PART A

SYNTHESES OF SANTALENES & SANTALOLS

CHAPTER - I

I N T R O D U C T I O N

(REVIEW ON EARLIER KNOWN SYNTHESES)

The powerful, sweet, woody fragrance of East Indian sandalwood oil places this isolate of Santalum album Linn. among the most prized of the oils, essential in the compounding of soap and cosmetic perfumes. α- and β-Santalols constitute >90% of the commercial oil. Corresponding santalenes are also present to the extent of ~4%. This chapter reviews the earlier work on the syntheses of α-and β-santalenes, α-and β-santalols and also the conversion of α-series of compounds to that of β-series in terms of number of carbon atoms present in the building blocks. Thus, all the known syntheses have been classified as follows and are discussed in the text in sequel.

(i) C_8+C_7/C_7+C_8
(ii) C_9+C_6
(iii) $C_{10}+C_5$
(iv) $C_{12}+C_3$
(v) C_{15}*

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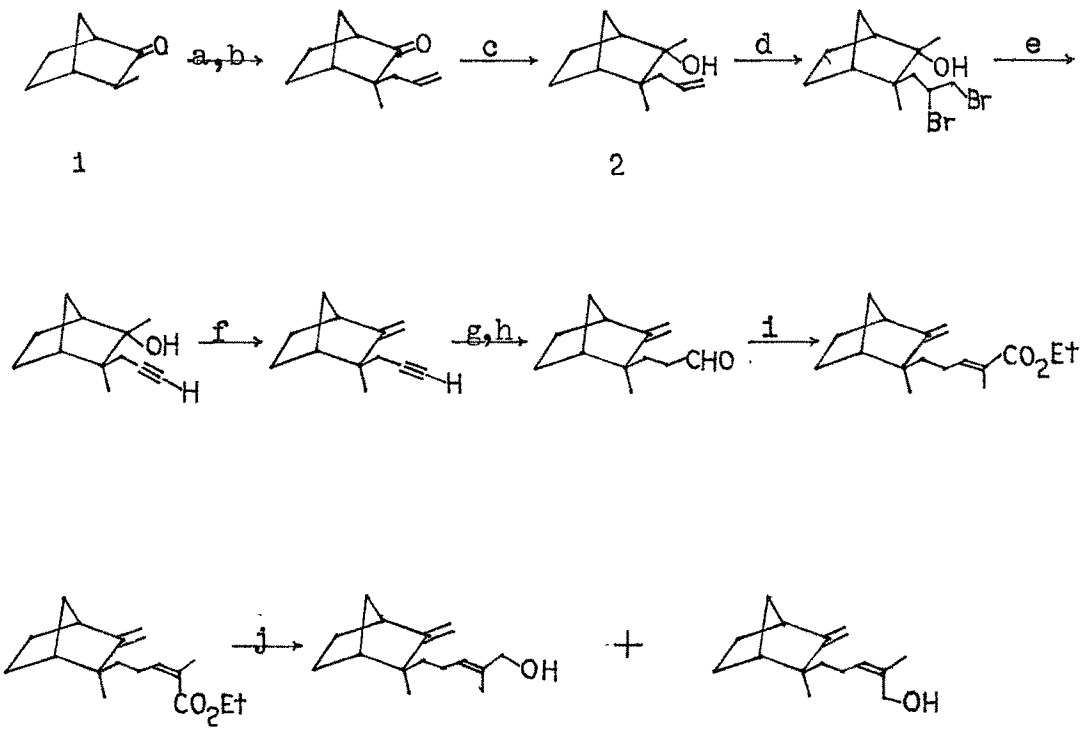
*According to this classification, it becomes obvious that conversion of α-to β-santalene, of α- to β-santalol and also that of C_{15} campherenone and isocampherenone to α- and β-series would fall under C_{15} heading.

(i) C_8+C_7/C_7+C_8

(a) 3-Methylnorcamphor(1) was used as a C_8 starting material in Erman's synthesis of β-santalol and its (E)-isomer (Scheme No.1)[1]. This was converted into a C_{12} intermediate(2)



Reagents: (a) NaH (b) $\sim\!\!\sim$Br (c) MeLi (d) Br_2 (e) $NaNH_2$/HMPA
(b) $SOCl_2$-C_5H_5N (g) R_2BH (h) H_2O_2 basic
(i) $\emptyset_3P{=}\underset{\underset{Me}{|}}{C}CO_2Et$ (j) lithium aluminum hydride

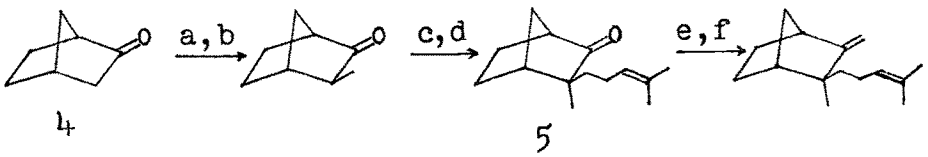
SCHEME NO.1: ERMAN'S SYNTHESIS OF β-SANTALOL AND ITS (E)-ISOMER

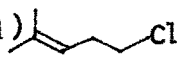
by sequential treatment with sodium hydride, allyl bromide, and methylithium. Acetylenic bond was next introduced in this C_{12} unit (2) by adding bromine to the olefinic moiety and dehydrobromination. Exocyclic methylene was incorporated by dehydration. Oxidative hydroboration of the acetylenic bond gave a C_{12} aldehyde(3) which also is an intermediate in Willis' stereospecific synthesis[2] of (±)β-santalol. Three carbon chain was introduced by Wittig reaction, wherein a cis- trans- isomeric mixture was obtained. Lithium aluminum hydride reduction of above mixture yielded a mixture containing β-santalol and its (E)-isomer.

This synthesis closely parallels Erman's synthesis[3] of α-santalol and its (E)-isomer.

(b_1) In the first stereospecific synthesis of (±)-β-santalene by Corey (Scheme No.2)[4], C_8 block was constructed from a C_7 precursor-2-norbornanone(4)- using tritylsodium and methyliodide, wherein the ratio of exo- to endo- methyl introduction was 30:1. C_6-Side chain was next introduced by treating the sodium enolate of C_8 unit with isohexenyl-chloride. The C_{14} unit (5), thus obtained, on treatment

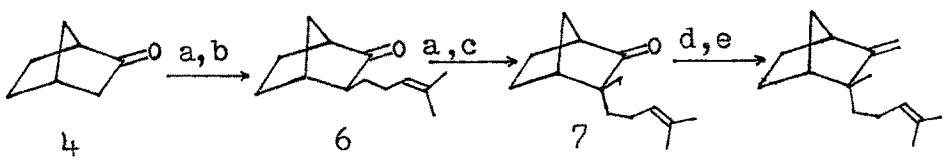
with methyllithium furnished a C_{15} alcohol which on dehydration gave (±)-β-santalene.

