,5,5-tetramethyl-3-hexene (di-*tert*-butylethylene), 3-hexene, 2-butene, and 4-methyl-2-pentene (isopropylmethylethylene). In later papers further investigations will be presented, involving additional complexing agents and olefins as well as solvents and reaction conditions.

Table I shows the cis–trans ozonide ratios obtained by ozonizing *cis*- and *trans*-1,2-diisopropylethylene with and without a complexing agent at two different temperatures and in two different solvents. It can be seen that the cis–trans ozonide ratios obtained at −155 °C with the cis isomer differ depending on the presence or absence of a complexing agent. This also appears to be true in two instances with the trans isomer in isopentane solution. However, the results portrayed in Table II show that the cis–trans ozonide ratios are the same, within experimental error, whether (1) the ozonolysis is performed with previously complexed ozone, (2) a mixture of the olefin and the complexing agent is ozonized, or (3) the complexing agent is added to the −155 °C reaction mixture after ozonolysis of the olefin is complete; in all three cases both the rate of warm-up and the work-up method were identical. In addition, it was shown that the characteristic ring proton doublet for the primary ozonide of *trans*-1,2-diisopropylethylene (δ 4.15–4.20 ppm) was present in equal intensity whether ozonolysis was performed with "free" or with complexes ozone. The primary ozonide of the cis olefin was similarly observed, although the ring proton peak (δ 4.35–4.40) was broad and unresolved, as also found by Greenwood and co-workers for other cis primary ozonides.[9] In the presence of a complexing

agent, toluene, the cis ring proton absorption shifted to δ 4.09 ppm. Careful NMR studies showed that the trans primary ozonide is stable up to about −78 °C, or slightly higher, while the cis primary ozonide decomposes at −130 °C ± 5. Incidentally, although the primary ozonide of *trans*-1,2-diisopropylethylene had been observed previously by Criegee,[10] ours is the first reported detection of the cis primary ozonide; it is also the first NMR characterization of either isomeric primary ozonide.

These results, along with the observation that ozonide yields are not affected, within experimental error, by the presence of a complexing agent (Table I), lead to the conclusion that the effect of the complexing agent occurs during the decomposition of, rather than the formation of, the primary ozonide, and that there is no difference in the mechanism of ozone attack with "free" or with complexed ozone. It was shown earlier[4] that ozone complexes form reversibly; thus, even though most of the ozone is complexed, the olefin reacts with "free" ozone in equilibrium with the complex.

This reasoning led us to propose in our 1976 communication[7] that, as the primary ozonide decomposes in the presence of the complexing agent, the carbonyl oxide intermediate, which is isoelectronic with ozone, becomes complexed, and this either prevents (or retards) equilibration of syn and anti zwitterions[11] or, perhaps, results in one stereoisomer being complexed preferentially.

Consistent with this general picture are the following observed facts. The data of Table I reveal that the differences in cis–trans ozonide ratios obtained in the presence or absence of a complexing agent at −155 °C are important, in general, only with the cis olefin (exceptions appear to be with the trans olefin in isopentane and using *o*-xylene or hexaethylbenzene as complexing agents). This is understandable from the viewpoint that the cis primary ozonide decomposes at a temperature low enough (−135 °C) for complexation of the carbonyl oxide to occur, whereas the trans primary ozonide is stable up to −78 °C or higher. Cis–trans ozonide ratios from ozonolyses of the cis olefin at −78° in the presence or absence of a complexing agent are identical (Table I). At this temperature complexation of the carbonyl oxide would not be expected to occur to any appreciable extent; similar ozone complexes are not stable above −130 °C, in general. This experiment also indicates that the differences noted at −155 °C are not simple solvent effects caused by the presence of the aromatic complexing agent.[12]

The data of Table I further show that the cis–trans ozonide ratios from the cis and trans isomeric olefins tend to converge as (1) the complexing agent is removed at −155 °C, (2) the temperature of the ozonolysis is raised, and (3) the solvent is

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Table I. Cis-Trans Ozonide Ratios from Ozonolyses of *cis*- and *trans*-1,2-Diisopropylethylene with Various Complexing Agents[a]

