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Articles

The Ozonolysis of Tetramethylethylene. Concentration and Temperature Effects

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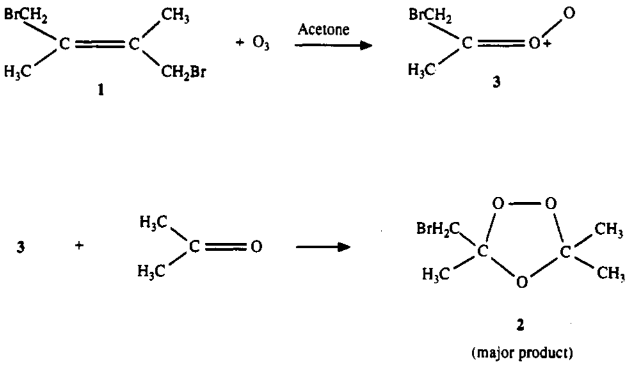
The products of the ozonolysis of tetramethylethylene in hexane or methylene chloride are remarkably dependent on the concentration of tetramethylethylene. Ozonolysis in neat tetramethylethylene gives mostly tetramethylethylene epoxide as product. As the concentration of tetramethylethylene is reduced, more acetone diperoxide is formed until it becomes the major product. The reaction also produces 3-hydroperoxy-2,3-dimethyl-1-butene. The product distribution is also quite dependent on reaction temperature. At a given concentration of the alkene the epoxide yield decreases as the temperature is lowered. Simultaneously the acetone diperoxide yield increases with lower temperature. The results are explained by postulating that energy-rich acetone oxide can be partially converted to dimethyldioxirane which is primarily responsible for the epoxidation. The proposed reaction scheme also has acetone oxide dimerize in a stepwise manner to give an intermediate which can either close to give diperoxide or lose singlet oxygen. The singlet oxygen would then react with tetramethylethylene to give the hydroperoxide.

Introduction

It has long been observed that tetrasubstituted linear alkenes do not usually give ozonides when treated with ozone.[1] Exceptions to this general observation occur when the substituents contain electron-withdrawing groups, that is, when the ketone produced in the ozonolysis is activated with respect to reaction with the ketonic carbonyl oxide.[1] On the other hand we have shown[2] that ozonolysis of *trans*-1,4-dibromo-2,3-dimethyl-2-butene, **1**, in acetone solvent gives, as the major ozonide product, the ozonide **2** resulting from reaction of carbonyl oxide **3** with acetone (Scheme I). Thus it is not the inherent unreactivity of acetone which is responsible for the failure of tetramethylethylene, **4**, to give an ozonide when ozonized in solution, as has long been assumed. When tetrasubstituted double bonds occur in four- and five-membered rings, then high yields of ozonide are obtained.[1] The formation of ozonides in these cases is presumably due to a combination of the proximity effect, i.e., the unsubstituted ketone and the carbonyl oxide are constrained to remain in each other's vicinity, and the relative ease of ring closure in these size rings. In the absence of these effects the ozonide-generating fragments are free to wander apart and give other products. In the case of **4** this process leads to the formation of acetone diperoxide, **5**, acetone triperoxide, **6**, and polymers of the carbonyl oxide[3] (Scheme II). In some cases ozonolysis of alkenes on silica gel has led to higher yields of the ozonides, presumably due to a favorable proximity effect.[4] Support for this explanation comes from the observation that ozonolysis of 2-pentene on silica gel did not give the cross ozonides 2-butene ozonide and 3-hexene ozonide[5] which are found in the solution ozonolysis of 2-pentene. Recently it has been shown[6,7] that ozonolysis of **4** on polyethylene did lead to the first synthesis of ozonide **7** (Scheme II). The method has been extended to other tetrasubstituted ethylenes[7] which also gave ozonides. These results may also reflect the favorable proximity effect achieved by partially immobilizing the reactive fragments on the polyethylene surface. The reaction with **4** also gave some **5** and **6** so that the reaction fragments do have some mobility. This achievment certainly demonstrates again that the earlier failure to form ozonide **7** in the solution ozonolysis of **4** was not due to the lack of reactivity of acetone.

Scheme I



Results

We have ozonized **4** in solution using hexane or methylene chloride as solvent. The ozonolyses were carried out on a series of solutions in which the amount of **4** present

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(1) Bailey, P. S. *Ozonation in Organic Chemistry*; Academic Press; New York, 1978; Vol. I, p 29.

(2) Murray, R. W.; Agarwal, S. K. *J. Org. Chem.* **1985**, *50*, 4698.

(3) Criegee, R.; Lohaus, G. *Justus Liebigs Ann. Chem.* **1953**, *583*, 6.

(4) Bailey, P. S. *Ozonation in Organic Chemistry*; Academic Press; New York, 1982; Vol. II, p 389.

(5) Den Besten, I. E.; Kinstle, T. H. *J. Am. Chem. Soc.* **1980**, *102*, 5968.

(6) Griesbaum, K.; Volpp, W.; Greinert, R. *J. Am. Chem. Soc.* **1985**, *107*, 5309.

(7) Griesbaum, K.; Volpp, W.; Greinert, R.; Greunig, H.-J.; Schmid, J.; Henke, H. *J. Org. Chem.* **1989**, *54*, 383.

