160.9, 153.8, 137.8, 127.4, 120.6, 76.1, 66.7, 44.1, 43.9, 34.2, 32.6, 28.1, 20.8, 20.5, 18.1, 16.5 ppm; IR (film) 2920, 1745, 1720, 1710 cm^{-1}; mass spectrum, m/z 320 (M^+).

Continued elution provided 8.0 mg of **53** (45%), which was homogeneous by TLC analysis (H:E, 1:1, R_f(**53**) = 0.48): ^1H NMR (300 MHz) δ 0.88 (s, 3 H), 0.92 (d, 3 H, J = 6.8 Hz), 1.74 (m, 2 H), 2.07 (m, 1 H), 2.14 (s, 3 H), 2.3-2.5 (m, 4 H), 2.71 (td, 1 H, J = 12.5 Hz, 3.9 Hz), 2.99 (dt, 1 H, J = 12.5 Hz, 6.3 Hz), 5.09 (s, 1 H), 5.35 (m, 1 H), 5.40 (s, 1 H), 5.56 (s, 1 H), 5.92 (d, 1 H, J = 5.3 Hz), 8.04 (s, 1 H); ^{13}C NMR (67.41 MHz) 208.5, 170.1, 160.8, 151.2, 137.8, 123.1, 115.1, 66.5, 46.2, 40.7, 40.3, 32.4, 29.6, 28.4, 26.7, 20.4, 20.1, 15.2 ppm; IR (film) 2920, 1740, 1720, 1710 cm^{-1}; mass spectrum, m/z 274 (M - 46).

Neolemnane (2). To a solution of 4.0 mg of **53** (0.012 mmol) in 2 mL of freshly distilled, dry methanol was added 0.1 mg of anhyd K_2CO_3. The resulting solution was stirred at 0 °C for 2 h and then quenched with 0.5 mL of water. Standard ethereal workup afforded 5 mg of a pale yellow oil. Purification by column chromatography (elution with H:E, 5:1) yielded 3.5 mg (95%) of **2**, which was homogeneous by TLC analysis (H:E, 1:4, R_f(**2**) = 0.35): ^1H NMR (300 MHz) δ 0.97 (d, 3 H, J = 6.8 Hz), 1.01 (s, 3 H), 1.68 (s, 3 H), 1.74 (m, 2 H), 2.13 (s, 3 H), 2.23 (m, 2 H), 2.43 (m, 1 H), 2.66 (m, 2 H), 4.19 (m, 1 H), 5.51 (s, 1 H), 5.86 (d, 1 H, J = 4.8 Hz), 6.80 (s, 1 H); ^{13}C NMR (67.41 MHz) 202.3 (s), 170.6 (s), 149.7 (s), 138.7 (d), 127.2 (s), 125.7 (d), 75.7 (d), 63.8 (d), 44.2 (s), 43.4 (t), 35.7 (t), 34.2 (d), 28.3 (t), 20.7 (q), 20.6 (q), 18.0 (q), 16.5 (q) ppm; IR (film) 3450, 2940, 1740, 1720, 1450, 1370, 1270, 1240, 1060, 1035, 1010, 930, 890, 750 cm^{-1}; mass spectrum, m/z 292 (M^+). These spectral data are identical with those of authentic neolemnane kindly provided by Professor William Fenical.

Acknowledgment. Support from the National Institute of General Medical Sciences through research grant 1 R01 GM39752 is gratefully acknolwedged. We wish to thank Dr. W. Fenical for a sample of natural neolemnane for comparison. G.M. thanks Dr. David Coffen of Hoffman LaRoche Corporation for helpful discussions concerning unusual epoxide openings. Special thanks are extended to Dr. Li-Qun Yan for doing the MM2 calculations on diols **48** and **49**.

Abbreviations. Aqeuous (aq), hexanes: ether (H:E), tetrabutylammonium fluoride (TBAF), and triethylamine (TEA).

Supplementary Material Available: NMR spectra of compounds studied (41 pages). Ordering information is given on any current masthead page.

Oxidation of 3,4-Di-*tert*-butylthiophene 1,1-Dioxide

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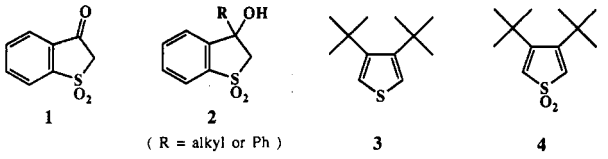
The oxidation of 3,4-di-*tert*-butylthiophene 1,1-dioxide (**4**) by a variety of reagents under various conditions was investigated in detail. Oxidation of **4** with peracids (MCPBA, trifluoroperacetic acid) affords the thiete 1,1-dioxide **6** and the sulfone **7**, both in moderate yield. The formation of these compounds can be explained as being the result of an acid-catalyzed rearrangement of the initial product, epoxy sulfone **5** via the carbocation **8**. Under basic conditions the rearrangement is suppressed and thus **5** can be isolated in good yield. Treatment of **5** with BF_3·Et_2O affords **6** and the sultine **10**. Oxidation of **4** with alkaline H_2O_2 involves a smooth Michael addition of HOO^- to give the hydroperoxide **17** in high yield. This represents the first example of the formation of an isolable β-hydroperoxy sulfone, a species which has been hypothesized to be an intermediate in the formation of epoxy sulfones by the oxidation of α,β-unsaturated sulfones with alkaline H_2O_2. Thermal decomposition of **17** affords the ketone **19** quantitatively. Reduction of **17** with $NaBH_4$ gives the alcohol **20**. On treatment with base, both **17** and **20** undergo ring opening to yield the alkene **18** in good yield.

