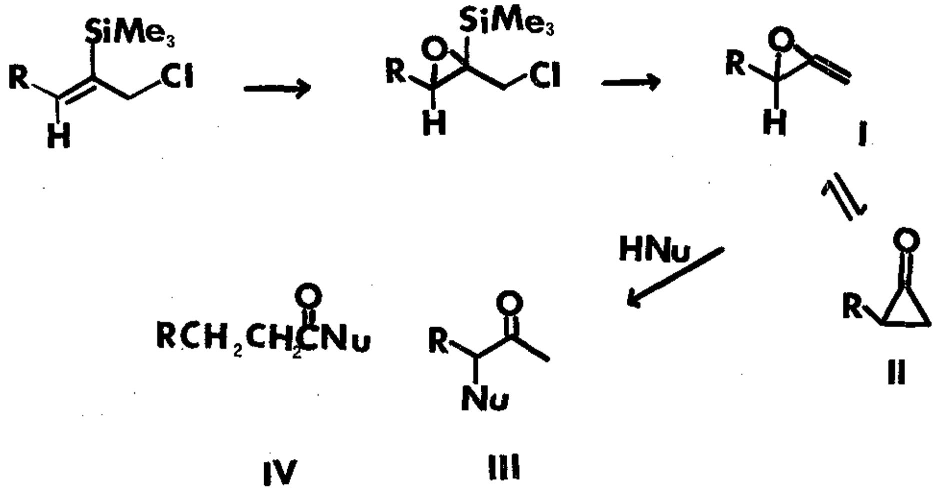
HETEROCYCLES, Vol. 7, No. 2, 1977

ENTRY INTO THE ALLENE OXIDE-CYCLOPROPANONE SYSTEM VIA VINYLSILANES. IV. REACTION OF ALLENE OXIDES WITH CYCLOPENTADIENE.[1,2]

Beng Soon Ong and Tak-Hang Chan*
Department of Chemistry, McGill University, Montreal, Canada

Alkyl-substituted allene oxides reacted with cyclopentadiene to give substitution products whereas aryl-substituted allene oxides reacted with cyclopentadiene and related heterocycles to give cycloaddition products. The difference is explained by a facile rearrangement of aryl-substituted allene oxides to cyclopropanones.

Allene oxide (I) may be considered as one of the smallest, and yet extremely reactive, heterocycle. Not much is known about the chemistry of this class of compound.[3] Recently, we have developed a novel method for the generation of allene oxides (Scheme 1).[4] With this method, 1-t-butylallene oxide (I,R=t-Bu) has been prepared, isolated and characterised.[5] Other monosubstituted allene oxides have been similarly generated, however, they were too reactive to survive isolation.[2] Their existence was inferred by trapping with external nucleophiles. From the product distribution (III or IV) it was concluded that, whereas aryl-substituted allene oxides (I, R=aryl) rearranged to the corresponding cyclopropanones II prior to reaction with the external nucleophiles to give IV, alkyl-substituted



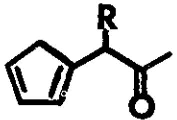
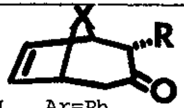
Scheme 1

allene oxides (I, R=alkyl or H) reacted as such to give III.[2]

We have now found that such a dichotomy of reactivity also exists in the reaction of allene oxides with cyclopentadiene and related heterocyclopentadienes.

Alkyl-substituted allene oxides (I a-d), when generated in the presence of cyclopentadiene, afforded the substitution products V a-d (scheme 2) in moderate yields (Table I). The assignment of the structure of V was based on the following considerations. The ir spectra of V displayed the expected strong carbonyl band at ca. 1705 cm^{-1}. Their UV spectra showed λ_{max} at 245 and 290 nm for the $\pi \rightarrow \pi^*$ [cf. cyclopentadiene, λ_{max} 239 nm] and $n \rightarrow \pi^*$ transitions respectively. Their nmr and mass spectra were entirely consistent

Table: Physical data of Compounds V and VI.