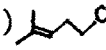


Reagents: (a) ϕ_3CNa (b) MeI (c) $NaNH_2$/THF (d)  (e) MeLi (f) $SOCl_2$-C_5H_5N

SCHEME NO.2: COREY'S SYNTHESIS OF (±)-β-SANTALENE

(b_2) In a synthesis of epi-β-santalene from the same school (Scheme No.3)[4], first a C_6 side chain was introduced using isohexenylchloride into a C_7 unit(4) as above to furnish (6). Tritylsodium and MeI was used to add the methyl group in the ring, resulting in a C_{14} compound(7). This(7) on treatment with methyllithium followed by dehydration furnished epi-β-santalene.

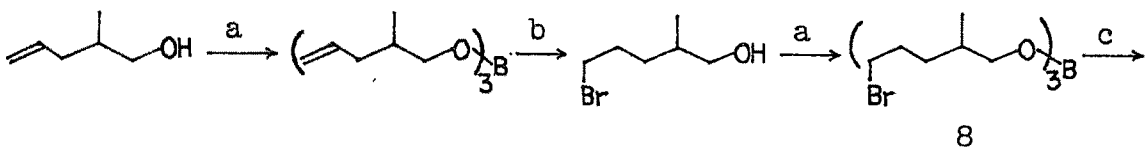


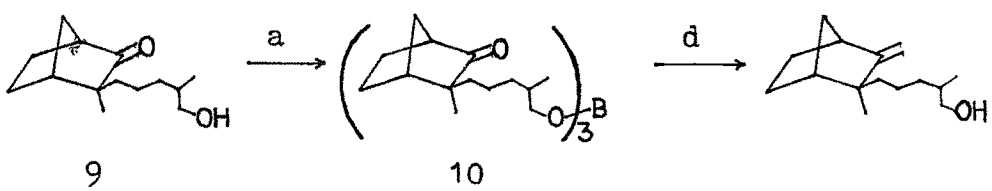
Reagents: (a) ϕ_3CNa (b)  (c) $NaNH_2$/THF (d) MeLi (e) $SOCl_2$-C_5H_5N

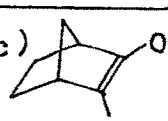
SCHEME NO.3: COREY'S SYNTHESIS OF EPI-β-SANTALENE

(c) Once again, in a synthesis of dihydro-β-santalol by Erman (Scheme No.4)[5] the starting material is the same C_8 compound-3-methylnorcamphor-as was used by Corey[4]. There is a novel approach in constructing the side chain and its condensation using a borate ester.

2-Methyl-4-pentenol was the C_6 side chain precursor and it was converted into a bromo-borate(8) by sequential treatment with boric acid and hydrobromic acid. This ester(8), on condensation with sodium salt of 3-methylnorcamphor furnished a C_{14} compound(9). The borate ester(10) of this C_{14} compound(9) gave, after Wittig reaction, dihydro-β-santalol.



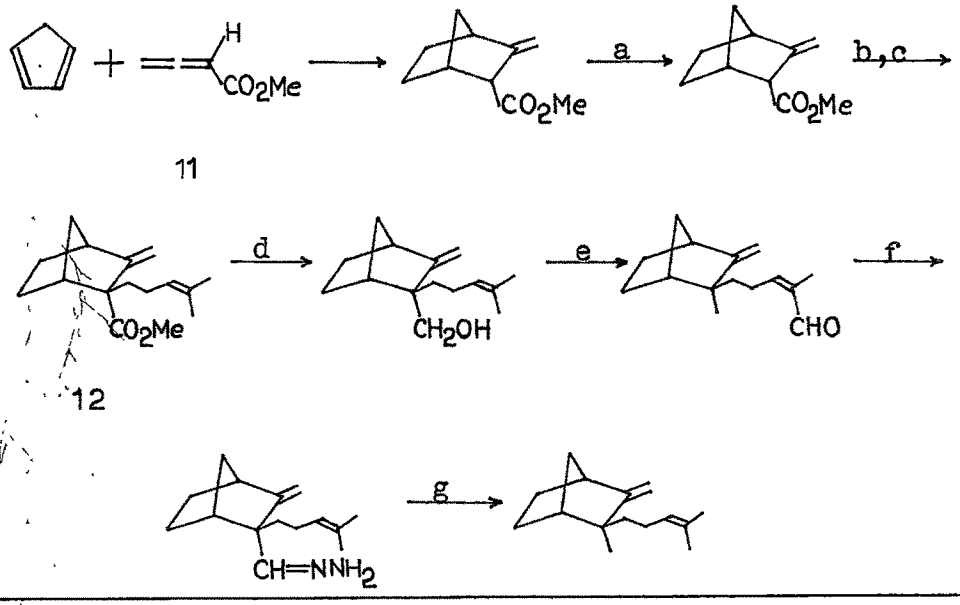


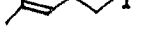
Reagents : (a) H_3BO_3 (b) HBr (c)  (d) $\phi_3P = CH_2$

SCHEME NO.4 : ERMAN'S SYNTHESIS OF DIHYDRO-β-SANTALOL

(ii) C_9+C_6

(a) Bertrand, Monti and Huong reported, very recently, a stereoselective synthesis of (±)-β-santalene (Scheme No.5)[6]. The C_9 unit was readily built up by Diels Alder reaction of a C_5 unit cyclopentadiene and a C_4 allene(11) in 85% yield. This was next selectively hydrogenated and treated with a C_6 unit isohexenyliodide to furnish(12), a C_{15} unit. This was next functionalized in three steps (via-LAH reduction, pyridinium chlorochromate oxidation[7], and Wolf-Kishner reduction[8], respectively) to the desired compound-(±)-β-santalene.

