CHAPTER II

'A NEW SYNTHESIS OF dl-CAMPHORONE'
During the thermal decomposition of thorium-D-camphorate Calas (81), in the year 1937, recorded the observation that, in addition to pulegoneone (XI) and a very small amount of 2-methyl-cyclopentanone, the principal product formed was dl-camphorone (XI).

The structure (XI) for this ketone was suggested by Koenigs (82) on the basis of its oxidation, with potassium permanganate, to α-methyl glutaric acid.

Further confirmation to the constitution (XI) was lent (83) through the formation of its derivatives with hydroxylamine; this parallels the formation of corresponding derivatives in pulegone (cf.84) which contains an exo-c=c - double bond in conjugation with the carbonyl function.
Physical evidence, embracing optical, spectral and polarographic studies, renders additional support to the structure (XI)\(^{(85, 86)}\).

The first recorded attempt at the synthesis of dl-camphorone is due to Cole\(^{67}\) who reported to have condensed 2-methyl-cyclopentanone with acetone in the presence of sodium methoxide.

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\begin{align*}
\text{CH}_3\text{O} + \text{CH}_3\text{CH}_3\text{C} & \rightarrow \text{CH}_3\text{O}\text{C} \text{CH}_3 \text{CH}_3 \text{C} \\
\text{CH}_3 & \text{CH}_3 \\
\text{CH}_3 & \text{CH}_3 \\
\end{align*}
\]

The aforementioned condensation, however, remains equivocal in so far as it admits of, at least, two alternative modes of reaction leading respectively to the formation of structures (XI) and (XII).

The synthetic route to the ketones (XI) presently envisaged further exploits fruitfully the technique of Salmi (43) whereby a keto group is not only protected, by its conversion into the cyclic ketal, but is rendered selectively defunct in a multi-functioned organic compound, thus enabling a host of reactions (viz., Grignard reaction, Reformatsky reaction etc.,) to be made at other reactive centres in the molecule. Such an approach engenders a simple
and an unambiguous pathway to the structure (XI). The following sequence of reactions illustrates the present route to the synthesis of dl-camphorone:

The starting material in the present investigations, namely, 2-methyl-5-ethoxycarbonyl-cyclopentanone (XIII) was secured exactly according to the procedure prescribed in the literature (88). 2-Methyl-5-ethoxycarbonyl-cyclopentanone (XIII) was converted into the corresponding ethylene cyclic ketal (XIV), in 75% yield, in the manner of Salmi (43). The ketal-ester (XIV) was then reacted upon with methyl magnesium iodide to obtain 3-methyl (2-keto-2-dioxolane)-cyclopentyl-dimethylcarbinol (XV) in 77% yield. The ketal-carbinol (XV) on being submitted to acid hydrolysis furnished 3-methyl-2-keto-cyclopentyl-dimethyl-carbinol (XVI) in 65% yield. Subsequent
The ultraviolet absorption spectrum of the ketone (XI) exhibited a strong absorption maximum in the region 254 μμ (log ε, 4.12) which is in conformity with the predictions of Woodward's rule (90) for exo-double-bonded trialkyl substituted cyclic ketones. The ketone (XI) was further characterised through its deep-red 2:4-dinitrophenylhydrazone and semicarbazone derivatives which melted at 203° and 197° respectively. Literature (91) records m.p. 197° for dl-camphorone semicarbazone. The colour of the D.N.P. derivative is suggestive of the α,β-nature of unsaturation. Again, though prepared under acidic conditions, this is assigned to have exo-c=c- double bond, because under the mild conditions employed the double bond is not expected to migrate into the cycle (cf. 92). Moreover, the 2:4-dinitrophenylhydrazone derivative of the isomeric structure (X) of pulegenone, described in chapter VIII (Part I), is observed to have much lower (105°) melting point.