assisted (acetates) heterolysis of the C–O bond yielding ion pairs, followed by direct proton loss or 1,2-hydride shift and subsequent proton loss from the cationic species.

Experimental Section[23]

Preparation of d_0- and 2-d_1-Labeled Xanthates and Acetates (1–8) and 2,6,6-d_3-2-Methylcyclohexyl-S-methyl Xanthate (20). —These materials were prepared and characterized as described earlier.[3]

Pyrolysis of *trans*-2-Methylcyclohexyl-S-methyl Xanthate (2) and 2,6,6-d_3-2-Methylcyclohexyl-S-methyl Xanthate (20) in the Liquid Phase.—The crude xanthate (containing a fair amount of dimethyl trithiocarbonate as an impurity) was pyrolyzed over powdered soft glass in a flask equipped with a nitrogen inlet tube and a Vigreux column by heating in a Wood's metal bath at 200–210°.[24] The pyrolysate was collected in a Dry Ice–isopropyl alcohol cooled trap. In each case, the pyrolysate was analyzed by vpc on a 15% Apiezon L column (10 × 0.25 in.) at 100°.

The pyrolysate from xanthate 20 was separated by preparative vpc employing the above conditions and the material corresponding in retention time to 3-methyl-1-cyclohexene (or methylenecyclohexane) was examined by nmr spectroscopy. The spectrum of this compound exhibited as its main features a signal centered at δ 5.55 ppm (1 H, HC=C) and a closely spaced doublet (J = 1 cps) centered at δ 0.95 ppm (3 H, –CH₃).

No signals were apparent for either terminal methylene (δ 4.6) or cyclopropane hydrogens (δ <1.0) in this material, nor was evidence found for the presence of cyclopropane hydrogens[3] in the nmr spectrum of the 1-methyl-1-cyclohexene fraction from this pyrolysis.

Conditions for All Other Pyrolysis Studies on 2-Methylcyclohexyl Acetates and S-Methyl Xanthates.—All pyrolyses were carried out in a Varian Aerograph Model 202A gas chromatograph fitted with either a 2 ft × 0.25 in. Greenville Tube, Inc., Type 304, W & D stainless steel tube equipped with a small plug of Pyrex glass wool at the entrance (and previously seasoned by *ca.* 30 pyrolyses of 10-μl samples of xanthates and acetates under the conditions listed below) or a 2 ft × 6 mm length of no. 7740 Pyrex tube with a small plug of Pyrex glass wool at the entrance. In both cases injector liners of 2-mm Pyrex tube were employed. The temperature conditions were as follows: xanthates, injector block 175°, column 250°, detector block 150°, helium flow *ca.* 20–60 ml/min over 5 min, estimated contact time with hot zone 0.5–1 min, sample size 2–10 μl; acetates, injector block 175°, column 400°, detector block 150°, helium flow conditions *ca.* 15–25 ml/min over 5 min, estimated contact time with hot zone 0.5–1 min, sample size 2–10 μl.

General Procedure.—The sample was injected at the requisite temperature and minimum flow rate. After 2 min, the flow rate was raised uniformly to the maximum value over the ensuing 3 min. The pyrolysate was collected in a 4-mm glass U-tube with liquid nitrogen cooling. When visible evidence of continued pyrolysate flow had ceased, the tube was removed, 20 μl of anhydrous ether added, and the sample examined by analytical gas chromatography on 20% Apiezon L column (10 ft × 0.25 in.) at 100°. Preparative gas chromatography employing the same conditions yielded the pure isomeric olefins whose isotopic contents were determined from the molecular ion regions of the 70-eV mass spectra. Olefinic compositions were determined by the cut and weigh method on the analytical vpc traces.

(23) All compounds were purified by vapor phase chromatography (vpc) and characterized by infrared spectroscopy and mass spectrometry as described in ref 3. Olefinic products were analyzed and purified by vpc on a Varian Aerograph Model 202B chromatograph employing the columns listed. Mass spectra of olefinic products were recorded by Dr. A. M. Duffield on an Atlas CH-4 mass spectrometer equipped with a Model TO-4 ion source and heated gas cartridge inlet system maintained at 200°. Ionizing conditions are as follows: ion source temperature, 200°; ionizing voltage, 70 eV; and ionizing current, 10 μA. Nmr spectra were run by Dr. Y. Kanazawa and Mr. R. C. Ronald on a Varian Associates Model A-60 spectrometer in deuteriochloroform solution and using tetramethylsilane (δ 0.00) as an internal standard.

