

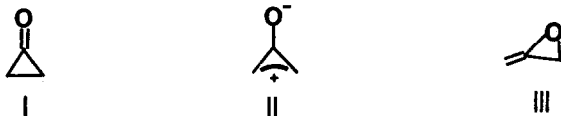
ENTRY INTO THE ALLENE OXIDE-CYCLOPROPANONE SYSTEM VIA VINYLSILANES

T.H. Chan*, Ming P. Li, W. Mychajlowskij and David N. Harpp

Department of Chemistry, McGill University
Montreal, Quebec, Canada

(Received in USA 10 July 1974; received in UK for publication 20 August 1974)

Cycloaddition of cyclopropanones (I)¹ or oxyallyls (II)^{2,3} with conjugated dienes represents a reaction of growing importance for the synthesis of seven-membered rings⁴. Tropones⁵, tropanes⁶ and various bicyclo-[3,2,1]-structures⁴ can be constructed by this method. The synthetic potential of the reaction appears to be limited only by the generation of cyclopropanones or oxyallyls.

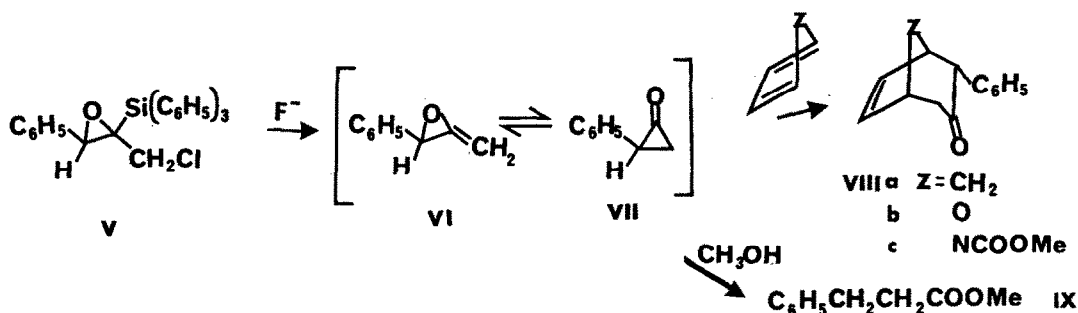


An interesting entry into the cyclopropanone structures is by way of allene oxides⁷ (III) which have so far been prepared by the epoxidation of allenes⁸. Recently, we reported a synthesis of allenes by the fluoride ion-promoted elimination of (α -chloromethyl)vinylsilane IV⁹. Since IV can be readily prepared by the reaction of vinylsilyl carbanions with carbonyl compounds^{9,10} followed by appropriate transformations⁹, it seemed to us that if the vinylsilanes IV could be converted to the epoxysilanes V, analogous elimination would offer a route to allene oxides under mild and selective conditions.

3-Chloro-2-triphenylsilyl-1-phenylpropene (IV, R=R'=C₆H₅, R''=H)^{9,11} mp 143-145° was epoxidized by *m*-chloroperbenzoic acid in refluxing chloroform for 5 days to give the epoxysilane V (R=R'=C₆H₅, R''=H) mp 101-103° in 75% yield¹²: nmr (CCl₄): 6.6-7.1 (m, 20H), 3.7 (s, 1H) and 3.1 (AB, J=10Hz, 2H) ppm. Its mass spectrum showed the molecular ion at m/e=426,428.



To demonstrate that the allene oxide-cyclopropanone system can indeed be generated, the fluoride ion-promoted elimination of V was carried out in the presence of various conjugated dienes. Thus, 204 mg (0.48 mmole) of V was stirred with 35 mg (0.60 mmole) of potassium fluoride in 5 ml of acetonitrile and 5 ml of cyclopentadiene at room temperature for 53 hrs in darkness under nitrogen. The reaction mixture was washed with water, dried and evaporated. The residue was separated by thin layer chromatography to give 121 mg of a mixture of triphenylfluorosilane and triphenylsilanol and 63 mg (66%) of compound VIIIa ($Z=CH_2$) mp 75-76¹². The infrared spectrum of VIIIa showed



carbonyl absorption at 1705 cm^{-1} (CCl_4). The nmr spectrum (CCl_4) showed the following absorptions: 6.9-7.3 (m, 5H), 6.1-6.3 (m, 2H), 3.75 (d, $J=3\text{Hz}$, 1H), 3.0 (m, 2H), 2.4 (m, 2H) and 2.05 (m, 2H) ppm. Its mass spectrum displayed a molecular ion at $m/e = 198$. The phenyl group is assigned to have the equatorial configuration¹³ on the basis of the coupling constant between the benzylic proton and the bridgehead proton (3Hz) as well as the low $n\rightarrow\pi^*$ band of the carbonyl group at 289 nm ($\epsilon=50$)¹³.

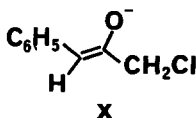
Similar generation of VI/VII in the presence of excess furan gave VIIIb ($Z=O$), mp 95-97¹². This compound showed carbonyl absorption at 1710 cm^{-1} (CCl_4); the assignment of structure with an equatorial phenyl group is consistent with its spectroscopic data¹³. Its nmr spectrum (CCl_4) showed 6.9-7.4 (m, 5H), 6.2-6.5 (m, 2H), 5.0-5.2 (m, 2H), 3.96 (d, $J=4\text{Hz}$, 1H), 2.6 (AB of ABX, $J_{AB}=15$, $J_{BX}=4\text{Hz}$, 2H) ppm. Its uv absorption featured λ_{max} at 259 nm ($\epsilon 220$) and 288 nm ($\epsilon 19$).