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Scheme II

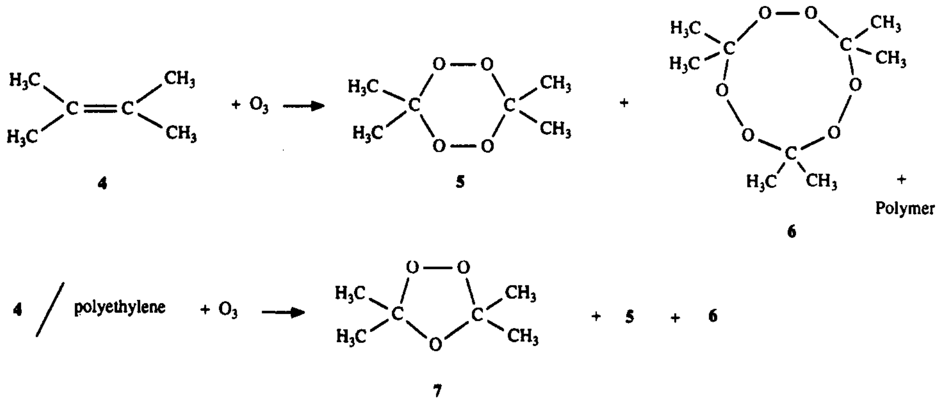

Table I. Product Yields (%) in Tetramethylethylene Ozonolyses

olefin concn (vol %)	solvent	acetone diperoxide (5)	epoxide (8)	hydroperoxide (9)	total reaction vol (mL)
1	hexane	12.81	0.0	0.0	60
10	hexane	5.98	1.88	1.25	30
10[a]	hexane	5.28	8.73	0.0	30
30	hexane	2.42	4.87	3.61	30
50	hexane	1.50	6.56	2.92	20
100		0.36	9.47	2.65	15
10	acetone	3.65	4.23	4.73	30
1	CH_2Cl_2	13.69	0.0	0.0	60
10	CH_2Cl_2	7.78	1.70	4.79	30
30	CH_2Cl_2	3.97	5.59	6.73	30
50	CH_2Cl_2	1.95	6.49	5.34	20
100		0.36	9.47	2.65	15

[a] Contains an equimolar amount of acetaldehyde.

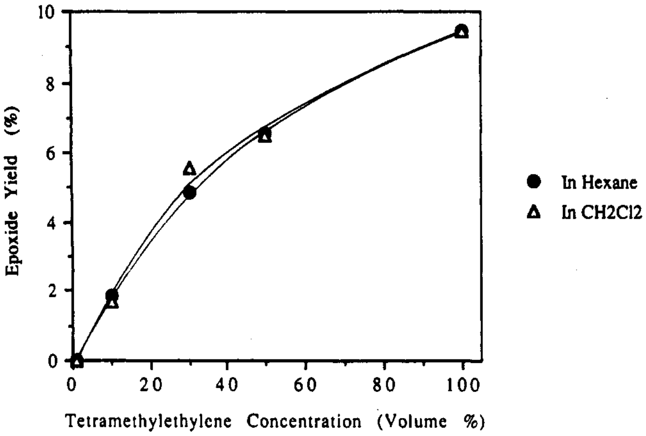

Figure 1. Yield of epoxide in the ozonolysis of tetramethylethylene in hexane and CH_2Cl_2.

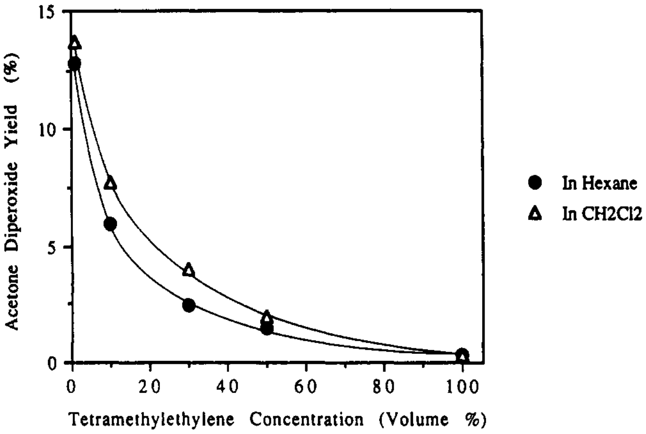

Figure 2. Yield of acetone diperoxide in the ozonolysis of tetramethylethylene in hexane and CH_2Cl_2.

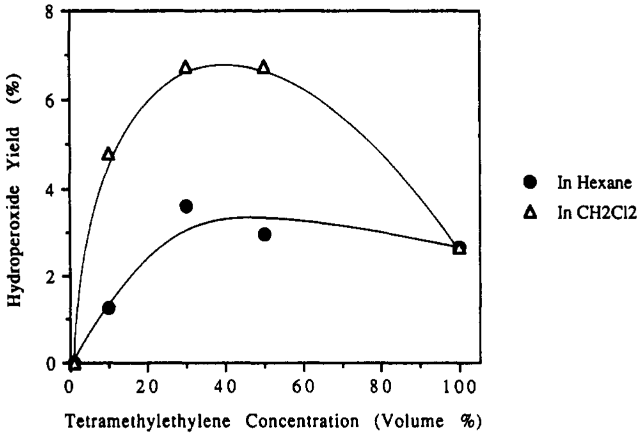

Figure 3. Yield of hydroperoxide in the ozonolysis of tetramethylethylene in hexane and CH_2Cl_2.

was varied from 1 to 100 volume %. Based on trial runs, the data were collected from reactions run to 2% conversion. When higher conversions are used it is more difficult to obtain precision in the data since the ozone/oxygen stream tends to carry away products even when a dry ice/acetone condenser is used. The major reaction products were tetramethylethylene epoxide, **8**, the hydroperoxide **9**, and acetone diperoxide, **5**. What is surprising is that the distribution of products is dependent on the amount of **4** in the reaction solution (Table I). The major product (77%) in neat **4** is the epoxide **8**. At the lowest concentration of **4** (1%) the only product is acetone diperoxide, **5**. Furthermore in both solvents the yields of the epoxide (Figure 1) and diperoxide (Figure 2) products varied in a smooth manner over the concentration range used. In a separate experiment it was shown that hydroperoxide **9** does not react with **4** to give epoxide. The yield of hydroperoxide **9** also varied with concentration (Figure 3) but not in the same smooth manner. Instead the yield of this product seems to be at a maximum at ca. 30% **4**. None of this product was observed at the lowest concentration used.

This remarkable departure from the existing reports on the ozonolysis of **4** has prompted us to conduct further investigation on the factors involved. Ozonolysis of *cis*- or *trans*-3-hexene in various concentrations in hexane gave mixtures of the ozonide stereoisomers as major products as expected. However these ozonolyses also gave low yields of the epoxides and in a stereospecific manner, i.e., *trans*-

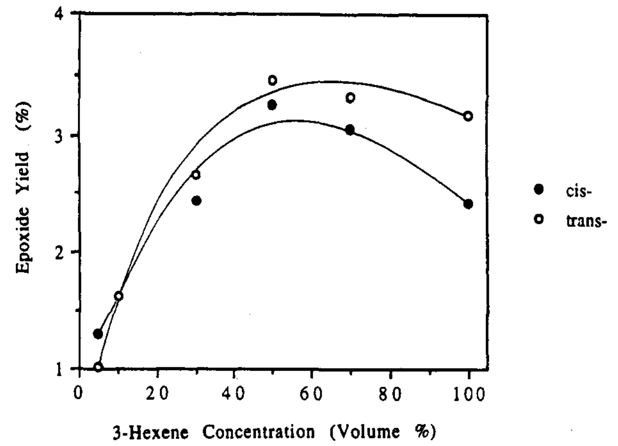

Figure 4. Epoxide yield in the ozonolysis of *trans*- and *cis*-3-hexene in hexane.