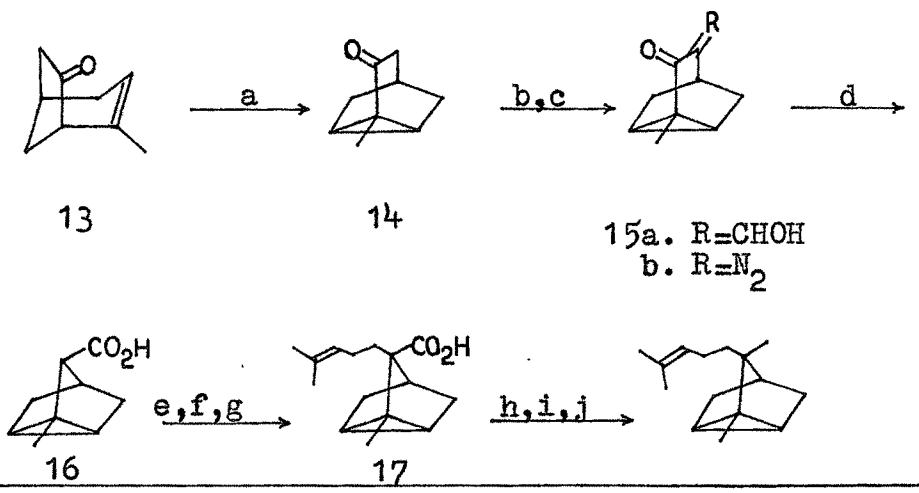


Reagents: (a) $H_2NiB(P11)$ (b) LDA (c)  (d) LAH (e) pyridinium chlorochromate (f) $NH_2.NH_2,H^+$ (g) KOH/DEG

SCHEME NO.5: HUONG'S SYNTHESIS OF (±)-β-SANTALENE

Obviously, major effort had been directed towards converting the carbomethoxy group into a methyl group in this synthesis.

(b) Similarly, ∝-santalene has been synthesized by Monti et al (Scheme No.6)[9], using a C_9 unit, i.e. 4-methyl-bicyclo 3.2.1 oct-3-en-6-one(13)[10], as the starting material. Irradiation of this β, γ-unsaturated ketone(13) in acetone resulted in a smooth rearrangement[11] to give the tricyclic ∝-methyl cyclopropylketone(14). Conversion of (14) into the ∝'-formyl derivative 15a followed by treatment with tosyl azide yielded the diazoketone 15b[12], which upon photolysis underwent ring contraction[13] to furnish the key intermediate, the C_9 tricyclic acid(16).



Reagents: (a) hv/><0, 25°C, 10 hrs. (b) NaH, HCO_2Et
(c) tosylazide, Et_3N (d) hv, $NaHCO_3$, THF/H_2O
(e) LDA (f) n-BuLi (g)  (h) LAH (i) TsCl
(j) $LiBEt_3H$

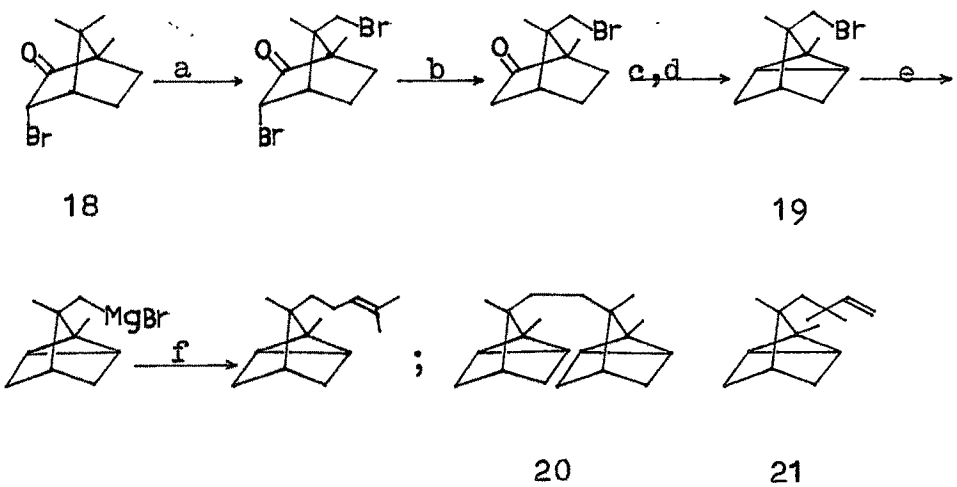
SCHEME NO.6: MONTI'S SYNTHESIS OF ∝-SANTALENE

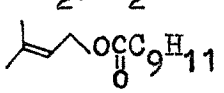
Side chain, which constitutes a 6-carbon unit, was elegantly built up in one step by reacting a dianion of the acid (16) with 5-iodo-2-methyl-2-pentene. Satisfactory generation of this dianion was achieved by exposure of(16) to lithiumdiisopropylamide(2.5 equiv, 50°C), followed by addition of n-butyllithium (1 equiv, 50°C)[9,14]. Conversion of the carboxyl function of (17) into methyl group in three steps gave the desired α-santalene.

(iii)$C_{10}+C_5$

(a) Corey, in his synthesis of α-santalene, preferred to start from a C_{10} unit, a halogenated monoterpene, i.e.trans- π-bromocamphor(18), which was converted, through steps depicted in Scheme No.7[15], into π-bromotricyclene(19).Grignard's product of this was treated with a C_5 unit(r,r-dimethylallylmesitoate) to give α-santalene. However, the yield of α-santalene was poor (~18%) and the major product in the key step was a dimer, i.e. bi-π-tricyclyl(20). When instead

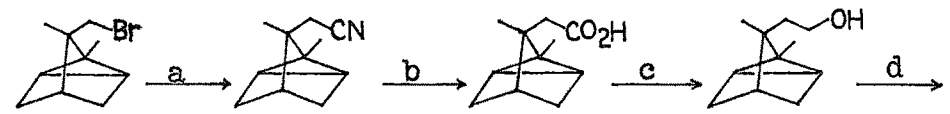
of r,r-dimethylallyl mesitoate,the C_5 source was the corresponding bromide (r,r-dimethylallylbromide), ∝-santalene did form but the major product (>50%) was its isomer (21).



