STUDIES ON SOME REACTIONS OF SMALL HETEROCYCLIC RINGS

By

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STUDIES ON SOME REACTIONS OF

SMALL HETEROCYCLIC RINGS

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A C K N O W L E D G E M E N T

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C O N T E N T S

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S U M M A R Y

S U M M A R Y

The work recorded in this thesis deals with the reactions of spiro[oxiran-2,9'-phenanthrenes] with nucleophilic reagents such as triphenylphosphine, triphenylphosphine benzylene, triphenylphosphine-1,2-bis(ethoxy-carbonyl) ethylidene and sodium azide.

The thesis is divided into five chapters, literature survey (chapter I) which is covered by 148 references, dealing with the preparation and reactions of epoxides.

The experimental results are presented in 22 tables and 64 figures.

Results and discussion are divided into three chapters (II-IV). Thus chapter II deals with the reaction of triphenylphosphine with spiro[3,3-diphenyl oxiran-2,9'-phenanthrene], spiro[3-benzoyl oxiran-2,9'-phenanthrene], spiro[3-phenyl-3-benzoyl oxiran-2,9'-phenanthrene] and spiro[3-fluorenylidene oxiran-2,9'-phenanthrene in presence of THF (compounds No 161a-d) to give products of 6-membered hetero ring (hexa-oxy-phosphoran compounds) (162a-d), respectively.

Whereas the reaction of triphenylphosphine with spiro [3-p-nitrophenyl oxiran-2,9'-phenanthrene] gives two products,

4-membered oxy-phosphorane (163) and 7-membered oxy-diphosphorane (164).

Chapter III describes the reaction of triphenylphosphine benzylene with spiro[oxiran-2,9'-phenanthrenes] in ether to give 5-membered phosphole compounds (167a-e). However, triphenylphosphine 1,2-bis(ethoxy carbonyl) ethylidene (168) reacts with spiro[oxiran-2,9'-phenanthrenes] in ether to give 5-membered phosphole compounds (169a-e). In case of fluorenylidene derivative two isomeric products are obtained, one is pink (169d) and the other is orange-red (169d'). The former is changed to the latter upon crystallization from ether.

In chapter IV the author describes the reaction of sodium azide with spiro[oxiran-2,9'-phenanthrenes] to give azido products via ring opening (170a-d) and the exceptional case is with the spiro[3-p-nitrophenyl-oxiran-2,9'-phenanthrene] where ring cleavage takes place to give p-nitrobenzyl azide (171e) and phenanthrenequinone.

The structures of the products are confirmed by elemental chemical analysis, IR, UV/visible, NMR and mass spectra.

Chapter V gives detailed experimental conditions, yields, melting points and chemical analysis.

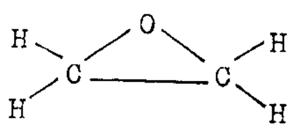
C H A P T E R I

I N T R O D U C T I O N

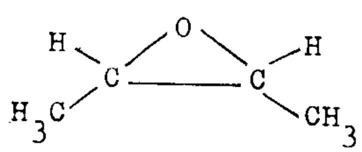
I N T R O D U C T I O N

Epoxides (Oxiranes)

Epoxides are compounds containing the three membered ring. It is one of the simplest classes of heterocyclic compounds which contain a strained ring of two carbon atoms and one oxygen atom. Electron diffraction studies on ethylene oxides (1) (oxirane) and the cis- and trans-2,3-epoxybutanes (2 and 3) show the expected internuclear distance (C–C 1.54 Å; C–O 1.43 Å, C–H 1.05 Å)[1], but distorted bond angles; thus the bond angle of oxygen is reduced to 67^{o}; and the $109^{o}28'$ tetrahedral value of carbon becomes $57^{o}26'$ and $117^{o}28'$. The transition in C–C bond type from ethylene to the cyclopropane is gradual, and contains features of the ethylenic linkage remain in the cyclopropane ring.



(1)



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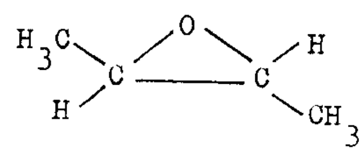
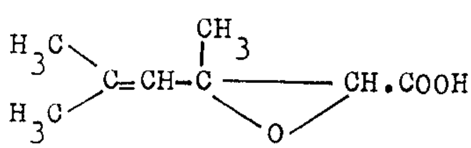


(3)

This situation has a parallel in the cyclic ether. The phenomenon of hyperconjugation[2] due to alkyl substitution in an olefin extends to substituted cyclopropanes, and a single effect appears to exist in the three-numbered heterocyclic ring.

In ethylene oxides this has a marked effect on the rate of oxide formation. As an olefinic linkage or carbonyl group can conjugate with another double bond or aryl group, so also can a three-membered ring[3,4].

Several observations have been made of the similarity of the absorption spectra of conjugated molecules which have an ethylenic oxide ring to the spectra of the corresponding molecules with an olefinic linkage or carbonyl group in its place. Measurements are available for such substances (4)[5] and (5)[6].



