Tetrahedron Letters No. 39, pp 3383 - 3386, 1975. Pergamon Press. Printed in Great Britain.

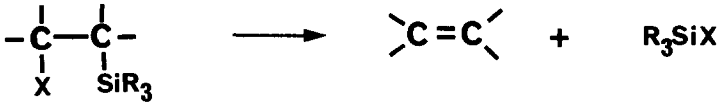
# ENTRY INTO THE CYCLOPROPENE SYSTEM VIA VINYLSILANES

T.H. CHAN* and D. MASSUDA

Department of Chemistry
McGill University,
Montreal, Quebec, Canada

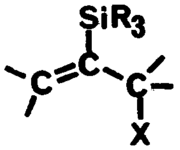
(Received in USA 24 June 1975; received in UK for publication 22 August 1975)

The facile elimination of β-functionalised silanes according to equation 1 ($R=CH_3$ or $C_6H_5$ ; $X=O^-$, Cl or other good leaving group) has now been developed into a general method of alkene synthesis[1-3].

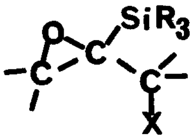


(1)

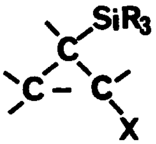
However, when the alkene to be generated is part of a strained system, the precursor β-substituted silicon compound (e.g. I, II or III) does not eliminate with ease. In the case of I and II, we found that the elimination can be promoted by fluoride ion under rather mild conditions to give allenes[4] and allene oxides[5] respectively. In the present communication, we wish to report the generation of cyclopropenes by the fluoride-ion promoted elimination of III (equation 2)[6].



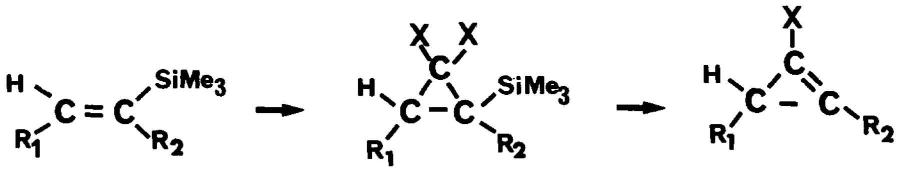
I



II



III



IV V VI (2)

a: $R_1=R_2=H$, X=Cl ; b: $R_1=R_2=H$, X=Br ; c: $R_1R_2=(CH_2)_4$, X=Cl

*1-Chlorocyclopropene (VIa)* 1,1-Dichloro-2-trimethylsilyl-cyclopropane (Va) was prepared from trimethylvinylsilane (IVa) by the method of Seyferth[6,7]. The preparation of 1-chlorocyclopropene was carried out as follows: a slow stream of dried nitrogen was passed through a mixture of Va (0.70g) and cesium fluoride (1.73g) in 7ml of diglyme. The mixture was heated at 80° and the volatile products were collected in a cold trap (-70°) containing carbon tetrachloride. The nmr of the distillate showed, in addition to the peaks of trimethylfluorosilane, a one proton triplet at δ 6.7 (J=2Hz) and a two proton doublet at δ 1.6 assigned to 1-chlorocyclopropene[8].

The formation of 1-chlorocyclopropene was also confirmed by carrying out the reaction in the presence of 1,3-diphenyl*iso*benzofuran. The adduct VIIa, m.p. 104-106° was isolated in 54% yield[9,10].

*1-Bromocyclopropene (VIb)* Similar reaction of 1,1-dibromo-2-trimethylsilylcyclopropane (Vb) with potassium fluoride in diglyme showed the formation of trimethylfluorosilane. Nmr of the distillate in cold-trap revealed the formation of 1-bromocyclopropene (VIb) as evidenced from the presence of doublet at δ 1.6 and triplet at δ 7.2 (J=2Hz). Attempt to further purity VIb was not successful however, presumably because of its greater instability. Its generation was also demonstrated by trapping it with 1,3-diphenyl*iso*benzofuran as well as with furan. The adduct VIIb, m.p. 107-109° was obtained in 77% yield[9,10]. The furan adduct of 1-bromocyclopropene was a mixture of *endo* and *exo* isomers (ratio 2:3 by nmr) which could be separated by thin layer chromatography.[11]

*7-Chlorobicyclo [4,1,0] -hept-6-ene[12]* Reaction of phenyl (bromodichloromethyl) mercury[7] with 1-trimethylsilylcyclohexene[13](IVc) in dried benzene for 4 hrs at 80° gave, on work-up, 7,7-dichloro-1-trimethylsilylbicyclo [4,1,0] heptane (Vc) b.p. 68°/0.1mm in 77% yield[7b]. When a mixture of Vc (0.29g), cesium fluoride (0.22g) and 1,3-diphenyl*iso*benzofuran (0.16g) in 10ml of dried diglyme was stirred at room temperature, the yellow color of 1,3-phenyl*iso*benzofuran was discharged after 24 hrs. On work-up and purification by TLC, there was obtained 55mg of adduct VIIc, m.p. 166-168°[9,10]. The mass spectrum showed the molecular ion at m/e 398.400. The nmr ($CDCl_3$) showed δ 2.8 (d of d, 1H), 1.2-2.2 (m, 9H) and 7.2-7.8 (m, 14H).

