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ALLENE OXIDE. V - OXIDATION OF β-ALLENIC ALCOHOLS BEARING A TRIMETHYLSILYL GROUP ON THE ALLENIC MOIETY. PROBE OF A CONCERTED MECHANISM IN THE δ-LACTONES FORMATION.

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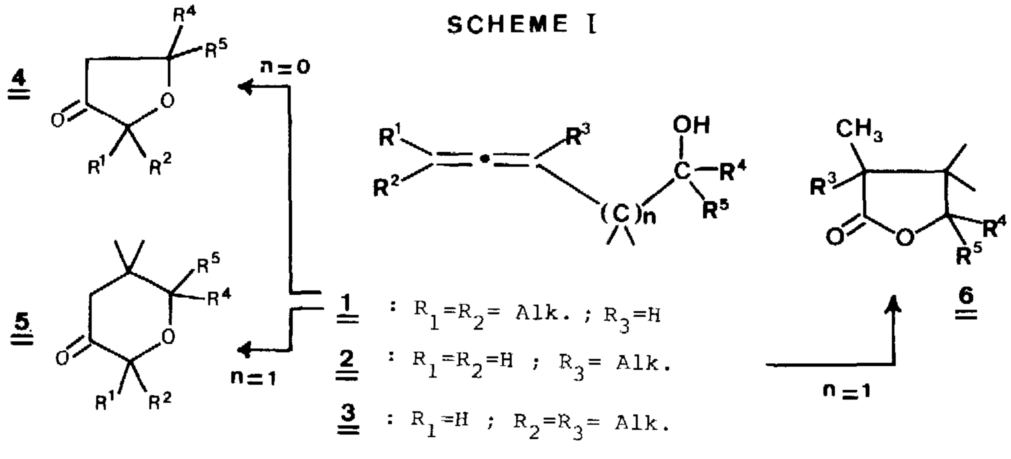
Summary : *β-allenic alcohols substituted by a trimethylsilyl group at the -1 or -3 position respectively give rise to γ or δ-lactones. In the last case, a concerted mechanism is involved.*

We previously reported (1) that two different pathways are involved in the α and β-allenic alcohols oxidation reaction, depending on the substituent position of the allenic moiety.

-1,1 disubstituted alcohols 1 submitted to H_2O_2/ØCN system (1a) exclusively produce tetrahydrofuranones 4 (n = 0) or tetrahydropyranones 5 (n = 1), while alcohols 2 (R_1 = R_2 = H) result in quantitative γ-lactones formation (1b) (Scheme I).



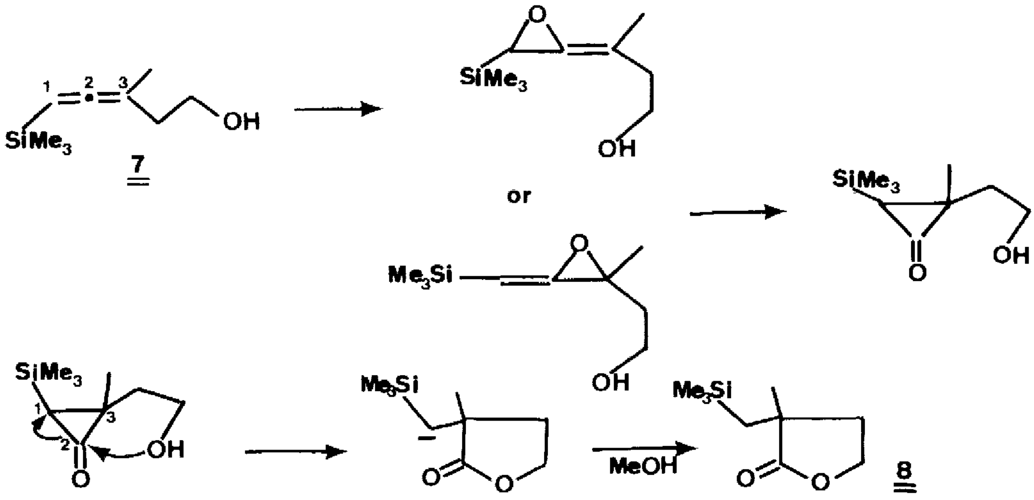
SCHEME I

In this last case, we proposed that the cyclopropanone issued from a preliminary isomerisation of the allene oxyde could be trapped in an intramolecular process to produce γ-lactones.

