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REACTION OF EPOXIDES WITH PHOSPHINE SELENIDES AND TRIFLUOROACETIC ACID. EVIDENCE FOR THE FORMATION OF EPISELENIDES

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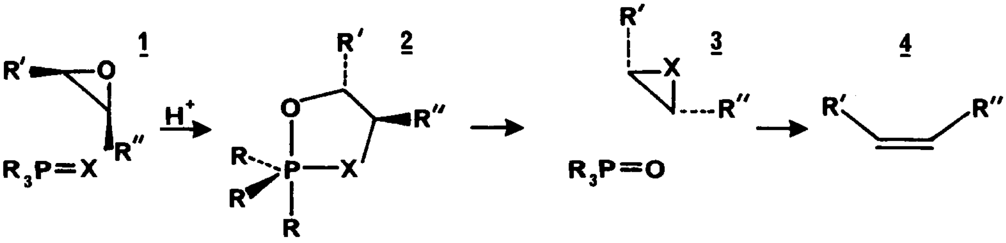
Episelenides[1] (3, X=Se) have been postulated as the intermediate in a number of reactions[2-5]. However, their existence has only been demonstrated in the gas phase by spectroscopic means[3,4] as a transient species. Recently we described the reaction of epoxides with phosphine sulfides to produce episulfides[6,7] ($1 \rightarrow 3$, X=S) under extremely mild conditions. We have been concerned with generation of episelenides (3, X=Se) by analogous reactions. The recent report by Clive and Denyer[5] describing conversion of epoxides to olefins by use of triphenylphosphine selenide prompts us to report some of our findings.



In agreement with Clive and Denyer[5], we observe deoxygenation of epoxides to olefins when using triphenylphosphine selenide and trifluoroacetic acid. In these reactions, selenium[8] was observed to deposit out of the reaction mixture within minutes. The suggestion was made that the olefin must arise by extrusion of selenium from the corresponding episelenide ($3 \rightarrow 4$), X=Se).

We wish to report here the reaction of epoxides with tri-n-butylphosphine selenide and trifluoroacetic acid and supply evidence to indicate the formation of episelenides.

(1) Reaction with cyclohexene oxide.

To an equimolar solution of cyclohexene oxide and tri-n-butylphosphine selenide in benzene at room temperature, one mole equivalent of trifluoroacetic acid in benzene solution was added with stirring. The reaction mixture remained clear with no deposition of selenium. VPC indicated the loss of epoxide as well as the conversion of tri-n-butylphosphine selenide to tri-n-butylphosphine oxide. The pmr spectrum of the reaction mixture showed the formation of a new multiplet at 3.6 p.p.m. On warming the reaction mixture, the signal at 3.6 p.p.m. disappeared to be replaced by an olefinic signal at 6.1 p.p.m. and selenium deposited out. Cyclohexene was identified as the olefinic product. We assign the pmr signal at 3.6 p.p.m. to be the methine protons of cyclohexene selenide[9]. Attempted column chromatography on silica gel of the reaction mixture led to decomposition as evidenced by the appearance of selenium.

The analogous reaction with propylene oxide as substrate gave similar results.

(2) Reaction with 1-octene oxide.

Reaction of 1-octene oxide and tri-n-butylphosphine selenide with trifluoroacetic acid in benzene was carried out in the usual manner. The reaction mixture could however be rapidly chromatographed over silica gel with benzene as eluent without decomposition. Fractions containing only episelenide could be obtained as demonstrated by the following experiments:

(a) VPC indicated the absence of 1-octene oxide, tri-n-butylphosphine selenide, tri-n-butylphosphine oxide and trifluoroacetic acid.

(b) Upon heating or concentrating the solution, selenium was observed together with the formation of 1-octene.

(c) Addition of triphenylphosphine to the solution gave triphenylphosphine selenide and 1-octene. This observation is consistent with the expected chemical behavior of episelenides in analogy with episulfides which are desulfurized by triphenylphosphine[10].

In addition, solutions of 1-octene selenide in 1-chlorobutane could be obtained by using 1-chlorobutane as reaction solvent and column eluent. This allowed the uv spectrum of 1-octene selenide to be determined and was found to have λmax at 237 nm. This is to be compared with the observation of Callear and Tyerman[11] who reported that ethylene selenide itself absorbs strongly in the gas phase at 226 nm. The absorption at 237 nm diminished as decomposition of the reaction mixture occurred.

Attempted concentration of these solutions, even at low temperature (-40°) led to decomposition with the formation of selenium. In this connection, it may be noted that the decomposition process may be bimolecular[4].

(3) Reaction with stilbene oxide.

The reaction of <u>trans</u>-stilbene oxide with tri-n-butylphosphine selenide and CF_3CO_2H was carried out in $CDCl_3$ at room temperature. Production of phosphine oxide ceased after 2 hours. The methine proton signal at 3.85 p.p.m. of the starting oxide was replaced by a new nmr signal at 5.1 p.p.m. which was assigned as the methine protons of stilbene selenide. In 2 days time, the signal at 5.1 p.p.m. disappeared completely concommittant with the formation of <u>trans</u>-stilbene (>98% pure). If it is assumed that <u>trans</u>-stilbene oxide is converted stereospecifically to <u>trans</u>-stilbene selenide[12], then the subsequent extrusion of Se must occur without loss of stereochemical integrity. Similarly <u>cis</u>-stilbene oxide gave only <u>cis</u>-stilbene.

References and Footnotes

(1) In the IUPAC nomenclature, these are known as seleniranes.

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(3) A.B. Callear and W.J.R. Tyerman, Trans. Faraday Soc., 62,2760 (1966); and references cited therein.

(4) W.J.R. Tyerman, W.B. O'Callaghan, P. Kebarle, O.P. Strausz, and H.E. Gunning, J. Amer. Chem. Soc., 88, 4277 (1966).

(5) D.L.J. Clive and C.V. Denyer, Chem. Commun., 253 (1973).

(6) T.H. Chan and J.R. Finkenbine, J. Amer. Chem. Soc., 94, 2880 (1972).

(7) T.H. Chan and J.R. Finkenbine, Int. J. Sulfur Chem., 8, 45 (1973).

(8) Selenium usually deposited in the red form from these reactions.

(9) The ring protons of episulfides resonate at a lower field than ring protons of epoxides. In addition, it was suggested that "the effect of selenium compared to sulfur and oxygen is deshielding when the heteroatom is part of an unsaturated system". See U. Svanholm, Ann. N.Y. Acad. Sci., 192, 124 (1972).

(10) D.B. Denny and M.J. Boskin, J. Amer. Chem. Soc., 82, 4736 (1960).

(11) A.B. Callear and W.J.R. Tyerman, Trans. Faraday Soc., 62, 371 (1966).

(12) The corresponding epoxide to episulfide conversion is stereospecific[6,7].

Acknowledgement

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