Introduction

It is well known that the oxidation of α,β-unsaturated sulfones with HOO^-,[1,2] t-$BuOO^-$,[2] ClO^-,[3] and m-$ClC_6H_4CO_3^-$[2] represents a convenient route to α,β-epoxy sulfones. To our knowledge, however, only one report describes the oxidation of thiophene 1,1-dioxides, a type of cyclic α,β-unsaturated sulfone. Thus, the oxidation of benzo[*b*]thiophene 1,1-dioxide with alkaline hydrogen peroxide affords 3-oxo-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide (**1**), whereas the oxidation of the 3-alkyl- or 3-phenyl-substituted derivatives produces the corresponding 3-hydroxy-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxides (**2**).[4] We recently developed[5] a simple synthesis of a sterically congested molecule, 3,4-di-*tert*-butylthiophene (**3**), and described its oxidation to 3,4-di-*tert*-butylthiophene 1,1-dioxide (**4**). This method enables the preparation of **3** and **4** in large quantities. We since became interested in developing methods for converting such heterocycles to other sterically congested molecules, those in which two bulky *tert*-butyl groups occupy adjacent positions.[6] With this in mind, we investigated the oxidation of **4** to determine the general behavior of thiophene 1,1-dioxides toward oxidizing agents and in expectation of obtaining the sterically congested epoxy sulfone **5**, which is representative of a new ring system.

(1) Zwanenburg, B.; ter Wiel, J. *Tetrahedron Lett.* **1970**, 935.
(2) Curci, R.; DiFuria, F. *Tetrahedron Lett.* **1974**, 4085.
(3) Clark, C.; Hermans, P.; Meth-Cohn, O.; Moore, C.; Taljaard, H. C.; van Vuuren, G. *J. Chem. Soc., Chem. Commun.* **1986**, 1378.
(4) Marmor, S. *J. Org. Chem.* **1977**, *42*, 2927.
(5) Nakayama, J.; Yamaoka, S.; Hoshino, M. *Tetrahedron Lett.* **1988**, *29*, 1161.
(6) (a) Nakayama, J.; Yamaoka, S.; Nakanishi, T.; Hoshino, M. *J. Am. Chem. Soc.* **1988**, *110*, 6598. (b) Nakayama, J.; Hirashima, A. *Heterocycles* **1989**, *29*, 1241. (c) Nakayama, J.; Sugihara, Y.; Clennan, E. L. *Tetrahedron Lett.* **1990**, *31*, 4473. (d) Nakayama, J.; Hirashima, A. *J. Am. Chem. Soc.* **1990**, *112*, 7648.
(7) (a) Hayashi, Y.; Nakamura, H.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 667. (b) Sedergran, T. C.; Yokoyama, M.; Dittmer, D. C. *J. Org. Chem.* **1984**, *49*, 2408.
(8) Beetz, T.; Kellogg, R. M.; Kiers, C. Th.; Piepenbroek, A. *J. Org. Chem.* **1975**, *40*, 3308.

0022-3263/91/1956-4001$02.50/0



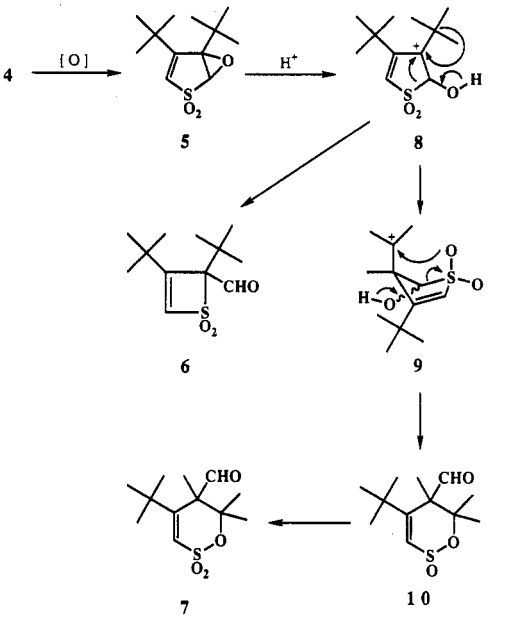
Results and Discussion

Oxidation of Thiophene 1,1-Dioxide 4 with Peracids. The carbon–carbon double bonds of **4**, each of which carries a bulky *tert*-butyl group and an electron-withdrawing sulfonyl functionality, are not very reactive toward oxidizing reagents and, thus, the oxidation of **4** required forcing conditions. Excess *m*-chloroperbenzoic acid (*m*-CPBA) (4.5 equiv) was needed to effect 100% conversion of **4** to a complex mixture of products. The mixture, on chromatographic workup, gave the ring-contracted product, thiete 1,1-dioxide **6** (31%) and the ring-expanded product, sulfone **7** (6%). The IR spectrum of **6** shows absorptions due to CH=O at 1718 cm^{-1} and to SO_2 at 1287 and 1141 cm^{-1}. The ^1H NMR spectrum of **6** displays signals due to two nonequivalent *tert*-butyl groups at δ 1.22 and 1.34 and signals due to vinyl and formyl hydrogen atoms, at δ 6.77 and 9.82, respectively. The ^{13}C NMR spectrum shows signals due to the ring carbons C_1, C_2, and C_3 at δ 143.4 (d), 167.9 (s), and 106.3 (s), respectively, and a signal due to the formyl carbon at δ 194.5 (d). The assigned structure of **7** was consistent with its ^1H and ^{13}C NMR, IR, and mass spectra.

Oxidation of **4** with a stronger oxidizing reagent, trifluoroperacetic acid, in refluxing dichloromethane also produced **6** (16%) and **7** (18%). Attempted oxidation with a milder reagent, magnesium monoperphthalate, failed under a variety of conditions, and **4** was recovered unchanged.

