¹⁸O Tracer Use in Ozonolysis Mechanism Studies. Results Using the Triphenylphosphine Reduction Method[1]

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Abstract: The use of specifically ¹⁸O-labeled ozonides permits demonstration of the validity of the triphenylphosphine reduction technique as a method of determining location of the ¹⁸O label in ozonides. For aryl-substituted ozonides this technique gives the same results as the direct mass spectral technique. For alkyl-substituted ozonides the methods give different results. The phosphine reduction method is considered more reliable and indicates that ozonolysis in the presence of labeled aldehyde leads to almost exclusive ether oxygen incorporation of the label contrary to some earlier literature reports. Possible reasons for the different results given by the direct mass spectral technique as well as consequences of this work for the ozonolysis mechanism problem are discussed.

In an attempt to rationalize some of the stereochemical consequences of the ozonolysis reaction, it has been suggested[2] that the Criegee zwitterion mechanism[3] may be accompanied by one or more additional pathways to ozonide under some circumstances. Attempts to determine whether or not a non-zwitterion path plays a role in the overall ozonolysis mechanism have usually relied on an ¹⁸O tracer technique. Such approaches are based on the assumption that the reaction of a zwitterion with an ¹⁸O-labeled aldehyde will lead exclusively to ozonide with labeling in the ether oxygen and no labeling in the peroxide oxygens. Using this approach it was concluded[4-6] that ozonolysis of phenylethylenes in the presence of ¹⁸O-labeled benzaldehyde leads exclusively to ether oxygen labeling and thus presumably only includes a zwitterion path to ozonide. Likewise the ¹⁸O tracer method leads to exclusive ether oxygen labeling in the ozonolyses of ethylene, propylene, and (E)- and (Z)-2-butene.[7,8]

On the other hand, ozonolyses of some higher molecular weight alkyl-substituted olefins have given results which lead to the conclusion that some peroxide oxygen ¹⁸O labeling had occurred and thus presumably allow for some contribution of a non-zwitterion pathway to ozonide formation. Ozonolysis of (E)-2,5-dimethyl-3-hexene (diisopropylethylene) in the presence of ¹⁸O-labeled acetaldehyde gave results which were interpreted as requiring the formation of ozonide with considerable peroxide oxygen labeling.[9] More recently a similar study was carried out on the same system with results that were interpreted as requiring largely ether oxygen labeling with the possibility of a maximum of 10% peroxide oxygen labeling.[10] It has also been reported that ozonolysis of ethylidenecyclohexane in the presence of ¹⁸O-labeled propionaldehyde leads to peroxide oxygen labeling.[11] Likewise we have studied the low-temperature ozonolysis of (E)- and (Z)-diisopropylethylene and obtained results which we interpreted as showing up to 90% peroxide oxygen labeling.[12]

The location of the ¹⁸O tracer in the ozonide has been determined by a variety of methods. In some cases the ozonides were reduced, and mass spectrometry was used to determine the ¹⁸O content of the alcohol products, from which the distribution in the ozonide was deduced.[9,11] In others, microwave spectroscopy has been used directly on the ozonides to determine the position of the ¹⁸O label.[7,8] Finally, the position of the ¹⁸O tracer has been determined by direct mass spectroscopy of the ozonides.[4-6,10,12]

Of these approaches, the use of microwave spectroscopy would seem to be least susceptible to errors of interpretation, but at present its use appears to be restricted to lower molecular weight ozonides.[7,8,13,14] The use of direct mass spectral analysis of the ozonides usually relies on a comparison between the ¹⁸O

content of the molecular ion and the ion which corresponds to loss of molecular oxygen, presumably from the peroxide bridge in the ozonide. The mass spectral peak corresponding to the latter ion is often weak, however,[10,12] and we have recently found that in some cases, primarily alkyl-substituted ozonides, it either does not appear consistently or is too weak to be reliable for analysis.

We have described a method of producing ozonides which does not require the use of ozone.[15-17] We have also shown that this method can be used to produce ozonides which are specifically labeled in the peroxide or ether oxygens.[1] We have now combined this latter technique with the use of triphenylphosphine reduction of the ozonides to give a method for determining the location of the ¹⁸O tracer which we believe is more reliable than the direct mass spectral techinque. It has been reported[18,19] that the triphenylphosphine reduction of ozonides proceeds quantitatively. Using ozonides which the direct mass spectral technique indicated to be labeled exclusively in the ether oxygen, Carles and Fliszar have concluded that the triphenylphosphine reduction occurs by exclusive attack at the peroxidic oxygen atoms of the ozonides.[20] We have confirmed this conclusion by studying the triphenylphosphine reduction of ozonides which were specifically labeled at either the ether or peroxide oxygen atoms.

Results

Direct Mass Spectral Analysis. The aryl-substituted ozonides to be used in these analyses were produced by photolyzing diphenyldiazomethane in the presence of ¹⁸O-labeled oxygen and unlabeled aldehyde, or by photolyzing the diazo compound in the presence of unlabeled oxygen and labeled aldehyde. Such reactions permit the synthesis of ozonides without using ozone and were originally formulated[15,16] as involving production of diphenylmethylene, followed by reaction of the carbene with oxygen to give a Criegee zwitterion, which then reacted with the aldehyde to give an ozonide. In this formulation we suggested that the carbonyl oxide was produced in its diradical form, a portion of which populated the dipolar or zwitterionic form which was seen as necessary for reaction with aldehyde to give ozonide. In this scheme the diradical form was viewed as possibly being involved in radical processes which decreased ozonide yield. Based upon generalized valence bond and configuration interaction calculations, Wadt and Goddard have recently proposed[21] that it is the singlet diradical form of the carbonyl oxide which is involved in the ozonide-forming reaction. Guided by the theoretical considerations expounded by Salem,[22] we had also been reexamining the possible role of diradicals in the formation of ozonides in the ozonolysis reaction and by the photooxidation of diazo compounds.[23,25]

Table I. Preparation of ^{18}O-Labeled Diisopropyl Ozonides by Ozonolysis of Diisopropylethylene in the Presence of Isobutyraldehyde-^{18}O

Olefin isomer	Ozonolysis method[a,b]	E/Z ozonide isomer ratio	% label in ozonide[c]		Method of analysis[d]
			E isomer	Z isomer	
E	A	61.1/38.9	15.9 ± 0.4	14.5 ± 0.7	Indirect
Z	B	25.3/74.7	15.2 ± 0.5	18.0 ± 0.9	Indirect
			18.2 ± 0.1	20.3 ± 0.5	Direct

[a] In pentane, olefin concentration, 0.2 M; isobutyraldehyde-^{18}O (32.35 atom %) concentration, 0.2 M. [b] Method A, 0.7 equiv of O_3; temperature -78 °C, fast warm up; method B, 0.5 equiv of O_3; temperature -110 °C, slow warm up. [c] Expressed as percentage of ozonide containing one ^{18}O atom. [d] Indirect analysis; reaction of ozonide with triphenylphosphine, followed by mass spectral analyses of the products; direct analysis; mass spectral analysis of the ozonide.

