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REGIOSPECIFIC SYNTHESIS OF αβ-UNSATURATED EPOXIDES (1)

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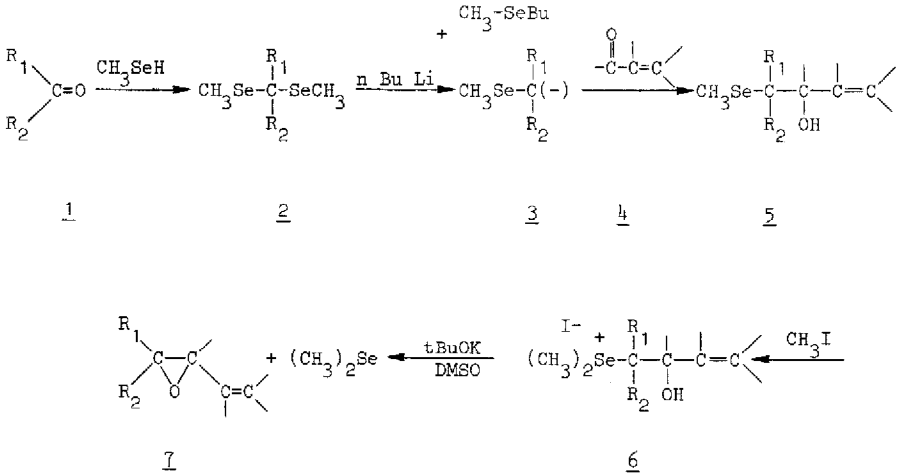
Until now the most powerful [C-C] connective (2) route to an αβ-unsaturated epoxide was the alkylidene transfer from a sulfur ylid (3) to an αβ-unsaturated aldehyde or ketone. This method is of wide application only in the methylene case; there is no report of mono alkylidene transfer and it was shown that isopropylidene diphenyl sulfurane reacts specifically on the carbon-carbon double bond of cyclohexenone (4), leading to a cyclopropane, instead of an epoxide.

Recently we described (5,6) a new general synthon for [C-C] connective synthesis of epoxides, using α-seleno carbanions 3 as one of the two building blocks. We report here an extension of our previous work (5) for the regiospecific synthesis of αβ-unsaturated epoxides 7 (Scheme I)

SCHEME I

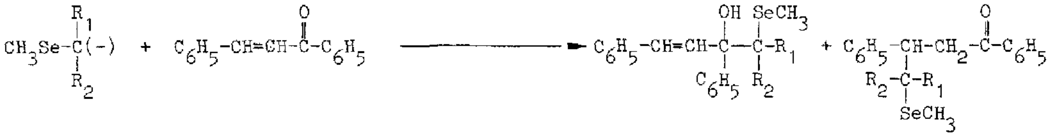


This synthon, which allows the synthesis even of tetrasubstituted epoxides, takes advantage of the easy formation of α-seleno carbanions from carbonyl compounds 1 [$1 \rightarrow 2$, selenol, H^+, ∿ 80 % yield] [$2 \rightarrow 3$ n-butyllithium, THF - 78°C, 1h] *and their high propensity to react on the* *carbon oxygen bond of an αβ-unsaturated aldehyde or ketone* [THF, - 78°C, 2h; - 25°C, 1h] *leading specifically to an αβ-unsaturated α'-seleno alcohol 5 in good yield (Table I).*

Seleno alcohol 5 is easily separated from by-products (7) and in some cases, eg. 7g, the separation of the two diastereoisomers is readily performed by preparative thick layer chromatography on silicagel (PLC). The seleno alcohol 5 is quantitatively transformed (8) to the corresponding selenonium salt 6 [CH_3I, 2 ∿ 4h, 25°C] , which is in turn transformed to the desired epoxide 7 in good yield [tBuOK in DMSO, 25°C, 1h]. In our hands these epoxides are quite labile and they are destroyed on silicagel PLC even when buffered (pH 7); they are generally obtained in good analytical purity without any purification. The dimethyl selenide formed during this reaction is highly volatile.

Of the different carbonyl compounds used, chalcone is the only case where α-seleno carbanions react to a large extent on the carbon-carbon double bond. This tendency of the 1-4 (9,10) versus the 1-2 (3b,3c) addition is well documented (Scheme II).

SCHEME II



R_1,R_2 = H	35 %	35 %
R_1,R_2 = CH_3	21 %	47 %

α-phenyl seleno carbanions react as in the methyl seleno case, leading to the corresponding β-hydroxy phenyl selenides (11), but as already mentioned (5) in the case of saturated carbonyl compounds, we were unable to synthesize β-hydroxy selenonium salts when R_1,R_2 = alkyl, and rearranged products are formed (12) (Scheme III).