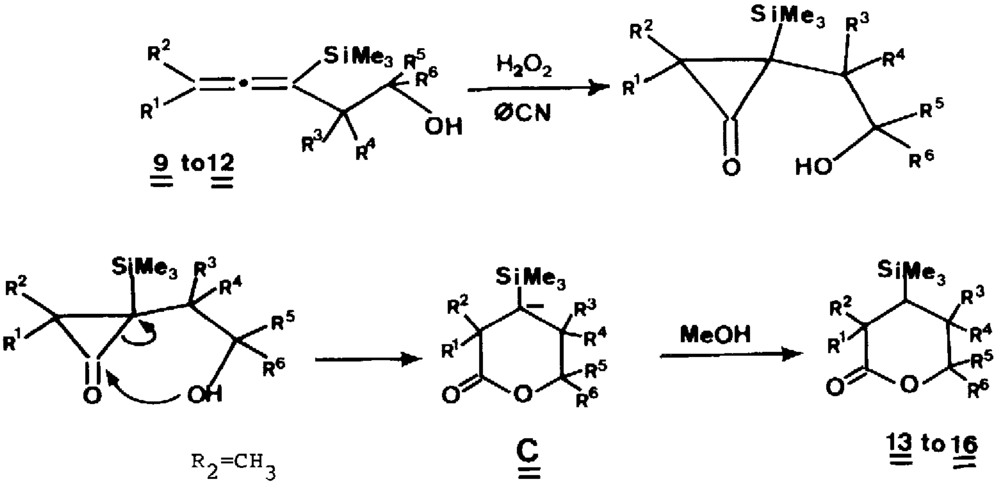
In exactly analogous reaction conditions, alcohols 3 (n = 1) never were converted in the corresponding tetrahydropyranone 5 or γ-lactone 6. (They were recovered after reaction).

This prompted us to study the reactivity of β-allenic alcohols substituted at the -1 or -3 position by a trimethylsilyl group.

Because of the negative charge localized on the carbon bearing the silicon atom (2), one can expect that the ability of both the epoxidation and lactonization steps will be enhanced.



SCHEME II



9 , 13 : $R_2=CH_3$ $R_1=R_5=R_6=R_3=R_4=H$

10 , 14 : $R_1=Et$, $R_2=CH_3$ $R_3=R_4=R_5=R_6=H$

11 , 15 : $R_1=H$ $R_2=R_3=R_4=CH_3$ $R_5=R_6=H$

12 , 16 : $R_1=Et$, $R_2=R_5=R_6=CH_3$ $R_3=R_4=H$

SCHEME III

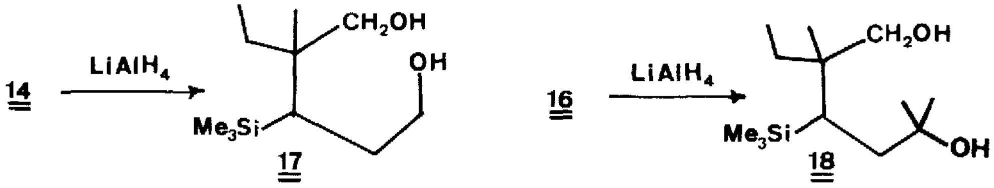
If our hypothesis is correct, alcohol 7 (3) must give rise after oxydation to a silylated γ-lactone 8 (Scheme II), while silylated δ-lactones 13 to 16 should be obtained by oxydation of alcohols 9 to 12 (Scheme III).

This was completly confirmed by the resulting data.

- The γ-lactone 8 is obtained in 92 % yield by oxydation of the alcohol 7.

- The δ-lactones 13 to 16 were the only products isolated in a quantitative yield after oxidation of the alcohols 9 to 12.

In order to make the assignments of the δ-lactones structures, 14 and 16 were reduced by LAH respectively in the diols 17 and 18 (Scheme IV).



