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Ozonolysis of *trans*-Di-*tert*-butylethylene. The Oligomer

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The oligomer obtained from ozonolysis of *trans*-di-*tert*-butylethylene (1) in hexane or methylene chloride is assigned a cyclic polycarbonyl oxide structure. The oligomer is reduced to pivalaldehyde by triphenylphosphine. It also slowly decomposes to an intermediate which can epoxidize olefins. The mechanism of the ozonolysis of 1 is discussed in the light of these new data.

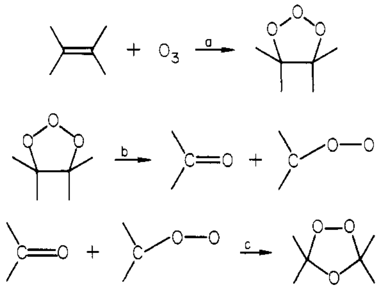
Recent suggested modifications[1-3] to the original Criegee mechanism for the ozonolysis reaction have gone a long way toward providing an explanation for much experimental data not adequately accounted for by the Criegee proposal, particularly as regards the stereochemistry of ozonide formation. There still remain some aspects of the reaction which appear not to be adequately accounted for by existing mechanisms, however. One of these still troublesome areas is the effect of added aldehyde[4-8] which can in some cases reduce or completely suppress ozonide formation. The ozonolysis process is generally regarded[9] as consisting of three separate steps (Scheme I) each of which is considered to be concerted in nature.

We have suggested[4,8] that the added aldehyde results could be explained by postulating nonconcertedness in step c. Such a nonconcerted addition of aldehyde and carbonyl oxide would generated an intermediate(s) which could be diverted to nonozonide products as, for example, by further reaction with excess aldehyde.

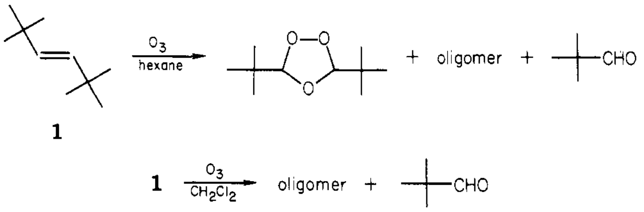
Still another problem area for current views of the mechanism is the influence of solvent on a variety of reaction parameters, including ozonide yield. The ozonolysis of *trans*-di-*tert*-butylethylene provides an extreme example of such an influence. In this case the general observation[8,10] is that ozonide is formed in nonpolar solvents, but no ozonide is obtained in polar solvents. That the ozonolysis of 1 lies at one end of a spectrum of such influences is presumably related to the steric bulk of the *tert*-butyl groups in 1.

An aspect of the ozonolysis process which has received less attention than others is the formation of oligomers.[9] These materials are usually colorless, viscous, higher molecular weight materials which have been variously characterized as polycarbonyl oxides,[11-14] as polyozonides,[15-22] or as having a more random arrangement of carbonyl and carbonyl oxide units. In some cases a trioxide bond has been suggested[23] as a contributing unit. A major contribution to an understanding of the structure of oligomers was provided by the work of Greenwood and Rubinstein,[23] who were able to show that their oligomers contained no carbon–carbon bonds since lithium aluminum hydride reduction did not yield α-diols.

Scheme I



Scheme II



We have begun a detailed study of ozonolysis oligomers in the hope that the structures of these materials and, in particular, the dependence of such structures on various reaction parameters might provide important new clues for the ozonolysis mechanism problem. In this paper we report data obtained on the oligomer produced in the ozonolysis of *trans*-di-*tert*-butylethylene (1). In subsequent reports we shall describe similar studies for olefins containing less bulky substituents. We hope to combine the results of such studies with those obtained on ozonide products and eventually make new suggestions regarding the ozonolysis mechanism. It should be pointed out, for example, that if oligomers are correctly characterized as polyozonides in some cases, then a nonconcerted reaction

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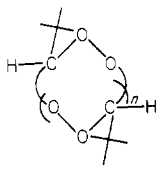
between carbonyl and carbonyl oxide fragments must be recognized. The question would then arise as to whether there are separate transition states for ozonide and oligomer formation, one concerted and one nonconcerted, or whether there is a single transition state in which subtle variations in structure and environment are responsible for the subsequent division between ozonide and nonozonide, including oligomer, products.

