

SYNTHETIC EXPERIMENTS IN TERPENOIDS

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SUBMITTED
IN FULFILMENT OF THE REQUIREMENTS OF
THE DEGREE OF DOCTOR OF PHILOSOPHY

TO THE
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
DECEMBER, 1978

CERTIFICATE

This is to certify that the thesis entitled " Synthetic Experiments in Terpenoids", being submitted by Mr.Lokesh Chander Rohela to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr.Rohela has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge, has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

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A_C_K_N_O_W_L_E_D_G_E_M_E_N_T_S

I wish to record my deep sense of gratitude to Dr.R.C.Anand, Department of Chemistry, Indian Institute of Technology, Delhi, for his guidance, interest and encouragement which made this work possible.

I am grateful to Professor J.C.Ahluwalia, Head, Department of Chemistry, for providing laboratory facilities.

I am also indebted to Professors R.D.Dua, I.K.Varma and R.P.Gandhi for their creative suggestions and help at various stages of this work.

The fruitful discussions and co-operations of Mr.M.Z.Kirmani and other colleagues are thankfully acknowledged.

My thanks are also due to I.I.T.Delhi for the award of research fellowship and to Mr.T.R.Sharma for typing the dissertation.

Lokesh Chander Rohela
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A_B_S_T_R_A_C_T

The thesis contains results of investigations towards the syntheses of following terpenoids:

i) 9-Isopropyl-6-methyl-trans-5,9-decadien-2-one (ii) Propylure
(iii) trans, trans-2,6-Nonadienol (All trans Violet leaf alcohol)
(iv) Dihydrojasmone and Tanacetophorone (v) Sesquichamaenol methyl ether.

The synthesis of 9-isopropyl-6-methyl-trans-5,9-decadien-2-one has been accomplished through the reduction of malonic ester anion to prepare 2-substituted allyl alcohol and Julia's cyclopropylcarbinyl rearrangement for the introduction of predominantly trans-trisubstituted double bond. Julia's method of conversion of cyclopropylcarbinol into homoallylic bromide has been utilized in the synthesis of propylure to generate trans-disubstituted double bond in the acyclic system. The synthesis of all trans violet leaf alcohol makes use of cyclopropylcarbinyl rearrangement for the creation of trans-disubstituted double bond coupled with 3-benzenesulphonyl propanal ethylene acetal as a synthon for α , β -unsaturated aldehyde with trans- conjugated double bond.

Two simple and convenient routes towards the syntheses of 2-cyclopentenones substituted at 2 and 3 positions, a moiety present in several biologically important compounds, have been elaborated. These approaches have been illustrated through the syntheses of dihydrojasmone and tanacetophorone. The first

route is based on the dual function of monosubstituted malonic ester, i.e., (i) Michael reaction of its anion with α , β - unsaturated ketone to have a suitably positioned carbonyl group (ii) conversion of gem- diacid (derived from malonic ester) into gem-diacetate. The second approach employs a recently developed one step oxidation of the terminal olefin to a methyl ketone with Jones reagent in the presence of mercuric propanoate.

Sesquichamaenol methyl ether has been synthesised by coupling lithium di(2-methoxy-5-methyl-phenyl)cuprate with 6-methyl-5-bromo-2-heptanone. This compound has also been synthesised through a four step reaction sequence: Wittig reaction with methoxymethylenetriphenylphosphorane, cleavage of enol ether, modified Wittig reaction with diethyl (2-oxo-propyl) phosphonate and hydrogenation over Pd/C.

C_O_N_T_E_N_T_S

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