SCHEME III

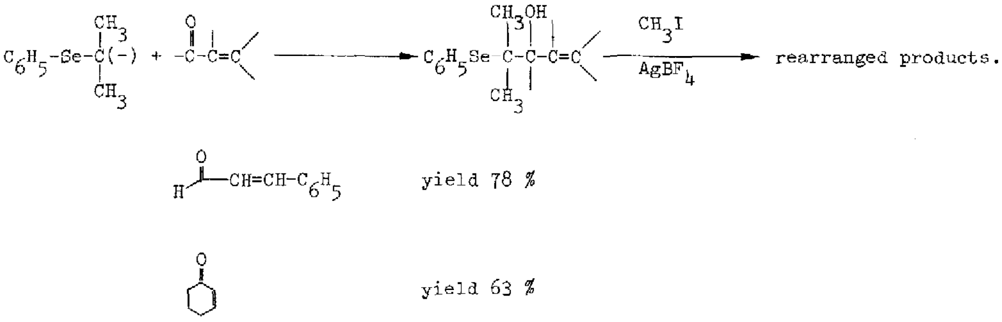
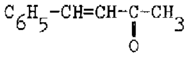
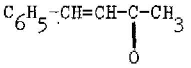
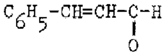
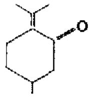
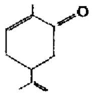
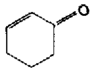
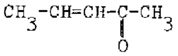
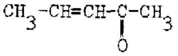


TABLE I

According to Scheme I

R_1	R_2	4	5[*][13]	7[**][13]	
H	H	 $C_6H_5-CH=CH-\underset{\underset{O}{\|}}{C}-CH_3$	87	75	a
CH_3	CH_3	 $C_6H_5-CH=CH-\underset{\underset{O}{\|}}{C}-CH_3$	80	89	b
H	CH_3	 $C_6H_5-CH=CH-\underset{\underset{O}{\|}}{C}-H$	90	94	c
H	CH_3		65	98	d
CH_3	CH_3		45	75	e
CH_3	CH_3		55	95	f
H	$CH_3(CH_2)_5$	 $CH_3-CH=CH-\underset{\underset{O}{\|}}{C}-CH_3$	65	40(80)	g
CH_3	CH_3	 $CH_3-CH=CH-\underset{\underset{O}{\|}}{C}-CH_3$	45	50	h

[*] *Yield of purified product*

[**] *Yield of analytically pure product (salt 6 washed with ether, without any purification at the epoxide stage), based on 5.*

() *Based on reacted 5.*

References

1) A preliminary report of this work was presented by the authors at the 25th I.U.P.A.C.Congres held in Jerusalem (Israel) Juli 1975

2) For definition of this term see E.J. Corey, Pure and Appl. Chemistry 14, 19 (1967)

3a) A.W. Johnson, Ylid Chemistry, Academic Press, New York (1966)

3b) E.J. Corey and M. Chaykovsky, J. Amer. Chem. Soc., 87, 1353 (1965)

3c) For selenium ylid case : W. Dumont, P. Bayet and A. Krief, Angew. Chem., Int. Ed. 13, 309 (1974)

4a) E.J. Corey and M. Jautelat, J. Amer. Chem. Soc., 89, 3913 (1967)

4b) For ylids derived from sulfoximines see C.R. Johnson, R.A. Kirchhoff, R.J. Reischer and G.F. Katekar, J. Amer. Chem. Soc. 95, 4287 (1973)

5) W. Dumont and A. Krief, Angew. Chem.Int. Ed. 14, 350 (1975)

6) D. Van Ende, W. Dumont and A. Krief, Angew. Chem. Int. Ed. 14, 700 (1975)

7) Methyl butyl selenide is easily removed by evaporation (0.1 mm Hg, 25°C)

8) The salt is washed with ether and sometimes some unreacted starting material is separated

9) A. Merz and G. Märkl, Angew. Chem. Int. Ed. 12, 845 (1973)

10) M.S. Kharasch and O. Reinmuth, Grignard Reactions of Nonmetallic Substances, Prentice-Hall, (1954)

11) αβ-unsaturated α'seleno alcohols 5 are easily transformed to αβ,α'β'-unsaturated alcohols in high yield : unpublished results from our laboratory

12) Work is in progress to determine the structure of these compounds

13) Spectroscopic data (IR, NMR, Mass Spectra) are in accord with the proposed structures.