We have also shown[17] in work subsequent to that reported here that the photooxidation of the diazo compound is better accomplished with singlet oxygen. This latter observation suggests that the photooxidations of diphenyldiazomethane described here may occur via singlet oxygen produced by self-sensitization with the diazo compound.

A solution of diphenyldiazomethane in acetonitrile was photooxidized in the presence of ^{18}O-labeled benzaldehyde (44.7 atom % ^{18}O), using an apparatus similar to one described in the literature.[27] The reaction mixture was worked up by dry column chromatography on silica gel, and the crude product was recrystallized from warm anhydrous methanol to afford 0.15 g (10%) of pure triphenylethylene ozonide. A similar procedure, except using unlabeled oxygen, was used to prepare an unlabeled sample of the ozonide. A photooxidation of diphenyldiazomethane in acetonitrile solution was then carried out in the presence of unlabeled benzaldehyde but using ^{18}O-labeled oxygen (63.3 atom % ^{18}O). This reaction gave a 7% yield of labeled triphenylethylene ozonide using the same workup as described above. Finally, a sample of labeled 1,1-diphenylpropene ozonide was obtained by photolyzing diphenyldiazomethane in the presence of acetaldehyde and ^{18}O-labeled oxygen.

The aryl-substituted ozonides were then analyzed by mass spectrometry. The fragmentation patterns observed were similar to those reported by Fliszár and co-workers.[4-6] The important mass spectral fragments are the following:
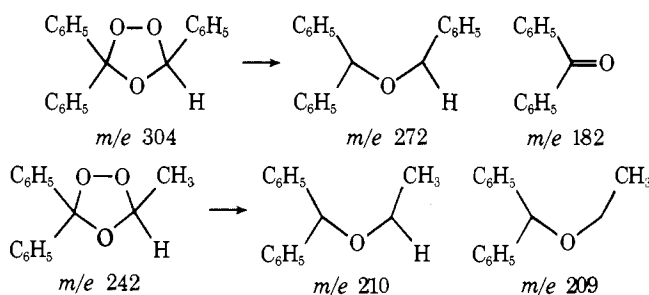
In the case of the triphenylethylene ozonide, no parent ion was observed. When this ozonide was obtained by carrying out the photooxidation of diphenyldiazomethane in the presence of labeled benzaldehyde, the fragment with m/e 272 contained 41.3 ± 0.2% ^{18}O, indicating that essentially all of the label was incorporated at the ether oxygen.[28] When the triphenylethylene ozonide was obtained by carrying out the photooxidation of diphenyldiazomethane in the presence of benzaldehyde and labeled O_2, the fragment with m/e 272, corresponding to loss of O_2 from the parent, contained 0.2 ± 0.5% label, while that with m/e 182 contained 51.1 ± 0.5% label. In both of these cases it appears that ozonide is formed by a direct reaction between carbonyl oxide and aldehyde with no significant exchange between oxygen atoms of the combining species.

In the case of 1,1-diphenylpropene ozonide, obtained by carrying out the photooxidation of diphenyldiazomethane in the presence of acetaldehyde and labeled O_2, the parent ion

with m/e 242 can be observed and was found to contain 46.2 ± 0.2% ions bearing one ^{18}O atom and 33.8 ± 0.2% ions bearing two ^{18}O atoms. The ion with m/e 210, arising from loss of O_2, contained 0.0 ± 0.9% label. Likewise the ion with m/e 209 arising from a further loss of hydrogen contained 0.0 ± 0.3% label. Thus, the ozonide is labeled exclusively in the peroxide oxygen atoms, indicating that it is formed by combination of the carbonyl oxide and aldehyde fragments with no interchange between oxygen atoms.[29] The results of the direct mass spectral analysis of these aryl-substituted ozonides can be summarized as follows:
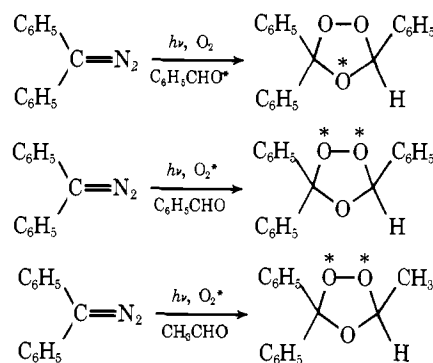
The alkyl-substituted ozonide chosen for study was that of diisopropylethylene. The ozonide was prepared both by ozonolysis of the olefin stereoisomers and by the sensitized photooxidation of isopropyldiazomethane. In the latter case the diazo compound, in methylene chloride solution containing methylene blue, was photolyzed in the presence of isobutyraldehyde and ^{18}O-enriched O_2 (20.6 atom % ^{18}O). This procedure gave a small yield (0.05%) of diisopropyl ozonide[31] which was isolated by VPC. As a result of decomposition and mechanical loss during isolation, only the E ozonide was isolated. This sample was subjected to triphenylphosphine reduction as described below, but in this case there was insufficient sample for direct mass spectral analysis. Labeled diisopropyl ozonide was then prepared by ozonizing the isomers of diisopropylethylene in the presence of ^{18}O-labeled isobutyraldehyde (32.4 atom % ^{18}O), under reaction conditions nearly identical with those used in our previous mechanistic study of this system.[12] The results of these experiments including the ozonide stereoisomer distribution and the ^{18}O content of the ozonide isomers are shown in Table I. The ozonide stereoisomer distributions obtained compare favorably with those found previously; e.g., ozonolysis of (Z)-diisopropylethylene at -110 °C in pentane gave 25.3% E ozonide as compared with the 26% reported[12] previously.

