

PREFACE

There has been considerable interest in the chemistry of strained polycyclic systems for the past three decades, which is still sustained. This is clearly indicated by the publication of a recent issue of 'Chemical Reviews' (Vol. 89, 1989) which is entirely devoted to the chemistry of strained organic molecules. Of a vast majority of the strained polycyclics such as Tetrahedrane, Cubane, Homocubane, Bishomocubane, Prismane and Dodecahedrane have held fascination among synthetic organic chemists. The present thesis, directed towards the synthesis of novel spirocage polycyclic systems and their chemical transformations, is therefore, an investigation of current interest.

The thesis entitled " Chemistry of Strained Polycyclic Systems " is divided into Five Chapters. The first Chapter of the thesis deals with the chemistry of various strained molecules to have an overview of this subject.

The Second Chapter describes the synthesis of novel polycyclic diones via $\pi^{4s} + \pi^{2s}$ cycloaddition of spiro dienes with various quinones followed by intramolecular $\pi^{2s} + \pi^{2s}$ photocycloaddition of the resulting endo Diels-Alder adducts. The Diels-Alder cycloaddition between the dienes and the quinones were studied in (i) Conventional homogeneous medium by refluxing in toluene (ii) in microheterogeneous micellar media at room temperature. A remarkable

catalytic effect of cetyltrimethylammonium bromide (CTAB) on all the $\pi^{4s} + \pi^{2s}$ cycloadditions has been observed.

In the case of cycloaddition between spirohepta-1,3-diene with benzoquinone, a bis addition was observed in aqueous medium containing higher amounts (much above its CMC) of CTAB. The extent of mono versus bis addition was found to be dependent upon surfactant concentration. The structure of the bis adduct has been determined by X-ray analysis.

In this context, we also developed a simple phase transfer method for the preparation of spirodienes required for the above objective, by bis alkylation of cyclopentadiene with appropriate halides in the presence of aqueous base and a phase transfer catalyst.

In the third Chapter of the thesis, a novel transformation of two cage diones, pentacyclo [5.4.0^{2,6}3,10^{5,9}] undecane-8,11-dione-4-spiro-1'-cyclopropane and pentacyclo [5.4.0.0^{2,6}3,10^{5,9}] undecane-8,11-dione-4-spiro-1'-cyclopentane with Ce(IV) ion is reported. Oxidation of the diones with ceric ammonium nitrate furnished a mixture of three compounds, a pair of isomeric anhydrides and a cyclopropyl lactone in each case.

Structures of all the products have been deduced from spectral and analytical data and a plausible mechanism has been advanced to explain the formation of various products.

A novel one step rearrangement of pentacyclo [5.4.0.0^{2,6}.0^{3,10}.0^{5,9}] undecane-8,11-dione-4-spiro-1'-cyclopropane and pentacyclo [5.4.0.0^{2,6}.0^{3,10}.0^{5,9}] undecane-8,11-dione-4-spiro-1'-cyclopentane is reported in Chapter IV. Reactions of the diones with sodium azide in methanesulphonic acid furnished two crystalline mesylates in each case, which have been assigned structures on the basis of complementary spectral data (¹HNMR, ¹³CNMR and IR). A plausible mechanism for the formation of mesylates under Schmidt reaction conditions is proposed.

In the last Chapter (V) an approach towards the synthesis of spirohomopentaprismane from readily available spiropoly-cyclic diones is described. The spiro cage dione on zinc reduction gave a reduced polycyclic dione, which on further reduction with lithium aluminium hydride furnished the key intermediate endo-endo diol, which was transformed into its dimesylate. However, the dimesylate failed to undergo elimination to give spirohomohypostrophene upon treatment with KO^tBu in DMSO.