Reagents: (a) Br_2/HSO_3Cl (b) Zn-HBr (c) NH_2,NH_2 (d) HgO
(e) Mg/diethylether (f) 

SCHEME NO 7: COREY'S SYNTHESIS OF ∝-SANTALENE

(b) Colonge, in his synthesis of α- and β-santalols (Scheme No.8)[16], also starts from a C_{10} unit – π-bromotricyclene-but here the additional five carbon chain has been added up in a stepwise(1+4) manner. One carbon was introduced by nucleophilic displacement of bromine to cyanotricyclene(22) followed by its



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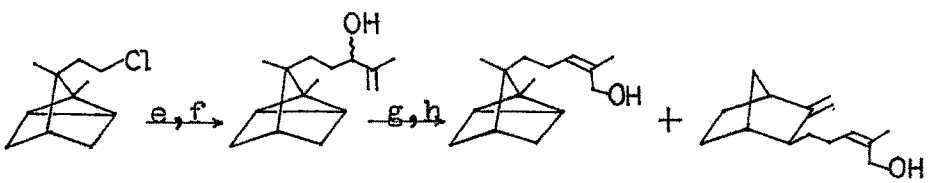


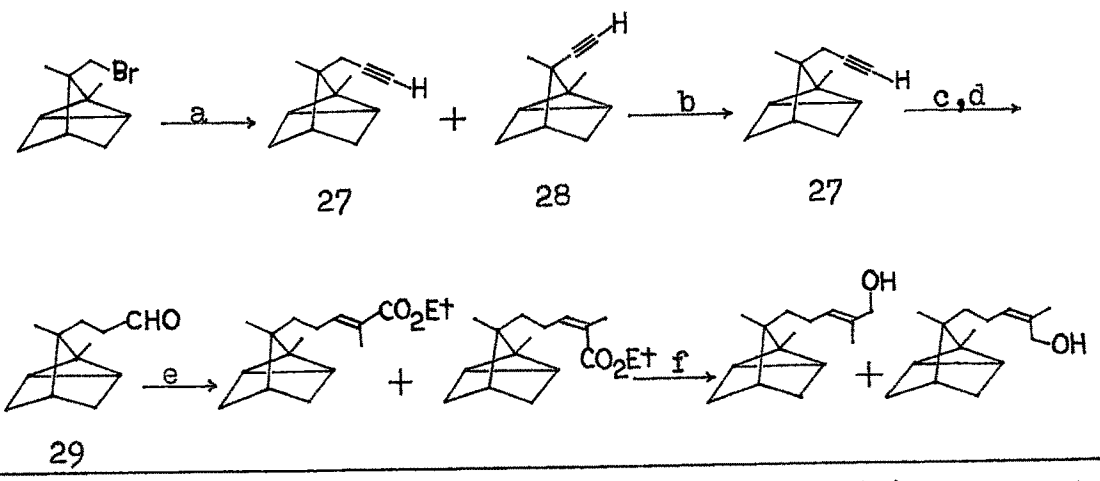
25 26

Reagents : (a) NaCN/DMSO (b) KOH (c) LAH (d) $SOCl_2$
(e) Mg (f)  (g) PBr_3 (h) KOH

SCHEME NO.8: COLONGE'S SYNTHESIS OF α- AND β-SANTALOLS

hydrolysis to the corresponding acid(23). The C_{11} alcohol(24), obtained from LAH reduction of the acid(23), was converted into the corresponding chloride(25), which,on condensation with C_4 α-methylacrolein,gave the C_{15} alcohol(26). This, on allylic rearrangement with PBr_3, followed by KOH treatment, furnished a mixture of α-and β-santalols and their trans-isomers.

(c) Erman's synthesis of α-santalol and its (E)-isomer again utilizes a C_{10} unit, in fact, π-bromotricyclene- the same starting material as is used by Colonge(see b-above)[16]. Here, instead of (1+4),(2+3) stepwise carbon chain addition has been realized, as is obvious from the scheme (No.9)[3] outlined below. The two-carbon chain was added by reaction of bromotricyclene with lithium acetylide, when a mixture of acetylenic isomers (27 and 28) was obtained in ~90% yield. The ratio of (27) to (28) was found to be time-, temperature-, and

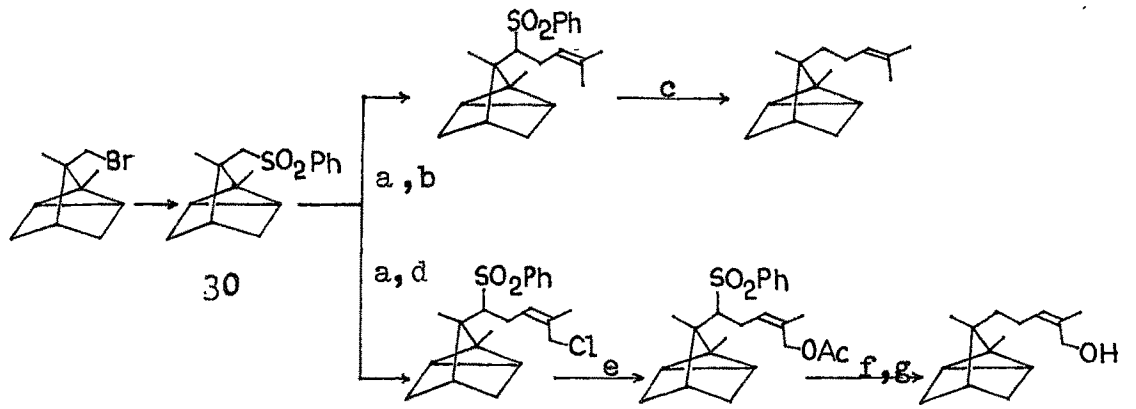


Reagents: (a) $LiC{\equiv}CH$ (b) $NaNH_2$/Xylene (c) R_2BH (d) H_2O_2-basic (e) $\emptyset_3P{=}C(Me)CO_2Et$ (f) LAH

SCHEME NO.9: ERMAN'S SYNTHESIS OF α-SANTALOL AND ITS (E)-ISOMER

solvent-dependent. Under optimized conditions(viz., using HMPA as solvent at 25-27°C for 160 hours) these workers obtained (28) as the sole product. This was isomerized to (27) by refluxing with sodamide in xylene. Oxidative monohydroboration of (27) yielded an aldehyde-tricycloekasantalal(29)-having the same number of carbon atoms. For adding the remaining three carbons in the side chain, these workers took recourse to Wittig reaction on this aldehyde(29). LAH reduction of the product from Wittig reaction produced ∝-santalol and its trans-isomer.