The ozonide stereoisomers obtained in one of these ozonolyses (Table I, line 2) were then individually subjected to direct mass spectral analysis. This analysis showed 18.2 ± 0.1% of the E ozonide isomer and 20.3 ± 0.5% of the Z isomer to contain one ^{18}O atom (no doubly labeled species were detected). Use of the direct mass spectral technique to obtain ^{18}O

Table II. Mass Spectral Analysis of the M − O₂ Fragment
of Diisopropyl Ozonides

| | Unlabeled sample | ¹⁸O-labeled sample | |
| | Rel peak | Rel peak | Corrected rel |
m/e	intensities[a]	intensities[a]	intensities[b]
130	0.78	1.80	0.99[c]
129	1.68	1.74	
128	13.63	73.46	12.64[d]
127	(10.00)	(10.00)	

[a] Average values from five scans; corrected for natural isotope abundances. [b] From the values for m/e 128 and 130 the atom % ¹⁸O in the M − O₂ fragment is calculated as 100%(0.99)/(0.99 + 12.64) = 7.3%. [c] Corrected on the basis of unlabeled sample peaks at m/e 129 and 130 and labeled sample peak at m/e 129: 1.80 − 0.78(1.74/1.68) = 0.99. [d] Because the value 73.46 appears spurious, the new value is assigned so that 12.64 + 0.99 = 13.63, or the intensity for m/e 128 in the unlabeled spectrum; see ref 32 regarding choice of correction method used.

distributions between ether and peroxide oxygen atoms proved to be rather frustrating. In some cases the fragment which presumably arises by loss of molecular oxygen was not present consistently and in other cases it was extremely weak. While the triphenylphosphine reduction work described below indicates that use of the direct mass spectral analysis method as applied to these ozonides may be misleading, we show in Table II the results obtained when this method was used for the labeled Z ozonide formed by the low-temperature (−110 °C) ozonolysis of (Z)-diisopropylethylene. The peak intensities of the ions ostensibly formed by loss of molecular oxygen from the parent, when corrected for spurious components on the basis of the mass spectrum of an unlabeled Z ozonide sample,[32] indicate that the M − O₂ fragment from the labeled ozonide contains only 7.3 atom % ¹⁸O (average of five determinations; Table II). Since 20.3% of the ozonide contained ¹⁸O, this method suggests that 13% of the ozonide, or 64% of the labeled species, bore the label in the peroxide position.
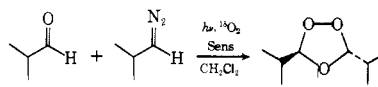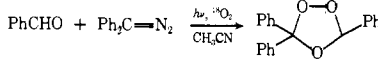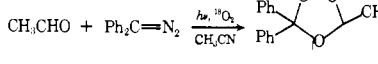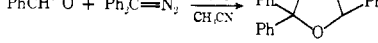
Triphenylphosphine Reduction Method. Using aryl-substituted ozonides which the direct mass spectral method indicated were labeled exclusively on the ether oxygen, Carles and Fliszar have shown[20] that triphenylphosphine reduction occurs by exclusive attack at the peroxide oxygen atoms. In order to confirm this result, a comparison was made between analysis by triphenylphosphine reduction and direct mass spectral analysis of several ¹⁸O-labeled ozonides prepared by the photooxidation of diazo compounds. A sample of 1,1-diphenylpropene ozonide, prepared by photooxidizing diphenyldiazomethane in the presence of acetaldehyde and labeled O₂, was

treated with triphenylphosphine, and the triphenylphosphine oxide thus obtained was analyzed by mass spectrometry. Whereas direct mass spectral analysis of this ozonide had indicated it to contain 56.9 atom % ¹⁸O in the peroxide oxygens and none (0.0 ± 0.9 atom %) in the ether oxygen, the triphenylphosphine oxide from its reduction was found to contain 54.4 atom % ¹⁸O (Table III). Similarly, a sample of triphenylethylene ozonide, obtained by the photooxidation of diphenyldiazomethane in the presence of benzaldehyde and labeled O₂, was analyzed by the triphenylphosphine reduction method. Direct mass spectral analysis of this ozonide had shown it to contain little or no label (0.2 ± 0.5 atom %) at the ether position, but had failed to reveal the total ¹⁸O content owing to the absence of parent ion. However, both the triphenylethylene ozonide and the 1,1-diphenylpropene ozonide samples were prepared using the same gas mixture containing labeled O₂, so it is reasonable to assume that the two samples had equal ¹⁸O contents. Evidence for the validity of this assumption as well as for the regiospecificity of the triphenylphosphine reaction was provided by the result that triphenylphosphine oxide from reduction of the triphenylethylene ozonide contained, by mass spectral analysis, 56.9 ± 0.2 atom % ¹⁸O (Table III).

The labeled triphenylethylene ozonide produced by photooxidation in the presence of labeled benzaldehyde was also reduced with triphenylphosphine. The results (Table III) indicate that the peroxide oxygens contain little or no ¹⁸O label. This result compares quite favorably with the direct mass spectral analysis result for the same ozonide which indicated essentially all of the label to be at the ether oxygen. Thus, we find that both the formation of aryl-substituted ozonides by photooxidation of diazo compounds and the reaction of those ozonides with triphenylphosphine are highly selective processes, since a loss of label integrity in either step would have been revealed by the above experiments. In addition, these results provide further evidence for the reliability of the direct mass spectral analysis method for determining ¹⁸O label position in aryl-substituted ozonides.

Next the labeled diisopropyl ozonide obtained from the photooxidation of isopropyldiazomethane in the presence of isobutyraldehyde and labeled O₂ was subjected to triphenylphosphine reduction. Mass spectral analysis of the triphenylphosphine oxide obtained showed it to contain 18.6 ± 0.2 atom % ¹⁸O (Table III). While there was insufficient sample to permit direct mass spectral analysis of the ozonide, the upper limit for its total oxygen labeling was the 20.6 atom % content of the labeled O₂ used in its preparation. Thus, as in the case of the aryl-substituted ozonides, it is apparent that the reaction of triphenylphosphine with diisopropyl ozonide proceeds with

Table III. Results of Mass Spectral Analysis of Triphenylphosphine Oxide from Reduction of ¹⁸O-Labeled Ozonides Prepared by the Photooxidation Method

| | % ¹⁸O in Ph₃P=O, based on analysis of fragments | | |
Reaction[a]	M	M − 1	M − 77
	18.6 ± 0.2	18.9 ± 0.2	18.2 ± 0.2
PhCHO + Ph₂C=N₂ $\xrightarrow[CH_3CN]{h\nu, {}^{18}O_2}$	56.9 ± 0.2	58.8 ± 0.1	
CH₃CHO + Ph₂C=N₂ $\xrightarrow[CH_3CN]{h\nu, {}^{18}O_2}$	54.4 ± 2.2	55.3 ± 1.3	55.6 ± 0.2
PhCH¹⁸O + Ph₂C=N₂ $\xrightarrow[CH_3CN]{h\nu, O_2}$	1.66	0.05	

[a] Product analyzed by Ph₃P reduction.

