Tetrahedron Letters No. 37, pp 3257 - 3260, 1976. Pergamon Press. Printed in Great Britain.

ENTRY INTO THE ALLENE OXIDE-CYCLOPROPANONE SYSTEM VIA VINYLSILANES.
III. SUBSTITUENT EFFECT ON THE ALLENE OXIDE-CYCLOPROPANONE ISOMERIZATION.[1]

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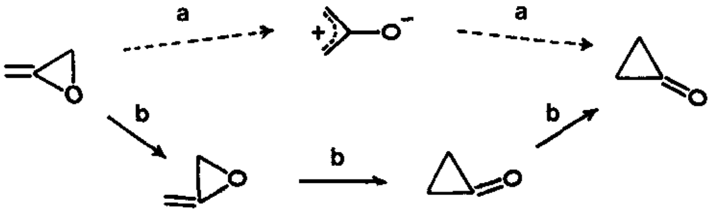
(Received in USA 11 June 1976; received in UK for publication 26 July 1976)

The allene oxide-cyclopropanone isomerization poses a challenging mechanistic problem. The inaccessibility and the unstability of both the allene oxide and the cyclopropanone render experimental investigation difficult. On the other hand, it is a fertile area for theoretical study. Indeed, several theoretical computations[2-7], not necessarily in general agreement, have appeared in the last several years. The latest CNDO/2 calculation[7] indicated a mechanism through the intermediacy of oxyallyl (Scheme 1, path a) to be energetically unlikely. Instead, a novel pathway involving bending of the molecule has been suggested (Scheme 1, path b). Existing experimental evidence[8] does not allow a distinction to be made between these two possibilities. We wish to report on our results which appear to cast some light on this difficult problem.

Scheme 1



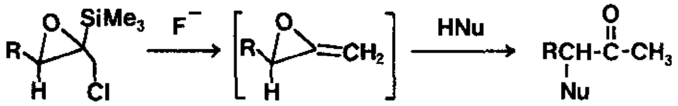
Recently we reported on the generation of the allene oxide system via vinylsilanes according to scheme 2[9]. The reaction was demonstrated by the isolation and characterisation of 1-t-butylallene oxide[1]. When the alkyl substituent is sterically less bulky than the t-butyl group, attempts to isolate the allene oxide have not been successful. The existence of the allene oxide was however demonstrated by trapping with external nucleophiles.

Scheme 2

Thus when the epoxide I (a-d, 1 mmole) was stirred with cesium fluoride (0.18g) in acetonitrile (4 ml) at 25° in the presence of a nucleophile (HNu, 3 mmole) for 2 days, the product isolated was the 3-substituted 2-ketone VII (See Tables). The formation of VII is attributed to the reaction of the nucleophile with the transient allene oxide IV, in analogy with the case of 1-t-butylallene oxide[1]. Under identical conditions, the epoxide IIa with cesium fluoride and a nucleophile gave as product the 1-substituted 2-ketone VIII exclusively. The regiospecific nature of the reaction argues convincingly for the nucleophilic opening of the epoxide structure in the isomeric allene oxides IV and V as the mechanism for the reaction. Conversely, it also rules out any common species, either the cyclopropanone or the oxyallyl, as the necessary intermediate for these reactions.

Table 1: Generation of allene oxide in the presence of nucleophile†

A.



I a: R = H

b: CH_3

c: $i\text{-}C_3H_7$

d: $n\text{-}C_{10}H_{21}$

IV

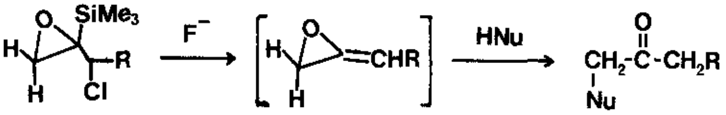
VII: Nu = OPh(77%)

Nu = $N(iPr)_2$(43%); OPh(78%)

Nu = SEt(83%); OPh(73%)

Nu = OCH_3(60%)**

B.



II

a: R = $n\text{-}C_{10}H_{21}$

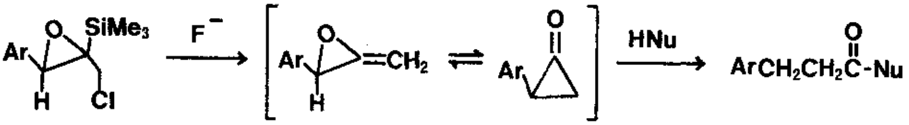
b: R = $p\text{-}CH_3C_6H_4$-

V

VIII: Nu = OCH_3(54%)**

Nu = SC_2H_5(81%)

C.



III

VIa

VIb

IX

a: Ar = Ph

b: Ar = $p\text{-}CH_3\text{-}C_6H_4$-

Nu = OCH_3(95%); SC_2H_5(92%); NHPh(93%)

Nu = OPh(88%)

† See text for experimental conditions. The isolated yields of IX to XII are given in parenthesis.

** pmr of the crude product mixture indicated the absence of the other isomer.

The moderate yield was due to the reaction of allene oxide with chloride ion.

A dramatic change in the course of reaction occurs when the substituent at C-1 is an aryl group. When the epoxide III was treated with cesium fluoride in the presence of a nucleophile under identical conditions, the sole product isolated was found to be the dihydrocinnamate IX. A reasonable pathway for the formation of IX from III is through the intervention of the allene oxide VIa, thence to the cyclopropanone VIb, followed by a Favorski type reaction of the nucleophile with VIb. Reaction of phenylcyclopropanone with nucleophiles to give dihydrocinnamates has been well documented.[10] On the other hand, an aryl substituent at C-3 does not lead to the intervention of the cyclopropanone intermediate. Reaction of the epoxide IIb with cesium fluoride and a nucleophile gave VIII as the product.