Temp, °C	Complexing agent	Isopentane		Freon-12[b]	
		Cis isomer[c]	Trans isomer[c]	Cis isomer[c]	Trans isomer[c]
−78	None	54:46	50:50	50:50	50:50
−78	Isodurene	55:45	45:55	52:48	49:51
−155	None	69:31 (86)	60:40 (35)	56:44 (85)	51:49 (42)
−155	Toluene[d]	74:26	60:40		52:48
−155	o-Xylene	75:25 (81)	65:35	61:39	48:52
−155	Isodurene	76:24 (83)	58:42	61:39	51:49
−155	MPE[e]	77:23 (88)	61:39	60:40	52:48
−155	HEB[f]	75:25	65:35		
−155	Anisole[g]	76:24			
−155	PMB[h]	77:23			
−155	TMB[i]	74:26			
−155	HFB[j]	69:31			

[a] Where complexing agents were employed, the ozone complex was prepared first, after which a solution of the alkene was added (see Experimental Section). In all cases the final concentrations were as follows: alkene (0.04 M), complexing agent (0.04 M, if present). A slow warm-up (see Experimental Section) was employed in all cases. [b] Dichlorodifluoromethane. [c] Values in parentheses are ozonide yields. [d] Toluene does not complex with ozone in Freon-12 except at lower temperatures. [e] MPE, 1-mesityl-1-phenylethane, [f] HEB, hexaethylbenzene. [g] A colored complex with ozone was not observed, but the results indicate its effectiveness with the carbonyl oxide. [h] PMB, pentamethylbenzene. Solubility difficulties prevented the observance of complexation with ozone. [i] TMB, 1,2,4-trimethoxybenzene. [j] HFB, hexafluorobenzene. No complex was observed with ozone or indicated with the carbonyl oxide.

Table II. Comparison of Normal, Inverse, and Mixed Ozonations with Complexing Agents[a]

DIPE[b] isomer	Solvent	Complexing agent	Cis-trans ozonide ratios		
			Normal[a]	Inverse[a]	Mixed[a]
Cis	Isopentane	Toluene	74:26	72:28	72:28
Cis	Isopentane	o-Xylene	75:25	75:25	76:24
Cis	Isopentane	Isodurene[c]	76:24	74:26	76:24
Cis	Isopentane	MPE[c]	77:23	77:23	
Trans	Isopentane	o-Xylene	65:35	66:34	
Trans	Isopentane	HEB[c]	65:35	65:35	
Cis	Freon-12[d]	o-Xylene	61:39	60:40	
Cis	Freon-12[d]	Isodurene[c]	60:40	62:38	

[a] All ozonolyses were at −155 °C and a slow warm-up was employed. "Normal" ozonation refers to preparing the ozone complex first, then adding the olefin. "Inverse" ozonation refers to carrying out the ozonolysis in the absence of the complexing agent, after which the complexing agent is added to the −155 °C solution and slow warm-up is allowed. "Mixed" ozonation refers to ozonolysis of a mixture of the olefin and complexing agent. [b] DIPE, 1,2-diisopropylethylene. [c] Isodurene, 1,2,3,5-tetramethylbenzene; MPE, 1-mesityl-1-phenylethane; and HEB, hexaethylbenzene. [d] Freon-12, dichlorodifluoromethane.

changed from isopentane to the more polar and nucleophilic Freon-12 (dichlorodifluoromethane). In Freon-12 at −155 °C (no complexing agent) the difference is 5% compared with 9% in isopentane, and at −78 °C in Freon-12 both isomers afford a 50:50 cis-trans ozonide ratio, compared with 54:46 for the cis olefin and 50:50 for the trans olefin in isopentane at −78 °C. With a complexing agent present at −155 °C, the two isomeric olefins give cis-trans ozonide ratios which differ by 10–18% in isopentane and 8–13% in Freon-12.

These results can be rationalized, at least in part, by one of, or more likely a combination of, two approaches, both of which assume that there is a finite, though short, lifetime for a carbonyl oxide and that the syn and anti isomers attempt to achieve equilibrium, as shown in Scheme I. From one viewpoint, the equilibration indicated is prevented, or impeded, by zwitterion complexation in the −155 °C experiments involving the cis olefin. In the absence of the complexing agent some equilibration occurs at −155 °C, but proceeds much faster at −78 °C. The equilibration is faster in the more polar and nucleophilic solvent, Freon-12, than in isopentane, perhaps owing to solvation of the transition state, **2**, by the nucleophilic solvent, thus facilitating free rotation. The equilibration, by this viewpoint, involves conversion of anti, **1**, to syn, **3**, zwitterion. Although, intuitively, for steric reasons, one might expect the anti isomer to be more stable, it is not unreasonable to suggest that this might be counteracted to some extent by stabilization of the syn isomer through hydrogen bonding, as illustrated by **4**. The necessity to assume conversion of anti to syn carbonyl