Table IV. Results of Mass Spectral Analysis of Triphenylphosphine Oxide from Reduction of Labeled Diisopropyl Ozonides Prepared by Ozonolysis

Starting olefin geometry	Ozonide geometry	% ^{18}O in Ph$_3$P=O, based on analysis of fragments			Av
		M	M − 1	M − 77	
E	E	0.40 ± 0.31	0.36 ± 0.29	0.21 ± 0.16	0.32
E	Z	0.30 ± 0.29	0.25 ± 0.22	0.44 ± 0.19	0.33
Z	E	0.39 ± 0.24	0.07 ± 0.11	0.31 ± 0.14	0.26
Z	Z	0.19 ± 0.17	0.28 ± 0.36	0.23 ± 0.14	0.23
Unlabeled standard		0.18 ± 0.26	0.36 ± 0.13	0.21 ± 0.11	0.25

either exclusive or highly selective abstraction of a peroxide oxygen atom.

The triphenylphosphine reduction method was then used to analyze the labeled diisopropyl ozonides obtained from ozonolysis of the olefin stereoisomers in the presence of labeled isobutyraldehyde. In these cases an approximate measure of total ^{18}O labeling in the ozonides could be obtained by analyzing the ^{18}O content of the triphenylphosphine oxide and isobutyraldehyde products of the reduction reaction (Table I). It will be noted that when the total ^{18}O content was determined both by this indirect method and by direct mass spectral analysis of the ozonide, the indirect method gave a smaller percent labeling. This may be due to loss of aldehyde ^{18}O label through exchange with traces of water or to a small amount of thermal or phosphine-catalyzed decomposition of the ozonide during the reduction.

Listed in Table IV are the results of the mass spectral analyses of the triphenylphosphine oxide samples obtained by reduction of these ozonides. As shown by the table, the determinations based on the peak intensities of the parent (M), M − 1, and M − 77 ions from the phosphine oxide samples all indicate a nearly complete absence of ^{18}O labeling. An unlabeled standard sample of triphenylphosphine oxide was also analyzed; the results, included in Table IV, indicate a slight systematic error in the determinations, correction for which would decrease the observed values for the other samples virtually to zero. Thus, within experimental error the triphenylphosphine oxide samples and, hence, the peroxide oxygens of the ozonides contained no label.

Discussion

The results obtained as described above with specifically labeled ozonides, prepared by photooxidation of diazo compounds, have established the validity of the triphenylphosphine reduction technique as a method of determining location of the ^{18}O label in ozonides. Excellent agreement was obtained between the results of direct mass spectral analysis and phosphine oxide analysis for peroxide oxygen-labeled 1,1-diphenylpropene ozonide. For triphenylethylene ozonides prepared by the photooxidation method, analysis by triphenylphosphine reduction also gives label location results which are totally consistent with the method of synthesis of the ozonides and with the results of their direct mass spectral analysis.

For the alkyl-substituted case, diisopropyl ozonide, use of the phosphine reduction method in analyzing a peroxide-labeled sample, prepared by photooxidation of isopropyldiazomethane, again gave results which were consistent with the method of ozonide synthesis. However, in the analysis of labeled diisopropyl ozonide prepared by ozonolysis of the olefin in the presence of labeled aldehyde, the phosphine reduction method gave results which conflict with those obtained by direct mass spectral analysis of the ozonide. Analysis by the latter method indicates the ozonide to contain considerable peroxide labeling, whereas the phosphine reduction results reveal little or no labeling in the peroxide position.

On the basis of the work described here, we are more confident of the results obtained by the phosphine reduction

method. We therefore conclude that ozonolysis of (E)- and (Z)-diisopropylethylene in the presence of labeled isobutyraldehyde may lead to some peroxide oxygen labeling, but only to the very small extent allowed by our experimental error. The label is incorporated exclusively, or nearly so, at the ether position.

We further conclude that while in some cases[10] direct mass spectrometry on alkyl-substituted ozonides apparently gives meaningful results, it can lead to a misleading fragmentation pattern. One possible explanation for our results is that the peak at m/e 128, which has been interpreted as arising from loss of molecular oxygen from the parent ion, actually has another origin. Because it is weak and is not observed consistently, it is conceivable that this peak originates from isobutyraldehyde trimer which can be formed in small amounts upon slight decomposition of the ozonide or from a fragmentation-recombination process in the mass spectrometer (eq 1 and 2).
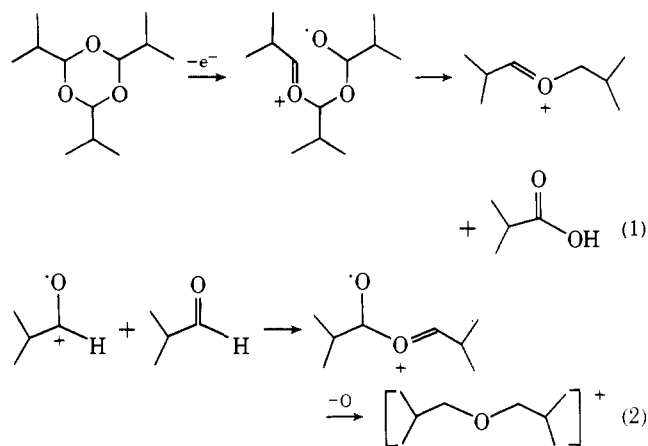
In this connection we have examined the mass spectrum of isobutyraldehyde containing a small amount of the trimer and did, in fact, observe a weak peak at m/e 128.

At any rate, we conclude that the extent of peroxide oxygen labeling reported[12] earlier by us is not supported by the present results using the phosphine reduction method. This conclusion has prompted us also to reexamine the ethylidenecyclohexane-propionaldehyde system using the triphenylphosphine reduction method. Our preliminary results suggest that the previously reported[11] extent of peroxide ^{18}O label incorporation in that case is also questionable.

We now turn to the question of the significance of these results to the ozonolysis mechanism problem. It appears that the amount of peroxide oxygen labeling allowed by the present results, or by those reported previously by Lattimer and Kuczkowski,[10] is too small to require any significant contribution from the specific aldehyde plus initial ozonide pathway to final ozonide via a seven-membered heterocyclic intermediate, which we proposed[2] earlier in the form of a working hypothesis. Even if this pathway is involved to a small extent, it in unlikely that it is responsible for the interesting stereochemical observations which led to its earlier consideration.