The initial step of the reaction described here apparently involves the formation of an epoxy sulfone (**5**), which undergoes acid-catalyzed rearrangement, via the carbocation **8**, to **6**. Acidic materials present in the system may act as catalysts. Such a rearrangement is precedented. Epoxy sulfones are generally labile and are known to undergo acid-catalyzed rearrangement to α-keto sulfones.[9] Migration of a methyl group of **8** leads to another tertiary carbocation, **9**. Therein, the sulfonyl group and the cationic center are in close proximity. Intramolecular attack by the sulfonyl oxygen on the cationic center leads to rearrangement of **9** to the sultine **10**. Oxidation of **10** with a peracid produces the final product **7**. The rearrangement of **9** to **10** is unusual. A literature survey reveals that there is only one report[10] of such neighboring group participation by a sulfonyl group which results in a similar rearrangement.[11]

Oxidation of 4 with Peracids under Basic Conditions. The mechanism proposed above involves the *acid-catalyzed* rearrangement of the epoxy sulfone intermediate **5**. If this is the case, oxidation under *basic* conditions should allow the isolation of **5**. In fact, when **4** was treated with *m*-CPBA (1.5 equiv) in the presence of Na_2CO_3 in refluxing 1,2-dichloroethane, **5** was obtained in 77% yield, based on consumed **4** (69% conversion). Similarly, treatment of **4** with trifluoroperacetic acid in the presence of Na_2HPO_4 in refluxing dichloromethane gave **5** in 98% yield, based on consumed **4** (41% conversion).



The IR spectrum of **5** shows two strong absorptions at 1308 and 1138 cm^{-1} (S=O stretchings). In the ^1H NMR spectrum, signals due to the vinyl and methine protons unexpectedly appeared as doublets (J = 3.1 Hz because of long-range coupling) at δ 6.22 and 4.42, respectively. Signals due to two nonequivalent *tert*-butyl groups appeared at δ 1.24 and 1.37 as singlets. The ^{13}C NMR spectrum displays four signals due to the four ring carbons at δ 65.6 (d) (sp^3 carbon carrying hydrogen), 72.2 (s) (sp^3 carbon carrying *tert*-butyl), 128.6 (d) (sp^2 carbon carrying a hydrogen atom), and 163.6 (s) (sp^2 carbon carrying a *tert*-butyl group) and four signals due to two nonequivalent *tert*-butyl groups. Because the long-range coupling mentioned above was unexpected, considering the structure **5**, the compound was subjected to a single-crystal X-ray structural analysis. This established the structure of **5** unambiguously.[12] Previously, to explain the observed coupling, what proved to be an incorrect structure, **16** was assigned to this compound.[13]

Compound **5** is a structurally interesting epoxy sulfone, representative of a new ring system. Its properties were investigated in some detail. Contrary to expectations, **5** was stable toward *m*-chlorobenzoic acid on prolonged reflux (20 h) in 1,2-dichloroethane. However, treatment of **5** with $BF_3{\cdot}Et_2O$ in refluxing dichloromethane afforded thiete 1,1-dioxide **6** (40%) and sultine **10** (3%). Oxidation of **10** with *m*-CPBA afforded the sultone **7** quantitatively. Heating neat **5** at 215–222 °C afforded a complex mixture which contained the thiophene **3** (10%) and the thiete **6** (13%). Flash vacuum pyrolysis of **5** at 300 °C (0.5–0.6 mmHg) also gave a complex mixture from which no identifiable compounds could be isolated. In both of these pyrolyses, no products that would arise from the expected carbonyl ylid intermediate **15** were detected. Interestingly, the reduction of **5** with $LiAlH_4$ gave 3,4-di-*tert*-butylfuran (**11**, 18%).[6c] The mechanism of formation of this compound is unclear. The reduction of **5** with Raney nickel produced 2,3-di-*tert*-butylbuten-3-ol (**12**, 96%). Treatment

(9) (a) Durst, T.; Tin, K.-C. *Tetrahedron Lett.* **1970**, 2369. (b) Tavares, D. F.; Estep, R. E.; Blezard, M. *Ibid* **1970**, 2373. (c) Houwen-Claassen, A. A. M.; McFarland, J. W.; Lammerink, B. H. M.; Thijs, L.; Zwanenburg, B. *Synthesis* **1983**, 628.

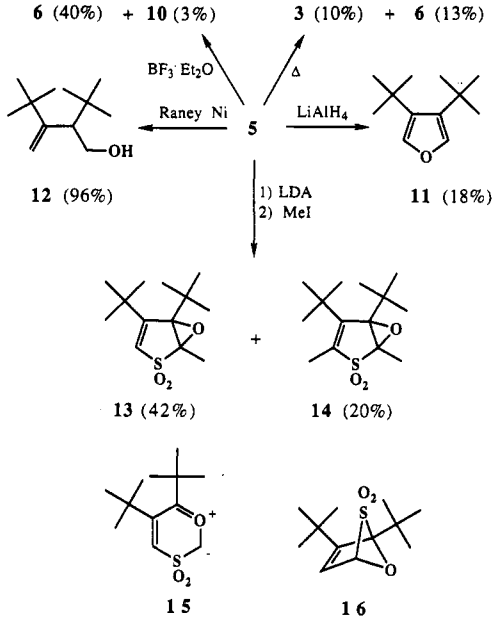
(10) Braverman, S.; Reisman, D. *J. Am. Chem. Soc.* **1977**, *99*, 605.

(11) For examples of neighboring-group participation by a sulfonyl oxygen, see: (a) Cadogan, J. I. G.; Cameron, D. K.; Gosney, I.; Highcock, R. M.; Newlands, S. F. *J. Chem. Soc., Chem. Commun.* **1986**, 766. (b) Modena, G.; Pasquato, L.; Lucchini, V. *Second International Conference on Heteroatom Chemistry*, Albany, New York, 1989; Abstract No. OC-4.

