Reaction of trans-anethole with m-chloroperoxybenzoic acid
(with buffer solution and without buffer solution)

Procedure A (No Buffer)

A solution of trans-anethole (0.50g, 3.4 mmol) in CH_2Cl_2 (10 ml) was efficiently stirred with a stir bar and cooled in an ice bath as a solution of mCPBA (0.92 g, 3.7 mmol) in CH_2Cl_2 (10 ml) was added dropwise via an addition funnel or a separatory funnel (if not available, use a 10 ml syringe and add through a vented septum). The resulting mixture was stirred in the ice bath for an additional 20 min. The mixture was washed with 10% Na_2CO_3 (5 X 15 ml) and saturated NaCl solution (15 ml).[1] The organic layer was dried (Na_2SO_4) and the solvent was removed on a rotary evaporator[2] to give 1.02 g of a viscous oil.

Procedure B (Buffered Reaction)

A biphasic mixture of a solution of trans-anethole (0.50g, 3.4 mmol) in CH_2Cl_2 (10 ml) and 10% Na_2CO_3 solution (10 ml) was efficiently stirred with a stir bar and well cooled in an ice bath as a solution of mCPBA (1.4 g, 5.7 mmol, 1.7 equiv) in CH_2Cl_2 (20 ml) was added dropwise via an addition funnel or a separatory funnel (if not available, use a 10 ml syringe and add through a vented septum). After the addition was complete, the mixture was stirred in the ice bath for an additional 20 min. The organic layer was separated and washed with 10% Na_2CO_3 (5 X 15 ml) and saturated NaCl solution (15 ml).[1] The organic layer was dried (Na_2SO_4) and the solvent was removed on a rotary evaporator[2] to give 0.52 g of a pleasant-smelling oil.

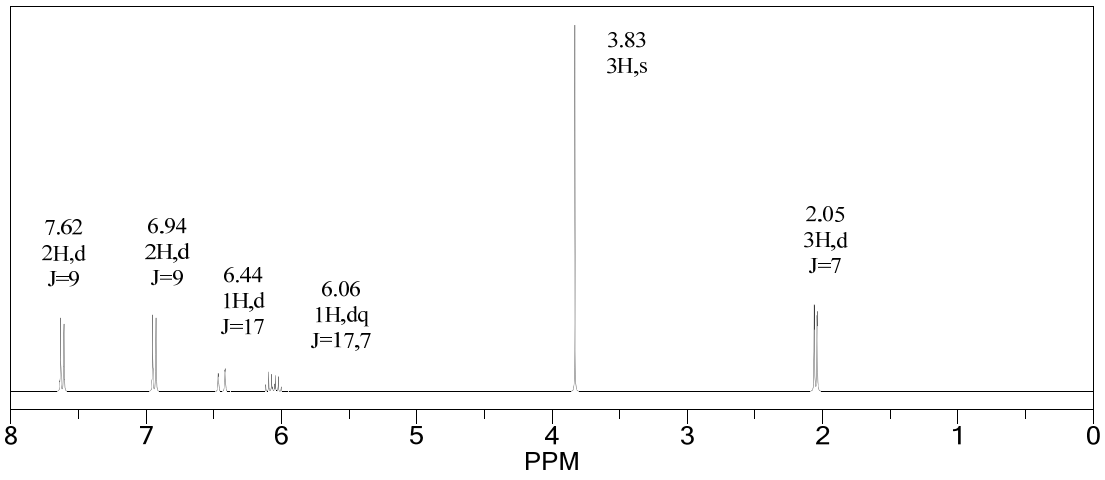
1. The excess peracid is removed by washing with 10% aqueous Na_2CO_3. The absence of peracid can be tested using starch-iodide paper.
2. Solvent can also be removed using a water bath maintained at 50°C.

Hazards

Dichloromethane vapor is harmful and inhalation should be avoided. MCPBA is shock sensitive and should not be ground in a mortar. The epoxide product has a pleasant but persistent odor and hence contact with skin and clothing should be avoided.