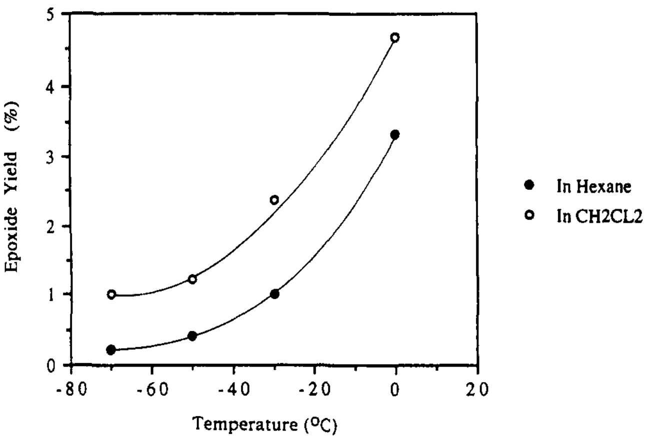

Figure 5. Temperature effect on the yield of epoxide in the ozonolysis of tetramethylethylene in hexane and CH_2Cl_2.

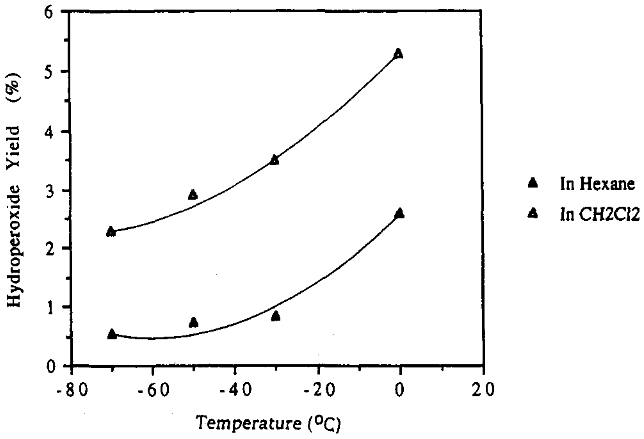

Figure 6. Temperature effect on the yield of hydroperoxide in the ozonolysis of tetramethylethylene in hexane and CH_2Cl_2.

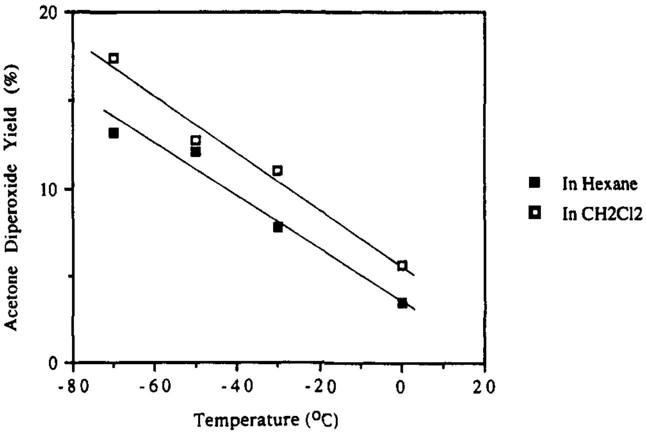

Figure 7. Temperature effect on the yield of acetone diperoxide in the ozonolysis of tetramethylethylene in hexane and CH_2Cl_2.

3-hexene gave only *trans*-epoxide and *cis*-3-hexene gave only *cis*-epoxide. Here again the yields of the epoxide products varied in a smooth manner with concentration of the alkene in the solvent (Figure 4). Epoxides have been reportedly formed in some earlier ozonolyses; however, most of these cases involve alkenes with halogen substituents[8] or large steric hindrance.[9] Ozonolysis of 4 in acetone solvent, using the same conditions as for hexane and methylene chloride, led to the formation of 5, 8, and 9. In this case, however, the yields of epoxide and hydroperoxide exceed that of diperoxide, in contrast to the results in hexane or methylene chloride solvent (Table I). The ozonolysis of 4 was also carried out in hexane containing an equimolar amount of acetaldehyde. In this case trimethylethylene ozonide is the major product followed by eopoxide and diperoxide. No hydroperoxide is detected under these conditions. A control reaction indicated that no epoxide is formed from peracetic acid (possible ozonation product of acetaldehyde) and 4 under the reaction conditions. A second control reaction showed that hydroperoxide is not consumed by acetaldehyde under the reaction conditions. Thus the absence of the hydroperoxide in the reaction mixture is not due to this possible side reaction. The ozonolysis of 4 was also conducted in the presence of phenanthrene. This procedure led to the formation of phenanthrene oxide, 10. A control experiment indicated that no oxide is formed when ozone is passed through the phenanthrene solution in the absence of 4.

In order to obtain further insight into the process or processes involved in these unusual results the ozonolyses of 4 in hexane and methylene chloride were carried out at several temperatures. As shown in Figures 5 and 6 the yields of epoxide and hydroperoxide, respectively, both decrease markedly at lower temperatures. At the same time there is an accompanying increase in the yield of diperoxide as the temperature is lowered (Figure 7).