(12) The analysis was performed by Professor F. Iwasaki of the University of Electro-Communications, Japan. Details will be reported elsewhere.

(13) Sugihara, Y.; Nakayama, J. *39th Symposium on Organic Reactions*; Matsuyama, Japan, 1989; Abstract No. O-3.

of **5** with lithium diisopropylamide (LDA) (1.4 equiv) in THF at −74 °C, followed by treatment with methyl iodide at the same temperature, afforded a mixture of compounds **13** (42%) and **14** (20%).



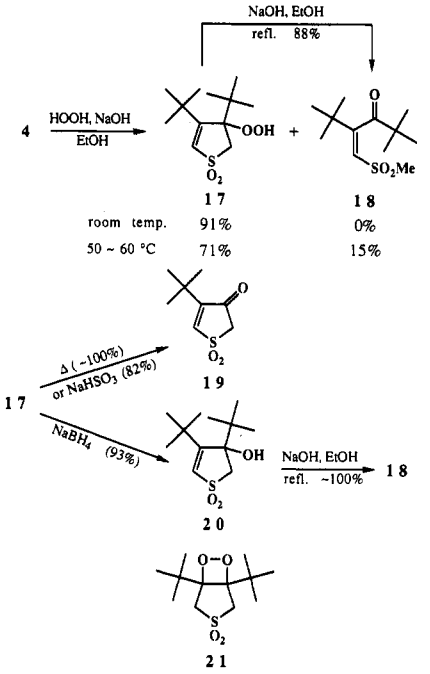
Oxidation of 4 with Alkaline Hydrogen Peroxide. Treatment of **4** with alkaline ethanolic hydrogen peroxide at room temperature afforded the crystalline hydroperoxide **17** (91%). At 50–60 °C the reaction produced the ring-opened product **18** (15%) and **17** (71%). The IR spectrum of **17** shows an absorption due to the OH of the hydroperoxy group at 3272 cm^{-1}. In the ^1H NMR spectrum, the signals due to the methylene hydrogens appear as doublets (J = 14.6 Hz) at δ 3.62 and 3.82. A singlet due to the vinyl hydrogen appears at δ 6.57. Compound **18** was designated the *Z* isomer from steric and mechanistic arguments.

The hydroperoxide **17**, when heated above its melting point, decomposes in a manner typical of hydroperoxides to give the ketone **19** quantitatively. Reductive cleavage of the O–O bond by treatment with $NaBH_4$ produces the alcohol **20** (93%). Interestingly, treatment of **17** with aqueous $NaHSO_3$ in a two-phase mixture afforded the ketone **19** (82%) but not the alcohol **20**. Under similar conditions **17** was unreactive toward Na_2SO_3.

The alkene **18** is also believed to be derived from **17**. Thus, refluxing **17** in ethanolic sodium hydroxide afforded **18** (88%). Neither intramolecular Michael addition of hydroxide ion to give the dioxetane **21** nor decomposition to the epoxide **5** occurred. Under the same conditions, alcohol **20** also yielded **18**, quantitatively, by a retro-aldol-type cleavage.[14] It is thus concluded that **18** is formed from **17** via **20**.[15]

Marmor[4] proposed that the initial step in the oxidation of benzo[*b*]thiophene 1,1-dioxides with alkaline hydrogen peroxide is the Michael addition of HOO^- to give the corresponding hydroperoxides. It was also reported[1,2] that the formation of epoxy sulfones from α,β-unsaturated sulfones by oxidation with HOO^- involves the intermediacy of hydroperoxides. In neither case, however, were hydroperoxides actually isolated. The reaction described here provides the first example of the formation of an isolable hydroperoxide by the Michael addition of HOO^- to an α,β-unsaturated sulfone.[16] That the Michael addition involves an attack at the sterically more crowded 3-position rather than the 2-position indicates that the electron density at C(3) is low because of the cross-conjugated nature of the system and also that attack at that position would result in the relief of strain by increasing the distance between the two *tert*-butyl groups so that the molecule assumes a gauche-like conformation.

Finally, the attempted addition of *t*-$BuOO^-$ to **4** failed, probably because of steric hindrance.



Experimental Section

General. Melting points are uncorrected. ^1H NMR spectra were recorded at 400 or 90 MHz. ^{13}C NMR spectra were recorded at 100.6 or 22.5 MHz. $CDCl_3$ was the solvent unless otherwise stated. Low- and high-resolution electron impact mass spectra were recorded at 70 eV unless otherwise noted. IR spectra of solids were of KBr disks. Column chromatography was performed with 70–230-mesh Merck silica gel 60. Preparative TLC was performed with Merck silica gel 60 F_{254}. Solutions obtained by reaction workup were dried with anhydrous $MgSO_4$. Elemental analyses were performed by the Analytical Center of Saitama University. *m*-CPBA (Tokyo Kasei) and magnesium monoperphthalate and *tert*-butyl hydroperoxide (Aldrich) were commercially available. Trifluoroperacetic acid[17] and 3,4-di-*tert*-butylthiophene 1,1-dioxide (**4**)[5] were prepared by literature methods.

Oxidation of 4 with *m*-CPBA. A solution of **4** (228 mg, 1 mmol), MCPBA (259 mg, 1.5 mmol), and 1,2-dichloroethane (5 mL) was refluxed for 3 h. TLC analysis showed that some **4** remained unchanged. More *m*-CPBA (259 mg) was added, and the mixture was again refluxed. After 3 h, still more *m*-CPBA (259 mg) was added, and the mixture was refluxed for another 3 h. The mixture was cooled and the *m*-chlorobenzoic acid that precipitated was removed by filtration. The filtrate was diluted with CH_2Cl_2 (50 mL), washed (aqueous saturated $NaHSO_3$, aqueous $NaHCO_3$, and H_2O), dried, and concentrated. The residue was purified by column chromatography on silica gel (40 g). Elution with benzene gave **6** (76 mg, 31%) and **7** (15 mg, 6%).