More recently, Klopman and Joiner[33] have presented evi-

dence for an alternative explanation for the occurrence of peroxide oxygen labeling. They find that labeled aldehyde in contact with ozone loses its label quite rapidly, presumably by means of a reaction of the aldehyde with ozone which regenerates the reactants but permits oxygen exchange. The results described above indicate that the extent of label scrambling is far less than previously concluded, so that the process proposed by Klopman and Joiner, if it occurs at all under ozonolysis conditions, is probably not an important reaction. It is possible that it is responsible for the very low peroxide oxygen labeling allowed by this work and that of Lattimer and Kuczkowski.[10] It has not been shown, however, that the ozone–aldehyde exchange reaction can compete significantly with the very rapid ozone–olefin reaction.

The possibility that the stereochemistry of the ozonolysis reaction could be influenced by the presence of zwitterions in discrete syn and anti forms has been considered by several research groups. Criegee first recognized[34] the possible existence of zwitterion stereoisomers. We had earlier[35] attempted to explain the then existing stereochemical data using syn and anti zwitterions, but were unable to provide a general mechanism on this basis.

More recently, Bailey and Bauld[36] and Kuczkowski et al.[14] have provided detailed schemes for the mechanism of ozonolysis. The essence of both of these proposals is that different olefins, and particularly cis–trans isomers, will give different syn/anti zwitterion distributions and that syn and anti zwitterions give different stereochemical results in the ozonide-forming reaction. Both schemes have achieved some success in correlating the now sizable amount of data on the stereochemical aspects of the ozonolysis reaction. These schemes depend to some extent on preferred conformations for the initial ozonide (1,2,3-trioxolane). Recent theoretical work[37] suggests, however, on the basis of calculated conformer energies, that several conformers of the trioxolane would be expected to decompose to carbonyl oxide and carbonyl compound.

Nevertheless, it seems to us that a scheme involving an important role for syn and anti configurations of the carbonyl oxide is probably required for a general ozonolysis mechanism. The schemes which have been presented[14,36] have put such an approach on a good foundation. There are still some problem areas to be resolved, however. The recent theoretical developments[21,22,24] regarding the ozonolysis mechanism present strong arguments that trioxolane decomposition will lead to an initial diradical form of the carbonyl oxide. If such an intermediate is formed from the trioxolane in a nonsynchronous manner, as has been proposed,[21] then it appears that the steric effects controlling carbonyl oxide syn/anti distributions may be somewhat different from those suggested previously.

One possibility which we believe must be considered in the formulation of any comprehensive mechanism of ozonolysis has been raised previously,[36] but has not received detailed attention, is that of carbonyl oxide syn/anti interconversion. Should such interconversion occur, one is then confronted with a problem of kinetic vs. thermodynamic control of carbonyl oxide geometry and, consequently, of ozonide stereochemistry. We had shown earlier[38] that one of the parameters which has an enormous influence on the stereochemistry of the ozonide is the concentration of the required aldehyde. This influence is at least as great as that of olefin stereochemistry, yet it has not been dealt with adequately by existing mechanistic schemes. We suggest that such an influence may reflect a time dependence of the carbonyl oxide syn/anti distribution. Thus, at high aldehyde concentrations it is more likely that a kinetically determined ratio of these configurations controls ozonide geometry, while at lower aldehyde concentrations the carbonyl oxide distribution may move partially or completely to equilibrium, with a consequent effect on ozonide stereochemistry.

This concept may also help to explain the fact that the sensitivity of ozonide stereochemistry to the conditions of ozonolysis (solvent, temperature, etc.) appears to vary as a function of the olefin geometry. Thus, decomposition of the trioxolane formed from a given olefin may produce a syn/anti carbonyl oxide distribution which is similar to the thermodynamic distribution, or quite different from it. In the latter event, factors which would be expected to affect the rate of carbonyl oxide syn/anti equilibration, such as solvent effects,[35] should exert a much stronger influence on the geometry of the final ozonide. Considered in this light, the data presently available suggest that cis olefin isomers, in general, may give rise to a carbonyl oxide distribution which is further removed from the equilibrium distribution than do their trans counterparts. Experiments to test this general hypothesis as an approach to the ozonolysis mechanism problem are in progress.

Experimental Section

Instrumentation. Mass spectra were obtained using an AEI Model MS 12 mass spectrometer operated at an ionizing potential of 70 eV. NMR spectra were recorded with a Varian T-60 spectrometer. Analytical and preparative VPC work was done on a Varian Aerograph A-705 gas chromatograph equipped with a thermal conductivity detector. The following columns, all in aluminum, were employed: column A, 0.375 in × 12 ft, 7% β,β'-oxydipropionitrile on 45/60 Chromosorb G-AW, DMCS; B, 0.375 in. × 6 ft, 10% Carbowax 20M on 40/60 Chromosorb P-AW, DMCS; C, 0.25 in. × 4 ft, 10% FFAP on 60/80 Chromosorb P-AW, DMCS; D, 0.25 in. × 6 ft, 7% β,β'-oxydipropionitrile on 60/80 Chromosorb G, DMCS; E, 0.375 in. × 6 ft, 10% β,β'-oxydipropionitrile on 45/60 Chromosorb G-AW, DMCS.

Materials. (E)- and (Z)-2,5-dimethyl-3-hexene (diisopropylethylene) were used as supplied by Chem Samples, Inc. Samples of the individual isomers were treated with an excess of m-chloroperbenzoic acid to give the corresponding epoxides, which were analyzed by VPC. Under conditions which would have revealed isomeric impurities in concentrations of less than 1%, neither of the epoxides was found to contain a detectable amount of the other isomer. Aldehydes were purified by distillation and if not used immediately were stored in the cold under nitrogen. Acetonitrile (reagent grade) was stored over Linde 3A molecular sieves for several days prior to use. Methylene chloride and pentane were purified by overnight stirring with concentrated sulfuric acid, washing with water and dilute aqueous base, preliminary drying over calcium chloride, and distillation under nitrogen from calcium hydride. Other reagents and solvents either were purified by standard procedures, or were reagent grade and used as obtained.