Results and Discussion

As previously reported[8,10] the ozonolysis of 1 proceeds as shown in Scheme II.

Oligomer was prepared and isolated from ozonolyses in both hexane and CH_2Cl_2 as the solvent. This oligomer, which is a colorless, glassy material, can be readily isolated by preparative TLC. The yield of oligomer in hexane was 47%. This yield combined with the previously reported[8] yield of ozonide (53%) in the same solvent indicates that all of the olefin can be accounted for by these two processes. The oligomers could be shown by GLC analysis of ether solutions to be free of ozonide, aldehyde, or any other volatile materials. The elemental analyses and NMR data suggest that the oligomers obtained in hexane and methylene chloride were virtually identical. In the case of the oligomer from hexane the chemical analysis and molecular weight data were combined in a best fit approach to suggest a structure for the oligomer. This method indicates that the oligomer is a polycarbonyl oxide. It seems to us to be reasonable to assume that the monomer units are combined in a cyclic structure as suggested earlier by Razumovskii.[19,20] The best fit approach also leads to the conclusion that the oligomer is not homogeneous. The simplest structural possibility is that the oligomer, 2, is composed of cyclic polycarbonyl oxides consisting of seven (44%) and eight (56%) carbonyl oxide units.



2, n = 6 or 7

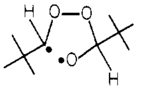
Thermal decomposition of 2 at 170 °C gives no chemiluminescence which is visible to the eye, but a similar experiment carried out in the presence of rubrene leads to the formation of a bright, reddish yellow luminescence. This chemiluminescence is presumably arising via transfer of energy, produced in the decomposition of 2, to the rubrene with subsequent emission from rubrene. Thermal decomposition of 2 in the presence of *cis*-stilbene leads to isomerization to *trans*-stilbene. No further work was done to characterize the process, but it seems clear that the thermal decomposition of 2 leads to the formation of excited states and/or luminescence.

Several approaches to chemical characterization of the oligomer were made. First, reduction of the oligomer with triphenylphosphine leads to the formation of pivalaldehyde consistent with structure 2. Next, samples of 2 in hexane were stored for 35 days with various olefins. A slow reaction occurs, leading to the formation of the olefin epoxides. Trans olefins gave only trans epoxide while cis olefins gave both epoxide stereoisomers with the cis isomer being slightly favored. In a separate experiment it was shown that storage of the oligomer in hexane with propionaldehyde did not lead to the formation of ozonide incorporating propionaldehyde.

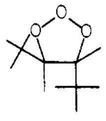
The expoxidation stereochemistry observed here is similar to that described earlier[24] when it was found that carbonyl oxides, from a nonozonolysis source, could expoxidize olefins. A possible explanation for these results then is that the oligomer 2 is slowly decomposing to carbonyl oxide monomer which is responsible for the epoxidation. The failure of this carbonyl oxide to react with propionaldehyde to give cross ozonide is consistent with our earlier observations[8] on the ozonolysis of 1 in the presence of propionaldehyde.

On the other hand, the small differences noted between the stereochemistry of the epoxidation reaction observed here and that previously observed by ourselves[24] and Hamilton and Keay[25] under conditions where carbonyl oxides are believed to be the epoxidizing reagents could be real and indicate another reaction pathway. One possibility for such a pathway would involve slow homolysis of a peroxy bond in the cyclic polycarbonyl oxide. The alkoxy radical so generated then could act as the epoxidizing reagent. Such epoxidations would permit rotation in the transition state or intermediate and be consistent with the observed stereochemistry provided that one assumes that the presence of the *tert*-butyl group in the alkoxy species would prevent complete rotation to trans epoxide in the case of cis olefin epoxidations.

