heated at 90 °C for 15 h. Progress of the reaction was monitored by IR ($Q^+N_3^-$ 2000 $cm^{-1}$, **42** 2100 $cm^{-1}$). Most of the toluene was then evaporated at 70 °C (300 mmHg). Short-path distillation of the residue [100 °C (< 0.01 mmHg)] afforded 69 mg (56%) of **42**, contaminated with traces of toluene. A solution of the crude **42** in 10 mL of ether was added dropwise to a suspension of 0.5 g of $LiAlH_4$ in 30 mL of ether. The mixture was then stirred for 20 h at room temperature before being quenched by dropwise addition of water. The precipitate was filtered and washed with ether. Anhydrous hydrogen chloride was then passed into the combined ethereal solutions. The precipitate was filtered and recrystallized from ethyl acetate–ethanol to give 95 mg (73%) of **43**·HCl, mp 221 °C sublimed. 1-Methylbicyclo[2.2.1]heptan-7-amine (**43**) was obtained from the hydrochloride with 5 N NaOH, extracted with ether, and purified by preparative GC (4.5-m Carbowax–KOH, 105 °C): $^1H$ NMR ($C_6D_6$) $\delta$ 0.75 ($NH_2$, s), 0.94 ($CH_3$, s), 1.0–1.6 (7 H, m), 1.7–2.1 (2 H, m), 2.43 (1 H, s). Anal. Calcd for $C_8H_{15}N$: C, 76.73; H, 12.07; N, 11.19. Found: C, 76.69; H, 12.12; N, 11.26.

The enantiomeric purity of optically active **43**, obtained from (*R*)-**40** via **41**, was determined by GC of the *N*-(trifluoroacetyl)-(*S*)-prolyl amides.[21] Within experimental error (±2%), the ee of **43** was found to be identical with that of **40**. The deaminations of **43** (12–20 mg) in water (10 mL) were performed as described for **11**. Ether (5 mL) was added in some runs in order to minimize the acid-induced rearrangement of **35**. Product distributions (Table I) and optical purities (Table II) were estimated as described for the solvolyses of **41**. The peak ratios on optically active PPG indicated that **40** from the deamination of **43** (*S*:*R* = 87:13) and **40** from the solvolysis of **41** (*S*:*R* = 12:88) had opposite configurations.

**5-Methylbicyclo[3.2.0]heptan-*exo*-2-amine (54).** 5-Methylbicyclo[3.2.0]heptan-2-one (**50**)[33] was processed to the amine **54** via *endo*-alcohol **51**[42] (90%), tosylate **52** (99%), and azide **53** (67%), as described for the parent compound (**11**). Reduction of **53** with $LiAlH_4$, followed by introduction of HCl, afforded 64% of **54**·HCl: mp 246–250 °C dec; $^1H$ NMR [of **54**] ($C_6D_6$) $\delta$ 0.65 ($NH_2$, s), 0.9–2.2 (9 H, m), 2.93 (1 H, d, $J$ = 4.4 Hz). Anal. Calcd for $C_8H_{15}N$: C, 76.73; H, 12.07; N, 11.19. Found: C, 76.77; H, 12.11; N, 11.23.

The nitrous acid deamination for **54** was performed in analogy to that of **11**. Products **35**,[27] **39**,[27] **40**,[27] **49**,[33] and **51**[33] were analyzed by GC (Table I) and identified by comparison on three different columns. An authentic sample of **49** was prepared from **51** via **52** by the standard inversion procedure (see above for **26** → **28**).

**Acknowledgment.** Financial support of this work by Fonds der Chemischen Industrie is gratefully acknowledged. We are indebted to Professor G. Snatzke and Dr. E. U. Würthwein for the communication of unpublished data.[20,25]

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# Products and Reaction Routes in the Diozonolysis of 2,3-Dimethyl-1,3-butadiene in Methanol

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Treatment of 2,3-dimethyl-1,3-butadiene (**1**) with 2 molar equiv of ozone in methanol afforded the abnormal products acetic acid (**12**) and methyl acetate (**13**), which resulted from cleavage of both the double bonds and the single bond of the conjugated diene system. In model experiments it was shown that the reaction proceeds stepwise by formation of an $\alpha,\beta$-unsaturated methoxy hydroperoxide (**3**) in the first and a $\alpha$-keto methoxy hydroperoxide (**8**) in the second ozonolysis step. The latter undergoes spontaneous decomposition at ambient temperatures to give rise to the abnormal cleavage products **12** and **13**. This cleavage is accompanied by emission signals in the $^1H$ NMR spectrum which are indicative of the occurrence of acetyl radicals and hence suggest at least a partial radical-type cleavage of the $\alpha$-keto methoxy hydroperoxide **8**.

Considering the importance of compounds having conjugated diene systems, including both natural and synthetic products, surprisingly little is known about their ozonolysis. In fact, not even a subchapter has been devoted to this theme in Bailey's recent comprehensive review on ozone chemistry.[2] The scarce reports in the literature are mainly concerned with the description of non-peroxidic stable end products of mono-[3–7] and of diozonolysis reactions[8–13] of acyclic and of cyclic diene compounds. By contrast, the nature of peroxidic intermediates has in most cases not been elucidated. Furthermore, the scattered data available do not provide a unifying view of the course of such reactions. Thus, in some cases it was reported that diozonolysis of a diene system followed a conventional pattern and resulted in the cleavage of the double bonds only, whereas in other cases abnormal reactions have been observed, in which the carbon skeleton has been cleaved both at the double bonds and at the central single bond.