Fluoride-ion promoted elimination of β-halosilanes thus appears to be a powerful method to generate strained alkenes. We are actively extending the scope of this reaction.

## References and footnotes.

(1) D.J. Peterson, J. Org. Chem. 33, 780 (1968).
T.H. Chan, A.E. Chang and E. Vinokur, Tetrahedron Letters, 1137 (1970).

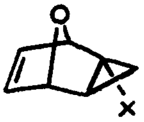
(2) T.H. Chan and E. Chang, J. Org. Chem. 39, 3264 (1974) and references cited therein.

(3) P.F. Hudrlik and D. Peterson, Tetrahedron Letters, 1133 (1974); J. Amer. Chem. Soc. 97, 1464 (1975).

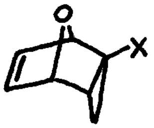
(4) T.H. Chan and W. Mychajlowskij, Tetrahedron Letters, 171 (1974).

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

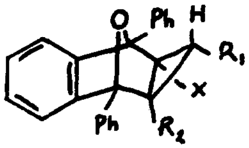
### Nmr data of various adducts (in $CDCl_3$)*



VIII



IX



VII

| | | |
|---|---|---|
| VIII | X=Cl | δ 6,8 (broad s, 2H), 4.9 (broad s, 1H), 4.7 (broad s, 1H), 2.2 (broad s, 1H), 1.5 (broad, 2H) |
| | X=Br | 6.8 (broad s, 2H), 4.95 (broad s, 1H), 4.75 (broad s, 1H) 2.2 (d, J=2Hz, 1H), 1.55 (broad, 2H) |
| IX[†] | X=Cl | 6.4 (d of AB, $J_{AB}$=6Hz, 2H), 5.2 (broad, 1H), 5.0 (t, 1H), 1.4-2.3 (m, 3H) |
| | X=Br | 6.4 (d of AB, $J_{AB}$=6Hz, 2H), 5.3 (broad, 1H), 5.15 (broad, 1H), 1.6-2.4 (m, 3H). |
| VIIa | X=Cl, $R_1=R_2=H$ | 7.0-7.8 (m, 14H), 2.35 (d of d, 1H) 1.7-2.0 (m, 2H). |
| b | X=Br $R_1=R_2=H$ | 7.1-8.0 (m, 14H), 2.45 (d of d, 1H), 1.7-2.0 (m, 2H). |

---

[*] Nmr in agreement with those reported for Diels-Alder adducts of other cyclopropenes. See R.W. La Rochelle and B.M. Trost, J. Chem. Soc. Chem. Commun. 1353 (1970), and reference (8).

[†] unstable on standing

(6) Similar elimination of dihalocarbene adducts of vinylsilanes under acidic or basic conditions was attempted and acetylenic products were observed. D. Seyferth and T.F. Jula, J. Organomet. Chem. 14, 109 (1968). See also reference 7 (b).

(7) (a) D. Seyferth, J.M. Burlitch, R.J. Minasz, J.Y. Mui, H.D. Simmons, A.J.H. Treiber and S.R. Dowd, J. Amer. Chem. Soc. 87, 4259 (1965).
(b) V. can also be prepared by the method of phase-transfer catalysis, R.B. Miller, Syn. Commun. 4, 341 (1974).

(8) 1-Chlorocyclopropene was first prepared by R. Breslow, G. Ryan and J.T. Groves, J. Amer. Chem. Soc. 92, 988 (1970) by treatment of tetrachlorocyclopropene with trinbutyltinhydride in 5-10% yield.

(9) Tentatively assigned to have the exo configuration. Compare with reference 8.

(10) Structures are consistent with spectroscopic and/or elemental analysis.

(11) Some decomposition occured during chromatography.

(12) Bicyclo [4.1.0] -hept-6-ene was postulated as the intermediate in the dehydrohalogenation of 7-bromobicyclo [4.1.0] heptane by strong base to give bicyclo [4.1.0] hept-2-ene. C.L. Osborn, T.C. Shields, B.A. Shoulders, J.F. Krause, H.V. Cortez and P.D. Gardner, J. Amer. Chem. Soc. 87, 3158 (1965).

(13) A.D. Petrov, V.F. Mironov, and V.G. Glinkhovtsev, Chem. Abstr., 52, 3668 (1958). For more experimental details, see V.F. Mironov, N.G. Maksimova and V.V. Nepomniva, Bull. Acad. Sc. U.S.S.R., 313 (1967).

Acknowledgement

We are grateful to the National Research Council of Canada for financial support of this research.