(d) The same C_{10} unit, i.e. π-bromotricyclene, is the starting material for Julia's stereospecific synthesis of ∝-santalene and ∝-santalol in ~68 and 80% yields, respectively (Scheme No.10)[17]. Bromotricyclene was first converted into a sulphone(30), the lithium salt of which gave ∝-santalene on treatment with a C_5 chain-cis-r,r-dimethylallylchloride, followed by removal of the sulphone moiety. The same lithium salt, when treated with cis-1,4-dichloro-2-methylbutan-2-ene,furnished(31), in which the chlorogroup was displaced by an acetate group. Saponification, followed by desulphonation, gave ∝-santalol. Highlight of this synthesis is that the C_5 carbon chain is suitably geometrized

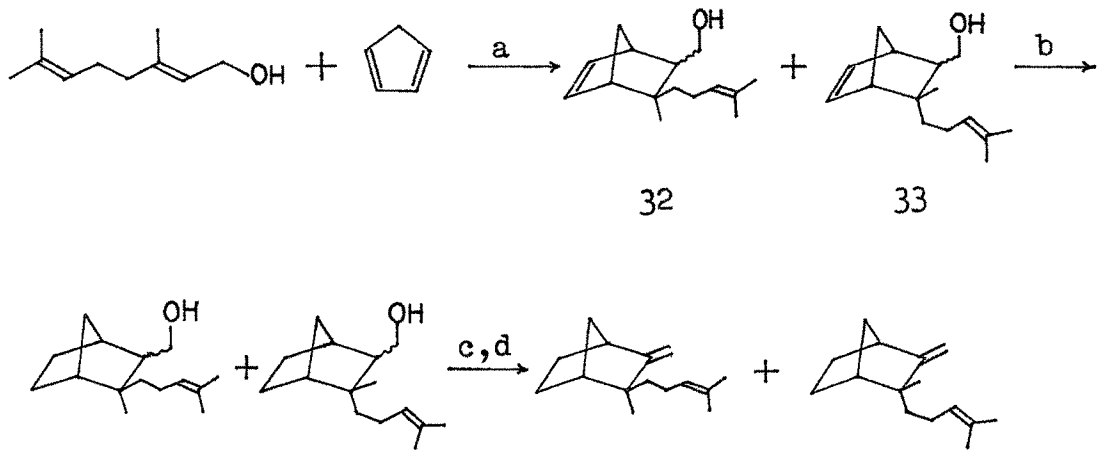


Reagents: (a) BuLi-$(Me_2N)_3PO$/THF (b) cis-$ClCH_2CH{=}CMe_2$ (c) Na-Hg/EtOH (d) cis-$ClCH_2CH{=}C(Me)CH_2Cl$ (e) NaOAc (f) saponification (g) desulphonation.

SCHEME NO.10: JULIA'S SYNTHESIS OF ∝-SANTALENE AND ∝-SANTALOL

before the condensation step itself, thus, leading to a stereospecific synthesis of ∝-santalol.

(e) An interesting approach for coupling a C_{10} unit with a C_5 component to synthesize β-santalene and epi-β-santalene is by Brieger (Scheme No.11)[18]. Here, the C_{10} unit is represented by geraniol and the C_5 unit by cyclopentadiene. These reactants were coupled in Diels Alder manner to furnish a mixture of (32) and (33) in, however, very poor yield (only ~4%). Catalytic hydrogenation of the more accessible olefinic bond in this C_{15} molecule followed by pyrolysis of corresponding



Reagents: (a) Δ ,170°C (b) H_2-Pd/$CaCO_3$ (c) Ac_2O-pyridine (d) Δ,575°C

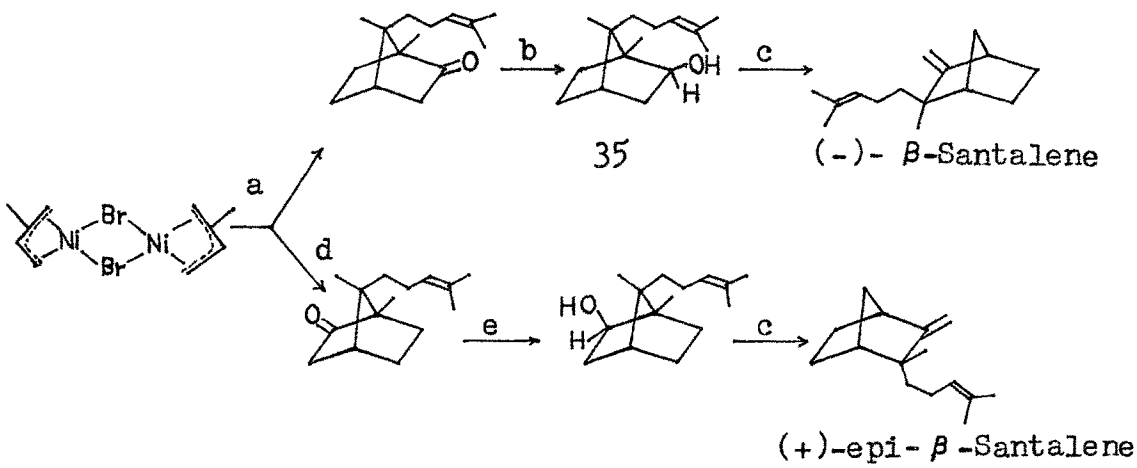
SCHEME NO.11: BRIEGER'S SYNTHESIS OF β-AND EPI-β-SANTALENES.

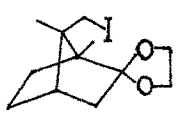
acetate yielded a 3:2 mixture of β-santalene and epi-β-santalene.

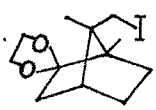
(f) The C_{10} unit, i.e (-)-8-iodocamphor, was the starting material in Money's synthesis of (-)-β-santalene (Scheme No.12)[19,20]. First,the acetal of (-)-8-iodocamphor was prepared and this acetal(34) was treated with π-allylnickel complex of a C_5 unit i.e. r,r-dimethylallyl bromide, to furnish, after

hydrolysis, followed by reduction with $LiAl(OMe)_3H$, (+)-isocamperenol(35). p-Toluenesulphonyl chloride-pyridine dehydration of this produced (-)-β-santalene in ~70% yield.

