1,5-Hydride Transfer in Acyclic Molecules

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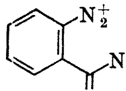
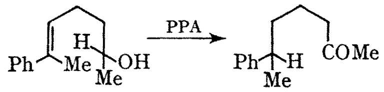
Summary A carbonium ion, generated by an intramolecular 1,5-hydride shift has been trapped intramolecularly with the formation of a C–C bond.

INTRAMOLECULAR 1,5-hydride transfer is favoured in those systems in which the transfer source and terminus are held in juxtaposition *e.g.* in medium-ring[1] and rigid polycyclic compounds.[2,3] Some aromatic diazonium salts, *e.g.* (I) also decompose *via* 1,5-hydride abstraction[4] but examples in other acyclic molecules are limited to the sapogenin–isosapogenin interconversion[5] and to the conversion of (II)→(III) with polyphosphoric acid.[3,6]



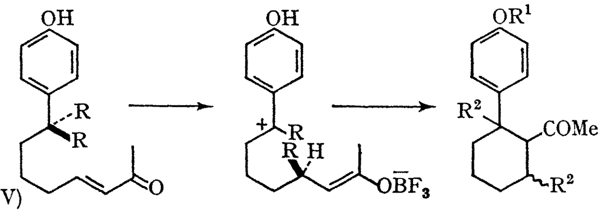
(I)



(II) (III)

The αβ-unsaturated ketone (IV; R = H) (*p*-nitrobenzoate m.p. 96—97·5°) is transformed on heating with boron trifluoride etherate in benzene to the isomeric ketone (Va; R^2 = H) in 77% yield. The structure of (Va; R^2 = H) was confirmed by synthesis of the methyl ether (Vb; R = H) by copper(I) chloride-catalysed conjugate addition of *p*-anisylmagnesium bromide to acetylcyclohexene[7] followed by demethylation with hydrobromic–acetic acid. Compound (Va) is assumed to have *trans*-stereochemistry by analogy with the case of 2-phenylcyclohexyl methyl ketone,[8] since it was recovered unchanged after treatment with base.

The αβ-unsaturated ketone (IV; R = H) was prepared by bromination–dehydrobromination of the corresponding saturated ketone (m.p. 67—68°), itself prepared by standard methods from γ-(*p*-anisoyl)butyric acid.



(IV)

(V) a, R^1 = H
b, R^1 = Me

In order to test the mechanism suggested above, the deuteriated compound (IV; R = D) was prepared. Catalytic exchange of the benzylic hydrogen atoms of the saturated ketone using deuterium and palladium–charcoal, followed by bromination–dehydrobromination, gave (IV; R = D) containing 92% D_2, 8% D_1. Treatment with boron trifluoride etherate yielded (Va; R^2 = D) whose mass spectrum showed no loss of deuterium and mass-spectrometric comparison of (Va; R^2 = H) and (Va; R^2 = D) was consistent with the mechanism postulated.

That the 1,5-hydride transfer is intramolecular was shown by treating a 1 : 1 mixture of (IV; R = H) and (IV; R = D) with boron trifluoride etherate. Mass spectrometric analysis of the resultant (V) showed the presence of D_2 and D_0 species only.

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