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(1) Visiting professor on leave from the University of Missouri–St. Louis.

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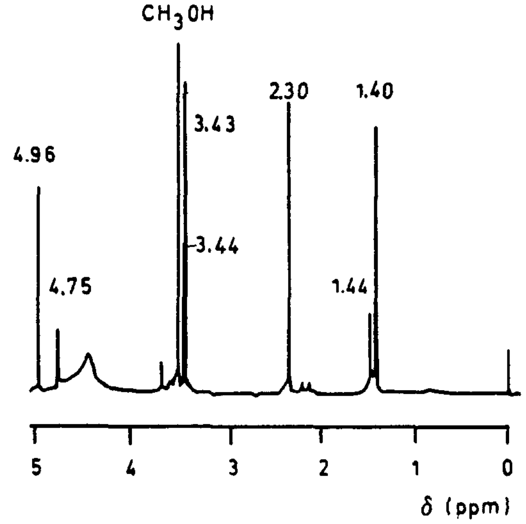
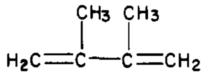


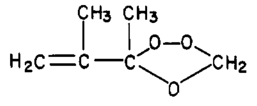
**Figure 1.** $^1H$ NMR spectrum of the ozonolysis product of 3 in methanol.

Recently, we reported that monoozonolysis of 2,3-dimethyl-1,3-butadiene (1) in pentane and in methanol occurs by attack of ozone at one of the two double bonds only and by a normal Criegee-type cleavage.[14] Major products were the monoozonide 2 from the reaction in pentane and the methoxy hydroperoxide 3 along with minor amounts of the peroxide 4 from the reaction in methanol.

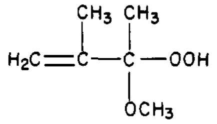


$H_2C{=}C(CH_3){-}C(CH_3){=}CH_2$

1

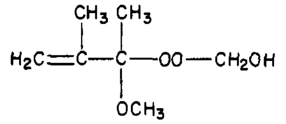


2



$H_2C{=}C(CH_3){-}C(CH_3)(OCH_3){-}OOH$

3



$H_2C{=}C(CH_3){-}C(CH_3)(OCH_3){-}OO{-}CH_2OH$

4

Attempts at carrying out diozonolysis reactions of 1 in pentane have been accompanied by some frustrating experiences, including violent explosions during the isolation of products. Diozonolysis of 1 in methanol, however, could be performed safely, as reported in the following.

## Results and Discussion

Complete ozonolysis of 1 in methanol at −78 °C afforded a peroxidic, slightly yellow viscous solution. Upon warming of this crude reaction product, a vigorous exothermic reaction began at ca. −10 °C which raised the temperature to the boiling point within a few seconds. During this period, approximately 7% of carbon dioxide and 1% of carbon monoxide were evolved,[15] the yellow color disappeared, and the solution became less viscous but remained peroxidic. Quantitative $^1H$ NMR analysis of this solution was consistent with the presence of compounds 6 (57%),[16] 7 (13%), 9 (9%), 10 (7%), 11 (7%), 12 (32%), 13 (44%), and 14 (2%), whereas compounds containing an intact $C_4$ skeleton such as 15 could not be detected either by $^1H$ NMR or by GLC analysis. By contrast, when the freshly ozonized solution was admixed with perdeuteriated dimethyl sulfide at −50 °C and subsequently warmed up to room temperature, no exothermic reaction occurred, and $^1H$ NMR analysis was consistent with the presence of 75% of 15, along with only 8% of 12, 7% of 13, 3% of 14, and ca. 95% of 6.

