Bifunctionally Catalysed 1,3-Proton Transfer Reaction of a Propene by a New Bicyclic Amidine

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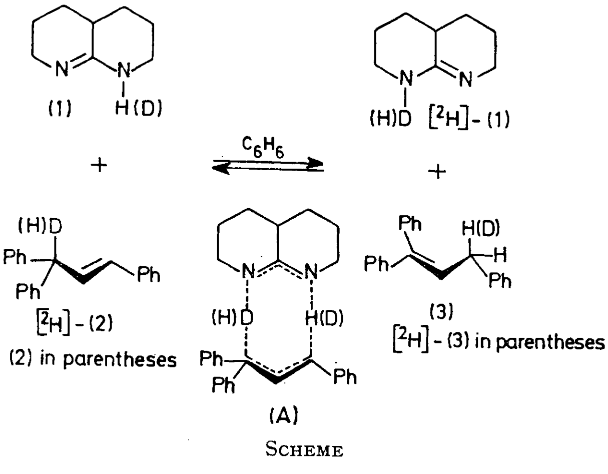
Summary Evidence is presented that the secondary amidine 1,2,3,4,4a,5,6,7-octahydro-1,8-naphthyridine catalyses the 1,3-proton transfer of 1,3,3-triphenylpropene to 1,1,3-triphenylpropene with a bifunctional mechanism.

A CLASSICAL example of multiple catalysis of the bifunctional type is the tautomeric catalysis by 2-pyridone of the mutarotation of tetramethylglucose in benzene.[1] We here present part of a study of the possibilities of having other bifunctionally catalysed 1,3-proton transfer reactions, enabling us more firmly to establish the nature of tautomeric catalysis.[2] The reaction system in the Scheme has therefore been partly investigated.

The bicyclic secondary amidine (**1**)[3] was found to catalyse the rearrangement of [^{2}H]-(**2**) into (**3**) in benzene at 75 °C. The reaction mixture was initially 1 M in the catalyst (**1**) and 0·05 M in the substrate [^{2}H]-(**2**). After *ca.* 1 h the reaction mixture was quenched and the mixture of isomeric propenes



SCHEME

was isolated. Analysis by g.l.c. showed that 40% of [^{2}H]-(**2**) had rearranged to (**3**). The propenes were separated by preparative g.l.c. and analysed by ^{1}H n.m.r. spectroscopy. Within experimental error the fraction containing (**2**) consisted solely of the deuteriated starting material [^{2}H]-(**2**), whereas the fraction containing (**3**) was largely (93%) the non-deuteriated compound.

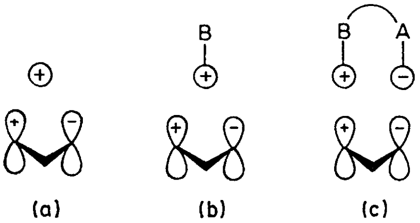


FIGURE. Interactions in important orbitals involved in (a) uncatalysed, (b) monofunctionally catalysed, and (c) bifunctionally catalysed 1,3-proton transfer reactions.

In a separate experiment employing [^{2}H]-(**3**) and (**1**) it was shown that exchange of the carbon-bonded deuteron with the amidine proton was much slower than the rate of catalysed isomerization of [^{2}H]-(**1**) to (**3**).

These results indicate that the rearrangement mainly involves an activated complex such as (A); *i.e.* the rearrangement is bifunctionally rather than monofunctionally catalysed.[2] Our results do not exclude the possibility of a multistep reaction and that the observed isotopic distribution in (**3**) is the result of rapid hydrogen–deuterium exchange within ion pair(s).[2]

It is interesting that the above results are in agreement with our recent CNDO/2 theoretical results on the formamidine catalysed rearrangements of propene, which could be rationalized as shown in the Figure.[2b,c] A suprafacial [1,3] sigmatropic rearrangement is forbidden according to the Woodward–Hoffmann rules[4] as illustrated by (a). A monofunctionally base-catalysed 1,3-proton transfer is less disfavoured than the non-catalysed reaction because of increased bonding of the hydrogen in the activated complex (b). With the bifunctional activated complex (c) on the other hand, the rearrangement becomes symmetry allowed.

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