Discussion

The results described here stand in great contrast to results on the ozonolysis of 4 reported over an extended period of time. In part this may be due to the fact that concentration and temperature effects apparently have not been studied for tetrasubstituted alkenes in the same way that they have for 1,2-disubstituted alkenes.[10] A general reading of the literature on the ozonolysis of 4[1] indicates that the major product expected is acetone diperoxide accompanied by some of the trimer and polymer of acetone oxide. In the results reported here the major product formed depends both on the concentration of 4 and the reaction temperature. The formation of hydroperoxide 9 is particularly puzzling. This material is well-known to be a product of the reaction of singlet oxygen with 4. We believe that our results can be rationalized by

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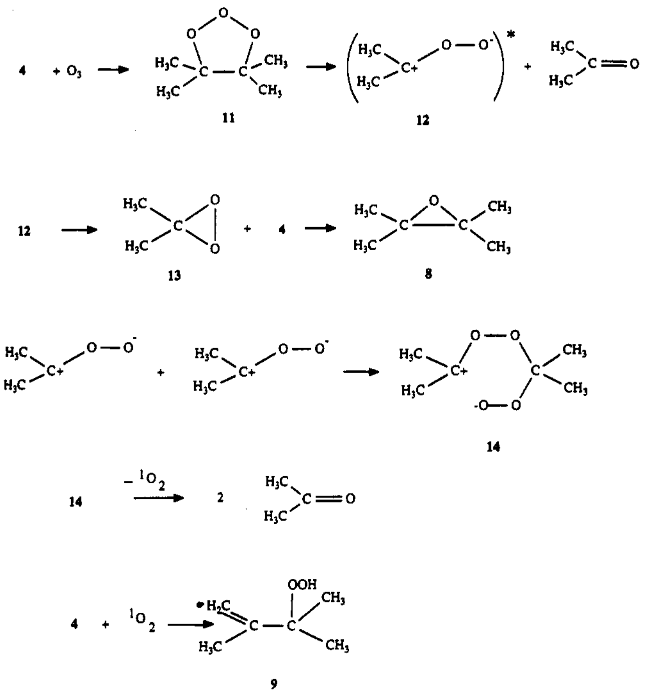
(8) Reference 1, p 8.

(9) Reference 1, p 197.

(10) Reference 1, Chapter 7.

Scheme III



the processes shown in Scheme III. This description has many of the same features as a similar scheme recently proposed by Kopecky and co-workers[11] to explain observations made on the ozonolysis of (*E*)- and (*Z*)-1,2-dimethoxy-1,2-diphenylethene. In Scheme III ozonolysis of 4 proceeds in the expected manner to give trioxolane 11 which decomposes to give carbonyl oxide 12 and acetone. Since the decomposition of 11 is expected to be very exothermic, carbonyl oxide 12 will be formed in an energy-rich form. In solution collisions with solvent molecules is expected to remove this excess energy for most molecules of 12. However we speculate that in some cases excited carbonyl oxide molecules may close to the isomeric dioxirane 13. Cyclization of an energy-rich carbonyl oxide has been invoked to explain some of the products of gas-phase ozonolysis of alkenes.[12] Indeed microwave spectroscopy has been used to detect the parent dioxirane in the gas phase as a product of the low-temperature ozonolysis of ethylene.[13]

Alternatively carbonyl oxide molecules may react with each other, ultimately to give 5. In the current scheme this dimerization process is shown as proceeding in a stepwise manner through 14. While many discussions of the formation of such dimers in ozonolysis imply a concerted process, we believe that the stepwise process is more appropriate. A concerted process in this case would be a 4 + 4 cycloaddition which is not allowed in a thermal process in which orbital symmetry is conserved.[14] The introduction of 14 as a precursor to 5 also provides an alternative reaction pathway which can explain some of the unusual results obtained here. We suggest that a competing pathway for 14 is loss of singlet oxygen accompanied by the formation of two molecules of acetone as shown in Scheme III. Under the conditions of the current experiments this singlet oxygen would be expected to undergo the ene reaction with the very reactive 4 to give the observed hydroperoxide 9. Dioxirane 13 would be expected to react rapidly with 4 to give epoxide 8. It is also possible that carbonyl oxide 12 could react with 4 to give the epoxide, but this process is known[15] to be inefficient. The details presented in Scheme III follow closely those given by Kopecky et al.[11] In their work these authors also included a stepwise dimerization of carbonyl oxides to give either diperoxide or singlet oxygen. In their case the evolved singlet oxygen gave the dioxetane of the starting alkene since the latter is devoid of allylic hydrogens. It is also the case that Kopecky et al.[11] observed an increase in the amount of diperoxide as the temperature is lowered. This result exactly parallels those obtained here in which the amount of acetone diperoxide produced increases as the temperature is lowered (Figure 7).

The mechanism shown in Scheme III also is nicely consistent with the results obtained in the temperature and concentration studies. Thus at high concentrations of 4 higher yields of epoxide are formed since dioxirane 13 (or carbonyl oxide 12) has a greater opportunity to react with 4 (Figure 1). Concurrently there is a decrease in the formation of the diperoxide 5 as the concentration of 4 is increased (Figure 2) since the carbonyl oxide precursor is removed by conversion to 13 and subsequent reaction with 4 to give epoxide. The dependence of hydroperoxide 9 formation on the concentration of 4 is more complex because its formation depends on the competing processes involved in epoxide versus diperoxide and singlet oxygen formation. Thus the dependence of the amount of 9 formed versus concentration (Figure 3) reaches a maximum at a concentration of 4 of ca. 30% for both hexane and methylene chloride solvents.

A similar scheme can explain the formation of the epoxide products in the ozonolyses of *cis*- and *trans*-3-hexene (Figure 4). In these cases the epoxide yield goes through a maximum as a result of the different competing process of ozonide formation. It is also noted that the epoxides formed are those expected for stereospecific processes, i.e., *cis*-alkene gave *cis*-epoxide and *trans*-alkene gave *trans*-epoxide. These results also suggest involvement of dioxiranes which are known[16] to epoxidize in this fashion whereas carbonyl oxides are associated with stereoselective and not stereospecific epoxidation.[15] In the experiment in which 4 is ozonized in hexane solution containing an equimolar amount of acetaldehyde, trimethylethylene ozonide is the major product, as expected. No hydroperoxide is formed in this case, presumably because the major portion of the available carbonyl oxide is converted to ozonide rather then going through 14 and then eliminating singlet oxygen for further reaction with

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[11] Kopecky, K. R.; Xie, Y.; Molina, J. *Abstracts Div. of Org. Chem.*, 203rd ACS National Meeting, San Francisco, CA, April 1992, p 25. *Can. J. Chem.*, submitted.

[12] (a) Herron, J. T.; Martinez, R. I.; Huie, R. E. *Int. J. Chem. Kinet.* 1982, *14*, 201. (b) Herron, J. T.; Martinez, R. I.; Huie, R. E. *Int. J. Chem. Kinet.* 1982, *14*, 225.