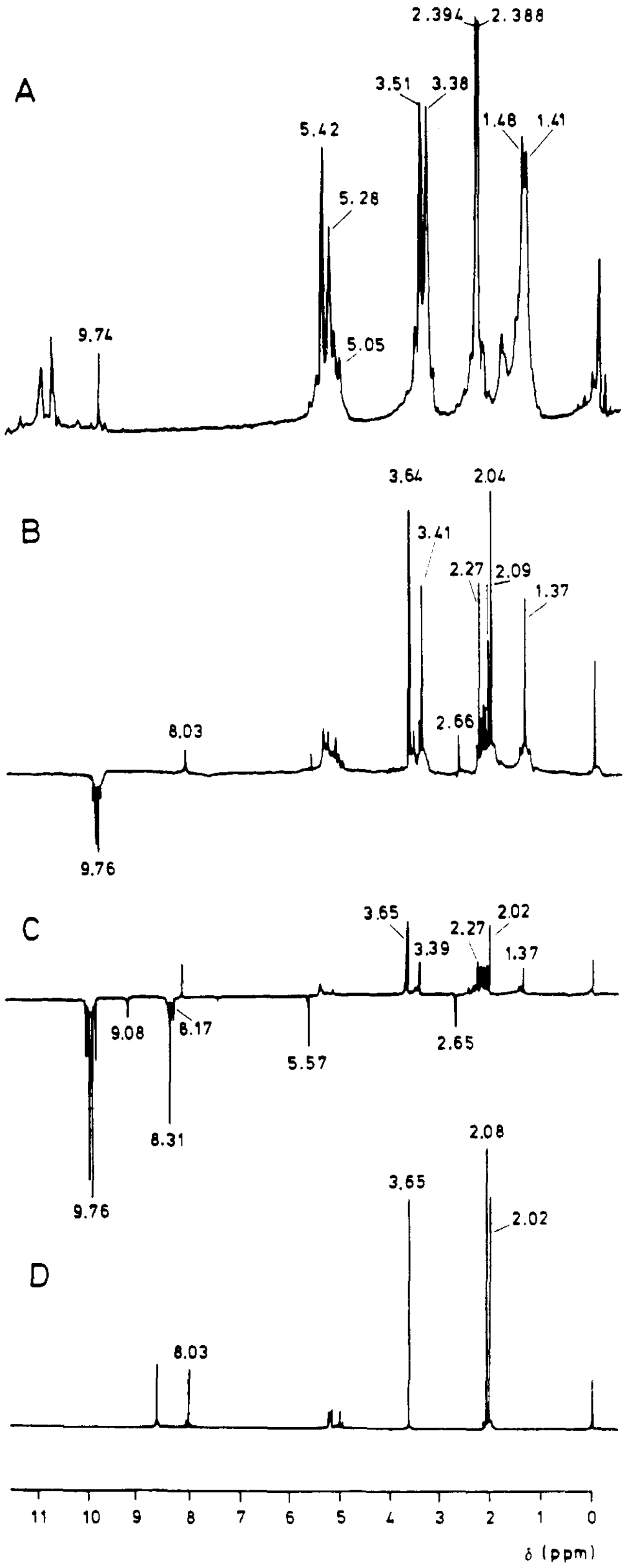


**Figure 2.** $^1H$ NMR spectra of the ozonolysis product of 3 in $CD_2Cl_2$ (A) at −78 °C, (B) after rapid warm-up to ca. 30 °C, (C) after immediate transfer of sample into probe at ca. 30 °C, and (D) after 24 h at room temperature.

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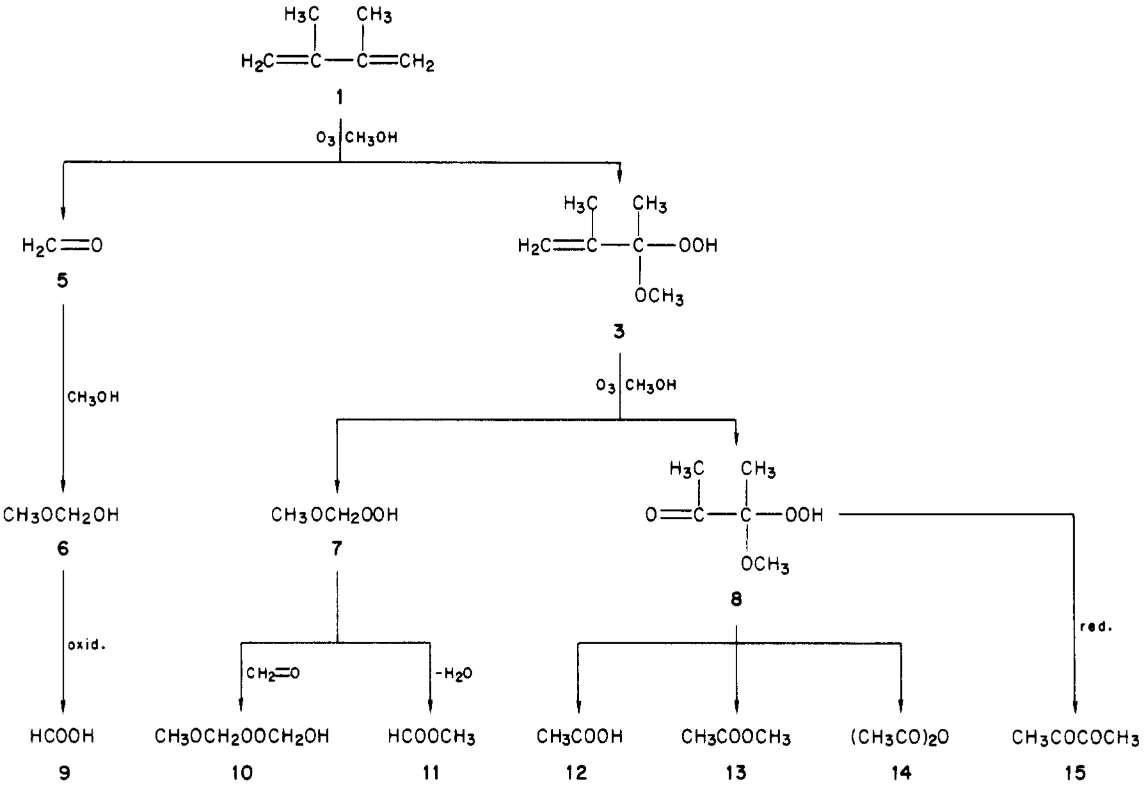
(14) Griesbaum, K.; Keul, H.; Agarwal, S.; Zwick, G. *Chem. Ber.* **1983**, *116*, 409.

(15) The percent figures are based upon theoretical total amounts of CO and $CO_2$, respectively, if all of 2,3-dimethyl-1,3-butadiene would be converted into these fragments.

(16) Yields are based on the presence of a measured amount of an added standard and calculated such that the maximum yields of the fragments derived from the $CH_2$ moiety(ies) and from the central $C_4$ moiety amount to 100% each.



