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THE DECARBOXYLATIVE ELIMINATION REACTION OF A β,γ-EPOXYACID. A ROUTE TO ALLYLIC ALCOHOLS

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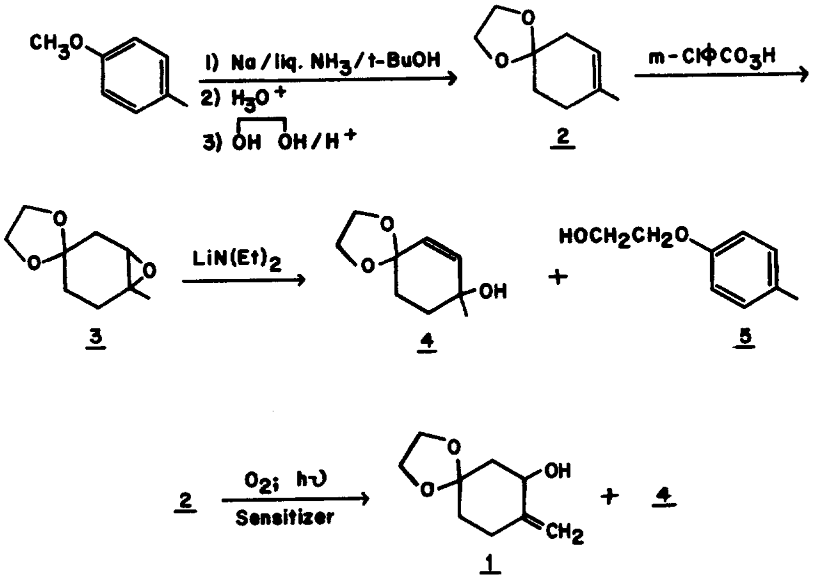
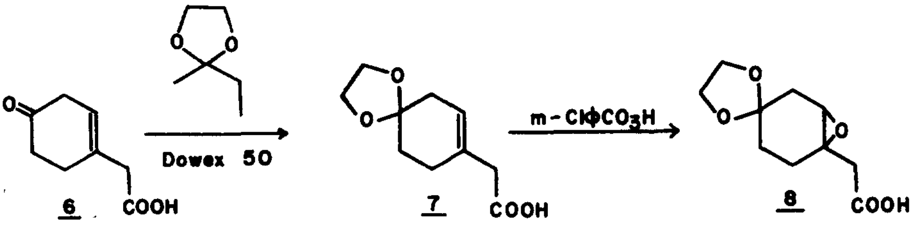
Recent communications by Sims[1,2] and Winstein[3] have described the utility of the decarboxylative elimination reactions of β,γ-cyclopropylcarboxylic acids in the synthesis of angularly methylated decalin systems. We wish to report here the finding that pyrolysis of a β,γ-epoxyacid leads via a decarboxylative-elimination pathway to an allylic alcohol; a potentially widely applicable route to this class of compounds.

As part of a terpene synthesis program we required the allylic alcohol 1. We attempted to prepare 1 by two relatively standard methods. First, dihydro-p-cresol methyl ether was converted directly to the unsaturated ketal 2[4]. Epoxidation of 2 with m-chloroperbenzoic acid yielded 3. Contrary to expectation from analogous published examples[5] when 3 was treated with lithium diethylamide in ether the endocyclic unsaturated tertiary alcohol 4 (nmr: δ 1.3, singlet, $-\overset{|}{\underset{|}{C}}-CH_3$; δ 5.63, AB quartet, J=10.4 Hz, H-C=C-H) was obtained rather than the methylene cyclohexanol 1. Accompanying 4, and in greater proportion, was the aromatic ether 5. Modification of the reaction conditions by the substitution of tetrahydrofuran for ether as solvent resulted only in an increase in the yield of 4.

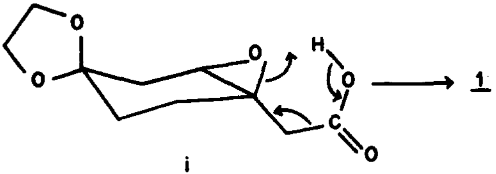


A second attempt to prepare 1 was made employing photosensitized oxygenation[6]. Treatment of 2 in pyridine solution with oxygen in the presence of hematoporphyrin afforded a mixture of allylic alcohols 1 and 4 in yields (glpc) of 48% and 37% respectively. (In view of published mechanistic suggestions[6] and previous synthetic applications[7] of this oxygenation reaction the factors resulting in the production of 4 by this process require further investigation.)

A successful route to 1 was developed in the following manner. Lithium-ammonia reduction of p-methoxyphenylacetic acid afforded 6 (95% yield). Transketalization between 6 and the dioxolane of methyl ethyl ketone in the presence of Dowex 50-W-X8 resin give 7 (m.p. 71-74; 93% yield; nmr: δ 3.03, multiplet, $-\underline{CH_2}-CO_2H$; δ 5.5, broad multiplet, $-C=\overset{H}{C}-$) and epoxidation of the latter (m-chloroperbenzoic acid) yielded the epoxyacid 8 (m.p. 103-104 (dec.); 94% yield; nmr: δ 3.06, triplet, $\overset{O}{C\text{—}C}$ - H; δ 2.56, singlet, $-\underline{CH_2}-CO_2H$).



By analogy with the thermal decompositions of β,γ-unsaturated acids[8] and β,γ-cyclopropyl acids *8* ought to undergo decarboxylative elimination as in *i* to *1*. This process was realized by heating *8* in toluene under reflux for 3.5 hours. Under these conditions a 98% yield of *1* (nmr: δ 3.83, singlet, 4H, $-O-CH_2CH_2-O-$; δ 4.0, multiplet, 1H, $O-\underset{|}{\overset{|}{C}}-H$; δ 4.65, broad, 1H; 4.83, broad, 1H, $C{=}C\begin{smallmatrix}\diagup H \\ \diagdown H\end{smallmatrix}$) was obtained.



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The general applicability of this route to the synthesis of other allylic alcohols is under investigation.

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