Scheme I
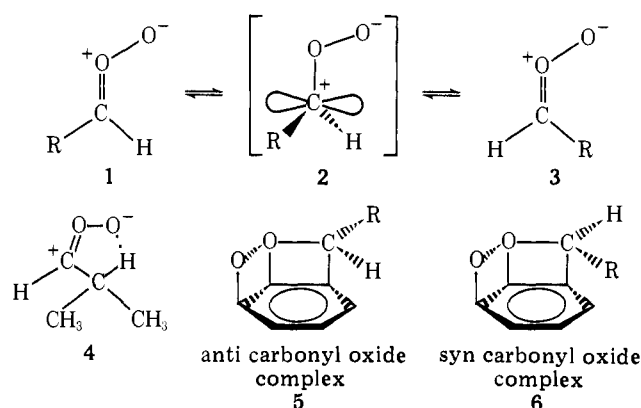
oxide in the above reasoning is based on the Bauld-Bailey[13] stereochemical refinement of the Criegee mechanism and the Kuczkowski[14] modification thereof, both of which propose that anti and syn carbonyl oxides lead predominantly to cis and trans final ozonides, respectively.[11]

The other approach suggests that anti carbonyl oxides complex more strongly than do syn carbonyl oxides. This would further account for the higher cis content of the ozonide mixture obtained from ozonolyses involving the presence of a complexing agent, especially with the cis olefin in isopentane solution (Table I). Such a preferential complexation is not unreasonable if it is assumed that complex formation requires

Table III. Cis-Trans Ozonide Ratios from Ozonolyses of *cis*- and *trans*-1,2-Di-*tert*-butylethylene with Various Complexing Agents in Isopentane[a]

Temp, °C	Complexing agent	Cis isomer			Trans isomer	
		N[b]	I[b]	M[b]	N[b]	M[b]
−78	None	70:30			15:85	
−155	None	70:30			19:81	
−155	Toluene	72:28		73:23		
−155	*o*-Xylene	89:11	82:18	89:11	20:80	20:80
−155	Isodurene	77:23	79:21		20:80	20:80
−155	MPE[c]	80:20	79:21	82:18	18:82	
−155	HEB[c]	71:29				
−155	*p*-Xylene	70:30				
−155	*p*-DTBB[c]			74:26		

[a] Reaction conditions and workup were same as those for Tables I and II. [b] N, normal ozonation procedure; I, inverse procedure; and M, ozonation of the mixture of olefin and complexing agent. See Table II. [c] MPE, 1-mesityl-1-phenylethane; HEB, hexaethylbenzene; and *p*-DTBB, *p*-di-*tert*-butylbenzene.

Table IV. Cis-Trans Ozonide Ratios from Ozonolyses of *cis*- and *trans*-3-Hexene with Various Complexing Agents in Isopentane[a]

Temp, °C	Complexing agent	Cis isomer	Trans isomer
−78	None	50:50	51:49
−155	None	54:46	45:55
−155	Toluene	56:44	44:56
−155	*o*-Xylene	57:43	48:52
−155	Mesitylene	58:42	47:53
−155	Isodurene	60:40	45:55

[a] All ozonolyses were by the normal procedure, as described in Table I and the Experimental Section.

Table V. Cis-Trans Ozonide Ratios from Ozonolyses of *cis*- and *trans*-2-Butene with and without a Complexing Agent in Isopentane[a]

Temp, °C	Complexing Agent	Cis isomer	Trans isomer
−78	None	38:62	37:63
−150	None	43:57	41:59
−150	*o*-Xylene	45:55	
−150	Isodurene	44:56	

[a] All ozonolyses were by the normal procedure, as described in Table I and the Experimental Section.

significant overlap of the carbonyl oxide and aromatic π electron systems, with alignments approaching those shown in **5** and **6**. Because of the bulk of the R group, complexation of the anti carbonyl oxide, **5**, might be expected to be stronger than that of the syn carbonyl oxide, **6**, since in the latter complex the R group overlaps the ring. With the stronger complexation of the anti carbonyl oxide, any equilibration such as shown in Scheme I involves conversion of syn to anti carbonyl oxide, in an attempt to replace the amount of anti carbonyl oxide effectively removed from the equilibrium mixture through the stronger complexation. At higher temperatures, where complexation ceases to be a factor, the anti isomer is no longer favored, and the equilibration, perhaps, starts to move from anti to syn, as suggested by the first viewpoint. This trend is also observed with the more nucleophilic Freon-12 even at −155 °C, where the solvation suggested earlier, of **2** perhaps decreases the importance of complexation. At −78 °C the rate of equilibration increases and the syn and anti contents apparently become equal. There is, however, in addition to this, another basic reason for lower cis-trans ozonide values at −78 °C (see the accompanying paper[15]).