[13] (a) Lovas, F. J.; Suenram, R. D. *Chem. Phys. Lett.* 1977, *51*, 453. (b) Martinez, R. I.; Huie, R. E.; Herron, J. T. *Chem. Phys. Lett.* 1977, *51*, 457. (c) Suenram, R. D.; Lovas, F. J. *J. Am. Chem. Soc.* 1978, *90*, 5117.

[14] Woodward, R. B.; Hoffman, R. *The conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, Germany, 1970.

[15] Hinrichs, T. A.; Ramachandran, V.; Murray, R. W. *J. Am. Chem. Soc.* 1979, *101*, 1282.

[16] (a) Murray, R. W. *Chem. Rev.* 1989, *89*, 1187. (b) Murray, R. W. In *Molecular Structure and Energetics. Unconventional Chemical Bonding*; Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1988; Vol. 6, pp 311–351. (c) Curci, R. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI Press: Greenwich, CT, 1990; Vol. 2, Chapter 1. (d) Adam, W.; Curci, R.; Edwards, J. O. *Acc. Chem. Res.* 1989, *22*, 205. (e) Adam, W.; Hadjiarapoglou, L.; Curci, R.; Mello, R. In *Organic Peroxides*; Ando, W., Ed.; Wiley: New York, 1992; p 195. (f) Griesbaum, K. Personal communication. We thank Prof. Griesbaum for this helpful information.

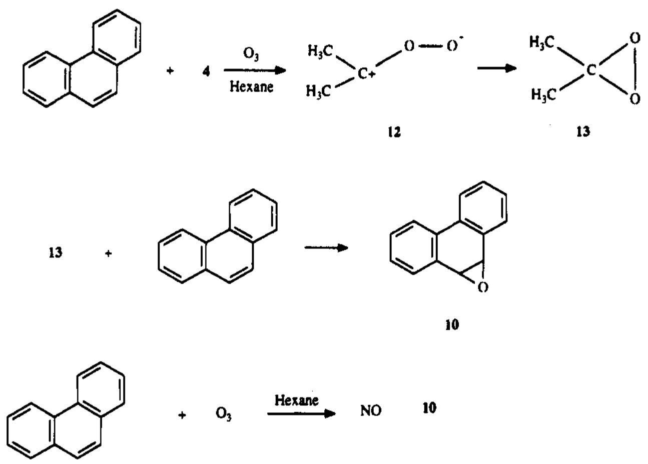
4 to give the hydroperoxide. On the other hand some 14 is presumably formed since some diperoxide is obtained.

The results obtained when 4 is ozonized in acetone solvent require some comment. In this reaction epoxide, diperoxide, and hydroperoxide are found in the reaction mixture. The diperoxide is formed in a lower yield than in hexane and CH_2Cl_2. However the epoxide yield in acetone is about 4.5 times that obtained in hexane. Perhaps the most surprising result of this experiment, however, is the failure to find tetramethylethylene ozonide, 7. If, as discussed earlier, the proximity effect is controlling for ozonide formation, as exemplified in the case of ozonolysis on polyethylene,[6,7] then one might have expected that surrounding carbonyl oxide 12 with acetone molecules would lead to the formation of some ozonide. Some additional factor must be playing a role here. A likely explanation is the low conversion used. Griesbaum and co-workers have found[16f] epoxide and ozonide (ca. 2:1) in very low yield in residues obtained by removing most of the acetone from ozonolysis solutions of 4 in acetone.

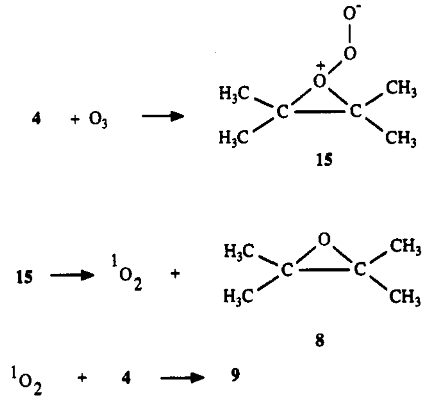
The elements of Scheme III also are nicely consistent with the variable-temperature results. Products which depend on the involvement of energy-rich carbonyl oxides, e.g., epoxide and hydroperoxide, are seen to decrease as the temperature is lowered (Figures 5 and 6, respectively). We suggest that at the lower temperatures less of the carbonyl oxide is converted to 13. Likewise dimer precursor 14 is less likely to lose singlet oxygen but is more prone to close to 5. A lowered production of singlet oxygen would lead to a decrease in hydroperoxide formation as observed. This explanation also requires an increase in dimer formation as the temperature is lowered which is also what is observed experimentally (Figure 7).

Scheme III contains a number of features which are not commonly associated with ozonolysis chemistry. There are, to the best of our knowledge, few examples of the invocation of the involvement of dioxiranes in ozonolysis. The recent work of Kopecky and co-workers[11] cited above is such an example. One very broad example is the frequent suggestion that the formation of esters or acids in ozonolysis occurs via a cyclic form of the carbonyl oxide, i.e., a dioxirane.[17] This reaction path is proposed as an alternative to the more unlikely direct rearrangement of the carbonyl oxide to the observed products. Another recent example of the invocation of dioxiranes in ozone chemistry occurs in our own work. We have suggested[18] that the ozonolysis of 4 in the gas phase leads to the formation of dioxirane 13 which subsequently reacts with polycyclic aromatic hydrocarbons (PAH), supported on model particulates, to give arene oxides. In an attempt to gain more evidence for the involvement of 13 in the current work we have carried out an ozonolysis of 4 in hexane containing phenanthrene. This reaction leads to the formation of phenanthrene oxide, 10. A control experiment indicated that ozone alone does not produce 10 under the reaction conditions. We interpret these results as demonstrating that an ozonolysis product of 4, most likely 13, is responsible for oxide production (Scheme IV). It should be noted, however, that we cannot rule out the possibility that 12 is responsible for the production of the oxide. On the other hand it is known[19] that carbonyl oxides carry out this reaction in an inefficient manner.

