Ready Formation of a Bredt Compound, Tricyclo[5,3,1,$0^{3,8}$]undec-2-ene. Conformational Preference Leading to Regiospecificity in a Planar *cis*-Elimination

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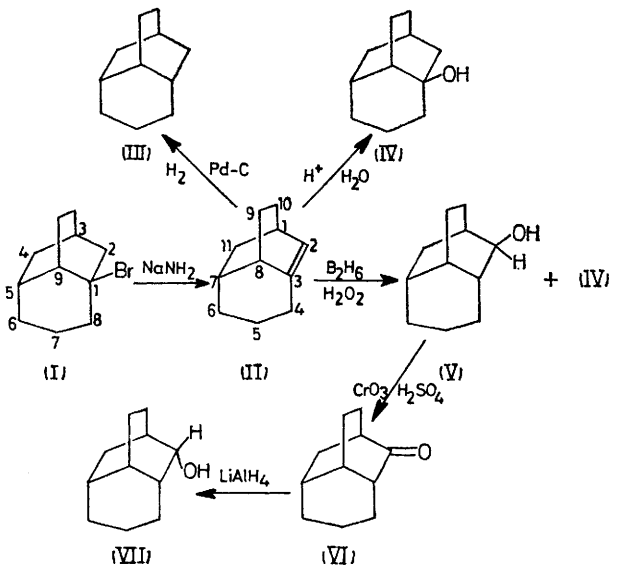
Summary Dehydrobromination of 3,9-ethanobicyclo[3,3,1]-non-1-yl (tricyclo[5,3,1,$0^{3,8}$]undec-3-yl) bromide (I) with sodium amide in refluxing toluene gave 3,9-ethano-bicyclo[3,3,1]non-1-ene (tricyclo[5,3,1,$0^{3,8}$]undec-2-ene) (II) in 52% yield.

No example seems to have been found of the formation of a Bredt compound in dehydrohalogenation of bridgehead halides.[1] Even bicyclo[3,3,1]non-1-ene, which is one of the most easily accessible strained bridgehead olefins, was obtained only with difficulty through a variety of methods.[1,2]

We discovered that dehydrobromination of 3,9-ethano-

bicyclo[3,3,1]non-1-yl (tricyclo[5,3,1,$0^{3,8}$]undec-1-yl) bromide (I)† with sodium amide in refluxing toluene led to the isolation in 52% yield of 4-homoisotwist-2-ene (tricyclo-[5,3,1,$0^{3,8}$]undec-2-ene) (II). The reaction was highly



regiospecific, giving neither 3(4)-ene nor 3(8)-ene at all. The olefin (II)‡ could be isolated from the mixture by distillation, b.p. 90—92° at 19 mmHg, ν_{max} 3020 and 1620 cm^{-1}, *m/e* 148 (41%, M^+), 105 (25%), and 94 (100%). The ^{1}H n.m.r. spectrum of (II) showed a 1H doublet at δ 5·9 (J 7 Hz) for the olefinic proton, indicating coupling with the 1-proton in accordance with structure (II). The olefin was fairly stable at room temperature in the absence of air.

Hydrogenation of (II) over Pd–C gave 4-homoisotwistane (III) quantitatively.[4] Hydration of (II) in the presence of a trace of perchloric acid[5] gave 4-homoisotwistan-3-ol (IV)‡ almost quantitatively, which was identical in every respect with (IV) obtained[3] by hydrolysis of the bromide (I). Hydroboration[6] of (II) gave a mixture comprising 23% (IV) and 77% 4-homoisotwistan-2-*exo*-ol (V),‡ m.p. 92—93°. An *exo* configuration was assigned to (V) on the basis of preferential *exo* attack of diborane.[6–10] The structure assignment is consistent with the result that the ketone (VI)‡ obtained by Jones oxidation of (V) was transformed exclusively into the *endo* alcohol (VII),‡ m.p. 95—96°, by $LiAlH_4$ reduction, which is known[9–11] to be subject to steric control of the reagent approach.

A rather ready and at the same time highly regiospecific dehydrobromination of (I) could be explained satisfactorily in terms of a planar *cis*-elimination of the 2-*exo* hydrogen and 1-bromine atoms[12] from the boat-form cyclohexane ring which is held rigidly in that conformation by the ethano bridge between the 3- and 9-positions in (I). High stereospecificity in hydroboration and $LiAlH_4$ reduction demonstrates the steric congestion on the *endo* side of (II).

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† Synthesised recently[3] by treatment of 4-homoisotwistane (III)[4] with excess of bromine at room temperature.

‡ Satisfactory elemental analyses were obtained for all new compounds.

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