Cycloaddition of VI to N-carbomethoxy pyrrole also gave the corresponding

adduct VIIIc ($Z=NCO_2CH_3$) in 49% yield. The stereochemistry of the phenyl group has not been firmly established¹⁴ in this case. Its uv spectrum however displayed λ_{max} at 260 (ϵ 384) and 289 nm (ϵ 137).

The formation of cyclopropanone VII as the intermediate was demonstrated by trapping it with methanol¹⁵. When 202 mg of V was stirred with 38 mg of potassium fluoride in 1 ml of methanol at room temperature for 24 hr, in darkness under nitrogen, two compounds were obtained in quantitative yield. They were identified by comparison with authentic compounds to be methyl dihydrocinnamate (IX) and triphenylmethoxysilane. It is reasonable to account for the formation of ester IX by the opening of cyclopropanone VII with methanol¹⁵, a reaction which bears analogy to the Favorski reaction¹⁶. Triphenylmethoxysilane was derived from the methanolysis of triphenylfluoro-silane under the reaction conditions¹⁷.

We believe that the formation of cyclopropanone VII occurred via the allene oxide VI and not by an alternative possibility involving opening of the epoxysilane to the enolate X¹⁸. Two arguments can be put forth to support this



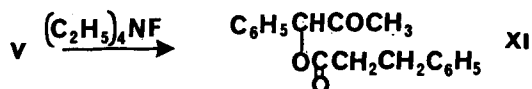
claim¹⁹: fluoride ion does not convert epoxysilanes to enolates under these conditions^{21,22} and β -elimination of chlorosilanes by fluoride ion is known to occur for a number of different substrates^{9,23,24}.

We are now actively extending the scope of this reaction.

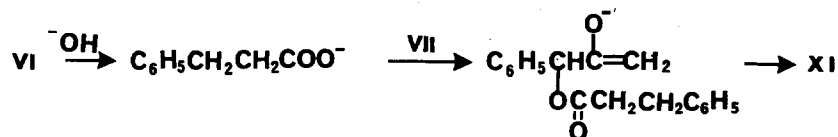
Acknowledgement: We are grateful to Ministère de l'Éducation, Gouvernement du Québec for financial support of this research.

1. N.J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).
2. R. Noyori, S. Makino and H. Takaya, *J. Amer. Chem. Soc.*, **93**, 1272 (1971).
3. A.E. Hill, G. Greenwood and H.M.R. Hoffmann, *ibid*, **95**, 1338 (1973).
4. For review, see H.M.R. Hoffmann, *Angew. Chem. Internat. Ed.*, **12**, 819 (1973).
5. R. Noyori, S. Makino and H. Takaya, *Tetrahedron Letters*, 1745 (1973).
6. R. Noyori, Y. Baba and Y. Hayakawa, *J. Amer. Chem. Soc.*, **96**, 3336 (1974).
7. J.K. Crandall, W.H. Machleden and S.A. Sojka, *J. Org. Chem.*, **33**, 1149 (1973) and references therein.

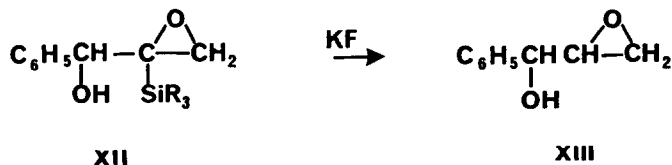
8. See for example, J.J. Havel, *J. Amer. Chem. Soc.*, **95**, 530 (1973).
9. T.H. Chan and W. Mychajlowskij, *Tetrahedron Letters*, 171 (1974).
10. B.T. Gröbel and D. Seebach, *Angew. Chem. Internat. Ed.*, **13**, 83 (1974). See also G. Stork and M.E. Jung, E. Colvin and Y. Noel, *J. Amer. Chem. Soc.* **96**, 3684 (1974).
11. The stereochemistry is tentatively assigned as Z. T.H. Chan and W. Mychajlowskij, unpublished results.
12. Correct elemental analysis was obtained for this compound.
13. See R.C. Cookson, M.J. Nye, G. Subrahmanyam, *J. Chem. Soc. (C)*, 473 (1967) for the basis of stereochemical assignment on similar compounds.
14. The coupling between benzylic proton and the bridgehead proton cannot be deduced because the signal overlaps with the methyl protons.
15. W.B. Hammond and N.J. Turro, *J. Amer. Chem. Soc.*, **88**, 2880 (1966).
16. N.J. Turro, R.B. Gagosian, C. Rappe and L. Knutsson, unpublished results, cited by N.J. Turro¹. For review of Favorski reaction, see A.S. Kende, *Organic Reactions*, **11**, 261 (1960).
17. C. Eaborn, *J. Chem. Soc.*, 2846 (1952).
18. G. Stork and E. Colvin, *J. Amer. Chem. Soc.*, **93**, 2080 (1971).
19. When V was treated with tetraethylammonium fluoride in dimethylsulfoxide, the major product obtained was identified to be XI by comparison with authentic sample synthesized by an independent route²⁰. A rationale for the formation of XI is to assume the presence of a trace of hydroxide in



the ammonium fluoride. The following mechanism can be proposed



20. Authentic XI was prepared from the reaction of sodium dihydrocinnamate with 1-chloro-1-phenyl-acetone in dimethylformamide.
21. Reaction of potassium fluoride with triphenylsilyloxirane in acetonitrile/methanol did not give acetaldehyde.
22. One particular example which has some bearing on this point is the reaction of XII with potassium fluoride in acetonitrile to give XIII. The mechanism of this reaction will be the subject of discussion in a future publication.



23. R.F. Cunico and E.M. Dexheimer, *J. Amer. Chem. Soc.*, **94**, 2868 (1972).
24. R.B. Miller and T. Reichenbach, *Tetrahedron Letters*, 543 (1974).