

A SIMPLE AND AN EFFECTIVE ROUTE TO CARYOPHYLLENE SYSTEM -  
SYNTHESIS OF DL-ISOCARYOPHYLLENE

A. Kumar, A. Singh and D. Devaprabhakara\*

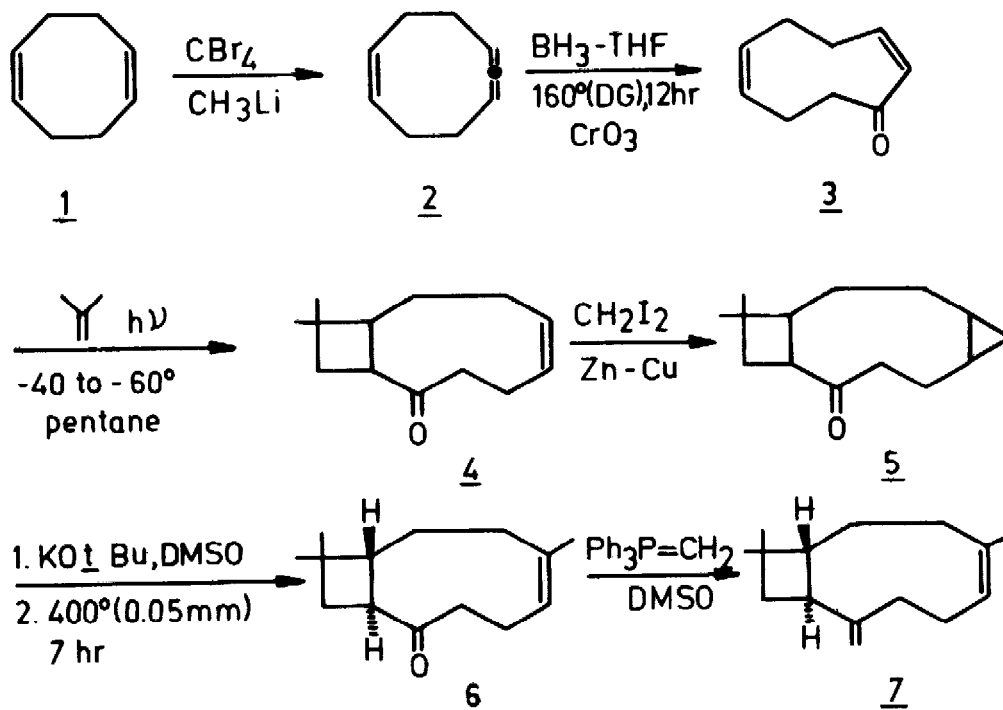
Department of Chemistry, Indian Institute of Technology,  
Kanpur 208016, India

(Received in UK 22 April 1976; accepted for publication 10 May 1976)

Our interest in the chemistry of a nine-membered ring<sup>1</sup> prompted us to devise and develop an efficient route to caryophyllene system from readily available starting material as the known methods of synthesizing caryophyllene sesquiterpenes involve multi-step sequences.<sup>2,3</sup> We describe herein a new and an improved 7-step procedure for the synthesis of dl-isocaryophyllene (7) from cis,cis-1,5-cyclooctadiene (1) as illustrated in the SCHEME.

The basic approach involves the synthesis of a nine-membered ring precursor, cis,cis-2,6-cyclononadienone (3) which can be converted into dl-isocaryophyllene (7) using well known transformations. One-step synthesis of allene provided 1,2,6-cyclononatriene (2)<sup>4</sup> from 1. Monohydroboration-isomerization-oxidation of 2 gave 3<sup>5</sup> in 60% yield. The photochemical addition of isobutylene to 2 at -40 to -60° afforded 10,10-dimethylbicyclo-(7.2.0)undec-5-en-2-one (4)<sup>5</sup> (40%). The separation of 4 from other minor unidentified photo products was carried out by adsorption chromatography. The bicyclic unsaturated ketone (4) was converted into 5<sup>5</sup> by addition of methylene to the double bond. The isomerization of ring fusion in 5 followed by thermolysis in a sealed tube at 400° (0.05 mm) for 7 hr gave 6 in 65% yield. A Wittig reaction transformed 6 into dl-isocaryophyllene (7) (70%). Identification of 7 was confirmed by comparison of IR and NMR with those of an authentic natural product.

## SCHEME



ACKNOWLEDGEMENT: We wish to thank CSIR, New Delhi for financial assistance.

## REFERENCES :

1. D. Devaprabhakara, Basudev Banerjee Memorial Lecture - Chemistry of Cyclo-nonadienes (Review), *J. Ind. Chem. Soc.*, **51**, 913 (1974) and references therein.
2. E. J. Corey, R. B. Mitra and H. Uda, *J. Amer. Chem. Soc.*, **86**, 485 (1964).
3. M. Bertrand and J-L. Gras, *Tetrahedron*, **30**, 793 (1974).
4. R. Vaidyanathaswamy and D. Devaprabhakara, *J. Org. Chem.*, **32**, 4143 (1967).
5. Analytical and spectroscopic data of all new compounds were in full agreement with the structures assigned.