Functionalizations and Bridgehead Reactivity of 4-Homoisotwistane (Tricyclo[5,3,1,$0^{3,8}$]undecane). Synthesis of 3-Substituted Derivatives

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Summary Bromination and hydride transfer–carboxylation of 4-homoisotwistane (tricyclo[5,3,1,$0^{3,8}$]undecane) (I) to give the 3-substituted derivatives (II) and (III) as well as ready hydrolysis of the 3-bromide (II) shows the high reactivity of the 3-bridgehead in the hydrocarbon (I).

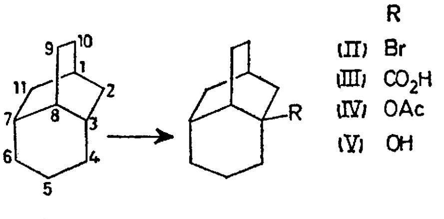
IT has been found[1,2] that 4-homoisotwistane (tricyclo[5,3,1,$0^{3,8}$]undecane) (I)[3] is the key intermediate in adamantane rearrangement of tricycloundecane precursors. Our recent discovery of a convenient synthesis of (I)[4] enabled us to study its functionalizations.

Reaction of (I) with excess of bromine at room temperature for 10 min gave in 85% yield the 3-bromo-derivative (II),[†] m.p. 59·5°, *m/e* (rel intensity) 230 (0·2%, M^+), 228 (0·3%, M^+), and 149 (100%), ^{1}H n.m.r. δ (CCl_4) 1·0—2·6 (complex m), ^{13}C n.m.r.[‡] ($CDCl_3$) 20·2 (t, 1), 24·7 (t, 2), 26·3

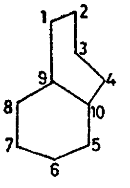
[†] Satisfactory elemental analyses were obtained for all the new compounds.

[‡] P.p.m. downfield from Me_4Si as internal standard. Fine structure on off-resonance proton decoupling and relative intensity of the signals are shown in parentheses.

(d, 1), 29·5 (t, 1), 31·3 (t, 1), 34·4 (d, 1), 42·7 (d, 1), 44·5 (t, 1), 45·0 (t, 1), and 73·5 (s, 0·5). The structure of the bromide was established as follows. Reduction of (II) by lithium metal in t-butyl alcohol gave the original hydrocarbon almost quantitatively. The bromide (II) showed no ^1H n.m.r. signal assignable to a proton geminal to the bromine atom, indicating that the substitution had occurred at a bridgehead. The ^{13}C n.m.r. spectrum of (II) showed the molecule to be asymmetrical, and excluded unambiguously the possibility of 1- and 8-bromides.



(I)



(VI)

Koch carboxylation of (I) using the t-butyl cation[5] also gave a 3-substituted derivative (III),† m.p. 95—96°, ν_{max} (neat) 2650br and 1680 cm^{-1}, *m/e* 194 (12%, M^+) and 149 (100%). The carboxylic acid (III) was decarboxylated with lead tetra-acetate[6] to the 3-acetoxy-derivative (IV),† which was then hydrolysed with KOH to the corresponding alcohol (V),† m.p. 104·5°, ν_{max} (Nujol) 3260 and 1100 cm^{-1}, *m/e* 166 (100%, M^+). The alcohol was identical with the sample obtained by hydrolysis of the bromide (II) in aqueous acetone at reflux for 1 h without added acid, base, or silver ion.[7] No isomerization of the hydrocarbon skeleton was thus observed in these reactions which proceeded through the 3-cation of (I), in spite of the rather easy adamantane rearrangement of (I) under carbonium ion-forming conditions.[1]

Bromination and carboxylation of (I) demonstrated that the 3-position of (I) was at least as reactive as the 1-position of adamantane,[8] while the 1- and 8-positions of (I) were quite unreactive. On comparison of the hydrolysis of bridgehead bromides, (II) was more reactive than 1-bromoadamantane.[7,9] The reactivity difference between the two kinds of bridgehead carbon atoms of (I) [1- (and 8-) and 3- (and 7-)] and the 1-carbon atom of adamantane may well be interpreted in terms of the relative stabilities of the bridgehead carbocations of bicyclo[2,2,2]octane, bicyclo[3,3,1]nonane, and adamantane, respectively, as shown by their bromination[8] and solvolysis.[10,11] Alternatively, the 3- and 8-bridgeheads in (I) might possibly have the same reactivity if it were not for the 11-methano-bridge in the molecule that transforms *cis*-decalin (VI) into (I). Methano-bridging between the 3- and 8-carbon atoms in (VI) would leave one of its bridgehead atoms [10-carbon atom in (VI), corresponding to 3- in (I)] unchanged with retention of high reactivity[11,12] while converting the other [9- in (VI), corresponding to 8- in (I)] into a bicyclo[2,2,2]octane bridgehead.

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