6: mp 71.5–72 °C (hexane); ^1H NMR δ 1.22 (s, 9 H, *t*-Bu), 1.34 (s, 9 H, *t*-Bu), 6.77 (s, 1 H, vinyl H), 9.82 (s, 1 H, CH=O); ^{13}C

(14) (a) Corey, E. J.; Lowry, T. H. *Tetrahedron Lett.* **1965**, 793. (b) Stirling, C. J. M. *Acc. Chem. Res.* **1979**, *12*, 198.

(15) For examples of the base-catalyzed decomposition of hydroperoxides to the corresponding alcohols, see: Hiatt, R. In *Organic Peroxides*; Swern, D., Ed.; Wiley-Interscience: New York; 1971; Vol. II, p 77.

(16) For examples the preparation of hydroperoxides by the acid-catalyzed addition of hydrogen peroxide to electron-rich alkenes, see: ref 15, p 34.

(17) Fung, S.; Siddall, J. B. *J. Am. Chem. Soc.* **1980**, *102*, 6580.

NMR δ 27.5 (q, Me), 28.7 (q, Me), 35.1 (s, CMe_3), 35.7 (s, CMe_3), 106.3 (s, C_4 of thiete ring), 143.4 (d, C_2 of thiete ring), 167.9 (s, C_3 of thiete ring), 194.5 (d, CH=O); IR 3070, 2974, 1718 (CH=O), 1557 (C=C), 1477, 1371, 1287 (S=O), 1238, 1204, 1179, 1141 (S=O), 1104, 827, 790, 671, 578, 554, 479, 450 cm^{-1}; MS (CI) m/z 245 ($M^+ + 1$). Anal. Calcd for $C_{12}H_{20}O_3S$: C, 58.98; H, 8.25; S, 13.12. Found: C, 59.10; H, 8.05; S, 12.97.

7: mp 143–144 °C (cyclohexane); ^1H NMR δ 1.22 (s, 9 H, *t*-Bu), 1.50 (s, 3 H, Me), 1.54 (s, 3 H, Me), 1.61 (s, 3 H, Me), 6.66 (s, 1 H, vinyl H), 9.79 (s, 1 H, CH=O); ^{13}C NMR δ 16.0 (q, Me), 24.3 (q, Me), 25.1 (q, Me), 30.4 (q, CMe_3), 38.9 (s, CMe_3), 59.6 [s, C(CH=O)Me], 91.6 (s, $OCMe_2$), 121.8 (d, =CH), 157.6 (s, =$CCMe_3$), 198.9 (d, CH=O); IR 3060, 2998, 1728 (CH=O), 1598 (C=C), 1488, 1403, 1379, 1340 (S=O), 1233, 1173 (S=O), 1140, 1111, 933, 897, 876, 803, 789, 609 cm^{-1}; MS (CI) m/z 261 ($M^+ + 1$). Anal. Calcd for $C_{12}H_{20}O_4S$: C, 55.36; H, 7.74. Found: C, 54.96; H, 7.71.

Oxidation of 4 with Trifluoroperacetic Acid. Trifluoroperacetic acid was prepared by adding 30% H_2O_2 (340 mg, 3 mmol) to a stirred mixture of trifluoracetic anhydride (2.3 mL) and CH_2Cl_2 (5 mL).[18] To this was added, drop by drop, a solution of **4** (228 mg, 1 mmol) in CH_2Cl_2 (1 mL). The mixture was refluxed for 5 h, cooled, and diluted with CH_2Cl_2 (30 mL) and ice water. The two liquid layers were separated. The organic layer was washed with aqueous saturated $NaHCO_3$ and water, dried, and concentrated. The residue was purified by column chromatography on silica gel (40 g). Elution with benzene gave **6** (39 mg, 16%) and **7** (46 mg, 18%).

Oxidation of 4 with *m*-CPBA in the Presence of Na_2CO_3. A solution of MCPBA (259 mg, 1.5 mmol) in 1,2-dichloroethane (5 mL) was added drop by drop to a stirred refluxing mixture of **4** (228 mg, 1 mmol), Na_2CO_3 (159 mg, 1.5 mmol), and 1,2-dichloroethane (5 mL) over 4 h. The mixture was refluxed for 8 h and then was cooled. The insoluble material that formed was removed by filtration. The solid was washed with CH_2Cl_2. The filtrate and washings were combined, washed (aqueous $NaHSO_3$, aqueous $NaHCO_3$, and H_2O), dried, and concentrated. The residue was purified by column chromatography on silica gel (30 g). Elution with benzene gave unchanged **4** (71 mg, 31%) and **5** (129 mg, 77% yield based on consumed **4**).

5: mp 111–112 °C (hexane); ^1H NMR δ 1.24 (s, 9 H, *t*-Bu), 1.37 (s, 9 H, *t*-Bu), 4.42 (d, 1 H, J = 3.1 Hz, methine), 6.22 (d, 1 H, J = 3.1 Hz, vinyl H); ^{13}C NMR δ 28.1 (q, Me), 30.3 (q, Me), 33.3 (s, CMe_3), 36.3 (s, CMe_3), 66.0 (d, methine), 72.2 (s, sp^3 C carrying *t*-Bu), 128.6 (d, sp^2 C carrying H), 163.6 (s, sp^2 C carrying *t*-Bu); IR 3084, 2972, 2932, 2884, 1574 (C=C), 1470, 1400, 1372, 1344, 1308 (S=O), 1252, 1232, 1136 (S=O), 1102, 976, 942, 884, 834, 572, 520, 490, 434 cm^{-1}; MS (CI) m/z 245 ($M^+ + 1$). Anal. Calcd for $C_{12}H_{20}O_3S$: C, 58.98; H, 8.25; S, 13.12. Found: C, 59.14; H, 8.25; S, 13.12.