It is evident from the above results, that an anomalous ozonolysis had occurred, in which both the double bonds and the central single bond of the conjugated diene system of **1** were cleaved. Since attack of ozone at the two double bonds of **1** occurs consecutively and leads to **3** and **5** with high selectivity in the first step,[14] the abnormal cleavage of the single bond must have occurred in conjunction with the ozonolysis of **3**. Therefore, we have ozonized authentic **3** under various conditions with the following results.

Ozonolysis of **3** in methanol in the presence of deuteriochloroform at −50 °C afforded a colorless solution. $^1$H NMR analysis of the crude reaction mixture showed the spectrum depicted in Figure 1. The signals at $\delta$ 4.75 and 4.96 are due to the $CH_2$ groups of **6**[14] and of **7**,[17] respectively. The relative intensities of these signals were 1:4, thus indicating that **3** has been cleaved such that at least 80% of its terminal methylene group was transformed into **7**. This is in contrast to the direction of cleavage observed in the monoozonolysis of **1**,[14] and the difference is presumably related to the relative stabilities of the zwitterions involved. In particular, the electron-withdrawing substituents in **17** are assumed to destabilize this zwitterion in accordance with the experience made by several authors.[2a] In line with the above finding, the three singlet signals of equal intensities at $\delta$ 1.40, 2.30, and 3.43 have been assigned to the $CH_3C$, $CH_3CO$, and $CH_3O$ groups, respectively, of **8**, i.e., to the expected complementary cleavage product of **7**. Of the additional signals in Figure 1, that at $\delta$ 3.44 is due to the $CH_3O$ group of **6**,[14] while that at $\delta$ 1.44 could not be definitely assigned, though it may be due to the $CH_3C$ groups of **18**, i.e., the expected complementary cleavage product of **6**. The $CH_3O$ signals of **7**[17] do and those of **18** may coincide with the $CH_3O$ signal of methanol and are, therefore, not observed.

When the ozonolysis product of **3** was kept at room temperature, the signals of **6**–**8** decreased, and concomitantly the signals of **10**–**13** appeared. After 22 h, the signals of **8** had completely disappeared and $^1$H NMR analysis was consistent with the presence of **7** (44%),[16] **10** (18%), **11** (11%), **12** (9%), and **13** (83%). By contrast, when an ozonolysis product of **3** was treated with perdeuteriated dimethyl sulfide immediately after it had reached ca. 0 °C, $^1$H NMR analysis showed the presence of **15** (67%),[16] along with only minor amounts of the abnormal cleavage products **12** (6%) and **13** (12%), as well as **6** (75%), **10** (9%),[18] **11** (3%), and **16** (5%).

Ozonolysis of **3** in perdeuteriodichloromethane at −78 °C afforded also a colorless solution. $^1$H NMR analysis at −78 °C gave the spectrum depicted in Figure 2A. Major signals had again chemical shift values similar to those attributed to the $CH_3C$, $CH_3CO$, and $CH_3O$ groups of **8** in the spectrum of Figure 1. However, in the spectrum of Figure 2A each of these signals appeared as two singlets, viz., at $\delta$ 1.41 and 1.48 for the $CH_3C$ group, at $\delta$ 2.388 and 2.394 for the $CH_3CO$ group, and at $\delta$ 3.38 and 3.51 for the $CH_3O$ group. This is attributed to intramolecular hydrogen bonding between the OOH and the $CH_3CO$ groups of **8** and the concomitant formation of a six-membered ring structure in the aprotic solvent perdeuteriodichloromethane and at the low temperature of −78 °C. The six-membered ring may undergo conformational isomerization, which leads to different magnetic environments for the $CH_3C$, $CH_3CO$, and $CH_3O$ groups in the two conformers **8a** and **8b**. It can be seen from formula **8a** and **8b** that the magnetic environment of the $CH_3CO$ group should be the least affected by this isomerization. In line with this, the two signals attributed to this group show the smallest shift difference of ca. 0.006 ppm, whereas the $CH_3C$ and $CH_3O$ signals in the two conformers exhibit shift differences of 0.07 and 0.43 ppm, respectively.

The group of signals between ca. $\delta$ 5.0 and 5.5 in the spectrum of Figure 2A may be partly due to the $CH_2$ groups of oligomers derived from zwitterion **21**, i.e., the

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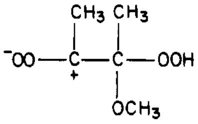
[17] Meister, M.; Zwick, G.; Griesbaum, K. *Can. J. Chem.* **1983**, *61*, 2385.

[18] Peroxide **10** undergoes only slow reduction with dimethyl sulfide.

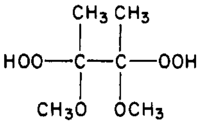
complementary cleavage product of **8**.[19] We have also considered the possibility that these absorptions could be partly due to a dioxetane formed either from intramolecular ring closure of **8** to give **19** or from intramolecular ring closure of **17** to give **20**. Although we have not been able to obtain confirmatory evidence for the formation of dioxetanes, **19** could be a reasonable precursor for the formation of the observed products acetic acid (**12**) and methyl acetate (**13**). The minor signals downfield from δ 9.5 in the spectrum of Figure 2A could not be assigned.