These results, taken together with the earlier observations of ourselves[4,8,24] and others,[6,7,10] present new challenges to the mechanism problem. We earlier had suggested[8] that the failure of 1 to give ozonide in polar solvents could be due to the diversion of intermediates such as 3,



3



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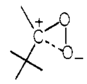

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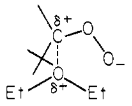

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produced by nonconcerted addition of carbonyl oxide and aldehyde units, to oligomers by further addition of carbonyl oxide and/or aldehyde, with such processes being favored by the polar solvents. A similar suggestion was made to explain the effect of added aldehyde which leads to a reduction[4] of ozonide formation in the case of *trans*-diisopropylethylene and complete suppression[8] of ozonide formation in the case of 1. The current results raise a serious objection to these earlier suggestions. The oligomer 2 from the ozonolysis of 1 is a polycarbonyl oxide whether it is produced in the nonpolar solvent hexane or in the polar solvent methylene chloride.

It now seems quite clear that the ozonolysis of 1 leads to the formation of the 1,2,3-trioxolane (4). The reduction experiments of Criegee and Schröder[10] and the NMR results of Bailey et al.[9] provide convincing evidence for this assignment. Both of these groups had also shown that the decomposition of 4 in the presence of methanol leads to the formation of the methoxy hydroperoxide expected from addition of methanol to the carbonyl oxide 5, arising from the cleavage of 4. Yet decomposition of 4 in nonpolar solvents gives ozonide while the same decomposition in polar solvents gives no ozonide.[8,10] Furthermore, all of the evidence, including that presented here, indicates that the carbonyl oxide 5 is produced in both solvent types.

It seems to us that all of these data are at least consistent with the following proposal. Ozonolysis of 1 in both polar

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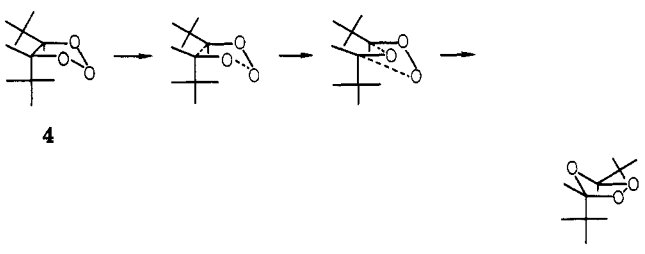
Scheme III



4

6

and nonpolar solvents leads to the formation of 4. In nonpolar solvents, i.e., hexane, cleavage of 4 occurs, following the principle of least motion,[1,27] with rapid recombination of carbonyl and carbonyl oxide fragments as shown in Scheme III. It should be noted that the use of the least motion principle in this instance makes no assumption regarding pseudoaxial or pseudoequatorial positioning of the *tert*-butyl groups in 4. The cleavage fragments are envisaged as recombining in a tight cage with the consequence that the trans arrangement in 4 leads predominantly to a trans arrangement in the ozonide 6. The conformation of 4 shown is the one calculated by Cremer[28,29] to be the most stable.

The results in polar solvents are more difficult to explain, but two possibilities seem reasonable. In these solvents the reaction proceeds as described above for nonpolar solvents except that the cleavage fragments are encouraged by the solvent to leave the cage. It would further have to be postulated that carbonyl oxide fragments once having left the cage have now fully rotated, perhaps assisted by the solvent, to a planar conformation with a dominant stereochemistry, presumably syn in the case of 5, as proposed by Bailey et al.[1] and Kuczkowski et al.[2] This form of the carbonyl oxide is presumably able to react with itself or methanol, but not with aldehyde. This assumption is not unreasonable since the syn configuration of the carbonyl oxide is extremely hindered and would find one-bond forming processes such as reaction with methanol or oligomerization more favorable than two-bond forming processes such as reaction with aldehyde to give ozonide. In this case the aldehyde is also sterically hindered, further adding to the difficulty of the ozonide-forming process.