Scheme IV



Scheme V



The other feature of Scheme 3 that is unusual in ozonolysis chemistry is the suggestion of singlet oxygen formation. The suggestion has been made[20] in some of those cases where ozone reacts with an olefin (usually a hindered example) via a σ complex or adduct, 15 (Scheme V). According to this scheme loss of singlet oxygen from the adduct, 15, leads to epoxide production. We believe that this scheme can be ruled out as a major source of epoxide in our current work. If this scheme were operating, then we would expect the singlet oxygen to react with 4 to give the hydroperoxide. In our results hyderoperoxide and epoxide production show a different dependence on the concentration of 4 than is predicted by Scheme V. This is most apparent when comparing epoxide production in methylene chloride (Figure 1) with hydroperoxide formation (Figure 3) in the same solvent. Contrary to the prediction of Scheme V, the maximum epoxide and hydroperoxide production do not occur at the same concentration of 4. The intervention of singlet oxyen in ozonolysis has also been suggested by Kopecky et al.[11] in the example cited above.

Experimental Section

Materials. Tetramethylethylene (98%) was purchased from Aldrich Chemical Co. and was passed through a column of alumina (Brockman neutral, activity grade 1, 80–200 mesh, Fisher)

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(17) Bailey, P. S. *Chem. Rev.* **1958**, *58*, 925.

(18) Murray, R. W.; Rajadhyaksha, S. N.; Jeyaraman, R. In *Polycyclic Aromatic Hydrocarbons* **1990**, *1*, 213.

(19) See, for example: Kumar, S.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 1040.

(20) (a) Bailey, P. S.; Ward, J. W.; Hornish, R. E.; Potts, F. E., III. *Adv. Chem. Ser.* **1972**, *112*, 1. (b) Bailey, P. S.; Ward, J. W.; Carter, T. P.; Nieh, E.; Fisher, C. M.; Khashab, A. Y. *J. Am. Chem. Soc.* **1974**, *96*, 6136.

immediately before use. GLC analysis of this tetramethylethylene indicated that no epoxide or hydroperoxide was present. In a separate experiment a sample of this material was stored at room temperature and periodically analyzed by GLC. Only after 3 h, 20 min could a trace of epoxide be detected. After 24 h both epoxide and hydroperoxide could be detected. The experiments in Table I required 15 min or less. Acetaldehyde (Eastman Kodak) was distilled immediately before use. *cis*-3-Hexene (96%) was purchased from Wiley Organics and used as received. *trans*-3-Hexene (96%) was obtained from Aldrich Chemical Co. and used as received. Phenanthrene (Aldrich) was recrystallized from methanol prior to use. Hexane, methylene chloride, and acetone, all obtained from Fisher Scientific Co., were distilled from calcium hydride or potassium carbonate before use. Sodium thiosulfate solution (N/10, certified, 0.1005–0.0995 N) and starch indicator solution (stabilized) were purchased from Fisher Scientific Co.

Instrumentation. NMR spectra were recorded on a 300-MHz NMR spectrometer using deuterated chloroform as solvent. Chemical shift values given are relative to tetramethylsilane. Analytical GLC analyses were carried out on a capillary gas chromatograph using a fused silica capillary column (30 m × 0.311 mm) with DB-210 as liquid phase (film thickness 0.5 μm); temperature 1, 40 °C; time 1, 5 min; rate 1, 10 °C/min; temperature 2, 100 °C; time 2, 2 min. Ozone was produced in a commercial generator with the concentration being measured using iodometry. Preparative GLC was performed on a preparative gas chromatograph using a 20-ft × $^3/_8$-in. column (liquid phase, 15% SE-30 on Chrom W, 30/60 mesh, (PIGV). Quantitative GLC data were obtained by using authentic samples of the products and determining response factors using dodecane as an internal standard. Electron impact mass spectra (at 70 eV ionizing voltage) were recorded on a twin EI and CI quadrupole mass spectrometer connected to a gas chromatograph fitted with an ultra 1 12-m × 0.2-mm × 0.33-μm cross-linked methyl silicone gum column.

General Ozonolysis Procedure. A reaction vessel containing the substrate or solution of substrate and solvent and equipped with a dry ice/acetone condenser was placed in an ice water bath at 0 °C for 30 min before commencing ozonolysis. The inlet tube of the reaction vessel was connected to the outlet of the ozone generator. An outlet tube from the vessel led to a gas wash bottle containing 100 mL of 5% KI solution. Total ozone absorbed was determined by first measuring the output of the generator, passing ozone for the required time, and then titrating the contents of the wash bottle in order to determine the precise amount of ozone absorbed. The titration uses sodium thiosulfate solution and starch indicator solution. Ozonolyses were carried out to 2% conversion of the olefin in order to gain the most accurate data on product distribution. In separate experiments it was shown that running the reactions to higher conversions causes loss of product, particularly epoxide, and particularly at high concentrations of tetramethylethylene where longer reaction times are required.

Ozonolysis of Neat Tetramethylethylene. The general procedure was followed with ozone (0.16 mmol/min) being passed through tetramethylethylene (15 mL, 126.2 mmol) for 15.5 min. The solution became pale yellow in color but returned to colorless when the solution was allowed to reach room temperature. Quantitative GLC analysis of the reaction mixture indicated that the following products were present: tetramethylethylene epoxide (0.231 mmol, 9.47%), 3-hydroperoxy-2,3-dimethyl-1-butene (0.064 mmol, 2.65%), and acetone diperoxide (0.004 mmol, 0.36%). The product mixture also contained trace amounts of other materials which were not identified. The products were identified by comparing their properties with those of authentic materials. The quantitative GLC was accomplished by using an internal standard and determining response factors for each of the products.

Ozonolysis of Tetramethylethylene in Hexane. The general ozonolysis procedure was used on solutions of tetramethylethylene in hexane at various concentrations (Table I). The products formed were acetone, tetramethylethylene epoxide, 3-hydroperoxy-2,3-dimethyl-1-butene, and acetone diperoxide. The yields of products were determined by quantitative GLC (Table I). Traces of 2,3-dimethylbut-3-en-2-ol were also formed.

Ozonolysis of Tetramethylethylene in Methylene Chloride. The procedure described for the ozonolyses in hexane was followed with the results shown in Table I. In this case traces of 2,2,3-trimethyl-3-buten-1-ol were formed.

