

Cyclopentenols from γ -Allenic Aldehydes

By MARCEL BERTRAND, MARIE-LOUISE ROUMESTANT, and PIERRE SYLVESTRE-PANTHET

(Laboratoire no. 109 associé au C.N.R.S., rue Henri Poincaré, 13397 Marseille, Cedex 4, France)

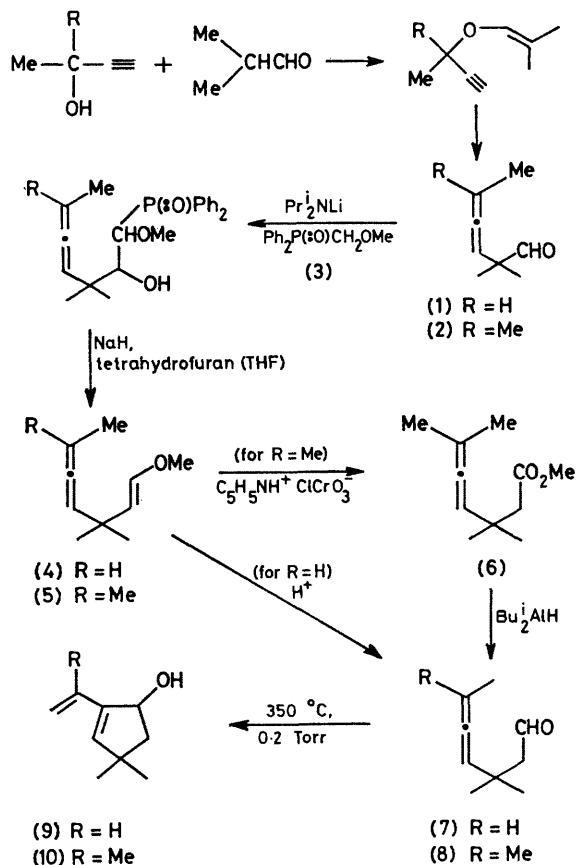
Summary Cyclopentenols can be easily obtained from γ -allenic aldehydes by intramolecular hetero-ene synthesis.

A RECENT review by Oppolzer and Snieckus¹ demonstrated the importance and the preparative power of the intramolecular ene-reaction. We report here preliminary

results obtained in the cyclisation of γ -allenic aldehydes. These compounds were prepared by homologation of the easily accessible (Scheme 1) β -allenic aldehydes² (**1**) and (**2**) via a Claisen rearrangement.

β -Allenic aldehydes may be converted into the homologous γ -aldehydes via vinyl ether formation by the Horner-Wittig reaction,³ and reaction of (**1**) and (**2**) with

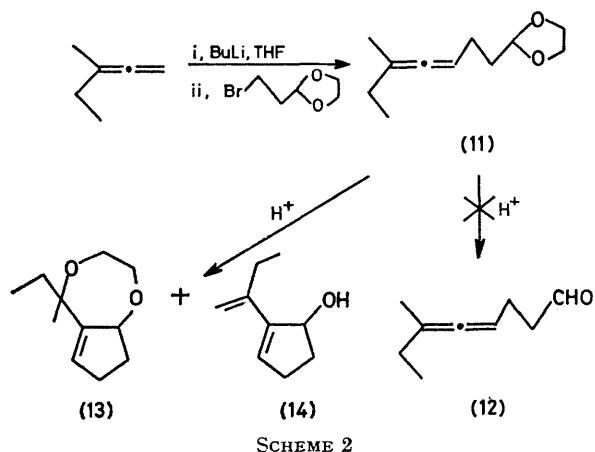
the phosphine oxide (3) gave the vinyl ether (4) and (5) (Scheme 1). [Attempted Wittig reactions of (1) and (2)



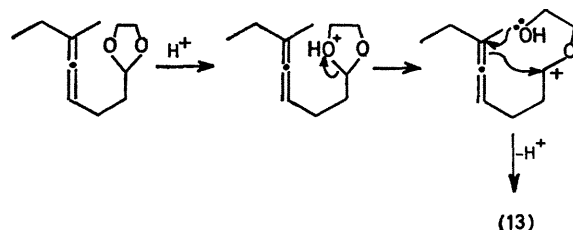
SCHEME 1

with the phosphonium ylide $\text{Ph}_3\text{P}^+\text{-CHOMe}$ were unsuccessful.] Treatment of (4) with acid gave the γ -allenic aldehyde (7) quantitatively [85% overall yield from (1)]; however, treatment of the ether (5) with acid gave a mixture of products. The aldehyde (8) was obtained⁴ [76% overall yield from (2)] by oxidation of (5) with pyridinium chlorochromate to give (6) followed by treatment of (6) with

di-isobutylaluminium hydride. Thermal cyclization of (7) and (8) gave the cyclopentenols (9) and (10), respectively, and (10) is also obtained quantitatively by chromatography of (8) on SiO_2 .



Attempted preparation of the γ -allenic aldehyde (12) by the sequence in Scheme 2 gave instead a mixture of the cyclopentenol (14) and the cyclopentadioxepan (13), whose formation can be rationalized by the cationic cyclization in Scheme 3.



SCHEME 3

We are now preparing an optically active γ -allenic aldehyde to see if the cyclisation would occur with transfer of chirality; if this were the case, an optically active cyclopentenol would be obtained from a chiral aldehyde.

(Received, 22nd February 1979; Com. 178.)

¹ W. Oppolzer and V. Snieckus, *Angew. Chem. Internat. Edn.*, 1978, 476.

² R. S. Bly and S. U. Kooek, *J. Amer. Chem. Soc.*, 1969, 91, 3292.

³ C. Earnshaw, C. J. Wallis, and S. Warren, *J.C.S. Chem. Comm.*, 1977, 314.

⁴ G. Paincatelli, A. Scettri, and M. D. Auria, *Tetrahedron Letters*, 1977, 3483.