A second possible explanation for the results obtained in polar solvents is that the cleavage process itself follows a somewhat different course. Thus, in such solvents the trioxolane may be heavily solvated throughout a concerted decomposition directly to a planar carbonyl oxide following the allowed disrotatory cleavage mode.[30] In such decompositions the carbonyl oxide would be directly produced in its more reaction-selective form as described above. It is interesting to note that while very few data are available which bear on these considerations, there are some which could be very revealing and which appear to be consistent with the view presented here. Mile et al.[31] have shown that E_a for decomposition of 4 in carbon disulfide is 14.1 kcal/mol. Furthermore, the *A* factor is very low and suggests heavy solvation with severe solvent reorientation requirements in the transition state. The same workers have also noted that the half-life of the trioxolane from *trans*-diisopropylethylene in pentane is about 5 times longer than in carbon disulfide. Thus the E_a for decomposition of this trioxolane is greater in pentane than in carbon disulfide. It appears that in both of these cases the decomposition in nonpolar solvents is slower and could be following a different decomposition mode. These higher energy decompositions could lead to energy-rich fragments which are more prone to recombine to ozonide prior to leaving the solvent cage. In such decomposition the first-produced carbonyl oxide structure probably lies closer to the nonplanar conformation which Harding and Goddard[32] have assigned to excited states of the carbonyl oxide.

The previously reported[8] effect of added aldehyde on the ozonolysis of 1 could, under the proposals made here, be regarded as a special case of the general solvent effect. Thus, increasing amounts of added aldehyde lead to a change in reaction type from the nonpolar, i.e., hexane, type to the polar type. In the latter case, the carbonyl oxide is converted to the less reactive planar form described above, thus accounting for the decreasing yields of parent ozonide and failure to incorporate added foreign aldehyde.

Finally, something more needs to be said about the reactivity of 5. We have been compiling data on the reactivity of carbonyl oxides as a function of a variety of parameters including the influence of solvent. This process had led us to the tentative conclusion that the reactivity of a given carbonyl oxide can be altered greatly depending upon structure, solvent, and the requirements of a potential substrate. We have recently described[33] an example of the latter influence in the case of oxygen atom transfer from carbonyl oxides to aromatic substrates. The ozonolysis of 1 provides an example, we believe, of carbonyl oxide reactivity being altered by solvent. Unlike Criegee and Schröder[10] we have found[8] that ozonolysis of 1 in diethyl ether does lead to ozonide formation (25% yield). While the yield is approximately half that obtained in hexane, it is the only case where any ozonide is obtained from the ozonolysis of 1 in a polar solvent. We believe that the ether is acting as a nucleophilic solvent and converts 5 to 7. The solvated carbonyl oxide 7 now has a weaker intramolecular dipolar attraction than that shown in 5 as well as a more nucleophilic terminal oxygen. This latter character should increase the likelihood of reaction with electrophiles such as aldehydes. In the present case this increased nucleophilicity of the terminal oxygen is presumably responsible for the observation of some ozonide formation in diethyl ether solvent. Bailey et al have previously described[1] the interaction of diethyl ether with other carbonyl oxides in connection with the possible isomerization of carbonyl oxide stereoisomers.

In our view the ozonolysis of 1 probably lies at one end of a spectrum of reaction possibilities in a series of olefins. The very exhaustive studies of Fong and Kuczkowski[34] on the ozonolysis of ethylene, including various deuterio derivatives, indicate that ethylene lies at the other end of the reaction spectrum; that is, it behaves in the simple Criegee[35-37] manner with little or no need for additional mechanistics amplification. Nevertheless, we feel that

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studies of 1 such as the present one, including accompanying mechanistic speculations are instructive and may serve as a basis for new proposals for a general mechanism of ozonolysis. At any rate we are continuing our studies of the chemistry and structure of oligomers as possible sources of key mechanistic information.

Experimental Section[38]

Instrumentation. NMR spectra were recorded with a Varian T-60 NMR spectrometer. Mass spectra were obtained by using an Associated Electronics Industries Model MS-12 mass spectrometer. Infrared spectra were recorded with a Perkin-Elmer Model 137 or 337 infrared spectrophotometer. Analytical and preparative GLC work was carried out on Varian HY-FI Model 600-D and Varian-Aerograph Model A-705 gas chromatographs. The GLC column used was a 0.125 in. × 20 ft aluminum column packed with 7% β,β'-oxydipropionitrile on 60/80 Chromosorb G treated with DMCS. Yields were determined by using a Perkin-Elmer Model 6300 digital integrator. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Materials. The olefins used were from Chemical Samples Co., Columbus, OH. The stated purity was 98% or 99%. *cis*-Stilbene and *m*-chloroperbenzoic acid were obtained from Aldrich Chemical Co. and used as received. All solvents used were reagent grade quality. Preparative TLC plates were made by using Mallinckrodt Silica-TLC-TGF silica gel.