$CH_3OCH_2OCH_3$

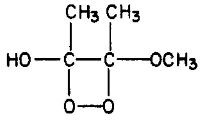
**16**



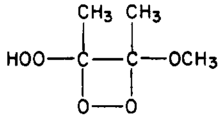
**17**



**18**



**19**

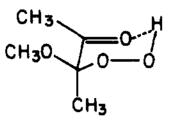


**20**

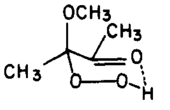
$\overset{+}{C}H_2{-}OO^-$

**21**

When an ozonolysis product of **3** in perdeuteriodichloromethane was repeatedly warmed up to temperatures near 0 °C and again cooled to −78 °C, $^1H$ NMR analyses at −78 °C showed a gradual decrease of the signals assigned to **8a** and **8b**, whereby the conformer with the respective signals in the higher field positions disappeared at a faster rate than the other one. Concurrent with the decrease of the signals of **8a**/**b**, there was the appearance of three singlet signals which were assigned to acetic acid (**12**) at δ 2.20 and to methyl acetate (**13**) at δ 2.10 and 3.67. The group of signals between ca. δ 5.0 and 5.5 and the signals downfield from δ 9.5 remained essentially unchanged.



**8a**



**8b**

When an ozonolysis product of **3** in perdeuteriodichloromethane was rapidly warmed up above 0 °C, $^1H$ NMR analysis at ca. 30 °C showed the spectrum depicted in Figure 2B. In this spectrum, the $CH_3C$, $CH_3CO$, and $CH_3O$ groups of **8** showed only one singlet, each, at 1.37, 2.27, and 3.41, respectively, which indicates that no apparent hydrogen bonding occurs at 30 °C. The intensity of these signals had considerably decreased, whereas the signals for acetic acid (**12**) at δ 2.09 and for methyl acetate (**13**) at δ 2.04 and 3.64 had increased. Furthermore, the group of signals at ca. 5.0–5.5 had also decreased. New signals of low intensities which appeared at δ 2.66 and 8.03 could be assigned to acetyl chloride and to formic acid (**9**), respectively. Finally, the spectrum showed also an emission signal, which appeared as a quartet centered at δ 9.76.

When an ozonolysis product of **3** in perdeuteriodichloromethane was immediately transferred into the probe of the NMR instrument kept at room temperature, $^1H$ NMR spectra of the type depicted in Figure 2C were obtained. They showed again the decreased signals of **8** at δ 1.37, 2.27, and 3.39, as well as the signals of acetic acid (**12**) at δ 2.09, of methyl acetate (**13**) at δ 2.02 and 3.65, and of formic acid (**9**) at δ 8.03. The most striking features of Figure 2C are, however, a series of emission signals, viz., a quartet centered at δ 9.76 as in Figure 2B and singlet signals at δ 9.08, 8.31, 8.17, 5.57, and 2.65 which were not present in the spectrum of Figure 2B. These emission signals are indicative of free-radical processes that occur during the warm-up period and the concomitant conversion of primary reaction products into non-peroxidic end products. In particular, the emission signals at δ 2.65 and 9.76 may be associated with the formation of acetyl chloride and of acetaldehyde, respectively, generated via abstraction of chlorine from $CD_2Cl_2$ and of hydrogen from an appropriate source, respectively, by an intermediate acetyl radical.

When an ozonolysis product of **3** in perdeuteriodichloromethane was left at room temperature for 24 h it showed the $^1H$ NMR spectrum depicted in Figure 2D. It exhibited major signals for acetic acid (**12**) at δ 2.08, for methyl acetate (**13**) at δ 2.02 and 3.65, and for formic acid (**9**) at δ 8.03, as well as minor signals for methyl formate (**11**) at δ 3.73 and 8.07. Quantitative $^1H$ NMR analysis showed, that the central $C_4$ moiety of **8** was essentially completely converted into approximately equimolar amounts of acetic acid (**12**) and methyl acetate (**13**). It should be noted, however, that the ratio of **12**:**13** varied from ca. 1:2.3 in the early stages of the warm-up period to ca. 1.3:1 after prolonged standing of reaction mixtures. The latter ratio may be due to the inadvertent admission of moisture and ensuing partial saponification of methyl acetate. The above described identification of products **11**–**13** by $^1H$ NMR spectroscopy has been supported by the results of GLC and GC/MS analyses.

When a fresh ozonolysis product of **3** in perdeuteriodichloromethane was admixed with perdeuteriated dimethyl sulfide at −78 °C and subsequently warmed up to room temperature, $^1H$ NMR analysis of the yellow product mixture showed the singlet for 2,3-butanedione (**15**) at δ 2.30 as the most intensive signal. This assignment was again ascertained by the results of GLC and of GC/MS analyses.

On the basis of the foregoing reported results, we formulate the diozonolysis of **1** in methanol in the following manner: In the first step, **1** is cleaved by ozone to afford predominantly the fragments **3** and **5**. In a subsequent ozone cleavage step, **3** is postulated to react predominantly to give fragments **7** and **8**. Of these, **7** can undergo subsequent reactions with **5** and/or **6** to form **10** and by acid catalysis[20] to form **11**, as we had previously demonstrated with authentic **7**.[17] Compound **8** is essentially completely cleaved at the central carbon single bond and at the peroxide bond to form **12**, **13**, and minor amounts of **14**. The predominance of **13** over **12** after 22 h of reaction time is probably due to partial esterification of **12** in the methanolic medium. This assumption is supported by the results of the ozonolysis of **3** in $CD_2Cl_2$, whereby **12** and **13** have been obtained in approximately equimolar amounts. Since **8** is not decomposed immediately, it can be reduced by dimethyl sulfide to give **15**. The latter result shows, that the anomalous cleavage of the central single bond in **1** does not occur in the ozonolysis step itself. Fragment **5** from the first ozonolysis step undergoes also further reactions, viz., formation of **6** and/or acid-catalyzed[20] formation of **16** with the excess methanol present, as well as formation of **9** by oxidation either by ozone attack or by peroxidic species present in the reaction mixtures.