Oxidation of 4 with Trifluoroperacetic Acid in the Presence of Na_2HPO_4. A solution of trifluoroperacetic acid [prepared by addition of 30% H_2O_2 (327 mg, 2.9 mmol) to a mixture of trifluoroacetic anhydride (2.3 mL) and CH_2Cl_2 (3 mL)] was added to a stirred refluxing suspension of **4** (228 mg, 1 mmol), Na_2HPO_4 (2.75 g, 19 mmol), and CH_2Cl_2 (12 mL) over 3.5 h. The mixture was refluxed for 1.5 h and then was cooled. The insoluble material was removed by filtration and was washed with CH_2Cl_2. The filtrate and washings were combined, washed (aqueous Na_2CO_3 and H_2O), dried, and concentrated. The residue was purified by column chromatography on silica gel (30 g). Elution with benzene gave unreacted (135 mg) and **5** (98 mg, 98% yield based on consumed **4**).

Pyrolysis of 5. Compound **5** (100 mg) was heated at 215–222 °C for 80 min in a small test tube. Purification of the mixture by silica gel column chromatography gave thiophene (8 mg, 10%), thiete **6** (13 mg, 13%), and a small amount of unidentified products. Flash vacuum pyrolysis of **5** (85 mg) at 300 °C (0.5–0.6 mmHg) gave a pyrolysate (46 mg) from which no pure identifiable product could be isolated.

Reduction of 5 with $LiAlH_4$. Compound **5** (61 mg, 0.25 mmol) in THF was treated with $LiAlH_4$ (38 mg, 1 mmol) at 0 °C for 30 min. Chromatographic purification of the mixture gave 3,4-di-*tert*-butylfuran (**11**, 8 mg, 18%), the ^1H and ^{13}C NMR of which were identical with those of an authentic sample:[6c] ^1H NMR δ 1.40 (s, 18 H, *t*-Bu), 7.20 (s, 2 H, furan ring); ^{13}C NMR δ 31.1 (s, CMe_3), 32.5 (q, Me), 133.9 (s, C_3 and C_4 of furan ring), 140.3 (d, C_2 and C_5 of furan ring).

Reduction of 5 with Raney Nickel. A mixture of **5** (100 mg), a large excess of Raney nickel W-2,[18] and ethanol was refluxed for 24 h. The usual workup gave nearly pure alcohol **12** (72 mg, 96%). Further purification by sublimation at 32–35 °C (0.3 mmHg) gave pure **12**, mp 39–40 °C; IR 3288 (OH), 3094, 2942, 1629, (C=C), 1462, 1384, 1358, 1205, 1069, 1025, 986, 896, 647 cm^{-1}; ^1H NMR δ 0.98 (s, 9 H, *t*-Bu), 1.09 (s, 9 H, *t*-Bu), 1.45 (broad s, 1 H, OH, disappears on addition of D_2O), 2.36 (m, 1 H, methine), 3.71 (m, 2 H, methylene), 4.95 (m, 1 H, vinyl H), 5.22 (m, 1 H, vinyl H): ^{13}C NMR δ 29.5, 30.2, 33.7, 36.8, 50.7, 65.0, 109.8, 157.9; MS m/z 166 ($M^+ - 18$). Anal. Calcd for $C_{12}H_{24}O$: C, 78.20; H, 13.12. Found: C, 77.70; H, 13.50.

Methylation of 5. To a solution of LDA [prepared by mixing *i*-Pr_2NH (0.09 mL, 0.65 mmol), BuLi (0.4 mL of a 1.6 M solution in hexane), and THF (3 mL)] at −74 °C was added a solution of **5** (112 mg, 0.46 mmol) in THF (0.5 mL). The mixture was stirred for 2 h at −74 °C. Then a solution of MeI (0.06 mL) in THF (0.6 mL) was added at −74 °C. The mixture was stirred for 2 h at −74 °C. Then the reaction was quenched by addition of wet THF. The mixture was diluted with Et_2O, washed with water, dried, and concentrated. The residue was purified by column chromatography on silica gel (15 g). Elution with hexane/Et_2O, 1:1, gave **13** (49 mg, 42%), **14** (20 mg, 20%), and an unidentified product (11 mg). **13**: mp 71–72 °C; ^1H NMR δ 1.30 (s, 9 H, *t*-Bu), 1.39 (s, 9 H, *t*-Bu), 2.05 (s, 3 H, Me), 6.29 (s, 1 H, vinyl H); ^{13}C NMR δ 12.3, 29.4, 31.3, 34.7, 37.2, 75.2, 125.7, 165.3; (C_6D_6) δ 12.5, 29.3, 31.0, 34.6, 36.9, 75.1, 75.6, 164.0; IR 1575 (C=C), 1294, 1117 cm^{-1} (SO_2); MS (CI) m/z 259 ($M^+ + 1$). Anal. Calcd for $C_{13}H_{22}O_3S$: C, 60.43; H, 8.58. Found: C, 60.16; H, 8.52. **14**: mp 74–75 °C; ^1H NMR ($CDCl_3$) δ 1.19 (s, 9 H, *t*-Bu), 1.41 (s, 9 H, *t*-Bu), 2.04 (s, 3 H, Me), 2.09 (s, 3 H, Me); MS (CI) m/z 273 ($M^+ + 1$). Anal. Calcd for $C_{14}H_{24}O_3S$: C, 61.73; H, 8.88. Found: C, 61.49; H, 8.81.