(24) Pyrolysis of xanthate 20 containing dimethyl trithiocarbonate under these conditions and that of a purified sample in the absence of powdered soft glass and with the bath temperature maintained at 250° yielded identical results.

Ozonolysis. X. The Molozonide as an Intermediate in the Ozonolysis of *cis* and *trans* Alkenes[1a]

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Low temperature (−130°) nmr spectral studies of the ozonation mixtures which were prepared from dichlorodifluoromethane solutions of the stereoisomers of 2-butene, 2-pentene, and 3-hexene gave evidence for the existence of molozonides. The *cis* molozonides could be observed to decompose at −130° to the usual ozonolysis products, whereas the *trans* molozonides required warming to −100° before they were converted into the usual ozonolysis products.

It was Staudinger[2] who first made the suggestion that the observed alkene–ozone reaction products were actually secondary reaction products which arose from a primary addition product. By analogy to the moloxide which at that time was postulated as the primary autoxidation product of alkenes and which was formulated as a 1,2-dioxetane, he called the primary alkene–ozone reaction product a molozonide and formulated it as

$$\begin{array}{c} \text{RCH}\!-\!\text{CHR} \\ |\qquad| \\ \text{O}\!-\!\!-\!\text{O}\!:\!\text{O} \end{array}$$
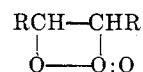
It was not until 1960 that firm, indirect experimental evidence for the existence of the molozonide appeared when Criegee and Schröder,[3] reported that treatment of the ozonation mixture from *trans*-di-*t*-butylethylene with isopropyl Grignard reagent gave rise to *dl*-2,2,5,5,-tetramethylhexane-3,4-diol. Subsequently, it

(1) (a) A preliminary report on part of this work has been published: L. J. Durham and F. L. Greenwood, *Chem. Commun.*, 843 (1967). (b) F. G. is indebted to the Chemistry Department, Stanford University, and particularly to Dr. H. S. Mosher, for their hospitality and to the Petroleum Research Fund of the American Chemical Society for partial financial support during sabbatical leave from Tufts University.

(2) H. Staudinger, *Ber.*, **58**, 1088 (1925).

(3) R. Criegee and G. Schröder, *Chem. Ber.*, **93**, 689 (1960).

TABLE I

NMR SPECTRAL DATA FOR *trans* ALKENE OZONATION MIXTURES[a]

Alkene	Aldehyde CHO, δ[b]	Ozonide CH, δ	Molozonide CH, δ	Propanal CH₂, δ	Ethanal CH₃, δ	Methylene, δ	Methyl, δ
			−130° Spectra				
trans-2-Butene	9.52 (d)	5.00 (q), 4.90 (q)[c]	4.12 (q)		1.98 (d)		1.15 (d)
trans-2-Pentene	9.62 (s)	4.95 (u)	4.08 (m)	2.38 (u)	2.05 (d)	1.52 (m)	1.27 (d), 0.85 (t)
trans-3-Hexene			4.07 (t)			1.60 (m)	0.90 (t)
			−70° Spectra				
trans-2-Butene	9.55 (d)	5.07 (q), 4.98 (q)[d]			1.97 (d)		1.13 (d)
trans-2-Pentene	9.57 (s)	4.98 (m)[d]		2.27 (q)	1.95 (d)	1.47 (u)	1.22 (d), 0.82 (t)
trans-3-Hexene	9.60 (s)	4.93 (t), 4.87 (t)[d]		2.27 (q)		1.48 (m)	0.80 (t)

[a] Authentic ozonides of 2-butene and 3-hexene, authentic 3-hexene ozonation oligomer, and aldehydes were used for peak assignments. [b] All δ values related to internal Me₄Si = 0.00. CHCl₂F was used as an internal standard. Abbreviations used were (d) doublet, (m) multiplet, (q) quartet, (s) singlet, (t) triplet, (u) unresolved. [c] Oligomer evidenced by weak absorption on low field side of peak. [d] Marked absorption, which disappeared on recooling the mixture to −130°, on low field side of peak indicated considerable oligomer.