Tables III, IV, and V portray the results of ozonolyses of the cis and trans isomers of 1,2-di-*tert*-butylethylene, 3-hexene,

and 2-butene in isopentane, to be compared with the results in Table I for the 1,2-diisopropylethylenes. It can again be seen that, in general, only the cis isomers afford differences in cis-trans ozonide ratios which depend upon the presence or absence of a complexing agent. These differences, however, tend to increase as the size of the ethylene substituents increases: negligible for *cis*-2-butene, 3–6% for *cis*-3-hexene, 5–8% for *cis*-diisopropylethylene, and 9–19% for *cis*-di-*tert*-butylethylene. The results were very scattered for the latter compound, with some complexing agents (toluene, *p*-xylene, and hexaethylbenzene) having essentially no effect at all. Toluene and hexaethylbenzene also were ineffective with *cis*-3-hexene. As a result of the above trends and the fact that the trans olefins are not appreciably affected by the presence of complexing agents, the cis-trans ozonide ratio differences between the cis and trans olefins also decrease as the ethylene substituents decrease in size (cf. Tables I, III, IV, and V). The 2-butenes require special consideration, which is given in the accompanying paper.[15]

These data are consistent with the hypothesis involving the stronger complexation of an anti than a syn carbonyl oxide. It is reasonable to expect that the larger the R group of the carbonyl oxide, the greater the stability of complex **5** over complex **6**. The great differences in the effect of the various complexing agents employed with *cis*-di-*tert*-butylethylene (Table III) are intriguing. These values have been checked several times. The differences among complexing agents were negligible with *cis*-diisopropylethylene and *cis*-3-hexene. Thus the bulk of the carbonyl oxide being complexed appears to be important. While further study involving other olefins and other complexing agents is required before any rationale can be established, it is, nevertheless, interesting to speculate that other important factors are (1) the strength, in terms of the ionization potential,[4] of the complexing agent (e.g., hexafluorobenzene is ineffective with *cis*-diisopropylethylene, and toluene has little or no effect with either of the other two cis olefins); (2) the steric effect of the substituents on the benzene ring of the complexing agent, in terms of number of substituents, orientation of substituents, and size or bulk of substituents. Although the ionization potential for hexaethylbenzene is low, the six ethyl groups apparently cause it to be ineffective in complexing the *tert*-butylcarbonyl oxides. The two factors seem to have a happy balance in the case of *o*-xylene, which has an ionization potential which falls between those of toluene and hexaethylbenzene, but offers four adjacent unsubstituted carbons to make it a more effective complexing agent (e.g., in **5**) than hexaethylbenzene. Isodurene and mesitylphenylethane, which fall in between *o*-xylene and hexaethylbenzene in both respects also give intermediate cis-trans ozonide ratios with *cis*-di-*tert*-butylethylene. Although, on the basis of the preceding trend one might expect *p*-xylene to be less effective than

Table VI. Cis-Trans Ozonide Ratios from Ozonolyses of *cis-* and *trans*-4-Methyl-2-pentene in Isopentane[a]

Temp, °C	Complexing Agent	Cis isomer NMW[b]	HMW[c]	Trans isomer NMW[b]	HMW[c]
-78	None	46:54	77:23	44:56	24:76
-155	None	70:30	85:15	41:59	21:79
-155	o-Xylene	67:33	78:22	45:55	26:74
-155	Isodurene	69:31	85:15	40:60	40:60
-155	MPE[d]	60:40	87:13	44:56	22:78

[a] All ozonolyses were by the normal procedure, as described in Table I and the Experimental Section. [b] NMW, normal molecular weight ozonide. [c] HMW, high molecular weight cross ozonide (diisopropylethylene ozonide). [d] MPE, 1-mesityl-1-phenylethane.