V 	isolated yield(%)	ir(cm^{-1})[a]	uv, λ_{max} nm(Σ)[b]	pmr, δ
R = CH_3	30	1704	243(2700) 290(400)	1.2 (d,3H), 2.0 (s,3H), 2.8 (d,2H) 3.4 (m,1H), 6.1 (m,3H)
iPr	48	1705	250(2060) 291(437)	0.8 (dd,6H), 2.0 (s,3H), 2.2 (m.1H) 2.8 (d,2H), 3.2 (d d,1H), 6.2 (m,3H)
n-$C_{10}H_{21}$	46	1707	245(2571) 290(393)	0.9 (t,3H), 1.3 (b,18H), 2.0 (s,3H) 2.9 (d,2H), 3.4 (m,1H), 6.4 (m,3H)
c-C_6H_{11}	43	1705	250(2110) 291(470)	0.9-1.9(b, 11H), 2.1 (s,3H), 2.9 (d,2H), 3.3 (dd,2H)6.3 (m,3H)
VI 				
X=CH_2, Ar=Ph	66 mp 75-6°	1705	289(50)	2.05 (m,2H), 2.4 (m,2H), 3.0 (m,2H), 3.75 (d,1H), 6.1-6.3 (m,2H), 6.9-7.3 (m,5H)
X=O, Ar=Ph	65 mp 95-7°	1710	288(19)	2.6 (AB of ABX,2H), 3.96 (d,1H), 5.0-5.2 (m,2H) 6.2-6.5 (m,2H), 6.9-7.4 (m,5H)
X=N-$\underset{\overset{\|}{O}}{C}$-OMe, Ar=Ph	49 c	1705,1715	260(384) 289(137)	2.0-3.0 (m,2H), 3.5 (b,1H), 3.8 (s,3H), 4.6-5.2 (m,2H), 6.1-6.4 (m,2H), 7.0-7.3(m,5H)
X=CH_2, Ar=p-Me-C_6H_4	72 mp 87-9°	1705	290(45)	2.1 (m,2H), 2.4 (bs,5H), 3.0 (m,2H), 3.7 (d,1H), 6.1-6.3 (m,2H), 7.0 (AB,4H)
X=O, Ar=P-Me-C_6H_4	68 mp 118-9°	1710	288(23)	2.6 (AB of ABX, 2H), 2.3 (s,3H), 3.9 (d,1H), 4.8-5.1 (m,2H), 6.1-6.4 (m,2H), 7.0 (AB,4H)
X=N-$\underset{\overset{\|}{O}}{C}$-OMe, Ar=P-Me-$C_6H_4$	47 c	1705,1715	260(390) 289(130)	2.1-3.0 (m,2H), 2.3 (s,3H), 3.4 (b,1H), 3.8 (s,3H), 4.6-5.0 (m,2H), 6.0-6.4 (m,2H), 6.9-7.2 (m,4H)

a. Neat for liquid sample and CCl_4 solution for solid. b. MeOH as solvent. c. viscous liquid.

V

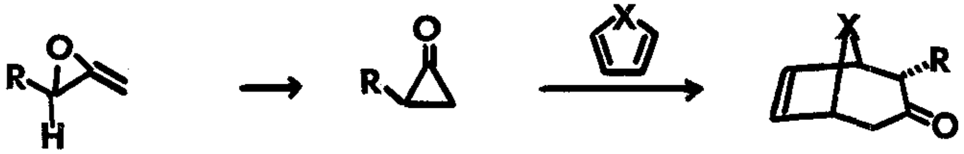
I a. R = Me
b. i-Pr
c. $n\text{-}C_{10}H_{21}$
d. cyclo-C_6C_{11}

Scheme 2

with the proposed structure. Compounds V polymerised after standing 3 days at room temperature.

No reactions were observed between the alkyl-substituted allene oxides and furan or N-carbomethoxypyrrole; only 3-chloro-2-ketones (III, Nu=Cl) were isolated from the reaction mixtures.

On the other hand, generation of aryl-substituted allene oxides (I, R=aryl) under identical conditions in the presence of cyclopentadiene gave exclusively the cycloadduct VI.[4] The formation



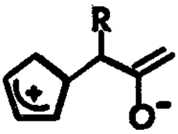
I R = C_6H_5-
or p-Me-C_6H_4

II X = CH_2, O, or $N\text{-}\underset{O}{\overset{\|}{C}}\text{-}OCH_3$ **VI**

of VI is in agreement with a prior rearrangement of the aryl-substituted allene oxides to the cyclopropanones II which are known to undergo cycloaddition with cyclopentadiene.[6]

Similar cycloadducts (VI, X = O, or $N-\overset{O}{\overset{\|}{C}}-OMe$) were formed when the aryl-substituted allene oxides were generated in the presence of furan or N-carbomethoxypyrrole.[6]

These results suggest that alkyl-substituted allene oxides are electrophilic. They could react with nucleophiles to give III.



VII

In the presence of cyclopentadiene, they could react to give the zwitterionic intermediate VII, thence to V. The regiospecific nature of the reaction (in all cases, 3-substituted ketones were obtained from I) is consistent with the proposed mechanism. For aryl-substituted allene oxides, however, their rearrangement to the cyclopropanones II is faster and the subsequent reactions are then those expected of cyclopropanones.[6]

An interesting conclusion of the present work is that the zwitterion species VII can be ruled out as the intermediate in the cycloaddition reactions between cyclopropanone and the cyclic 1,3-diene. Such a conclusion is consistent with a concerted mechanism for the cycloaddition.[7]

ACKNOWLEDGEMENT Financial support by the National Research Council of Canada, The Ministry of Education of Quebec and the Petroleum Research Fund, administered by the American Chemical Society is gratefully acknowledged.

REFERENCES AND FOOTNOTES

1 This paper is dedicated to the 60th birthday of Prof. R.B. Woodward.

2 Part III, B.S. Ong and T.H. Chan, Tetrahedron Letters, 3257 (1976).

3 For a review on the chemistry of allene oxides, see F.D. Greene, R.L. Camp, L. Kim, J.F. Pazos, D.B. Sclove and C.J. Wilberson, Proc. Internat. Congr. Pure Appl. Chem., 2, 325 (1971).

4 T.H. Chan, M.P. Li, W. Mychajlowskij and D.N. Harpp, Tetrahedron Letters, 3511 (1974).

5 T.H. Chan, B.S. Ong and W. Mychajlowskij, Tetrahedron Letters, 3253 (1976).

6 For a review on the chemistry of cyclopropanones, see N.J. Turro. Accounts Chem. Res., 2, 25 (1969).

7 R.B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry". Academic Press, 1970, p. 86.

Received, 10th September, 1977