was reported[4] that α-diols could be isolated from a variety of other alkenes by ozonation of the alkene in ether solution at −115° and treatment of this reaction mixture with the isopropyl Grignard reagent. By this reaction sequence with the geometric isomers of the lower alkenes, the α-diols which would result from the stereospecific *cis* addition of ozone to the *trans* alkenes were isolated in good yield, but no α-diol could be obtained from the *cis* alkenes. These data supported the molozonide as a stable species under the proper conditions in the case of *trans* and a few other alkenes. The structure of the *trans* molozonide as a 1,2,3-trioxolane

$$\underset{\diagdown_{O}\diagup}{\overset{RHC-CHR}{\underset{O}{\diagdown}\,\overset{O}{\diagup}}}$$
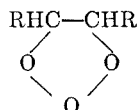
appears rather well established by the obtention of α-diols of the proper configuration[3,4] and by the more recent nmr spectral study of Bailey, *et al.*[5] Some crude evidence has appeared[4b] that the *cis* molozonide may be formed by the reaction of a *cis* alkene and ozone, and that the *cis* molozonide was less stable than the corresponding *trans* isomer. Other than this crude evidence, however, experimental data supporting the existence of the *cis* molozonide has not been published.

The data that have appeared on the molozonide indicate that it can be an observable alkene–ozone reaction product, but the data do not necessarily prove that the molozonide is an intermediate in the ozonolysis of alkenes. This paper reports the results of low temperature nmr spectral studies which support the formation of the molozonide as an intermediate in the ozonolysis of both *cis* and *trans* alkenes.

In these studies the crucial region for observation was the methine proton region. The −130° nmr spectrum (*cf.* Table I) of the ozonation mixture which was prepared from *trans*-3-hexene had one methine triplet at δ 4.07 which can be assigned to the *trans* molozonide methine protons. After 7 hr at −130° the spectrum of such a solution was identical with the spectrum initially recorded. The −130° spectrum from *trans*-2-pentene had a very weak methine absorption at δ 4.95 which may be assigned to ozonide methine

(4) (a) F. L. Greenwood, *J. Org. Chem.*, **29**, 1321 (1964); (b) F. L. Greenwood, *ibid.*, **30**, 3108 (1965).
(5) P. S. Bailey, J. A. Thompson, and B. A. Shoulders, *J. Amer. Chem. Soc.*, **88**, 4098 (1966).

TABLE II

NMR SPECTRA OF REFERENCE COMPOUNDS[a]

Compd	Aldehyde CHO, δ[b]	Methine, δ	Methylene, δ	Methyl, δ
cis-3-Hexene		5.30 (t)	2.05 (m)	0.98 (t)
Ethanal	9.42 (q)			1.83 (d)
Propanal	9.50 (t)		2.20 (q)	0.85 (t)
2-Butene-ozonide[c]		5.23 (q), 5.17 (q)		1.27 (d)
3-Hexene ozonide[c]		5.03 (t), 4.98 (t)	1.67 (m)	0.95 (t)
3-Hexene ozonation oligomer[c]		5.73–4.83 (u)	1.72 (m)	0.97 (t)

[a] Spectra of 8% solutions in dichlorodifluoromethane recorded at −50°. [b] *Cf.* footnote *b*, Table I. [c] For preparation, *cf.* ref 6.

by comparison with the methine absorption of authentic ozonides (*cf.* Table II); the principal methine absorption was at δ 4.08 (molozonide), and weak absorptions indicative of ethanal and propanal were also present. With *trans*-2-butene the areas of the ozonide and molozonide methine peaks indicated that these two components were present in the ratio 1.0:3.1, ethanal was clearly present, and weak absorption on the low-field side of the ozonide methine peak indicated a small amount of oligomer. The methine absorption of the alkene ozonation oligomer was broad and overlapped the ozonide methine absorption, but the former extended further downfield than did the latter (*cf.* Table II). The spectra from *trans*-2-pentene and *trans*-2-butene did not change as long as the ozonation mixtures were kept at −130°. These data indicated that these *trans* molozonides were stable at −130°. They also suggest that with a certain portion of the smaller alkene molecules the energy liberated during the formation of the molozonides could not be dissipated sufficiently rapidly in the small molecule and into its environment with the result that these species continued to react to give ozonolysis products. One might expect to observe this phenomenon with higher alkenes if the alkene and ozone concentrations used for the ozonation were sufficiently high. The single molozonide methine quartet that was observed with *trans*-2-butene and the single molozonide methine triplet that was observed with *trans*-3-hexene provide additional support for the 1,2,3-trioxolane structure of the molozonide.