BF_3·Et_2O-Induced Rearrangement of 5. To a stirred solution of **5** (192 mg, 0.79 mmol) in CH_2Cl_2 (7 mL) was added a catalytic amount of BF_3·Et_2O (ca. 20 mg). The mixture was refluxed for 5 h, cooled, washed with water, dried, and concentrated. The residue was purified by column chromatography on silica gel (40 g). Elution with benzene gave **6** (76 mg, 40%). Elution with CH_2Cl_2 afforded sultine **10** (5 mg, 3%) as colorless crystals: ^1H NMR δ 1.20 (s, 9 H, *t*-Bu), 1.36 (s, 3 H, Me), 1.48 (s, 3 H, Me), 1.65 (s, 3 H, Me), 6.66 (s, 1 H, vinyl H), 9.41 (s, 1 H, CH=O); ^{13}C NMR δ 15.5, 24.9, 25.7, 30.2, 39.4, 57.6, 82.4, 129.6, 151.7, 199.9; MS (CI) m/z 245 ($M^+ + 1$).

Oxidation of 10 to 7. Compound **10** (5.7 mg, 0.023 mmol) was treated with *m*-CPBA (9.7 mg, 0.056 mmol) in CH_2Cl_2 at room temperature. The usual workup afforded **7** (6.1 mg, 100%), identical with that obtained by oxidation of **4**.

Oxidation of 4 with Alkaline H_2O_2. (a) At Room Temperature. To a stirred mixture of H_2O_2 (0.3 mL, 2.6 mmol), **4** (114 mg, 0.5 mmol), and EtOH (5 mL) was added ethanolic NaOH (3.0 mL, 2.8 mmol, of a 0.93 M solution). The mixture was stirred for 6 h at room temperature, diluted with ice water, acidified with 12 M aqueous HCl, and extracted with CH_2Cl_2. The extracts were washed with water, dried, and concentrated to give **17** (119 mg, 91%): mp 144 °C (CCl_4); IR 3272 (OH), 3098, 3094, 2966, 1592 (C=C), 1402, 1370, 1268 (S=O), 1124 (S=O), 1069, 989, 958, 839, 653, 572 cm^{-1}; ^1H NMR δ 1.16 (s, 9 H, *t*-Bu), 1.40 (s, 9 H, *t*-Bu), 3.62 (d, 1 H, methylene H, J = 14.4 Hz), 3.82 (d, 1 H, methylene H, J = 14.4 Hz), 6.57 (s, 1 H, vinyl H), 8.60 (s, 1 H, OOH, disappears on addition of D_2O); ^{13}C NMR δ 27.9 (q, Me), 32.4 (q, Me), 36.5 (s, CMe_3), 40.0 (s, CMe_3), 55.9 (t, methylene), 99.5 (s, sp^3 C carrying *t*-Bu), 132.2 (d, sp^2 C carrying H), 167.0 (s, sp^2 C carrying *t*-Bu). Anal. Calcd for $C_{12}H_{22}O_4S$: C, 54.93; H, 8.45. Found: C, 54.85; H, 8.25.

(b) At 50–60 °C. To a stirred ice-cooled mixture of **4** (228 mg, 1 mmol) and 30% H_2O_2 (0.4 mL, 3.4 mmol) was added ethanolic NaOH (4.1 mL of a 0.93 M solution). The mixture was then immediately heated to 50–60 °C and was kept at that temperature for 4 h. The reaction was cooled, diluted with ice–water, acidified

(18) Mozingo, R. In *Organic Syntheses*; Wiley: New York, 1965; Collect. Vol. 3, p 181.

with 12 M aqueous HCl, and extracted with CH_2Cl_2. The extract was washed with water, dried, and concentrated. The residue was recrystallized (CCl_4) to give **17** (167 mg). The mother liquor was concentrated. The concentrate was purified by prepartaive TLC (CH_2Cl_2) to give **17** (19 mg, total yield 71%) and **18** (36 mg, 15%). **18**: mp 66.5–67 °C (pentane); IR 3052, 3020, 2974, 1680 (C=O), 1595 (C=C), 1482, 1460, 1398, 1371, 1361, 1325, 1286 (S=O), 1136 (S=O), 1089, 968, 940, 915, 792, 750, 543, 498, 444 cm^{-1}; ^1H NMR δ 1.24 (s, 9 H, *t*-Bu), 1.31 (s, 9 H, *t*-Bu), 2.92 (s, 3 H, SO_2Me), 6.24 (s, 1 H, vinyl H); ^{13}C NMR δ 28.0 (q, Me of *t*-Bu), 30.5 (q, Me of *t*-Bu), 37.2 (s, CMe_3), 43.8 (q, SO_2Me), 44.5 (s, CMe_3), 124.9 (d, sp^2 C carrying H), 167.5 (s, sp^2 C carrying *t*-Bu), 214.0 (s, C=O); MS (CI) *m/z* 247 ($M^+ + 1$). Anal. Calcd for $C_{12}H_{22}O_3S$: C, 58.50; H, 9.00. Found: C, 58.31; H, 8.85.