It appears therefore that the nature of the substituent at C-1 of allene oxide has a decisive effect on its rate of isomerization to cyclopropanone. When the substituent is either an alkyl group (as in I b-d) or hydrogen (as in Ia and II), the allene oxide suffers nucleophilic attack faster than rearrangement to cyclopropanone. When the substituent is an aryl group, isomerization of the allene oxide to cyclopropanone is faster than the nucleophilic attack. Such a substituent effect does not appear to be compatible with a mechanism based solely on the bending of the molecule as outlined by path b, scheme 1. A reasonable interpretation of the substituent effect is that, in the allene oxide-cyclopropanone isomerization process, the rate determining step must involve rupture of the C-1 -oxygen bond with considerable charge developing at C-1. An oxyallyl intermediate, as outlined by path a, scheme 1, would be in agreement with such a substituent effect.

Acknowledgement. We are grateful to the National Research Council of Canada, and the Ministry of Education, Government of Quebec for financial support of the research. The award of a NRCC scholarship to B.S.O. is also acknowledged.

References and Footnotes

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Table 2. Physical and Spectroscopic Data of Compounds According to Table 1.

Precursor	Products[a]
Ia. b.p.81-3°/35mm pmr.0.2(s,9H),2.7(s,2H) 3.5(AB,J=11Hz,2H)	VII Nu=OPh;pmr:2.15(s,3H),4.4(s,2H),6.6-7.4(m,5H); ir:1720 cm^{-1}.
Ib. b.p.96-8°/48mm pmr:0.2(s,9H),1.3(d, J=6Hz,3H),2.75(q,J=6Hz, 1H),3.25(AB,J=10Hz,2H)	VII Nu=N(iPr)$_2$;pmr:0.9-1.2(m,15H),2.15(s,3H),2.6-3.3(m, 2H),3.4(q,J=7Hz,1H);ir:1705 cm^{-1} VII Nu=OPh;pmr:1.4(d,7Hz,3H),2.0(s,3H),4.4(q,J=6Hz,1H), 6.7-7.3(m,5H);ir:1720 cm^{-1}
Ic. b.p.86-7°/14mm pmr:0.2(s,9H),1.05(d, J=6Hz,6H),1.2-1.7(m,1H), 2.4(d,J=9Hz,1H),3.35(AB, J=11Hz,2H)	VII Nu=SC$_2$H$_5$;pmr:0.9-1.3(m,9H),2.15(s,3H),2.45(q,J=7Hz,2H), 2.9(d,J=10Hz,1H);ir:1700 cm^{-1} Nu=OPh;pmr:0.9-1.2(dd,J=7Hz,6H),2.1(s,3H),1.9-2.4(m, 1H),4.15(d,J=6Hz,1H),6.7-7.5(m,5H);ir:1715 cm^{-1}
Id. b.p.107-108.5°/0.1mm pmr:0.25(s,9H),0.8-1.8 (br,21H),2.75(t,J=6Hg, 1H),3.35(AB,J=11Hz,2H)	VII Nu=OCH$_3$;pmr=0.7-1.7(br,21H),2.15(s,3H),3.4(s,3H), 3.55(t,J=6Hz,1H);ir:1720 cm^{-1}
IIa. b.p. -[b] pmr:0.0(s,9H),0.6-1.8(br, 21H),2.4-2.8(m,2H),3.8- 4.2(m,1H)	VIII Nu=OCH$_3$;p,r:0.7-1.7(br,21H),2.3(t,J=6H,2H),3.3 (s,3H),3.65(s,2H);ir:1720 cm^{-1}
IIb.[c] b.p. -[b] pmr:0.0(2s,9H),2.4(s, 3H),2.95(m,2H),5.2(2s, 1H),7.1-7.6(m,4H)	VIII Nu= SC$_2$H$_5$;pmr:1.35(t,J=7Hz,3H),2.4(s,3H),2.6(q,J= Hz,2H),3.35(s,2H),3.95(s,2H),7.2(s,4H);ir:1700 cm^{-1}
IIIa. b.p.62-4°/0.05mm pmr:0.2(s,9H),3.25(AB,J= 11Hz,2H),3.95(s,1H),7.25 (s,5H)	IX Nu=OCH$_3$;pmr:(2.4-3.1(m,4H),3.6(s,3H),7.2(s,5H); ir:1735 cm^{-1} Nu=SEt;pmr:1.2(t,J=7Hz,3H),2.6-3.1(m,6H),7.2(s,5H); ir:1685 cm^{-1} Nu=NHPh;pmr:2.3-3.05(m,4H),6.7-7.4(m,10H),8.0(broad s,1H);ir:3410,1680 cm^{-1}
IIIb. b.p.80-3°/0.1mm pmr:0.2(s,9H),2.3(s,3H) 3.25(AB,J=11Hz,2H),4.0 (s,1H),7.1(s,4H)	Nu=OPh;pmr:2.3(s,3H),2.65-3.1(m,4H),6.9-7.5(m,9H); ir:1750 cm^{-1}

a: All products were purified by TLC

b: Decomposed on attempted distillation

c: IIb is a mixture of two diastereomers