The decomposition of the molozonide was observed by projecting the molozonide methine peak and the

TABLE III

NMR SPECTRAL DATA FOR *cis* ALKENE OZONATION MIXTURES[a]

Alkene	Aldehyde CHO, δ[b]	Ozonide CH, δ	Molozonide CH, δ	Ethanal CH₃, δ	Methylene, δ	Methyl, δ
			−130° Spectra			
cis-2-Butene	9.50 (u)	5.05 (q), 4.97 (q)[c]	4.52 (u)[e]	1.80 (d)		1.17 (d), 1.08 (d)
cis-2-Pentene	9.65–9.56 (m)	4.93 (m)[c]	4.35 (m)		Overlapping multiplets 2.02–0.42	
cis-3-Hexene		4.95 (t), 4.87 (t)[c]	4.53 (u)[e]		1.48 (u)	0.80 (u)
			−50° Spectra			
cis-2-Butene		5.17 (q), 5.10 (q)[d]		1.93 (d)		1.23 (d)
cis-2-Pentene		5.70–4.80 (m)[d]			2.27–1.30 (m)	1.27 (d), 0.87 (t)
cis-3-Hexene		5.05 (t), 5.00 (t)[d]			1.58 (m)	0.88 (t)

[a–d] Cf. footnotes, Table I.   [e] Gianni, *et al.*,[7a] have observed multiplicity of *cis* vicinal methine absorption in other cyclic systems.

ozonide methine region on an oscilloscope. With all three *trans* alkenes the molozonide peak did not begin to disappear until the mixture was warmed. As the temperature of each ozonation solution reached −100° the ozonide methine peak began to appear downfield from the molozonide peak. The former could be observed to increase as the latter diminished, and when a temperature of −90° was reached the molozonide peak had disappeared completely. The solutions were warmed to −70°, and their nmr spectra verified the usual[6] ozonolysis products of ozonide, aldehyde, and oligomer (cf. Table I). The presence of considerable oligomer in the ozonation mixtures was indicated by marked absorption on the low field side of the ozonide methine peak in the −70° spectra and the virtual disappearance of this absorption when the mixtures were recooled to −130°. This behavior may be explained by oligomer coming into and going out of solution.

The first spectra at −130° were taken about 30 min after the start of the ozonation. With all of the *cis* alkenes the two methine absorptions (cf. Table III) in the first spectra indicated the presence of both ozonide and molozonide; now, however, the molozonide methine absorption was at a lower field than in the case of the *trans* molozonides. These ozonation mixtures were kept at −130°, and the spectra were recorded at various times. The molozonide methine absorption diminished as the ozonide methine absorption increased, and the areas of these peaks were used to obtain an approximation of the relative amounts of ozonide and molozonide in the mixtures. Illustrative data are recorded in Table IV. After the disappearance of the molozonide methine absorption, the ozonation mixtures were warmed to −50° and the spectra indicated the presence of ozonide and oligomer. Again, the oligomer in each case was indicated by weak absorption on the low field side of the ozonide methine peak of the −130° spectra, a marked increase in intensity of this low field absorption in the −50° spectra, and the near loss of this absorption when the ozonation mixtures were recooled to −130°. Under the usual ozonation conditions, *cis* alkenes gave little aldehyde;[6] in these ozonations the only clear evidences of aldehyde were those shown in Table III. The larger amount of oligomer in these ozonations is interesting in light of the fact that *cis* alkenes on ozonation under usual conditions gave rise to little oligomer, whereas with *trans* alkenes oligomer was the principal product.[6] It has been suggested[6] that the

(6) F. L. Greenwood and H. Rubinstein, *J. Org. Chem.*, **32**, 3369 (1967).