^{18}O-Labeled Isobutyraldehyde. A 1.84-ml portion of isobutyraldehyde (1.44 g, 20 mmol) was combined in a small flask with 0.36 ml (20 mmol) of ^{18}O-labeled water (Miles Laboratories, 42.04 atom % ^{18}O, deuterium normalized). One drop of N-ethylaniline was added to stabilize the aldehyde,[39] the flask was tightly stoppered, and the mixture was stirred magnetically overnight. The aqueous layer was then saturated with sodium chloride (0.13 g) and withdrawn with a syringe. This process was repeated using a fresh 0.36-ml portion of labeled water. The aldehyde was then purified by preparative VPC (column A) and was stored in sealed ampules at −30 °C until use. Analysis of this material by mass spectroscopy showed it to contain 32.35 ± 0.02 atom % of ^{18}O (theoretical ^{18}O content, 31.5 atom %).[40]

^{18}O-Labeled Benzaldehyde. A 1.20-g (6.7-mmol) sample of benzaldehyde diethyl acetal[41] was combined with 120 μl (6.7 mmol) of 60 atom % ^{18}O-enriched water and several mg of p-toluenesulfonic acid, and the mixture was stirred vigorously for 2 days in a stoppered cantainer. The acid was then neutralized by the addition of a few particles of anhydrous sodium carbonate, and the labeled benzaldehyde was isolated by preparative VPC (column 8). The purified product was obtained in only moderate yield (0.353 g, 50%), presumably as a result largely of inefficient collection from the gas chromatograph.[42] The ^{18}O enrichment of this material was determined by mass spectroscopy to be 63.8 atom %. The sample was made up to 0.50 g by the addition of unlabeled benzaldehyde, diluting the label to 44.7 atom % as determined by mass spectroscopy (calculated, 44.7 atom %).

Diphenyldiazomethane. A procedure similar to that described by Reimlinger[43] was employed. A mixture of 5.89 g (30 mmol) of benzophenone hydrazone, 3.0 g of anhydrous magnesium sulfate, and 60

ml of methylene chloride was stirred rapidly at 0 °C and to it was added in one portion 9.2 g of active manganese dioxide.[44] Stirring was continued for 2 h at 0 °C and then for 1 h at room temperature. Solid material was removed from the reaction mixture by suction filtration through a sintered glass Buchner funnel and was washed with 40 ml of methylene chloride. Solvent was removed from the combined solutions by rotary evaporation to give the crude product as a dark maroon oil, which upon crystallization from 60 ml of anhydrous methanol afforded 4.06 g (70%) of diphenyldiazomethane as long, fine needles, mp 28–30 °C (lit.[43] mp 35 °C).

Isopropyldiazomethane. Isopropyldiazomethane was generated by vacuum pyrolysis of the lithium salt of isobutyraldehyde p-tosylhydrazone (65 mmol) as described in the literature.[45] Upon completion of the pyrolysis, a 20-ml portion of methylene chloride was distilled under vacuum into the trap containing the diazo compound, and the resulting solution was redistilled under vacuum at room temperature. The concentration (1.6 M) and approximate yield (55%) of diazo compound were determined ebulliometrically by adding an aliquot of the solution to a stirred, cold solution of acetic acid in methylene chloride. The solution was stored in the dark at −78 °C until use.

Ozonolysis of Diisopropylethylene (General Procedure).[46] Ozone in a stream of oxygen from a Welsbach Model T-408 ozone generator was bubbled through the solution of olefin and aldehyde at the rate of 0.25–0.27 mmol of O_3/min. The exact 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. The total volume of the reaction solution was 5 ml for the ozonolysis of (E)-diisopropylethylene and 10 ml in the case of the Z isomer.

Upon completion of ozonolysis, and following either fast or slow warm-up,[46] the product mixtures were stored overnight in the refrigerator prior to isolation of the ozonides. Most of the solvent was then removed by rotary evaporation at 0 °C, and the isomeric diisopropylethylene ozonides were isolated by preparative VPC in sufficient quantity for subsequent analyses [column A, 65 °C, 180 ml of He/min; injector and detector temperature 135 °C; retention times ca. 30 min (E isomer) and 39 min]. Isomer ratios were determined from xerographic copies of the recorder traces by the cut-and-weigh method; the thermal conductivities of the two isomers were assumed equal. The ^{18}O distributions in the isolated ozonides were determined by means of reduction with triphenylphosphine, as described below. Rough measurements of the total ^{18}O contents were also obtained by this method, but in some cases these were obtained more directly (and more accurately) by mass spectrometric analysis of the ozonides themselves.

Photooxidation of Diazo Compounds. A. General. The photolysis apparatus used was similar to one described in the literature[27] and consisted of a Pyrex vessel equipped with a jacketed immersion well, a side neck, and a fritted gas inlet at the bottom. During the photooxidations the reaction mixtures were maintained at 12–15 °C (except as otherwise noted below) by immersion of the apparatus in an ice–water bath and by circulation of ice–water through the jacket of the immersion well. Irradiation was from a General Electric DWY 650-W lamp operated at 90 V.

B. Unlabeled Triphenylethylene Ozonide. A solution of 0.5 ml (5 mmol) of benzaldehyde in 90 ml of acetonitrile was placed in the photolysis apparatus and to it was added 2 ml of a solution of diphenyldiazomethane (0.971 g, 5 mmol) in 20 ml of acetonitrile. Oxygen flow through the fritted inlet was begun at the rate of 100 ml/min and maintained throughout the subsequent photolysis. The remaining diphenyldiazomethane solution was added in 1-ml aliquotes at 5-min intervals during the photolysis. Irradiation was terminated 5 min after the addition of the final aliquot. Solvent was removed by rotary evaporation, and the crude product was purified initially by dry column chromatography through a 3 × 36 cm column packed with silica gel (Woelm, activity grade III) using benzene as eluent. The material so obtained was recrystallized from a mixture of ca. 3 ml of benzene and 20 ml of hexane to give white crystals of triphenylethylene ozonide, mp 93–95 °C (lit.[5] mp 95 °C); NMR (CCl$_4$) δ 7.24 (m, 15) and 6.26 (s, 1, >CH−).

C. Labeled Triphenylethylene Ozonide from Benzaldehyde-^{18}O. The photooxidation was carried out as described above except that ^{18}O-labeled benzaldehyde (44.7 atm %) was used. Initial purification by dry column chromatography, followed by recrystallization from 20 ml of warm anhydrous methanol, afforded 0.15 g (10%) of the ozonide as white glittering plates, mp 93–94 °C.

