INTRODUCTION

The major part of this dissertation comprising Part I is concerned with the development of a general method for the construction of the basic tricarbocyclic skeleton of ophiobolins. The synthesis of the bicyclic ketone, 1β(H)-3, 7α, 11β-Trimethyl-cis-bicyclo(6.3.0)undecan-4-one, was completed and was included in a previous dissertation from this laboratory (T. K. Das, Ph.D. dissertation, Calcutta University, January 1975) and the results have already been published (T. K. Das and P. C. Dutta, Synth. Comm., 1976, 6, 253). Subsequently the synthesis of 3β(H), 7β(H)-13-Keto-1β,4β,8α-trimethyl-tricyclo(9.3.0.0^3,7) tetradec-11-ene has been completed with the characteristic A/B cis ring junction and with well-defined stereochemistry at each of the five asymmetric centres. The stereochemistry of these centres has been deduced from mechanistic course of reactions and confirmed from X-ray crystallographic analysis of an eight-membered acid. The orientation of the tertiary methyl group in the final tricarbocyclic compound has been deduced from force field calculations and confirmed from model studies. The successful entry into this virgin field resulting in the synthesis of the tricarbocyclic framework of ophiobolins opens up immense synthetic possibilities, since this basic skeleton is also encountered in the diterpenoids, viz., fusicoccins, aglycones of cotylenols and also in another group of sesterterpenes, ceroplastols. The double bond in
the central eight-membered ring which is always found to be present in ophiobolins may be generated from the intermediate bicyclo(6.3.0)undecan alcohol derivative through the corresponding aldehyde.

Conformational studies on eight-membered ring compounds are quite a significant point of interest in the present studies. The available data in the literature on the conformations of simple cyclooctanes and cyclooctanones fail to fulfil the requirements to make a meaningful deduction on the conformations of the compounds synthesised during these studies. Hence recourse has been taken for an independent study towards their conformational aspects. It is expected that the studies reported herein and the conclusions drawn therefrom may throw some light on conformational behaviour of medium-sized ring compounds particularly when these are heavily substituted or fused to other ring systems.

Part II of the dissertation details out synthetic studies towards developing the pentacarbocyclic system of trachylobanes. With the isolation of trachylobanes the theoretically conceivable array of diterpenoid types may be considered to be completed. A notable feature in this group is the "C-3 hydroxyl" substitution, a rarity among diterpenoids, although frequently encountered in triterpenoids and steroids.

With considerable amount of experience having been accumulated in this laboratory during the synthesis of tetracyclic diterpenoids, it was considered worthwhile to bring into the synthetic orbit the pentacyclic framework
of trachylobanes. Preliminary attempts towards model compounds without ring A was reported in an earlier dissertation from this laboratory (A. Dasgupta, Ph.D. dissertation, Calcutta University, November 1970) and this represented the bicyclic unsaturated acid which was then isolated in a poor yield. The synthesis of tricyclo (3.2.1.0\textsuperscript{2,7}) ring system of trachylobane without ring A has been completed with significant improvement in yield of the intermediates. Two different approaches were conceived with model studies with intermediates having rings A and C aromatic respectively and the aromatic ring may ultimately serve as a convenient handle for further elaboration to the desired ring-system. A few interesting observations have been encountered in the course of this investigation and these have been discussed in the proper context. In a series of studies which utilised podocarpic acid as a starting material, an interesting case of C-11 substitution during an attempted regiospecific para-formylation of the aromatic ring was observed. A probable mechanistic interpretation for this interesting reaction has been put forward, though it demands a detailed probe into the aspects of the unusual course of this reaction. From the analytical values of the final compound, it appears that the formation of the desired trachylobane net-work with ring A aromatic has been achieved. Detailed experimentations are, however, necessary to confirm this conclusion.

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