Tetrahedron Letters No.54, pp. 4687-4688, 1970. Pergamon Press. Printed in Great Britain.

STEREOSPECIFIC CYCLIZATION OF *cis,cis*-1,5-CYCLONONADIENE to *cis*-HEXAHYDROINDANE DERIVATIVES *via* C^+-π INTERACTION

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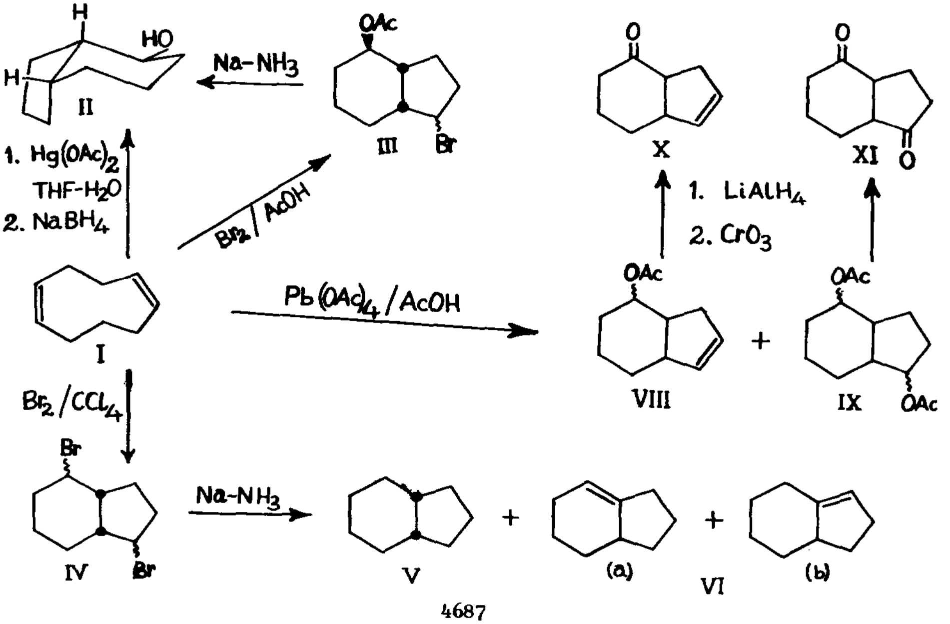
(Received in UK 13 October 1970; accepted for publication 21 October 1970)

The medium ring compounds, because of their intrinsic angle deformation, bond opposition and steric interference between nonadjacent atoms, exhibit unique physical and chemical properties. Since very little chemistry of nine-membered cyclic system is known as compared to that of eight and ten-membered systems[1], we wish to report here the transannular reactions of *cis,cis*-1,5-cyclononadiene (I) brought about by electrophilic attack on carbon-carbon double bond.

Monooxymercuration by Brown's procedure[2] of I gave a bicyclic alcohol (II)[3] in 68% yield as the sole product of the reaction which was shown by its spectral properties and by the physical properties of its derivatives to be β-*cis*-hexahydroindan-4-ol[4].



Addition of bromine to I in AcOH and CCl_4 also led to transannular addition products (III and IV), the structures of which were confirmed by spectral and analytical data. Sodium-ammonia reduction of III led to the formation of II, whereas the reduction of IV in sodium-liquid ammonia gave V, VI and an unidentified product in the ratio 46:48:6. Compound (V) was identified as *cis*-hexahydroindane from a comparison of its ir[5] and nmr[6] spectra with reported data. The other product (48%) had ir and nmr spectra consistent with the bicyclic olefin VI formed by elimination of HBr from IV. The compound VI was found actually to be a mixture of (VIa) and (VIb) by hydroboration and oxidation of the resulting alcohols to ketones.

The reaction of HBr in AcOH with I gave a saturated bicyclic monobromo compound (VII), the structure of which was based on its spectral properties as well as the fact that we get β-*cis*-hexahydroindan-4-ol (II) in the earlier reactions.

Lead tetraacetate oxidation of I in AcOH at room temperature gave three acetates in the ratio of 19:78:3. After separation, the first two products were shown to be the monoacetate (VIII) and the diacetate (IX) by elemental analysis[3], ir and nmr spectral data. Because of insufficient amount the third component could not be identified. The $LiAlH_4$ reduction of VIII followed by chromic acid oxidation afforded the ketone (X) which showed carbonyl absorption at 5.85μ indicating the presence of the acetate group in the six-membered ring. A similar sequence of reactions with IX provided a diketone which showed two carbonyl bands at 5.85 and 5.75μ indicating the presence of both a six and a five-membered cyclic ketone. Further work is in progress, and will be reported in the forthcoming paper.

Acknowledgement: We thank CSIR, New Delhi for an award of SRF to G.N.

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