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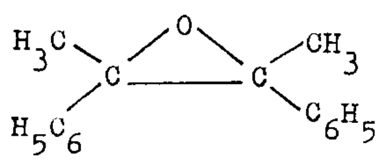

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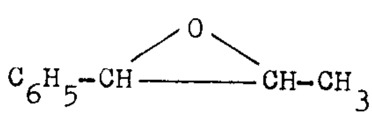
Comparison of the spectra of acetophenone and 1-phenyl-1,2-epoxypropane (6) shows losely similar curves with maxima shifted 20-30 nm towards the ultraviolet for oxide[7].

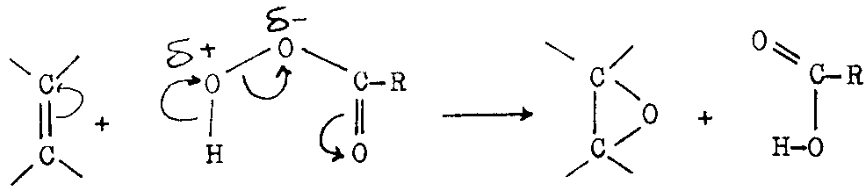


(6)

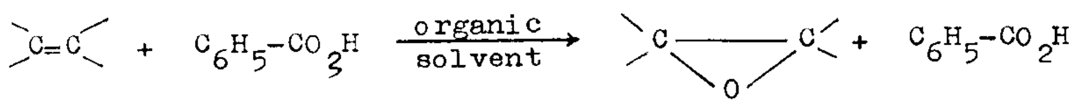
1. Methods of Preparation:

a. Oxidation of olefins:

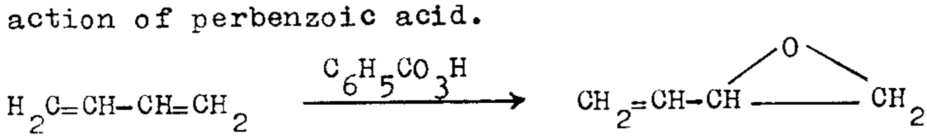
Alkenes are oxidised by peracids, $R-\overset{\overset{\displaystyle O}{\|}}{C}-O-OH$ to give an alkene oxide or epoxides.



Perbenzoic acid[7] is an efficient oxidising agent for the epoxidation of the isolated double bond.

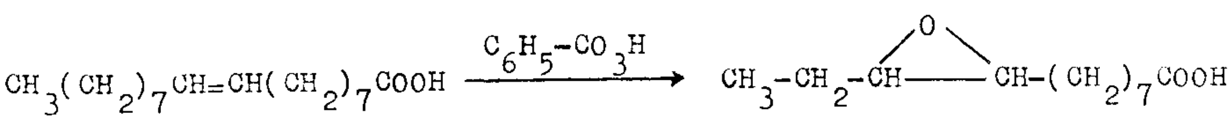


Butadiene may be converted to the monoxide[8] by the action of perbenzoic acid.



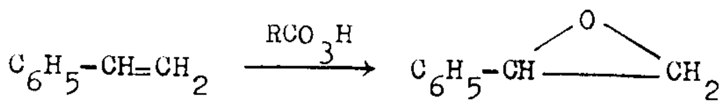
In the epoxidation of dienes[9] the first attack is at the double bond carrying an alkyl substituent.

9,10-Epoxystearic acid (7) was best prepared by epoxidation of oleic acid with perbenzoic acid.



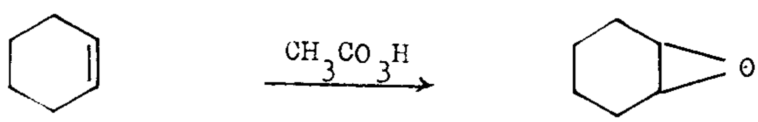
(7)

Styrene reacts with perbenzoic acid or peracetic acid to give the corresponding epoxide[10] (8).



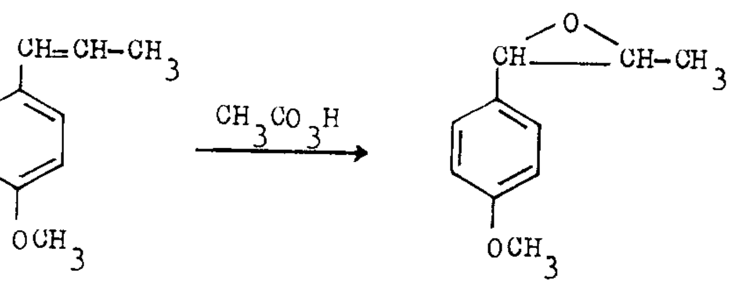
(8)

Cyclohexene reacts with peracetic acid to give the corresponding epoxide[11] (9).



(9)

Anethole reacts with peracetic acid to give the corresponding epoxide[11] (10).



(10)

The rate of the oxidation of olefinic compounds is quite sensitive to the number and kind of substituents on the ethylinic carbon atoms.