TABLE IV

OZONIDE/MOLOZONIDE RATIOS IN *cis* ALKENE OZONATION MIXTURES

Alkene	Minutes after start of ozonation	Ozonide/molozonide
cis-2-Butene	31	1.00:0.67
	68	1.00:0.11
cis-2-Pentene	39	1.00:1.32
	60	1.00:0.75
	121	1.00:0.20
cis-3-Hexene	25	1.00:0.57
	49	1.00:0.09

molozonide is the principal source of the ozonation oligomer, and that the different behaviors of *cis* and *trans* alkenes may be explained by the relative stability of *cis* and *trans* molozonides. If the experimental conditions were such that the *cis* molozonide were stable for some time, then one might expect reasonable amounts of oligomer from the ozonation of *cis* alkenes. The presently reported data support this thesis.

The 1,2,3-trioxolane structure for the *trans* molozonide would appear to be rather firmly established. There are a number of instances[7] where, with cyclic compounds having vicinal methine protons, the *cis* isomer absorbs at a lower field than does the *trans* isomer. This pattern is followed uniformly by the *cis* and *trans* molozonides (cf. Tables I and III). The chemical shift of the methine proton of the *cis* molozonide differs from that of the *trans* isomer by approximately the same amount that has been observed in other ring systems.[7] This suggests that the *cis* molozonide has the same ring system as the *trans* isomer rather than a ring system of a different size. It is not really known, but the σ structure might not be expected for the *cis* molozonide which had been suggested by Murray, *et al.*,[8] to exhibit the varied stabilities which were observed with the *cis* molozonides (cf. Table IV). Simply by analogy with the *trans* molozonide we favor the 1,2,3-trioxolane structure for the *cis* molozonide.

The data of Table IV indicate some differences in stability of the various *cis* molozonides. The high initial ozonide/molozonide ratio which was observed with *cis*-2-butene may be explained by considerable formation of ozonide during the alkene-

(7) (a) M. H. Gianni, E. L. Stogryn, and C. M. Orlando, Jr., *J. Phys. Chem.*, **67**, 1385 (1963); (b) D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. E. Knipmeyer, *J. Amer. Chem. Soc.*, **83**, 4838 (1961); (c) F. A. L. Anet, *ibid.*, **84**, 747 (1962).

(8) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *ibid.*, **89**, 2429 (1967).

ozone reaction (*cf.* comments on *trans*-2-butene–ozone reaction). Once the decomposition of this molozonide began to be observed, however, it did so at roughly the same rate as the *cis* molozonide of 2-pentene, the most stable of the *cis* molozonides that were studied. In considering the stability of the 1,2,3-trioxolane system, two factors may be involved. First, one has a system that is inherently unstable. Examination of Briegleb models indicates that a steric factor must also be considered. The experimental facts[4b,5] would indicate that alkyl groups in a *trans* configuration in a 1,2,3-trioxolane effect no instability in the molecule, and models support the absence of interaction between the alkyl groups of such a configuration. With the alkyl groups in a *cis* configuration in such a system, however, models suggest interaction of the alkyl groups. This interaction becomes of some consequence with two ethyl groups, and one might predict that, with *cis* alkenes having groups larger than ethyl, the stability of the *cis* molozonide will be markedly less than that observed for the *cis* molozonide of 3-hexene.

In the studies[4] with the *trans* isomers of 2-butene, 2-pentene, and 3-hexene the α-diols that were obtained were entirely of the configuration that one would expect from the stereospecific *cis* addition of ozone to the carbon–carbon double bond. The current studies supported the stereospecific *cis* addition of ozone to both *cis* and *trans* alkenes. The methine absorptions of the two molozonide stereoisomers were quite different (*cf.* Tables I and III). In the −130° spectra that were obtained from the *trans* alkene ozonation mixtures there was no indication of *cis* molozonide methine absorption, and, likewise, in the −130° spectra which were obtained from the *cis* alkene ozonation mixtures there was no indication of *trans* molozonide methine absorption.