Tetramethylethylene Epoxide. Tetramethylethylene (0.5 mL) in 10 mL of acetone was added to 60 mL of freshly prepared dimethyldioxirane (0.07 M, acetone solution). The reaction mixture was stirred at room temperature for 1 h. Excess acetone was removed by fractional distillation. The epoxide was isolated from the residue by preparative GLC (column: 8% SF-96, column temperature, 60 °C, injector temperature, 80 °C, detector temperature, 105 °C, collector temperature, 20 °C). ^{1}H NMR: δ 1.24 (s). ^{13}C NMR: δ 21.09 and 62.02.

3-Hydroperoxy-2,3-dimethyl-1-butene. The procedure of Foote and Wexler[21] was followed. To a solution of 7.2 mL (60.6 mmol) of tetramethylethylene in 300 mL of methanol was added 12.4 g of H_2O_2 (50%, 182 mmol). The solution was stirred at 5 °C, and 204 mL of commercial bleach (contains 5.25% by wt of NaOCl) was added in 60 min. The reaction solution was diluted with H_2O (100 mL) and extracted with ether (2 × 250 mL). The ether was removed by distillation. A pure sample was obtained by preparative GLC (column SE-30, column temperature, 72 °C, detector temperature, 95 °C, injector temperature, 84 °C). ^{1}H NMR: δ 1.32 (s, 6 H), 1.77 (m, 3 H), 4.91 (m, 1 H), 4.96 (m, 1 H), and 7.71 (s, 1 H). ^{13}C NMR: δ 18.75, 23.9, 84.28, 111.74, and 147.85.

Tetramethylethylene Ozonide. The procedure of Griesbaum et al.[6,7] was followed. Polyethylene (Microethene FN 500, purchased from Serva Feinbiochemica Heidelberg, Germany, spherical particles, maximum size 20 μm) was extracted with diethyl ether for 24 h, followed by drying on a vacuum line for 24 h. The polyethylene (5 g) was placed in an air condenser. Tetramethylethylene, carried by dry Ar, was passed through the polyethylene at room temperature. The condenser was cooled to −78 °C (dry ice/acetone), and ozone (0.16 mmol/min) was passed through the tetramethylethylene/polyethylene for 20 min. The polyethylene was washed with diethyl ether (40 mL) and then filtered off the reaction solution. The ether solution was concentrated by distillation. The pure ozonide was isolated by preparative GLC (column SE-30, column temperature 80 °C, detector temperature, 90 °C, injector temperature, 100 °C). ^{1}H NMR: δ 1.45 (lit.[6,7] δ 1.46). ^{13}C NMR: δ 24.74 and 108.58 (lit.[6,7] δ 24.60 and 108.65).

Acetone Diperoxide. A sample was prepared by ozonizing tetramethylethylene in methylene chloride at 0 °C. A pure sample was obtained using preparative GLC (column SE-30, column temperature, 80 °C, detector temperature, 75 °C). ^{1}H NMR: δ 1.34 (s) and 1.77 (s). ^{13}C NMR: δ 20.56, 22.42, and 107.48.

2,3-Dimethylbut-3-en-2-ol. This material was isolated as a colorless liquid from the reaction mixtures in the ozonolysis of tetramethylethylene in hexane. The isolation was via preparative GLC (column SE-30, column temperature, 60 °C, detector temperature, 105 °C, injector temperature, 80 °C). ^{1}H NMR: δ 1.31 (s, 6 H), 1.62 (bs, 1 H), 1.77 (m, 3 H), 4.73 (m, 1 H), 4.96 (m, 1 H). Lit. values[22] δ 1.35, 1.81, 4.77, 5.00. ^{13}C NMR: δ 19.21, 28.88, 73.09, 100.32, 151.77. GC/MS: 101 (0.2), 100 (1.9, M$^+$), 85 (100), 59 (67), 43 (50).

2,2,3-Trimethylbut-3-en-1-ol was isolated as a colorless liquid from the reaction mixtures in the ozonolysis of tetramethylethylene in methylene chloride. The isolation used preparative GLC (column SE-30, column temperature, 70 °C, detector temperature, 95 °C, injector temperature, 90 °C). ^{1}H NMR: δ 1.05 (s, 6 H), 1.73 (m, 3 H), 3.38 (bs, 2 H), 4.81 (m, 1 H), 4.92 (m, 1 H). Lit. values[23] δ 1.01, 1.73, 3.28, 4.78. ^{13}C NMR: δ 19.63, 23.87, 41.31, 69.60, 111.87, 149.38.

Ozonolysis of Tetramethylethylene in Acetone. The general ozonolysis procedure was used, modified as follows. Ozone (0.163 mmol/min) was bubbled through the acetone solution of tetramethylethylene (3 mL, 25.2 mmol, in 27 mL of acetone) for 3 min, 15 s (0.504 mmol of O_3, 2% conversion). GLC analysis of the reaction mixture indicated the formation of epoxide (0.023

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mmol, 4.23%), 3-hydroperoxy-2,3-dimethyl-1-butene (0.026 mmol, 4.73%), and acetone diperoxide (0.01 mmol, 3.65%) (Table I).

Ozonolysis of Tetramethylethylene in Hexane Containing Acetaldehyde. The general ozonolysis procedure was followed, modified as follows. Ozone (0.161 mmol/min) was bubbled through a solution of tetramethylethylene (3 mL, 25.2 mmol) and acetaldehyde (1.42 mL, 25.4 mmol) in hexane (27 mL) for 3 min, 8 s (2% conversion of tetramethylethylene). GLC analysis indicated the formation of epoxide (0.044 mmol, 8.73%), acetone diperoxide (0.014 mmol, 5.28%), and trimethyl ozonide (0.103 mmol, 20.29%) (Table I). The ozonide was separated using preparative GLC (column SE-30, column temperature, 50 °C, detector temperature, 95 °C, injector temperature, 75 °C). ^{1}H NMR: δ 1.39 (d, J = 4.95 Hz, 3 H), 1.45 (bs, 3 H), 1.46 (bs, 3 H), 5.27 (q, J = 4.95 Hz, 1 H) (lit.[24] δ 1.40, 1.49, 5.38). ^{13}C NMR: δ 23.29, 26.20, 100.39. A control experiment was run in which peracetic acid (Fisher, 40%, 4.8 g, 25.2 mmol) in hexane was stored with 4 for 3 min and 10 s. GLC analysis indicated that no epoxide was formed under these conditions. A second control was run in which hydroperoxide 9 (0.205 g, 1.8 mmol) in 2 mL of hexane was combined with acetaldehyde (0.1 mL, 1.8 mmol) for 1 min. GLC analysis indicated that neither reagent was consumed in this period.