Table VII. Comparison of Cis-Trans Ozonide Ratios from Various Alkenes Using Fast or Slow Warm-up[a]

R and R' in RCH=CHR'	Alkene config'n	Slow warm-up NMW[b]	HMW[c]	Fast warm-up NMW[b]	HMW[c]
R = R' = t-Bu	Cis	70:30		69:31	
	Trans	19:81		06:94	
R = R' = i-Pr	Cis	69:31		65:35	
	Trans	60:40		47:53	
R = R' = Et	Cis	54:46		50:50	
	Trans	45:55		41:59	
R = R' = Me	Cis	43:57		37:63	
	Trans	41:59		40:60	
R = CH₃; R' = i-Pr	Cis	70:30	85:15	48:52	68:32
	Trans	41:59	21:79	45:55	24:76

[a] All ozonolyses were carried out at -155 °C by the normal procedure without a complexing agent. See Experimental Section and Tables I, IV, V, and VI. [b] NMW, normal molecular weight ozonide. [c] HMW, high molecular weight cross ozonide.

Table VIII. Effect of Rate of Warm-up upon Cis-Trans Ozonide Ratios from *cis*-1,2-Diisopropylethylene

Temp,[a] °C	Complexing agent None	MPE[b]
-155	69:31	77:23
-128	70:30	76:24
-113	70:30	76:24
-93	65:35	67:33
-78	66:34	65:35
25	65:35	62:38

[a] The initial temperature was -155 °C. For the other listed temperatures, the reaction mixture was allowed to rise quickly to that temperature, after which the warm-up was slow (see Experimental Section). The change between -113 and -93 °C indicates that the effect is associated with the rapid decomposition of the primary ozonide in this range. [b] MPE, mesitylphenylethane.

o-xylene, owing to the positions of the methyl substituents, it is totally inconsistent that it should have no effect at all, especially in comparison with isodurene and mesitylphenylethane. Further studies with different complexing agents are in progress.

Table VI exhibits cis-trans normal and high molecular weight cross ozonide ratios obtained from ozonolyses of *cis*- and *trans*-4-methyl-2-pentene, the only unsymmetrical olefin studied. Except for three peculiar instances which are at present unexplanable, the complexing agents appear to have little or no effect on the cis-trans ozonide ratios obtained at -155 °C. The ratios obtained for the cross ozonide, diisopropylethylene ozonide, however, are much different from those obtained from ozonolyses of the diisopropylethylenes themselves (Table I); the values in Table VI are higher than those in Table I in comparing the cis olefins and lower in comparing the trans olefins. Obviously, factors other than complexation of and equilibration of carbonyl oxide zwitterions are more important with this and, perhaps, other, unsymmetrical olefins. This will be discussed in the accompanying paper.[15]

The importance placed on complexation and equilibration of carbonyl oxide stereoisomers is best understood from the viewpoint of the zwitterionic structure of these species. Although recent calculations indicate that both ozone and carbonyl oxides are singlet diradicals in the ground state,[16] it is important to realize that a singlet diradical can have a whole spectrum of character ranging from a zwitterion to a pure diradical.[17]

One other comparison gleaned from these studies is important to our further consideration of the ozonolysis mechanism. Table VII compares cis-trans ozonide ratios obtained from fast and slow warm-ups of the ozonolysis reaction mixtures of the ten olefins studied. These results were obtained in the absence of complexing agents. However, similar differences were noted with the diisopropylethylenes when complexing agents were present (e.g., Table VIII). It is noteworthy that the differences range from small to profound with *cis*- and *trans*-3-hexene, *cis*-2-butene, *cis*- and *trans*-1,2-diisopropylethylene, *trans*-1,2-di-*tert*-butylethylene, and *cis*-methylisopropylethylene, in which cases higher cis-trans ozonide ratios were obtained by the slow warm-up. On the other hand, the rate of warm-up did not affect the results which *cis*-di-*tert*-butylethylene or *trans*-2-butene, and the cis-trans ozonide ratios from *trans*-methylisopropylethylene were lower from a slow than from a fast warm-up. Murray and Hagen[8] have previously reported large differences with *trans*-1,2-diisopropylethylene, but noted only slight differences with the cis olefin. Our results show the same trend as theirs, but our cis-trans ozonide values are considerably higher than theirs, perhaps owing to the fact that our ozonolysis temperature was much lower (-155 °C) than the lowest (-120 °C) that they employed.