In a similar fashion, (+)-epi-β-santalene was synthesized using (-)-9-iodocamphor(36) the C_{10} unit as the starting material (see Scheme No.12)



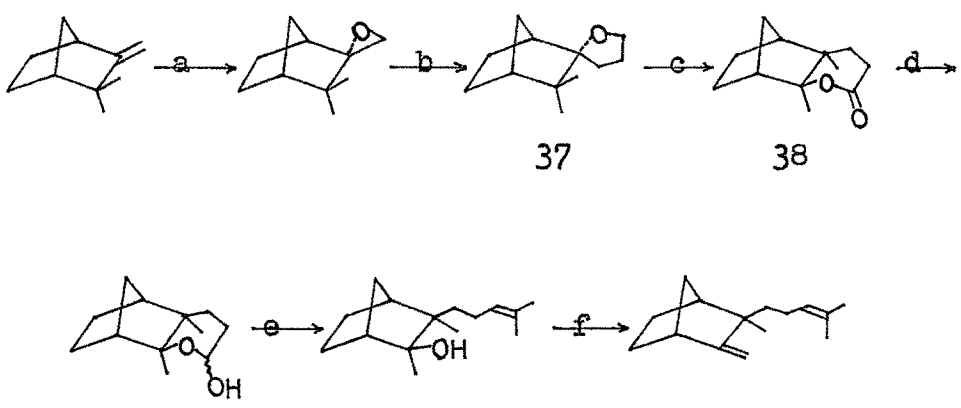
Reagents: (a)  (34) (b) Na-PrOH or $LiAl(OMe)_3H$

(c) C_7H_7SOCl-C_5H_5N (d)  (36)

(e) $LiAl(OMe)_3H$

SCHEME NO.12: MONEY'S SYNTHESIS OF β-AND EPI-β-SANTALENES

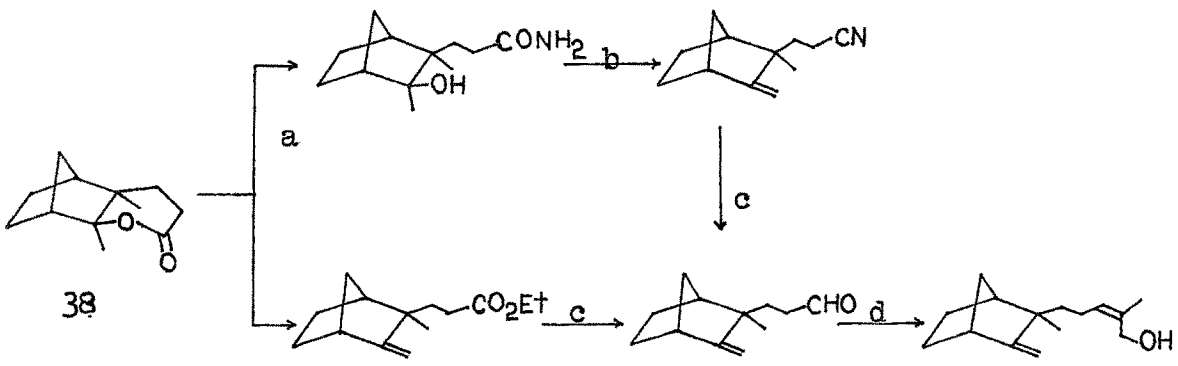
(g) The staring C_{10} unit in Willis' stereospecific synthesis of (±)- β-santalene (Scheme No.13)[2] is camphene, which was converted into a C_{10} oxirane using peracetic acid. Two carbon unit was added in the oxirane ring with the anion of acetic acid to furnish after lactonization a C_{12} γ-lactone(37). The γ-lactone(37), on treatment with cold sulphuric acid, gave two different lactones in a 5:1 ratio; the δ-lactone(38) was the major one. The C_{12} δ-lactone was reduced with diisobutylaluminum hydride(DIBAL) to the corresponding lactol(39). Remaining three carbon unit was introduced with the incipient chain(lactol) by Wittig reaction, followed by dehydration to furnish the targetted β-santalene.



Reagents : (a) peracetic acid (b) CH_3CO_2H/n-BuLi/$(Me_2CH)_2NH$
(c) cold H_2SO_4 (d) DIBAL (e) $\phi_3P{=}\swarrow$ /DMSO
(f) $POCl_3$-C_5H_5N.

SCHEME NO.13: WILLIS' SYNTHESIS OF (±)- β-SANTALENE

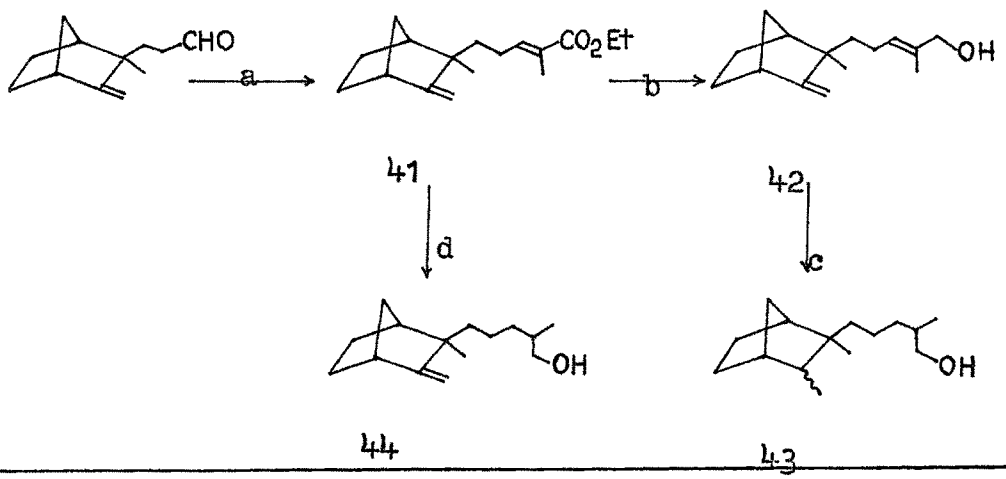
Similarly, Willis also synthesized β-santalol and tetrahydro-β-santalol using the key compound C_{12} δ-lactone(38). This lactone(38) was converted into C_{12} aldehyde(40) by two different routes as depicted in Scheme No.14[2]. Aldehyde(40), under Corey's modified conditions of Wittig reaction, furnished (±)-β-santalol, stereospecifically.