General Ozonolysis Procedure. Ozone was produced in a Welsbach Model T-408 ozone generator and was delivered as an ozone/oxygen stream at a rate of 0.11–0.18 mmol of O_3 min^{-1}. In most cases ozonolyses were carried out to less than 100% of the theoretical requirement of the olefin.

Synthesis of Oligomer from *trans*-Di-*tert*-butylethylene. A solution of *trans*-di-*tert*-butylethylene (1 mL, 5 mmol) and 10 mL of hexane was cooled to −90 °C in an acetone/solid acetone cooling bath. The solution was purged with argon for 5 min, and then ozone (0.14 mmol min^{-1}) was passed through the solution for 4 min. The reaction solution was again purged with argon for 5 min and then allowed to warm to room temperature. The volatiles, including the solvent, were removed on the rotary evaporator to give a viscous, colorless residue. Trace amounts of volatiles remaining were removed in vacuo (1 mm) over a 3-h period. The glassy residue remaining (240 mg, 47%) was chromatographed on three 1-mm silica gel TLC plates with hexane and hexane/ether (85:15) successively as the developing solvents. This procedure gave a single band on the TLC plates. This band was removed with ether. GLC analysis of the ether solution indicated that there was no ozonide, aldehyde, or any other volatile material present in the oligomer fraction. Evaporation of the ether gave the colorless, glassy oligomer. The purified oligomer had a TLC R_f value of 0.6–0.7 (diethyl ether/hexane, 30:70).

The average molecular weight of the oligomer, as determined by the freezing point depression method was 772 ± 10: IR (neat) 2950, 1470, 1400, 1370, 1050, 970 cm^{-1}; NMR ($CDCl_3$) δ 1.03 (s, 9 H), 5.1–5.7 (m, 1 H). Anal. Calcd for $(C_5H_{10}O_2)_n$ (polycarbonyl oxide): C, 58.79; H, 9.87. Found: C, 58.74, 58.65; H, 9.91, 9.90.

An oligomer was prepared in the same manner as described above except CH_2Cl_2 was used as the solvent: NMR ($CDCl_3$) δ 1.01 (s, 9 H), 5.0–5.5 (m, 1 H). Anal. Calcd for $(C_5H_{10}O_2)_n$ (polycarbonyl oxide): C, 58.79; H, 9.87. Found: C, 57.15, 58.96; H, 10.82, 10.99.

Reactions of Olefins with the Oligomer. The oligomer obtained in hexane was stored with various olefins in hexane at room temperature for a period of 1 month. These solutions were analyzed by GLC periodically during the storage period. These analyses revealed that the olefins were being slowly converted to the correponding epoxides. Epoxide yields were determined by GLC using peak areas calibrated with authentic samples. The epoxides were identified by comparing their GLC, NMR, and mass spectral data with those of the authentic materials. In a control experiment it was shown that storage of *trans*-di-*tert*-butylethylene in pentane for 1 month in the absence of oligomer gave no epoxide formation. The results of the epoxidations were as follows: *trans*-2,2,5,5-tetramethyl-3-hexene (314 mg) plus oligomer (162 mg) gave *trans*-2,2,5,5-tetramethyl-3-hexene epoxide (12 mg); *cis*-3-hexene (423 mg) plus oligomer (123 mg) gave *cis*-3-hexene epoxide (8.7 mg) plus *trans*-3-hexene epoxide (7.7 mg); *trans*-3-hexene (326 mg) plus oligomer (153 mg) gave *trans*-3-hexene epoxide (8.4 mg); *cis*-2,5-dimethyl-3-hexene plus oligomer (177 mg) gave *cis*-2,5-dimethyl-3-hexene epoxide (11.3 mg) plus *trans*-2,5-dimethyl-3-hexene epoxide (9.5 mg); *trans*-2,5-dimethyl-3-hexene (393 mg) plus oligomer (150 mg) gave *trans*-2,5-dimethyl-3-hexene epoxide (14 mg).