Control Reaction of 1-Hydroperoxy-2,3-dimethyl-1-butene with Tetramethylethylene. To a solution of the hydroperoxide in CDCl$_3$, cooled to 0 °C for 20 min, was added tetramethylethylene (0.3 mL, 2.52 mmol). The reaction mixture was stirred for 15 min. GLC analysis showed that no epoxide was formed.

Ozonolysis of *cis*- and *trans*-3-Hexene in Hexane. The general ozonolysis procedure was followed. Ozone was passed through a solution of the hexene in hexane for the time required to give 2% conversion of the hexene. Details of the experiments with *cis*-3-hexene are as follows:

hexene used (mmol)	concn (vol, %)	epoxide yield (%)	ozonide yield (%)	O$_3$ used (mmol)
0.77	5	1.3	60.8	0.015
1.55	10	1.63	65.0	0.030
4.65	30	2.44	57.9	0.092
7.76	50	3.27	62.1	0.153
10.86	70	3.06	44.96	0.219
15.51	100	2.42	28.9	0.306

Details of the experiments with *trans*-3-hexene are as follows:

hexene used (mmol)	concn (vol, %)	epoxide yield (%)	ozonide yield (%)	O$_3$ used (mmol)
0.77	5	1.01	17	0.015
1.52	10	1.62	29.1	0.03
4.56	30	2.67	22.8	0.092
7.61	50	3.46	24.8	0.153
10.65	70	3.32	19.8	0.214
15.22	100	3.18	12.2	0.306

***cis*- and *trans*-3-Hexene Ozonides.** These materials were isolated as a mixture from the reaction mixture in the ozonolysis of 3-hexene in hexane. The isolation used preparative GLC (column SE-30, column temperature, 75 °C, detector temperature, 100 °C, injector temperature, 110 °C). ^{1}H NMR (CDCl$_3$): δ 0.96 (2 t, J = 7.52 Hz, 2 × 6 H), 1.70 (m, 2 × 4 H), 5.12 (2 t, J = 5.10, 4.64 Hz, 2 × 1 H), (lit.[25] δ 1.39, 1.66, 5.05). ^{13}C NMR: δ 7.81, 8.00, 24.05, 25.59, 104.87, 104.91. GC/MS (EI): 132, 103, 57.

The Ozonolysis of Tetramethylethylene in the Presence of Phenanthrene. The general ozonolysis procedure was followed by passing the ozone stream (0.16 mmol/min) through a solution of phenanthrene (0.1 g, 0.56 mmol) and tetramethylethylene (0.5 mL, 4.2 mmol) in 20 mL of hexane at 0 °C for 14 min. A colorless solution was obtained. The solvent was removed on the Rotovapor and the residue dissolved in CDCl$_3$. The ^{1}H NMR spectrum showed the characteristic methine proton of phenanthrene oxide at δ 4.54. Using dichloromethane (0.4 μL, 0.006 mmol) as an internal standard, the yield of phenanthrene oxide was determined to be 0.8%. The experiment was repeated without tetramethylethylene. In this case no phenanthrene oxide was formed.

The Ozonolysis of Tetramethylethylene in Hexane at Various Temperatures. The general ozonolysis procedure was followed, modified as follows. The reaction vessel containing the tetramethylethylene (1 mL, 8.41 mmol, 50% in hexane) was precooled in a cooling bath at the desired temperature (vide infra) for 20 min. Ozone (0.154 mmol/min) was passed through the reaction solution for 1 min (2% conversion). The reaction solution was kept at the reaction temperature for an additional period (−70 °C, 40 min; −50 °C, 30 min; −30 °C, 20 min) before warm-up to room temperature and analysis. The results of the GLC analyses at the various temperatures are as follows:

T (°C)	O$_3$ used (mmol)	epoxide (%)	acetone diperoxide (%)	hydroperoxide (%)
0[a]	0.153	3.32	3.43	2.59
−30	0.153	1.02	7.8	0.84
−50	0.153	0.42	12.09	0.75
−70	0.153	0.21	13.61	0.55

[a] Differences between these data and those in Table I (50 vol %) are due to the different scale of the reactions. The data in Table I are obtained using a reaction volume of 20 mL while those given here are from a 2-mL reaction. At the lower volume the epoxide yields are lower presumably because more material was lost during the ozonolysis.

The Ozonolysis of Tetramethylethylene in Methylene Chloride at Various Temperatures. The same procedure as for the hexane case was followed with these results:

T (°C)	O$_3$ used (mmol)	epoxide (%)	acetone diperoxide (%)	hydroperoxide (%)
0[a]	0.157	4.68	5.60	5.28
−30	0.157	2.37	11.08	3.50
−50	0.157	1.22	12.73	2.92
−70	0.157	1.02	17.36	2.30

[a] See footnote for hexane above.

***cis*-3-Hexene Epoxide.** To a solution of 100 mL of dimethyldioxirane (0.05 M) in acetone was added 0.6 mL of *cis*-3-hexene (4.7 mmol). The solution was stirred at room temperature for 2 h. Most of the acetone was removed by fractional distillation. Pure *cis*-3-hexene epoxide was isolated by preparative GLC (column, SE-30, column temperature, 80 °C, detector temperature, 90 °C, injector temperature, 100 °C). ^{1}H NMR (CDCl$_3$): δ 1.02 (t, J = 7.47 Hz, 6 H), 1.52 (m, 4 H), 2.86 (m, 2 H). ^{13}C NMR: δ 10.69, 21.07, 58.49.

***trans*-3-Hexene Epoxide.** The same procedure as for the cis compound was followed. The pure *trans*-3-hexene epoxide had ^{1}H NMR (CDCl$_3$): δ 0.97 (t, J = 4.9 Hz, 6 H), 1.54 (m, 4 H), 2.63 (m, 2 H). ^{13}C NMR: δ 10.02, 25.24, 59.70.

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