Reagents: (a) NH_3 or Me_2AlNH_2 (b) C_7H_7SOCl-C_5H_5N
(c) DIBAL (d) $EtOH/H^+$ (e) $\phi_3P{=}CHCH_3$, n-BuLi, CH_2O, -78^oC

SCHEME NO.14: WILLIS' SYNTHESIS OF (±)-β-SANTALOL

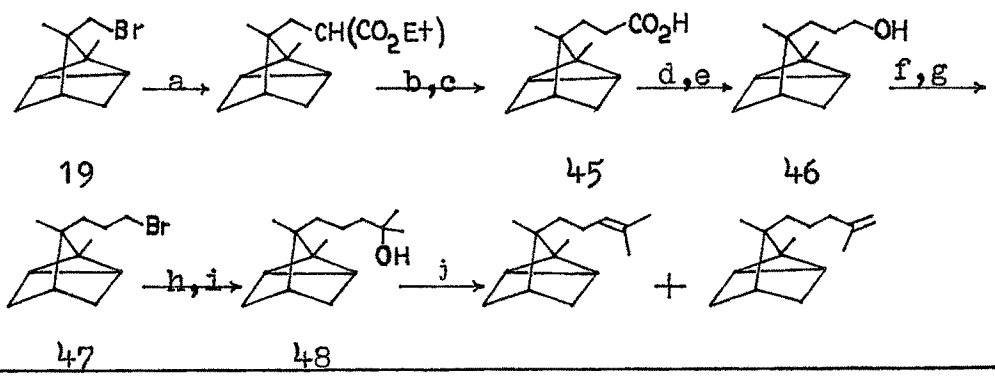
Wittig reaction, using sodiotriphenylphosphono-propanoate, on aldehyde(40) gave olefinic ester(41) as a mixture of trans/cis-(85/15) isomers. Aluminium hydride reduction of (41) produced(±) trans- β-santalol (42), which contained ~15% of the cis-isomer. Hydrogenation of this isomeric mixture over poisoned platinum oxide resulted in an isomeric (endo/exo) mixture of tetrahydro- β-santalol(43). Birch reduction of the olefinic esters(41) furnished (±) dihydro- β-santalol (44)(Scheme No.15)[2].



Reagents : (a) $\phi_3P=CMeCO_2Et$ (b) AlH_3 (c) H_2/PtO_2
(d) $Li-NH_3$.

SCHEME NO.15: WILLIS' SYNTHESIS OF DI-AND TETRAHYDRO-β-SANTALOLS

(h) The starting material in Bhattacharya's synthesis of α-santalene and its isomer (Scheme No.16)[21] is a C_{10} compound- π-bromotricyclene(19). Two carbon chain is added by treating(19) with potassium salt of diethylmalonate, followed by alkaline hydrolysis and decarboxylation to furnish a C_{12} acid-tricyclo-ekasantalic acid(45). This acid, on esterification and LAH reduction of the ester, gave a C_{12} tricyclic compound-tricyclo-ekasantalol(46). Remaining three carbons in the side chain were introduced by treating Grignard of C_{12} bromocompound(47) with acetone to produce a C_{15} tertiary carbinol(48). Dehydration of (48) gave a mixture of α-santalene and its double bond isomer.

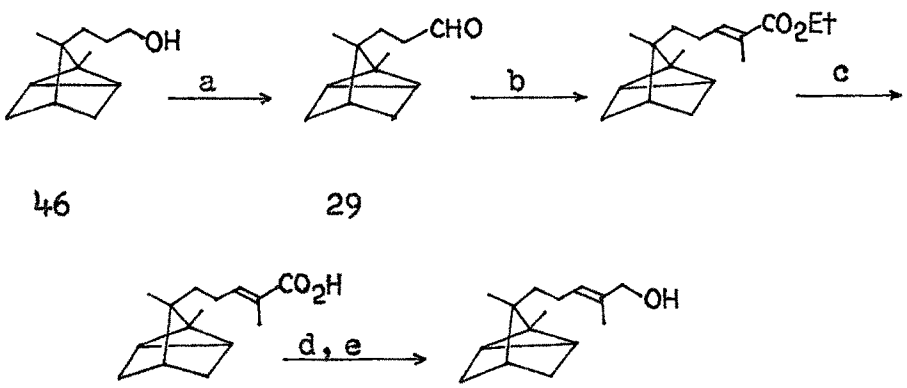


Reagents: (a) $KCH(CO_2Et)_2$ (b) KOH (c) $H_3\overset{+}{O}$ (d) CH_2N_2
(e) LAH (f) p.TsCl-C_5H_5N (g) NaBr
(h) Mg (i) $\rightleftharpoons O$ (j) p.TsCl-C_5H_5N

SCHEME NO.16: BHATTACHARYA'S SYNTHESIS OF α-SANTALENE AND ITS ISOMER

(iv) $C_{12}+C_3$

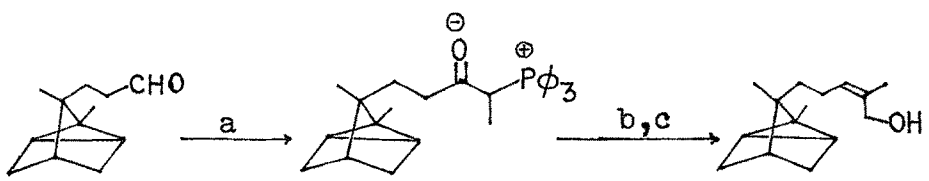
(a) Bhattacharya et al., in their synthesis of ∝-santalol (Scheme No.17)[21], have used a C_{12} starting material-tricycloekasantalol(46). This (46),on oxidation with CrO_3-pyridine,gave tricycloekasantal(29). Three carbon atoms were added in the side chain by Wittig reaction. Through sequential treatment with KOH, diazomethane and LAH, these workers prepared ∝-santalol which,in fact, turned out to be its (E)-isomer.



Reagents : (a) CrO_3-C_5H_5N (b) $\emptyset_3P{=}\overset{|}{C}{-}CO_2Et$ (c) KOH
(d) CH_2N_2 (e) LAH

SCHEME NO.17: BHATTACHARYA'S SYNTHESIS OF (E)-∝-SANTALOL

(b) The C_{12} compound(tricycloekasantalal), which is also an intermediate in Bhattacharya's synthesis[21] of (E)-isomer of α-santalol,is the starting material in Corey's stereospecific synthesis of (±)- α-santalol (Scheme No.18)[22]. The problem of (Z)-geometry of the olefinic bond in the side chain has been elegantly solved by adding the remaining C_3 unit in a stepwise (C_2+C_1) manner. Two carbon unit was introduced by a simple modification[22] of Wittig reaction on tricyclo-ekasantalal(29). The treatment of n-butyllithium salt of the C_{14} unit(49), thus produced, with formaldehyde at -78°C afforded (±)- α-santalol as the sole product.