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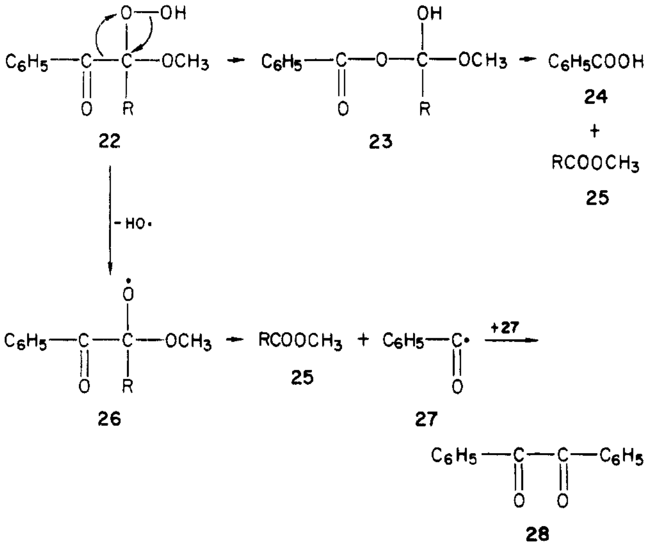
(19) In recent unpublished work concerned with the ozonolysis of 2,3-di-*tert*-butyl-1,3-butadiene in pentane, these products could be isolated as a colorless, peroxidic solid, which upon reduction in acidified methanol afforded formaldehyde dimethyl acetal.

(20) The acid may be partly provided by partial decomposition of the added $CDCl_3$, as we have observed at other occasions that acid-sensitive hydroperoxides underwent spontaneous decompositions in $CDCl_3$.

The formation of the α-keto methoxy hydroperoxide **8** has been postulated previously in the ozonolysis of 2-butyne in methanol.[21] As in our work, **8** could not be isolated, and its existence was inferred from the formation of 2,3-butanedione (**15**) after reduction of the ozonolysis product. The lability of **8** and its fragmentation into a mixture of **12** and **13** is in line with similar observations that have been made with other α-keto methoxy hydroperoxides such as **22**.[22,23] It was reported,[22] that such decompositions "are typical heterolytic cleavages of the peroxide group", and the authors have favored concerted rearrangements via intermediates of type **23** to give the final products of types **24** and **25**. In one instance, a minor route via a radical-type cleavage has been postulated also.[22] This proposal was based on the observation that in some experiments minor amounts of **28** have been formed. Its occurrence was formulated by the reaction sequence **22** → **26** → **27** → **28**.



We feel, that the observed CIDNP effects in the foregoing described experiments provide evidence for a fragmentation pathway for **8** which is radical in character, although this pathway may be a minor one.

## Experimental Section

**General Methods.** $^1$H NMR spectra were recorded on a Bruker WP 60 instrument, GC/MS and mass spectra on a Hewlett-Packard 5985 B instrument, and IR spectra on a Beckman IR 4260 instrument. GLC analyses were carried out on a Shimadzu GC 6A instrument. GLC conditions were as follows: glass column 0.3 × 500 cm, 5% Carbowax 20M on Chromosorb G; 60–160 °C at 4 °C/min. The same conditions were used for the GC/MS analyses.

**Diozonolysis of 1 in Methanol.** A solution of 1.55 g (18.9 mmol) of **1** in 14 mL of methanol was ozonized at −78 °C with a $O_3/O_2$ stream containing 48 mg (1 mmol) of ozone per liter.[24] During this treatment the reaction mixture became slightly yellow and very viscous. When the mixture turned blue, ozone addition was terminated, and it was flushed with nitrogen to remove excess ozone. The reaction vessel was equipped with a reflux condenser, which was connected to a gas-collecting device; flushing with nitrogen was resumed, and the cold bath was removed. When the mixture had reached ca. −10 °C, an exothermic reaction began which caused the mixture to reflux within a few seconds. After the reaction had ceased, there remained 13.6 g of a colorless, mobile, peroxidic liquid. The collected gases (1600 mL) were shown to contain 1.96 vol % of carbon dioxide and 0.18 vol % of carbon monoxide by analysis with the help of the Leybold-Heraeus IR photometer "Binos 4.3". This corresponds to carbon equivalents of 7% and 1%, respectively, on the basis of the amount of **1** applied. Of the peroxidic liquid reaction product, 1.15 g (8.5%) was removed and admixed with 0.19 g (1.16 mmol) of 1,1,2,2-tetrachloroethane and $Me_4Si$. Quantitative $^1$H NMR analysis of this mixture showed the presence of **6** [$\delta^{14}$ 3.43 (3 H) and 4.74 (2 H; 57%)], **7** [$\delta^{17}$ 4.95 (2 H); 13%], **9** [$\delta$ 8.03 (1 H); 9%], **10** [$\delta^{17}$ 3.52 (3 H), 5.04 and 5.17 (2 H each); 7%], **11** [$\delta$ 3.76 (3 H) and 8.07 (1 H); 7%], **12** [$\delta$ 2.07 (3 H); 32%], **13** [$\delta$ 2.05 and 3.67 (3 H each); 44%], and **14** [$\delta$ 2.23 (6 H); 2%). The quantitative analysis is based on a comparison of the intensities of the signals of the individual components with that of 1,1,2,2-tetrachloroethane at $\delta$ 5.96. GLC analysis showed the peaks of **11** ($t_R$ 4.1 min), **12** ($t_R$ 27.8 min), and **13** ($t_R$ 5.0 min), along with some minor peaks of ca. 1% intensity, each. Coinjection of **15** ($t_R$ 8.2 min) showed that the latter was not present in the reaction mixture.