Questions

1. What is the structure of mCPBA?
2. Interpret the proton NMR spectra for the starting material, product A and product B. Are there peaks for epoxide hydrogens in any of the ^1H NMR spectra?
3. How many aromatic carbons can be seen in the ^{13}C NMR spectrum of starting material, A and B? Is this reasonable?
4. Are there any other carbons in the ^{13}C spectra? If so, what are the likely functional groups on the basis of the chemical shift in the ^{13}C NMR spectra?
5. What functional groups are indicated by the IR spectra (starting material, product A and product B)?
6. What is the theoretical yield of the product, assuming it is the epoxide? How does this compare to the observed yields? Explain any discrepancies (product A versus product B).
7. The pK_a of a peracid is about 8. How does this compare to the pK_a of benzoic acid (about 4)…to the pK_a of benzyl alcohol (about 16)? Are these reasonable values? Explain their differences.
8. Why are Na_2CO_3 extractions performed?
9. Propose what products are formed (A and B) and write mechanisms for each probable reaction. Explain any differences in reaction pathways.



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128.7,s
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114.2,d (x2)
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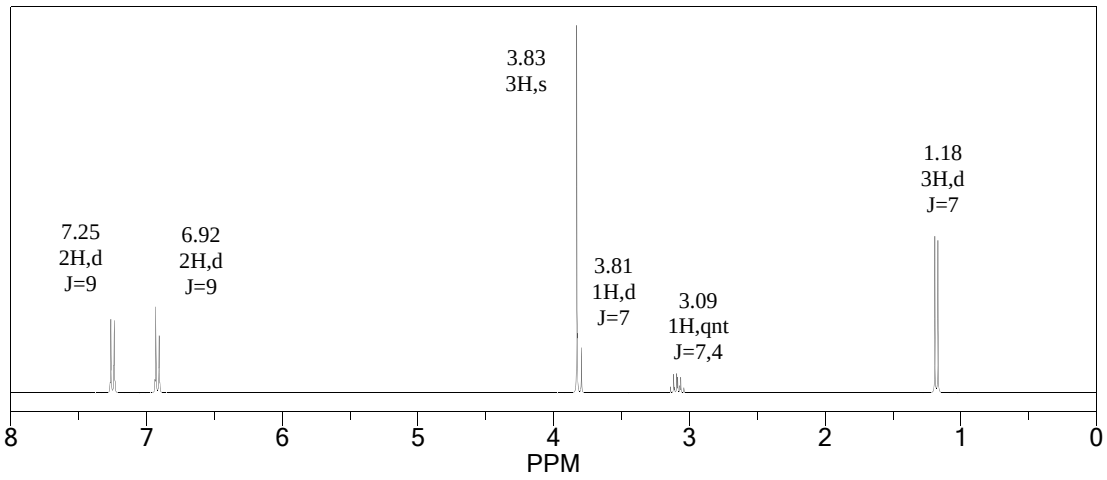

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60.3,d
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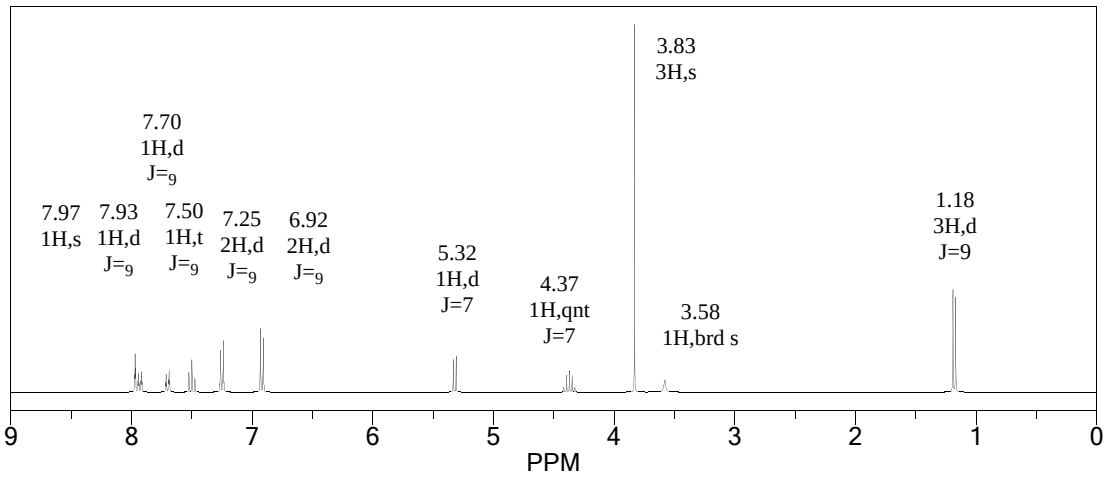
18.1,q



165.9,s
157.9,s
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134.2,s
133.1,d
130.0,d
129.9,d
128.7,s
128.0,d
128.0,d (x2)
114.4,d (x2)
80.7,d
70.4,d
55.8,q
18.7,q