$NaHSO_3$-Induced Decomposition of 17. A two-phase mixture of a solution of **17** (66.2 mg, 0.25 mmol) in CH_2Cl_2 (10 mL) and a solution of $NaHSO_3$ (104 mg, 1 mmol) in H_2O (5 mL) was stirred at room temperature for 1.5 h. The two liquid layers were separated. The organic layer was washed with water, dried, and concentrated to give **19** (39.1 mg, 82%): mp 190–191 °C (CCl_4); IR 3064, 3020, 2970, 2876, 1716 (C=O), 1598 (C=C), 1463, 1361, 1304 (S=O), 1245, 1203, 1145 (S=O), 1118, 1097, 1041, 980, 876, 849, 578 cm^{-1}; ^1H NMR δ 1.28 (s, 9 H, *t*-Bu), 3.85 (s, 2 H, methylene), 7.35 (s, 1 H, vinyl H); ^{13}C NMR δ 28.2 (q, Me of *t*-Bu), 33.8 (s, CMe_3), 56.2 (t, methylene), 144.4 (d, sp^2 C carrying H), 157.8 (s, sp^2 C carrying t-Bu), 189.2 (s, C=O); high-resolution MS, calcd for $C_8H_{12}O_3$ 188.0507, found 188.0489.

Thermolysis of 17. Compound **17** (7.5 mg) was heated at 145–150 °C for 20 min in a small test tube. The mixture was purified by preparative TLC (CH_2Cl_2) to give **19** (5.4 mg, 100%).

Reduction of 17 with $NaBH_4$. To a stirred, ice-cooled solution of **17** (131 mg, 0.5 mmol) in MeOH (3 mL) was added $NaBH_4$ (38 mg, 1 mmol). The mixture was warmed to room temperature and was stirred for 4 h. The mixture was then cooled in ice water and was acidified by 12 M aqueous HCl (the pH of the mixture was adjusted to ca. 6–7). The mixture was extracted with Et_2O. The extract washed with water, dried, and concentrated. The residue was recrystallized (CCl_4) to give pure alcohol (114 mg, 93%): mp 161 °C; IR 3488 (OH), 3086, 2964, 1613 (C=C), 1585, 1461, 1396, 1375, 1281 (S=O), 1234, 1213, 1130 (S=O), 1081, 1011, 956, 822, 580 cm^{-1}; ^1H NMR δ 1.16 (s, *t*-Bu), 1.38 (s, *t*-Bu), 3.10 (s, 1 H, OH, disappears on addition of D_2O), 3.28 (d, 1 H, methylene, J = 14.3 Hz), 3.85 (d, 1 H, methylene, J = 14.3 Hz), 6.51 (d, 1 H, vinyl H); ^{13}C NMR δ 27.6 (q, Me of *t*-Bu), 32.8 (q, Me of *t*-Bu), 36.8 (s, CMe_3), 40.1 (s, CMe_3), 62.8 (t, methylene), 89.6 (s, sp^3 C carrying OH), 130.5 (d, sp^2 C carrying H), 167.5 (s, sp^2 C carrying *t*-Bu). Anal. Calcd for $C_{12}H_{22}O_3S$: C, 58.50; H, 9.00. Found: C, 58.42; H, 8.65.

NaOH-Induced Decomposition of 17. To a stirred solution of **17** (26.2 mg) in EtOH (1 mL) was added aqueous NaOH (0.1 mL of a 1 M solution). The mixture was heated at 58–60 °C for 30 h. The usual workup, followed by purification by preparative TLC (hexane/Et_2O, 1:1) afforded **18** (21.6 mg, 88%).

NaOH-Induced Decomposition of 20. To a stirred solution of **20** (12.3 mg) in EtOH (1.6 mL) was added aqueous NaOH (0.075 mL of a 1 M solution). The mixture was heated at 60 °C for 7 h. Workup in the manner described above gave **18** (12.3 mg, 100%).

Ozonides of Substituted Norbornenes with Exo- and Endo-Positioned Peroxide Bonds

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Ozonolyses of three methyl-substituted norbornenes **1a–c** on polyethylene gave in each case the corresponding ozonide **2** with an endo-positioned peroxide bridge. From **1b**, ozonide **3b** with an exo-positioned peroxide bridge was obtained, too. Thermally and photolytically induced decompositions of the ozonides are described.

Introduction

Ozonides of norbornenes (bicyclo[2.2.1]heptenes) have remained unknown for a long time. Thus, early work on the ozonolysis of norbornene itself in inert solvents resulted in the formation of intractable peroxidic materials,[2a] and it was only very recently that we have been able to prepare the ozonide of norbornene as the first example of its kind by application of the modified ozonolysis on polyethylene.[3] However, due to its instability, this ozonide could not be analyzed by X-ray diffraction and, hence, it remained uncertain whether it has the peroxide bridge in the endo or exo position. Since it is known that the ozonide of 1,2-dimethylcyclopentene is more stable than that of cyclopentene, we have now tried the ozonolysis of the methyl substituted norbornenes **1a–c** on polyethylene with the goal of preparing the corresponding ozonides and assigning them to structures **2** and/or **3**.

Results and Discussion

After treatment of **1a** with ca. 23 molar equiv of ozone on polyethylene at −75 °C, we isolated 16% of unreacted **1a**,[4] 7% of ozonide **2a**, and 12% of the diketone **4a**. The structure of the crystalline ozonide **2a** has been assigned based on a positive peroxide test, correct elemental analysis in conjunction with an $[M + 1]^+$ ion at *m/z* 171 in the CI mass spectrum, and the formation of **4a** as the sole product of reduction with triphenylphosphine. The stereochemical identity, i.e. the endo position of the peroxide group, has been demonstrated by X-ray diffraction, which showed additional salient features: the 1,2,4-trioxolane ring assumes an envelope conformation, in which—in contrast to monocyclic[3] or dispiroozonides[5]—the O atom of the ether

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(4) Incomplete olefin conversions even after using ozone in a large excess are usual in ozonolyses on polyethylene. We assume that it is caused by partial migration of the olefinic substrates into the polymer particles and limited diffusion of ozone into the polymer.

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