29 49

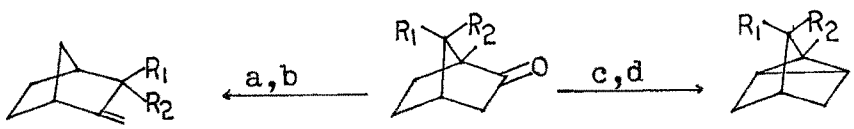
Reagents: (a) $\phi_3P = CHCH_3$/THF, -78°C (b) n-BuLi,-78°C
(c) CH_2O, 0°C.

SCHEME NO.18: COREY'S STEREOSPECIFIC SYNTHESIS OF α-SANTALOL

(v) C_{15}

(a) The hydrazones of C_{15} precursors-campherenone[23](50) and isocampherenone[23](51)-were prepared and heated with mercuric oxide to furnish α-santalene(52) (Scheme No.19)[24].

Money et al using the same C_{15} precursor-campherenone-also synthesized β-santalene(53) by sequential treatment with lithiumaluminum hydride and p-toluenesulphonyl chloride and pyridine. Using the above set of reactions, isocampherenone has also been converted into epi-β-santalene(54) by these workers(Scheme No.19)[24].



53: $R_1=CH_2CH_2CH=CMe_2$, $R_2=CH_3$

54: $R_1=CH_3$, $R_2=CH_2CH_2CH=CMe_2$

50: $R_1=CH_3$, $R_2=CH\ CH\ CH=CMe_2$

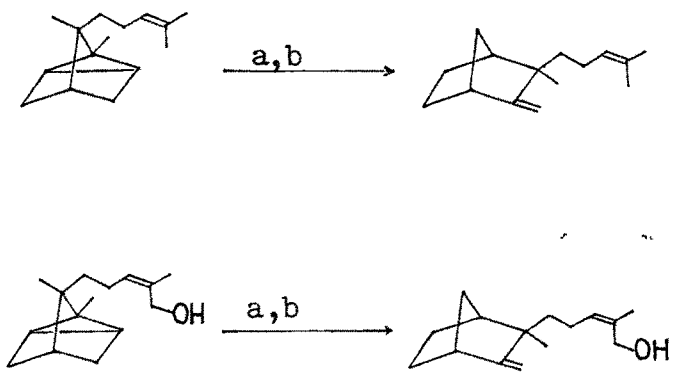
51: $R_1=CH_2CH_2CH=CMe_2$, $R_2=CH_3$

52: $R_1=CH_3$, $R_2=CH_2CH_2CH=CMe_2$

Reagents : (a) LAH (b) p-TsCl/C_5H_5N (c) NH_2NH_2,H^+ (d) HgO/Δ

SCHEME NO.19: MONEY'S SYNTHESIS OF α-, β-AND EPI-β-SANTALENES

(b) The transformation of α-santalene to β-santalene and of α-santalol to β-santalol was achieved by Bhattacharya by passing dry HCl gas in acetic acid solutions of the above starting materials and hydrolyzing the resulting product with alkali(Scheme No.20)[25].



Reagents: (a) dry HCl gas in AcOH (b) alcoholic KOH

SCHEME NO.20: BHATTACHARYA'S TRANSFORMATION OF α-SANTALENE TO β-SANTALENE AND OF α-SANTALOL TO β-SANTALOL

REFERENCES

1. H.C.Kretschmer and W.F.Erman, Tetrahedron Letters, 41(1970).
2. P.Christenson and B.J.Willis, J.Org.Chem, 44 2012 (1979).
3. R.G.Lewis, D.H.Gustafson and W.F.Erman,Tetrahedron Letters 401(1967).
4. E.J.Corey, R.Hartmann, and P.A.Vatakencherry, J.Am.Chem.Soc., 84 2611(1962).
5. W.I.Fanta and W.F.Erman, Tetrahedron Letters, 4155(1969).
6. M.Bertrand, H.Monti, and K.C.Huong, Tetrahedron Letters,15(1979).
7. E.J.Corey and J.W.Suggs, Tetrahedron Letters, 2647(1975).
8. D.Todd, Organic Reactions 4 378(1948); Huang-Minlon, J.Am. Chem.Soc. 68 2487(1946).
9. S.A.Monti and S.D.Larsen, J.Org.Chem., 43 2282(1978).
10. S.D.Larsen and S.A.Monti, J.Am.Chem.Soc. 99 8015(1977); S.A.Monti and G.L.White, J.Org.Chem., 40 215(1975).
11. R.K.Murray and K.A.Babiak, Tetrahedron Letters, 319(1974); K.Yano, Tetrahedron Letters, 1861(1974); R.S.Givens, W.F. Oettle, R.L.Coffin, and R.G.Carlson, J.Am.Chem.Soc., 93 3957(1971).
12. M.Regitz and J.Ruter, Chem.Ber., 101 1263 2622(1968).
13. L.R.Smith and J.Meinwald, J.Org.Chem., 40 415(1977); A.Stojilijkovic and R.Tasovac,Tetrahedron, 33 65(1977); T.Gibson and W.F.Erman, J.Org.Chem., 31 3028(1966).
14. P.A.Grieco and Y.Masaki, J.Org.Chem., 40 150(1975).
15. E.J.Corey, S.W.Chow, and R.A.Scherrer, J.Am.Chem.Soc., 79 5773(1957).

16. J.Colonge, G.Descotes, Y.Bahurel and A.Memet, Bull.Soc. Chim.France, 374(1966).

17. M.Julia(Agence Nationale de Valorisation de la Recherche) Ger.Offen. 2,341,872; Chem.Abstr. 80 146381y(1974).

18. G.Brieger, Tetrahedron Letters, 1949(1963).

19. C.R.Eck, G.L.Hodgson, D.F.MacSweeney, R.W.Mills, and T.Money, J.Chem. Soc. Perkin I, 1938(1974).

20. G.L.Hodgson, D.F.MacSweeney, and T.Money, J.Chem.Soc.Perkin I, 2113(1973).

21. S.C.Bhattacharya, Sci. and Cult., 13 208(1947); S.Y.Kamat, K.K.Chakravarti, and S.C.Bhattacharya, Tetrahedron, 23 4487(1967).

22. E.J.Corey and Hisashi Yamamoto, J.Am.Chem.Soc., 92 226(1970)

23. G.L.Hodgson, D.F.MacSweeney, and T.Money, J.Chem.Soc.(Chem. Commun.), 766(1971).

24. G.L.Hodgson, D.F.MacSweeney, and T.Money, Tetrahedron Letters, 3683(1972).

25. S.C.Bhattacharya, Sci. and Cult., 13 158(1947).