CHAPTER II

Synthesis of Dehydro-α-Curcumene

Monocyclic sesquiterpene hydrocarbon dehydro-α-curcumene has recently been isolated from the wood of T-oriental (84) by the Japanese workers. On the basis of spectroscopic data and correlation with α-curcumene (VI), it has been assigned structure (V).

Salient features characterising dehydro-α-curcumene are the presence of a p-substituted toluene system, having isopropylidene and methylenic types of double bonds in the side chain.

In continuation of our work on the synthesis of terpenoids involving Wittig reaction, we describe herein the first unambiguous synthesis of the structure (V), suggested for dehydro-α-curcumene by Bunichiro et al (84). The reaction
sequence is depicted as follows:

The keto-ester, ethyl-4-oxo-4(p-tolyl)-butanoate (VII) (85), which had been characterised through its I.R. spectrum showing bands at 1745 (ester), 1700 (ketone) and 1625, 810 (1,4-disubstituted benzene nucleus) cm$^{-1}$, when subjected to Wittig reaction with methyl triphenyl-phosphonium iodide in dimethyl sulfoxide and sodium hydride, as described by Corey et al (46), resulted in the formation of the methylene ester (VIII) in 75 per cent yield. I.R. characteristic absorption bands were observed at 1750 (ester) 1615, 895 (conjugated terminal methylene) and 1525, 810 (1,4-disubstituted benzene nucleus) cm$^{-1}$. The methylene ester (VIII) was smoothly reduced with lithium aluminium hydride to the corresponding carbinol (IX) in 93 per cent yield. I.R.
spectrum did not show any absorption in the carbonyl region but had characteristic bands at 3350 (-OH), 1610, 895 (conjugated methylene) and 1540, 810 (1,4-disubstituted benzene nucleus) cm$^{-1}$.

Oxidation of the carbinol (IX) with excess of Collin's reagent (86) furnished the aldehyde (X) which was characterised through its semicarbazone (m.p. 142-44$^\circ$) and I.R. spectrum. The spectrum showed absence of absorption in the hydroxyl region but had characteristic bands at 1700 (-CHO) and also an aldehydic shoulder at 2720 cm$^{-1}$. The aldehyde (X) was submitted to Wittig reaction with isopropylidene triphenyl-phosphorane to provide the title compound which was purified by chromatography over neutral alumina and elution with petroleum ether (40-60$^\circ$). The purity of the synthetic sample was determined by t.l.c. (single spot, Rf value 0.83, silica gel, petroleum ether (40-60$^\circ$) used as eluent) and again by I.R. and N.M.R. spectral characterisation. I.R. spectrum showed absorption bands at 3050, 2920, 1630, 1570, 1620, 1450, 1380, 1180, 1040, 1020, 890, 820, 775 and 730 cm$^{-1}$. Lit.(84) reports characteristic

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peaks at 1630, 1570, 1520, 890, 826 and 730 cm$^{-1}$.

N.M.R.* showed the characteristic signals $\tau = 2.8$
(m,4H, aromatic), 4.8 (b. 1H, trisubstituted double bond),
5.0 (bs. 2H, terminal methylene), 7.60 (s,3H methyl group
directly attached to benzene ring) and 8.6 (d, 6H gem-
dimethyl on the double bond) in fair comparison with the
reported values (84).

* N.M.R. spectrum of the synthetic sample was
kindly recorded by Dr. Baldev Vig, Department of
Chemistry, Oakland University, Rochester, Michigan
(U.S.A.).