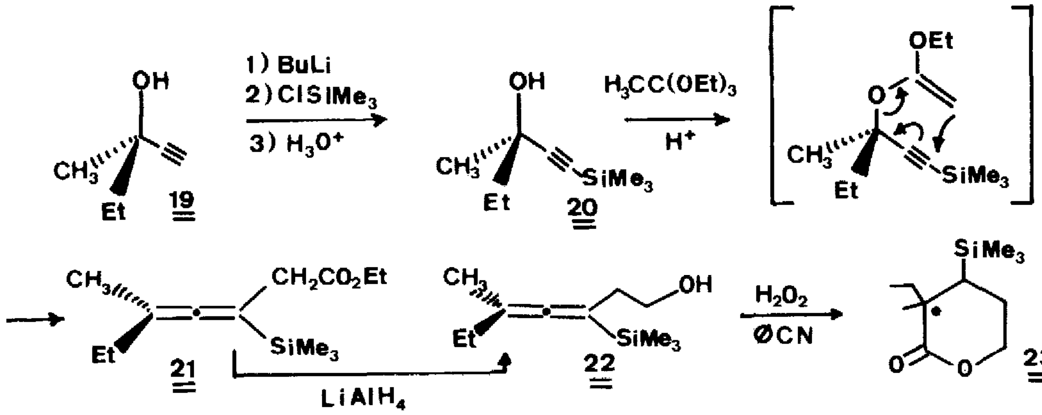
SCHEME IV

Each of the lactones 13 to 16 consists of a mixture of two diastereoisomeric forms issued by a protonation of the carbanion C. (Scheme III)

Probe of a concerted mechanism in the δ-lactone formation

In order to determine the δ-lactone mechanism formation, the chiral β-allenic alcohol 22 was submitted to the oxydation reaction.

22 was prepared from the optically active propargylic alcohol 19 (R (-) $[\alpha]_D^{20}$ = -2,54 (neat)) according to the subsequent reactions shown in Scheme V.



SCHEME V

The transformation 19 → 20 do not produce any modification of the asymmetric carbon configuration, while a 35 % racemization of the alcohol 20 occurs during the Claisen step (starting alcohol 20 : $[\alpha]_D^{20} = + 4,82$ (dioxane), recovered alcohol 20 after the Claisen step : $[\alpha]_D^{20} = + 3,16$, C = 0,2 g/ml).

Stereochemistry of the Claisen reaction is well known (4) so, configuration S can be deduced for the ester 21 and the alcohol 22.

Oxidation of 22 gives rise to a mixture of two diastereoisomeric lactones, one of which 23 was isolated in a pure state by GLC; 23, whose absolute configuration has not yet been established indicates an optical activity $[\alpha]_D^{20} = 21°,84$, C = 0,16 g/ml (dioxane).

This result involves a concerted mechanism during the ring opening of the cyclopropanone intermediate.

In conclusion, by the utilization of trimethylsilyl β-allenic alcohols derivatives, this work enhances the impact of both the nature and position of substituent groups during the epoxidation reaction process.

Either tetrahydropyranones (1a), γ-lactones (1b) or δ-lactones can be obtained in very high yield, depending on the substitution of the β-allenic alcohol.

REFERENCES AND NOTES

For earlier works, see reference 1.

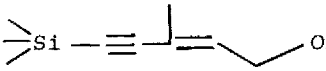
1 - a) M. BERTRAND, J.P. DULCERE, G. GIL, J. GRIMALDI and P. SYLVESTRE-PANTHET, Tetrahedron Letters, 1507, (1976).

b) M. BERTRAND, J.P. DULCERE, G. GIL, J. GRIMALDI and P. SYLVESTRE-PANTHET, Tetrahedron Letters, 3305, (1976).

c) M. BERTRAND, J.P. DULCERE and G. GIL, Tetrahedron Letters, 3807, (1977).

d) M. BERTRAND, J.P. DULCERE and G. GIL, Tetrahedron Letters, 4403, (1977).

2 - E. EHLINGER and P. MAGNUS, J. Chem. Soc., Chem. Comm., 421, (1979), and reference therein.

3 - Reduction by LAH of the silylated alcohol  gave the allenic alcohol 7 in a 73 % Yield.

4 - R.B. WOODWARD and R. HOFFMANN, The conservation of orbital symmetry, p. 126, Verlag Chemie, (1970).

All the spectroscopic values (I.R., U.V., Mass and N.M.R.) are consistent with the assigned structures.

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