D. Labeled Triphenylethylene Ozonide from $^{18}O_2$. The general photolysis procedure was modified as follows: The fritted inlet and the gas outlet of the photolysis vessel were connected by Tygon tubing to a gas circulating pump to form a closed system. To this system were connected, by two lengths of Tygon tubing branching from the main loop, an oil-filled 500-ml gas buret with leveling bulb and a 250-ml glass bulb, closed with a break-seal, containing ^{18}O-labeled O_2 (Miles Laboratories, 63.3 atom % ^{18}O). Connection to this bulb was made by a two-necked adapter, the second neck affording straight-line access to the break-seal via a serum cap closure.

The system was flushed with nitrogen, and the photolysis vessel was charged with 135 ml of an acetonitrile solution containing 0.971 g (5 mmol) of diphenyldiazomethane and 1.0 ml (10 mmol) of benzaldehyde. The gas circulating pump was then switched on, the seal of the bulb containing the labeled oxygen was broken, and the bulb was filled with acetonitrile introduced via a long syringe needle passed through the serum cap and opened seal, displacing the oxygen into the system. The reaction mixture was then photolyzed for 40 min as gas circulation was maintained at ca. 100 ml/min. Upon completion of photolysis the pale-red product solution was withdrawn from the vessel with a syringe. Solvent was removed in vacuo, and the residue was purified as described above (part C) to give 98 mg (7%) of triphenylethylene ozonide, mp 94–95 °C.

E. Labeled 1,1-Diphenyl-1-propene Ozonide from $^{18}O_2$. Using the gas mixture remaining from the reaction described in part D above and the same apparatus and procedure, 0.971 g (5 mmol) of diphenyldiazomethane in 135 ml of an acetonitrile solution containing 3 ml (53 mmol) of acetaldehyde was photooxidized for 40 min. Upon termination of photolysis the pale-red product solution was transferred from the photolysis vessel, and solvent was removed by rotary evaporation. The residue was purified initially by dry column chromatography as described in B above and then was further purified by perparative thin-layer chromatography on silica gel (PF-254, EM Reagents) using benzene–cyclohexane (60:40) as eluent, followed by a second chromatography using ether–pentane (20:80). The product, a cloudy oil obtained in ca. 5% yield, was identified as the pure ozonide by its NMR spectrum[16] (CCl$_4$): δ 7.3 (m, 10, (C$_6$H$_5$)$_2$C<), 5.51 (q, 1, J = 5.0 Hz, >CH-), and 1.40(d, 3, J = 5.0 Hz, -CH$_3$).

A similar procedure, except using unlabeled oxygen, was followed to obtain a sample of unlabeled 1,1-diphenyl-1-propene ozonide.

F. Labeled Diisopropylethylene Ozonide from $^{18}O_2$. A closed-system photolysis apparatus with provision for the introduction of $^{18}O_2$ was assembled as described above, but with he added feature of methanol coolant circulated between the immersion well jacket and a metal coil immersed in a bath of methanol and dry ice. The system was flushed with nitrogen, and the photolysis vessel was immersed in a methanol–dry ice bath. In the vessel were combined 16 ml of methylene chloride and 5.0 ml of a solution of isopropyldiazomethane in methylene chloride (1.6 M, 8.0 mmol). The side neck of the vessel was then closed with a serum cap, gas circulation was begun, and ^{18}O-enriched oxygen (250 ml, 20 atom % ^{18}O claimed, British Oxygen Co. Ltd.) was displaced with solvent from its break-seal container and into the system. A solution of 10 mg of methylene blue in 10 ml of methylene chloride was injected from a syringe into the photolysis vessel through the serum cap; this was quickly followed by 7.25 ml (5.76 g, 80 mmol) of isobutyraldehyde introduced in the same way, and photolysis was immediately begun. At this point gas circulation slowed and almost stopped, owing to precipitation of the sensitizer and clogging of the fritted gas inlet at the bottom of the vessel. The dry ice bath was therefore removed, circulation of coolant was stopped, and the reaction mixture was allowed to warm to ca. 0 °C, with the result that gas circulation was restored. Irradiation was discontinued while another 5-ml portion of isopropyldiazomethane solution was added to the reaction mixture, together with 2 ml of a saturated solution of methylene blue in methylene chloride. Photolysis was then resumed for 3 min, while coolant was again circulated through the immersion well jacket to maintain the temperature of the reaction mixture at ca. 0 °C.[47] A sample of the gas mixture in the reaction system was withdrawn into a gas syringe through the serum cap; subsequent mass spectral analysis of this sample showed it to contain, relative to total O_2, 28.8 ± 0.4% of ^{16}O ^{18}O and 6.2 ± 0.6% of $^{18}O_2$, or 20.6 ± 0.5 atom % of ^{18}O.

Solvent and most of the aldehyde were removed from the product mixture by rotary evaporation at 0 °C, and carbon tetrachloride was added to the residue to precipitate methylene blue, which was then removed by filtration. An NMR spectrum of the crude product mixture showed it to consist largely of 2,5-dimethyl-3-hexanone, while

Table V

m/e	276	277	278	279	280
Rel peak height	6.1	(100)	68.6	11.6	1.3

Table VI

m/e	Peak height	Contributing ions
276	A	U-2
277	B	U-1
278	C	(U) + (L-2)
279	D	L-1
280	E	L

Table VII

m/e	199	200	201	202	203
Rel peak height	59.6	9.5	(100)	14.6	1.5

Table VIII

m/e	Peak height	Contributing ions
199	A	U-79
200	B	U-78
201	$C(=C_U + C_L)$	(U-77) + (L-79)
202	D	L-78
203	E	L-77

only a trace of the desired ozonide was found to be present as shown by a very weak doublet at δ 4.77 (J = 5.3 Hz, ring protons of both isomers).[2] A preliminary purification of the mixture was effected by preparative thin-layer chromatography on silica gel (EM Reagents, PF-254; ether–pentane, 20:80; product recovery with methylene chloride). The partially purified material, still containing only a trace concentration of ozonide, was then twice subjected to preparative VPC, first on column C (60 °C, 60 ml of He/min) and finally on column D (52 °C, 60 ml of He/min). As a result of decomposition and mechanical loss during purification, only the E ozonide was isolated, in a yield of approximately 2 µl (ca. 0.05% of theory). Approximately one-half of this product was analyzed by reaction with triphenylphosphine; an attempt was made to analyze the remainder of the sample for total ^{18}O content by mass spectroscopy, but this met with failure owing to an insufficiency of sample.