It has been mentioned previously[7] that *cis* vicinal methine protons in cyclic systems absorb at a lower field than do *trans* ones, and the molozonides examined in this work follow this pattern. If one assumes that the same phenomenon will be exhibited by 1,3-methine protons in cyclic systems, then one has an indirect method of assigning stereochemical configurations to ozonides. In the nmr spectrum of authentic 2-butene ozonide[6] the peak height of the lower field methine quadruplet is about half that of the higher field methine quadruplet. In vapor phase chromatography of this same ozonide[9] the peak area of the steroisomer of longer retention time is about half that of the stereoisomer of shorter retention time. Thus, one may make the assignment that the *cis* ozonide is the one of longer retention time in gas chromatography and the one of lower field methine absorption in the nmr spectrum. This assignment is in agreement with that already made by Murray, *et al.*[10] A number of other instances where the methine absorption of a *cis* ozonide is at lower field than that of the corresponding *trans* isomer have been published.[8]

If one assumes that peak height and peak area in an nmr spectrum are directly proportional, then one can

obtain an approximation of the *cis/trans* ratio of the ozonides produced in the presently reported ozonolyses. In the −70° spectrum of the *trans*-3-hexene ozonation mixture and the −50° spectrum of the *cis*-3-hexene ozonation mixture the methine triplets of the stereoisomeric ozonides were well resolved and of equal heights. Thus, where the molozonide is clearly rearranging to ozonide in dichlorodifluoromethane solvent each alkene stereoisomer gave the stereoisomeric ozonides in about a 50:50 ratio. In the spectra obtained from the 2-butene ozonation mixtures the methine quadruplets were not completely resolved, but were resolved sufficiently well that one could calculate an approximate *cis/trans* ozonide ratio. From the −70° spectrum of the *trans*-2-butene the *cis/trans* ozonide ratio was 31:69. From the first −130° spectrum from *cis*-2-butene the *cis/trans* ozonide ratio was 31:69, and, from the last −130° spectrum, when nearly all of the molozonide had disappeared, the *cis/trans* ozonide ratio was 33:67. These data may be added to those already published[9,11] which show that experimental conditions, particularly solvent, have a marked effect on the *cis/trans* ozonide ratio formed in alkene ozonolyses. It is impossible to draw any conclusions about the ozonide which was formed in the 2-pentene ozonations. If this alkene behaved here as under other ozonation conditions,[9,12] it gave rise to stereoisomeric pairs of three different ozonides. The methine protons of all of these absorb in the same region, and it was impossible to draw any conclusions from the complex pattern of the methine region of the 2-pentene ozonation spectra.

Experimental Section

The 2-pentenes and 3-hexenes were API standard samples. The 2-butenes (CP grade) and the fluorocarbons were purchased from Matheson Scientific Co.

An ozonizer of the type described by Bonner[13] at an oxygen flow rate of 1.35 l./hr produced 2–3 vol % ozone. Spectra were recorded with a Varian HR-60, Model 4300-B, using a V-4331 nmr probe which was equipped with a V-4340 variable-temperature modification. The theoretical amount of ozone was introduced into an nmr tube, which was immersed in a −130° bath, containing 0.30 ml of liquid dichlorodifluoromethane, 0.24 mmol of alkene, and a small amount of dichlorofluoromethane as an internal standard. After the ozonation, helium was bubbled through the reaction mixture for 10 min to remove dissolved oxygen, and the nmr tube was then transferred to the probe which was precooled to −130°. With the *cis* alkenes, spectra were recorded at −130° at intervals until the molozonide methine absorption disappeared. The ozonation mixtures were then warmed to −50°, and the spectra were recorded at this temperature. With the *trans* alkenes the spectra were recorded at −130°. The molozonide methine peak and the ozonide methine region were projected onto an oscilloscope, and the ozonation mixtures were warmed slowly to observe the molozonide-ozonide rearrangement. The mixtures were then warmed to −70° and the spectra were recorded.

Registry No.—*trans*-2-Butene molozonide, 15981-77-8; *trans*-2-pentene molozonide, 15981-76-7; *trans*-3-hexene molozonide, 2028-40-2; *cis*-2-butene molozonide, 15981-73-4; *cis*-2-pentene molozonide, 15981-74-5; *cis*-3-hexene molozonide, 2946-58-9.

(9) F. L. Greenwood, *J. Amer. Chem. Soc.*, **88**, 3146 (1966).
(10) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *ibid.*, **88**, 3655 (1966).

(11) *Cf.* references cited in ref 8.
(12) L. D. Loan, R. W. Murray, and P. R. Story, *J. Amer. Chem. Soc.*, **87**, 737 (1965).
(13) W. A. Bonner, *J. Chem. Educ.*, **30**, 452 (1953).