In a separate experiment it was shown that a solution of oligomer in 5 mL of hexane containing 0.2 mL of propionaldehyde did not lead to the formation of cross ozonide after storage at room temperature for 2 months.

Oligomer Decomposition Experiments. A mixture of oligomer and rubrene dissolved in decane was immersed abruptly in an oil bath heated to 170 °C. The mixture gave off a bright reddish yellow chemiluminescence.

In a separate experiment a mixture of *cis*-stilbene (261 mg) and oligomer (130 mg) in hexane was heated in a sealed tube for 2 h at 150 °C. The reaction mixture was cooled to room temperature and then chromatographed on three 1-mm silica gel plates with hexane as the developing solvent. A band with an R_f value corresponding to that of authentic *trans*-stilbene was extracted with ether. The ether was evaporated to give a white solid. The crude product was recrystallized three times from hexane to give white crystals, mp 123–124 °C (lit. mp 124–125 °C). A mixture melting point between the product and authentic *trans*-stilbene gave no depression. In a control experiment the above procedure was repeated but with no oligomer present. In this case no *trans*-stilbene could be detected after the heating period.

Synthesis of Authentic Epoxides. The epoxides were synthesized by using an established procedure. A slight molar excess of *m*-chloroperbenzoic acid was allowed to react with the olefin in hexane at room temperature for 24 h. At the end of the reaction period excess *m*-chloroperbenzoic acid was removed by washing with aqueous sodium bicarbonate solution. The hexane layer was dried with anhydrous potassium carbonate and the epoxide isolated and purified by preparative GLC. The epoxides all gave correct elemental analyses. Spectroscopic data obtained on the epoxides are as follows. *trans*-3-Hexene: NMR δ 2.65 (t, 2 H), 1.2–1.8 (m, 4 H), 0.95 (t, 6 H); mass spectrum, *m/e* (relative intensity) 100 (M^+), 85, 71, 58 (100). *cis*-3-Hexene: NMR δ 2.9 (t, 2 H), 1.2–1.8 (m, 4 H), 1.03 (t, 6 H); mass spectrum (*m/e* (relative intensity) 100 (M^+), 85, 71, 58, 43 (100). *trans*-2,5-Dimethyl-3-hexene: NMR δ 2.5 (d, 2 H), 1.2–1.8, (br m, 2 H), 1.06 (d, 6 H) 0.95 (d, 6 H); mass spectrum, *m/e* (relative intensity) 128 (M^+), 95, 85, 74, 56 (100). *cis*-2,5-Dimethyl-3-hexene: NMR δ 2.65 (d, 2 H), 1.2–1.8 (br m, 2 H), 1.1 (d, 6 H), 1.0 (d, 6 H); mass spectrum, *m/e* (relative intensity) 128 (M^+), 95, 85, 74, 56 (100). *trans*-2,2,5,5-Tetramethyl-3-hexene: NMR δ 2.6 (5, 2 H), 0.95 (5, 18 H); mass spectrum, *m/e* (relative intensity) 156 (M^+), 141, 125, 87, 70 (100).

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Registry No. 1, 692-48-8; 2 (*n* = 6), 84649-01-4; 2 (*n* = 7), 84649-02-5; 4, 13866-82-5; 5, 84649-03-6; *trans*-3-hexene, 13269-52-8; *cis*-3-hexene, 7642-09-3; *trans*-2,5-dimethyl-3-hexene, 692-70-6; *cis*-2,5-dimethyl-3-hexene, 10557-44-5; *trans*-2,2,5,5-tetramethyl-3-hexene epoxide, 17615-94-0; *trans*-3-hexene epoxide, 36611-93-5; *cis*-3-hexene epoxide, 36611-94-6; *trans*-2,5-dimethyl-3-hexene epoxide, 54644-32-5; *cis*-2,5-dimethyl-3-hexene epoxide, 59175-38-1; triphenylphosphine, 603-35-0.

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[38] While no diffficulties were encountered in this work, the oligomers involved are polyperoxides and should be handled with caution.