Analysis of Ozonide Labeling. A. By Reaction with Triphenylphosphine. A small sample of ozonide, 1.1 equiv of triphenylphosphine, and hexane in the approximate quantity of 1.5 ml/0.1 mmol of ozonide were sealed in a glass ampule, care being taken to exclude air and moisture. The ampule was heated in an oil bath at 70 °C for a minimum of 5 h; whereas before heating the reaction mixture was homogeneous at or above room temperature, crystals were observed to form slowly during heating. Upon removal from the bath the ampule was cooled in an ice bath before opening to effect further crystallization of triphenylphosphine oxide, which was then collected by filtration (mp 151–154 °C). In most cases of diisopropylethylene ozonide analysis, the ^{18}O content of isobutyraldehyde produced in the reaction was determined by subjecting a sample of the mother liquor (withdrawn into a syringe from the ampule immediately upon opening) to VPC–mass spectrometry (column E, 60 °C, 50 ml of He/min).

Excellent mass spectra of the triphenylphosphine oxide samples were obtained using a direct-introduction probe and an ion source temperature of 90 °C, provided that the samples were positioned near enough to the source to ensure temperature equilibration. At lower source temperatures only a very weak spectrum was obtained, while higher temperatures resulted in distorted and unreliable spectra. Multiple sweeps of two five-peak groups were recorded, one at m/e 276–280 (molecular ion M, M − 1, and M − 2), and the other at m/e 199–203 (M − C_6H_5 and M − C_6H_7). A computer program was written to aid in the interpretation of the resulting data. This program was designed to correct the data for natural isotope abundance and to compute the averages and standard deviations of the final results obtained from the various measurements for a given sample. Between these initial and final operations, the program also effected the less obvious data manipulations described below.

1. Molecular Ion Group. For unlabeled triphenylphosphine oxide, the relative peak heights (Table V), uncorrected for natural abundance of isotopes, are representative. It was assumed that in the spectrum of a partially labeled sample, the peak heights after correction for natural abundances correspond to the relative populations of ions as shown in Table VI, where U and L designate the unlabeled and labeled molecular ions, respectively. Owing to the superimposition of ions U and L-2, it was necessary to assume the loss of two hydrogen atoms from the labeled or the unlabeled parent occurs with equal probability; that is, that there is no ^{18}O isotope effect in formation of ions U-2 and L-2. On the basis of this assumption, the corrected peak height C', corresponding to the contribution of the unlabeled parent to the total peak height at m/e 278, was calculated using the equation $C' = C - D(A/B)$. The percentages (P) of ^{18}O in both M and M − 1 were then

calculated, according to the equations of $P_M = 100 [E/(E + C')]$ and $P_{M-1} = 100 [D/(D + B)]$.

2. Parent-Minus-Phenyl Group. In the case of the unlabeled phosphine oxide, the uncorrected peak heights are typical (Table VII). Following corrections for natural abundance of isotopes, the spectra of labeled samples were interpreted in accordance with the assignments in Table VIII. In order to separate the peak height at m/e 201 into its labeled and unlabeled components, the proportionality $E/C_L = C_U/A$ was assumed, where C_U and C_L represent the components of peak height C corresponding to fragments U-77 and L-79, respectively. From this is derived the following expression for C_L (since $C_U = C - C_L$): $C_L = (C/2) \pm 1/2 (C^2 - 4AE)^{1/2}$. The correction of height E for natural isotope abundance varies slightly with variations in the height C_L relative to total height C; a final correlation for this effect was made following solution of the above equation, and the percentage of ^{18}O in the sample was then calculated as $p = 100 [E/(E + (C - C_L)]$.

B. Direct Mass Spectral Analysis of Ozonides. Diisopropylethylene ozonide (ca. 2 µl) was placed in a 1-mm melting-point tube, the open end of which was then drawn down to a very fine capillary. Volatilization of the ozonide was thus restricted sufficiently to permit its introduction into the mass spectrometer via the solid-sample probe, and troublesome decomposition in the volatile-sample inlet line was thereby avoided. The ion source temperature was maintained at 50–70 °C. Samples of aryl-substituted ozonides were run using the direct introduction probe in the normal manner at ion source temperatures of 110–130 °C. At least two peak heights were corrected for natural isotope abundances; additional corrections for variations from natural abundances and/or contributions to peak heights by extraneous ions were made on the basis of spectra of unlabeled compounds.

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# Electronic States of Acenaphthylene. Linear Dichroism in Stretched Polyethylene and Magnetic Circular Dichroism

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Abstract: Low-temperature absorption, linear dichroic, and magnetic circular dichroic spectroscopy of acenaphthylene (I) and five of its simple derivatives are used to confirm previous assignments of five electronic states, detect a new one, and determine the directions of magnetic dipole transition moments between excited states. Energies, intensities, polarizations, and signs of *B* terms are in good agreement with results of π-electron calculations. Systematic introduction of doubly excited configurations has little effect on the results for excited states assigned to the first five observed transitions. It suggests, however, that the newly observed excited state is predominantly doubly excited. The energy of the lowest triplet state of I was measured by the oxygen perturbation technique. Measurement of polarized absorption in stretched polyethylene ("stretched sheet method") yields the correct absolute polarizations even for a nearly circular molecule such as I. The expected reversal of preferred orientation on going to the 1,2-dibromo derivative is observed. The results clearly demand a two-parameter description of the orientation distribution and provide a good example for the inadequacy of one-parameter evaluation methods which are still occasionally used. A detailed discussion of the problem is given.

Acenaphthylene (I) is one of the most easily available nonalternant hydrocarbons, and the nature of its excited electronic states has been a subject of spectroscopic[1-7] and photochemical[8] as well as theoretical[1,4,9-17] interest. Also, I can be considered as a parent compound for a large number of more complex nonalternant hydrocarbons such as fluoranthene (II), benzofluoranthenes, etc., and a good understanding of its electronic states is useful for derivation of correlations between excited states within this group of compounds.

Previous measurements of the solution absorption spec-

I   II   III
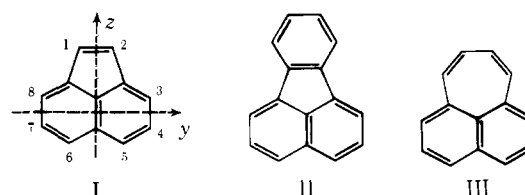
trum,[1] substituent effect,[2] linear dichroism in stretched polyethylene,[3] polarized fluorescence,[4] vapor phase absorption,[5]