Most noteworthy are the high cis-trans ozonide ratios obtained from ozonolysis of *trans*-1,2-diisopropylethylene using a slow warm-up, both with and without complexing agents (Tables I and VII). With a fast warm-up procedure the cis-trans ozonide ratios were <1. Neither the Bauld-Bailey[13] nor the Kuczkowski schemes,[14] in their present forms, will explain either the differences observed due to rate of warm-up or the

high cis–trans ozonide values obtained from *trans*-diisopropylethylene with a slow warm-up. The accompanying paper[15] will amplify upon this problem and propose further refinements to the Bauld–Bailey mechanism which will allow the most complete rationale so far available for the intricacies of ozonide formation.

Experimental Section

Materials. Most of the olefins studied were obtained from Chemical Samples Co. and were 99% pure. *cis*-1,2-Di-*tert*-butylethylene was synthesized from 1,2-di-*tert*-butylacetylene by the method of Puterbaugh and Newman.[18] The di-*tert*-butylacetylene was prepared by the method of Hennion and Banigan.[19] The isopentane and dichlorodifluoromethane (Freon 12) were pure solvents obtained from MCB Chemical Co.

Ozonolysis Procedures. The ozonator, ozonation vessels, and equipment and general techniques employed were as described or referenced in earlier publications.[4,13,20] Simple ozonolyses and "*mixed*" ozonolyses involving a mixture of the olefin and of the complexing agent were performed either in a simple single-cell vessel[4] or in a two-cell vessel[4,20] in which the olefin (or mixture of olefin and complexing agent) was transferred, by means of a stream of nitrogen, from one cell to a cell containing a solution of ozone in the same solvent. The "normal" ozonolyses with complexing agents were carried out in the two-cell vessel, with the ozone complex[4] being prepared in one cell, after which the solution of the olefin was blown over into it from the other cell. The "inverse" ozonolyses were performed by completely ozonizing the olefin in one cell and blowing a solution of the complexing agent from the other cell into the ozonolysis mixture. All procedures were carried out at the selected ozonolysis temperature, usually -155 °C (see Tables I–VII). Cooling solutions were as follows: -155 °C, isopentane + liquid nitrogen; -128 °C, *n*-pentane + liquid nitrogen; -113 °C, ethanol + liquid nitrogen; -93 °C, toluene + liquid nitrogen; -78 °C, 2-propanol + dry ice.

The final ozonolysis mixture usually was 0.04 M in regard to both olefin and complexing agent and the final volume 15 mL; when mixing of solutions was brought about in the two-cell vessel, each solution was 0.08 M in a volume of 7.5 mL.

With a "fast" warm-up, the reaction vessel was immediately transferred from the -155 °C bath to a water bath at room temperature. Most "slow" warm-ups were brought about by letting the -155 °C cooling bath gradually come to room temperature over a 24-h period. In some cases the reaction vessel was first transferred from the -155 °C bath to a -128 °C bath and then in slow succession to the -113, the -93, and the -78 °C bath, the temperature of which was then allowed to rise gradually to room temperature.

Gas Chromatographic Techniques. The equipment and general procedures were as described in earlier publications.[4,13] Cis–trans ozonide ratios are arithmetic means of a minimum of two reactions of each type and a minimum of three injections per reaction. Reproducibility was ±1%. For total ozonide yields, the reaction mixtures were evaporated, a known weight of toluene and a known volume of isopentane were added, and determinations were based upon the known weight of toluene standard and the flame-ionization detector response values of the ozonides relative to toluene.

Low-temperature NMR spectra were recorded on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe. For example, 26 mg (0.28 mmol) of toluene, 23.7 (0.2 mmol) of *cis*-1,2-diisopropylethylene, and a small amount of Me$_4$Si was added to a thin-wall NMR tube, after which the tube was cooled to -78 °C and enough of a 2:5 solution of CF$_3$Br-CF$_2$Cl$_2$ was added to produce a final volume of ~0.6 mL. The tube was cooled to ca. -160 °C and 0.222 mmol of O$_3$ in a nitrogen stream[21] was passed into the reaction mixture. The NMR tube was then capped and transferred, quickly with wiping, to a liquid nitrogen bath and then to the HA-100 probe cooled to -144 °C. The spectra was taken at several different temperatures. The primary ozonide (ring protons, broad multiplet at δ 4.35–4.40 ppm) disappeared in a short time when the temperature reached -130 °C, giving way to the final ozonide mixture.

References and Notes

(1) The major portion of the experimental data of this paper was taken from the Ph.D. dissertation of T. M. Ferrell, The University of Texas at Austin, 1977. Much of the pioneering work, however, was done by Professor Dr. A. Rustaiyan while on leave of absence from the National University of Iran, 1973–1974.

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