**Diozonolysis of 1 in Methanol and Subsequent Reduction with Dimethyl Sulfide-$d_6$.** A solution of 20.5 mg (0.25 mmol) of **1**, 69.2 mg (0.41 mmol) of 1,1,2,2-tetrachloroethane, and 43.3 mg (1.45 mmol) of methanol in 0.3 mL of $CDCl_3$ was ozonized to completion at −50 °C. The solution was purged with nitrogen to remove unreacted ozone, ca. 15 drops of $Me_2S$-$d_6$ was added, and the mixture was allowed to warm up to ca. −10 °C and after 20 min to room temperature. Quantitative $^1$H NMR analysis ($Me_4Si$) showed the presence of **6** ($\delta$ 3.43 (3 H); 95%], **12** [$\delta$ 2.07 (3 H); 8%], **13** [$\delta$ 3.67 (3 H); 7%], **14** [$\delta$ 2.23 (6 H); 3%], and **15** [$\delta$ 2.33 (6 H); 75%]. GLC analysis showed the peaks of **12** ($t_R$ 27.8 min), **13** ($t_R$ 5.0 min), and **15** ($t_R$ 8.2 min). GC/MS *m/e* (relative intensity): **12**, 60 (65, $M^+$), 45 (100, $(COOH)^+$), 43 (95, $(CH_3CO)^+$); **13**, 74 (50, $M^+$), 59 (15, $(M - CH_3)^+$), 43 (100, $(CH_3CO)^+$); **15**, 86 (20, $M^+$), 43 (100, $(CH_3CO)^+$).

**Ozonolysis of 3 in Methanol.** A solution of 77.3 mg (0.58 mmol) of **3**,[14] 86.4 mg (2.7 mmol) of methanol, and 144.2 mg (0.86 mmol) of 1,1,2,2-tetrachloroethane in 0.7 mL of $CDCl_3$ was ozonized at −50 °C until it turned blue. The solution was purged with nitrogen to remove unreacted ozone. Immediate $^1$H NMR analysis of the reaction mixture in the presence of $Me_4Si$ (Figure 1) showed the signals of **6**[14] at $\delta$ 3.44 ($OCH_3$) and 4.75 ($CH_2$), of **7**[17] at $\delta$ 4.96 ($CH_2$), of **8** at $\delta$ 1.40 ($CH_3C$), 2.30 ($CH_3CO$), and 3.43 ($OCH_3$), as well as a singlet at $\delta$ 1.44, which was tentatively assigned to the $CH_3C$ signals of **18**. Intermittent $^1$H NMR analyses of the reaction mixture after it had reached room temperature showed a continuous decrease of the singlet signals assigned to **8** at $\delta$ 1.40, 2.30, and 3.43, and the concomitant appearance of new signals. Quantitative $^1$H NMR analysis after 22 h showed the presence of **7** [$\delta$ 4.95 (2 H); 44%], **10** [$\delta$ 5.04 and 5.17 (2 H each); 18%], **11** [$\delta$ 3.76 (3 H) and 8.07 (1 H); 11%], **12** [$\delta$ 2.07 (3 H); 9%], and **13** [$\delta$ 2.05 and 3.67 (3 H) each); 83%]. GLC analysis showed the peaks of **11** ($t_R$ 4.1 min), **12** ($t_R$ 27.8 min), and **13** ($t_R$ 5.0 min).

**Ozonolysis of 3 in Methanol and Subsequent Reduction with Dimethyl Sulfide-$d_6$.** A solution of 34.0 mg (0.26 mmol) of **3**,[14] 40.7 mg (1.27 mmol) of methanol, and 27.0 mg (0.20 mmol) of 1,1,1-trichloroethane in 0.3 mL of $CDCl_3$ was ozonized at −50 °C until it turned blue. The solution was purged with nitrogen to remove unreacted ozone, warmed up to room temperature, and immediately admixed with 10 drops of $Me_2S$-$d_6$. Quantitative $^1$H NMR analysis ($Me_4Si$) after 70 min showed the presence of **6** [$\delta$ 3.43 (3 H); 75%], **10** [$\delta$ 3.52 (3 H), 5.04 and 5.17 (2 H each); 9%], **11** [$\delta$ 3.76 (3 H) and 8.07 (1 H); 3%], **12** [$\delta$ 2.07 (3 H); 6%], **13** [$\delta$ 2.05 and 3.67 (3 H each); 12%], **15** [$\delta$ 2.33 (6 H); 67%], and **16** [$\delta$ 3.37 (6 H) and 4.58 (2 H); 5%].

