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FORMATION OF SULFINES IN THE PEROXYACID OXIDATION OF NEOPENTYL NEOPENTANETHIOLSULFINATE

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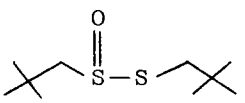
Abstract. Low temperature ^{1}H NMR and ^{13}C NMR, and IR suggest that the m-chloroperbenzoic acid (MCPBA) oxidation of neopentyl neopentanethiolsulfinate leads to the formation of (E)- and (Z)-2,2-dimethylpropanethial S-oxide, neopentyl neopentanethiolsulfonate, and other products.

Although the formation of α-disulfoxides and/or sulfenyl sulfinates as intermediates in the peroxyacid oxidation of disulfides or thiolsulfinates to thiolsulfonates have been suggested, neither species has been observed or isolated.[1]

We have investigated the m-chloroperbenzoic acid (MCPBA) oxidation of neopentyl neopentanethiolsulfinate (1) in $CDCl_3$ solution via low temperature ^{1}H NMR, ^{13}C NMR, and IR spectroscopy and found that (E)- and (Z)-2,2-dimethylpropanethial S-oxide (2,3),[4] neopentanesulfinic acid (4)[5], and neopentanesulfonic



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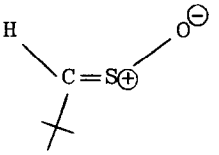

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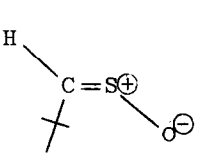

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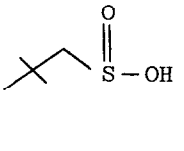
acid (5)[7] are formed in addition to neopentyl neopentanethiolsulfonate (6).[8]



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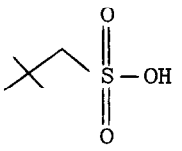

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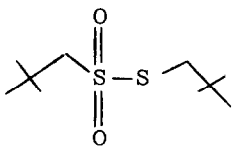

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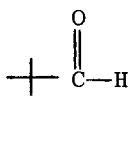

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The thiolsulfinate 1 was oxidized with one equiv of MCPBA at -20° in an inert atmosphere (1 h reaction time). The reaction mixture was filtered under nitrogen at -45°. The ^{1}H NMR spectrum of the filtrate at -20° is tabulated in Table I. After 3 hours at 25°, the ^{1}H NMR and ^{13}C NMR resonances and IR bands

Table I. ^{1}H NMR Chemical Shifts of the Products From the MCPBA Oxidation of 1 in $CDCl_3$ at -20°[a,b]

Compound	Chemical Shift (δ)	Relative Integral (%)
1	1.03,1.15	51
2	1.24	11
3	1.39	7
4	1.12	19
6	1.04,1.22	12

(a) TMS used as internal standard. Spectrometer frequency = 250 MHz. (b) Only the t-butyl groups are tabulated. Compounds 2 and 3 also show singlets for protons at δ 9.09 and 7.62, respectively.[4]

for 2 and 3 disappeared and new signals (δ 1.08, 9.58) appeared for the expected decomposition product, 2,2-dimethylpropanal (7).[4,9,10] Storage of this filtrate at -18° for 28 days led to a gradual decrease of 1 and 4 and a corresponding increase of 6 (to 26% via NMR).[11]

In another experiment the reaction mixture was warmed to 0° and stirred with ice cold 5% $NaHCO_3$ solution for 10 minutes. The layers were separated and the organic phase dried (Na_2SO_4). Table II shows the NMR analysis of the two phases.

Analytical HPLC[12] (UV detector, 254, nm) of the organic phase showed the presence of 1 and two other peaks, presumably 2 and 3. Flash chromatography of the organic phase on silica gel (20% ether-hexanes) showed that 2 and 3 decomposed when the eluted fractions were concentrated. After the organic phase was allowed to stand overnight at 25° in the dark, compounds 2 and 3 disappeared and the concentration of aldehyde 7 increased (^{1}H NMR assay). HPLC analysis

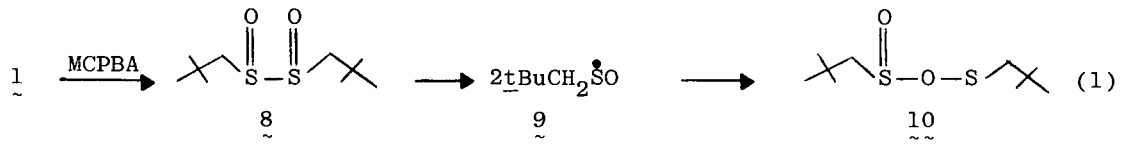
also showed 1 as the only other UV active component.

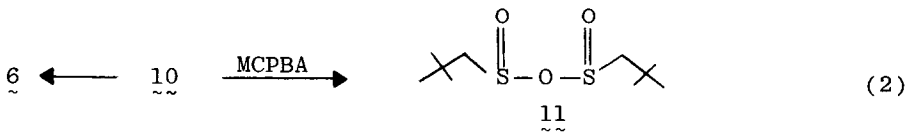
Table II. Product Distribution From the MCPBA Oxidation of 1 (-20°) Followed by Treatment with 5% $NaHCO_3$ at 0°[a]

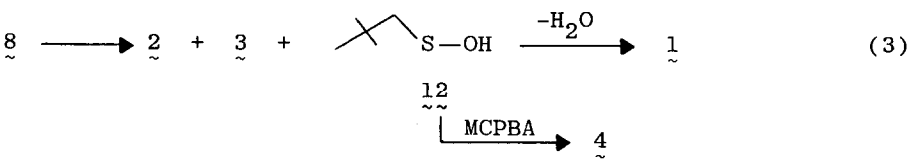
Compound	Yield,%[b]
1	48
2	13
3	8
4	29
5	4
6	13

(a) NMR yields are given. (b) Based on moles of starting material. Approximately 10% m-chlorobenzoic acid (MCBA) remained in the organic phase.

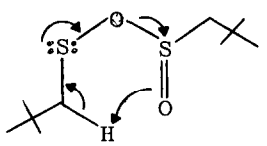
Formation of thiolsulfonate 6 could result from combinative termination of two $tBuCH_2\dot{S}O$ radicals (9), followed by rearrangement of the sulfenyl sulfinate (10). Sulfines 2 and 3 may be formed from the α-disulfoxide (8),[1,13]







from rearrangement of 10, and/or from fragmentation of the sulfinic anhydrides



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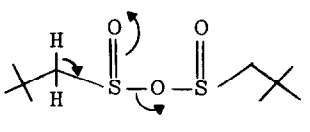

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(11). Dehydration of neopentanesulfenic acid (12) can lead to 1.[3] Sulfinic acid 4 can also arise from the hydrolysis of 11.

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5. Compound 4 was prepared by a recently reported method.[6]

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7. Oxidation of neopentyl mercaptan with nitric acid afforded compound 5 which was purified by decomposition of its lead salt with hydrogen sulfide. Since 5 is only observed in the $NaHCO_3$ extraction, it may not be a direct oxidation product of 1.

8. Compound 6 was prepared by the thermal decomposition of 4, m.p. 59-60°. Calculated: C,50.38, H, 9.30. Found: C, 50.28, H, 9.55.

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12. HPLC was performed on an EM Hibar 5 μm silica gel column with 3% EtOAc-isooctane as eluant.

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