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THE REARRANGEMENT OF 1-ALLYL-1,2-DIHYDROISOQUINOLINES

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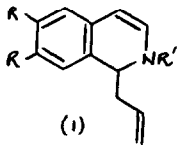
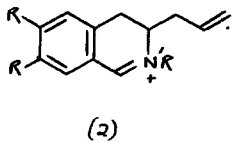
We have recently shown[1] that 1-allyl-2-methyl-1,2-dihydroisoquinoline (1, R = H, R' = Me) rearranges to the 3-allyl-2-methyl-3,4-dihydroisoquinolinium salt (2, R = H, R' = Me) when treated with dilute HCl. In a discussion of the chemistry of benzylaminoacetaldehyde dimethyl acetals we[2] have also reported that the compound (3, R = H), when treated with dilute HCl, is transformed into the 3-allyl-3,4-dihydroisoquinolinium salt (2, R = OMe, R' = H) in almost quantitative yield. Since we were able to isolate the 1-allyl-4-hydroxy-1,2,3,4-tetrahydroisoquinoline (4), and since these compounds are easily dehydrated with acids, it was clear that the reaction proceeded via the 1,2-dihydroisoquinoline (1, R = OMe, R' = H). Knabe and Holtje, who[3] have just confirmed this finding, state their intention to study the mechanism of the reaction.

We have[2] viewed the reactions as an example of a suprafacial sigmatropic [3, 3] reaction, and have[4] supported this view by an examination of the reaction of (5) with dilute HCl under conditions similar to those used above. The 3-trans-crotyl-3,4-dihydroisoquinolinium salt (6) was formed[4] in 96% yield. An intramolecular course for the reaction is also supported by (a) the fact that when a mixture of (3, R = Me) and (5) was treated with dilute HCl, only the TWO products (2, R = OMe, R' = Me) and (6) were formed (GLC and mass spectral analysis and comparison with authentic specimens) and (b) the fact that the 1-propargyl-2-methyl-1,2-dihydroisoquinoline (7) rearranges to the allene derivative (8) when treated with HCl. [This latter experiment was conducted with Mr. F. L. Hall.]



(1)



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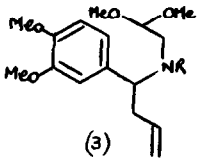

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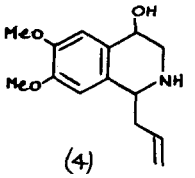

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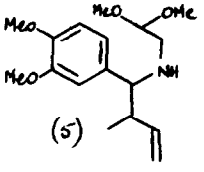

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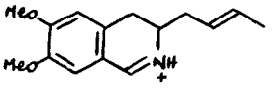

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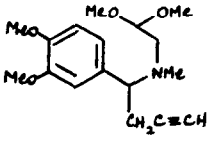

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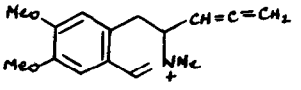

(8)

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1. M. Sainsbury, D. W. Brown, S. F. Dyke, R. G. Kinsman and B. J. Moon, Tetrahedron, 24, 6695 (1968).

2. D. W. Brown, S. F. Dyke and M. Sainsbury, Tetrahedron, 25, 101 (1969)

3. J. Knabe and H. D. Holtje, Tetrahedron Letters, 433 (1969)

4. D. W. Brown, S. F. Dyke, R. G. Kinsman and M. Sainsbury, Autumn Meeting Chemical Society, Keele, September 1968.

5. Satisfactory analytical and spectral data have been secured for all new compounds described.