**Ozonolysis of 3 in $CD_2Cl_2$.** A solution of 376.0 mg (2.85 mmol) of **3**[14] in 3 mL of $CD_2Cl_2$ was ozonized to completion at −78 °C. A sample was immediately submitted to $^1$H NMR analysis ($Me_4Si$) at −78 °C (Figure 2A). Then the $^1$H NMR sample was repeatedly warmed up to temperatures near 0 °C and cooled to −78 °C and monitored by $^1$H NMR spectroscopy at −78 °C. A second sample of the crude ozonolysis product was rapidly warmed up and immediately analyzed by $^1$H NMR spectroscopy ($Me_4Si$) at 30 °C (Figure 2B). A third sample of the crude ozonolysis product was immediately transferred into the probe of the NMR instrument, kept at room temperature, and monitored by $^1$H NMR

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analysis (Me$_4$Si) to give spectra as that depicted in Figure 2C. A fourth sample of the crude ozonolysis product was kept at room temperature. $^1$H NMR analysis (Me$_4$Si) after 24 h showed the spectrum depicted in Figure 2D and GLC analysis showed the peaks of **11**, **12**, and **13**. GC/MS *m/e* (relative intensity): **11**, 60 (100, M$^+$), 45 (4, M − CH$_3$)$^+$); **12**, 60 (69, M$^+$), 45 (100, (COOH)$^+$], 43 (92, (CH$_3$CO)$^+$); **13**, 74 (42, M$^+$), 59 (16, M − CH$_3$)$^+$), 43 (100, (CH$_3$CO)$^+$). A fifth sample of the crude ozonolysis product was admixed with an excess of Me$_2$S-$d_6$ and warmed up to room temperature. The sample turned yellow, and $^1$H NMR analysis (Me$_4$Si) showed the most intensive signal at $\delta$ 2.30 for compound **15**. GLC analysis showed the peaks of **12**, **13**, **15**, and **16**. GC/MS *m/e* (relative intensity): **12**, 60 (69, M$^+$); **13**, 74 (42, M$^+$); **15**, 86 (14, M$^+$), 43 (100, (CH$_3$CO)$^+$); **16**, 76 (7, M$^+$), 75 (100, M − H)$^+$), 45 (73, M − OCH$_3$)$^+$).

**Quantitative $^1$H NMR Analysis of Reaction Products from the Ozonolysis of 3 in CD$_2$Cl$_2$.** A solution of 376.0 mg (2.85 mmol) of **3**[14] and 397.0 mg (2.98 mmol) of 1,1,1-trichloroethane in 3 mL of CD$_2$Cl$_2$ was ozonized to completion at −78 °C. A sample was kept at room temperature for 24 h. Quantitative $^1$H NMR analysis (Me$_4$Si) showed the presence of **9** [$\delta$ 8.03 (1 H); 40%[16]], **11** [$\delta$ 3.73 (3 H); 10%], **12** [$\delta$ 2.08 (3 H); 50%], and **13** [$\delta$ 2.02 and 3.65 (3 H each); 50%]. The quantitative analysis is based on a comparison of the intensities of the signals of the individual components with that of 1,1,1-trichloroethane at $\delta$ 2.74.

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# Stereochemical and Regiochemical Course of Isodicyclopentadiene–Tropone Cycloaddition Reactions[1]

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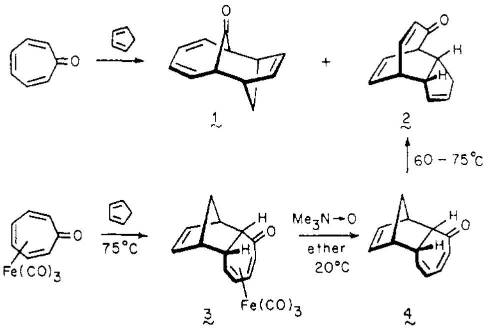
The reactions of isodicyclopentadiene and two spirocyclic derivatives with tropone, 2-methyltropone, and 2-methoxytropone have been investigated. Cycloaddition of the two parent molecules occurred predominantly by a [6 + 4] bonding pathway with a marked above-plane selectivity. The presence of a 2-substituent on the tropone rendered this process inoperative. Instead, capture of the [1,5] sigmatropic diene isomers **15** and **30** was seen. In the latter instance, a Diels–Alder mode was kinetically favored, with the tropones functioning as 4$\pi$ donors. The regioselectivity that distinguishes the methyl and methoxyl examples was accountable in terms of frontier molecular orbital theory. When the pure spirocyclic systems were heated with tropone in benzene solution, no reaction occurred. However, condensations with isomeric contaminants were seen to occur. The various phenomena are discussed at the mechanistic level.

Tropone is well recognized to undergo cycloaddition with cyclopentadiene. Whereas a reaction temperature of 80 °C provides **1**, heating of the reactants to 145 °C delivers **2**.[2] Formation of these adducts has been attributed to the operation of concerted exo [6 + 4] and endo [4 + 2] pathways, respectively.[3] An alternative mechanistic formulation that would lead with equal stereospecificity to **1** and **2** involves initial formation of the simple Diels–Alder adduct **4**, followed by thermally allowed [1,5] and [3,3] sigmatropic carbon migration.[4] Franck-Neumann and Martina have recently found it possible to prepare **4** by an independent method.[5] Through condensation of tropone–iron tricarbonyl with cyclopentadiene, access to **3** was realized. Subsequent to decomplexation of **3** under mild conditions, the thermally labile **4** was obtained and shown to undergo only the Cope rearrangement to **2** at 60–75 °C ($E_a$ = 28.5 kcal/mol). Consequently, ketone **1** probably results directly from [6 + 4] cycloaddition.



Although tropone is reported to react similarly with other dienes,[6–10] several other processes can compete effectively with the [6 + 4] bonding scheme. In particular, successful operation of the latter pathway is especially sensitive to substitution in either addend. 2-Chlorotropone

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