

SINGLE, DOUBLE, AND TRIPLE HYDROGEN REARRANGEMENT REACTIONS
IN IONIZED 2-BENZYL-1-INDANOLS

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An unexpected variety of hydrogen rearrangement reactions has been found in the mass spectrometric fragmentation of the metastable molecular ions of 2-benzyl-1-indanols and related compounds. Single (1H), double (2H), and triple (3H) rearrangements have been observed, the course of reaction being strongly affected by steric and substituent effects. Illustrative examples are given in Fig 1.

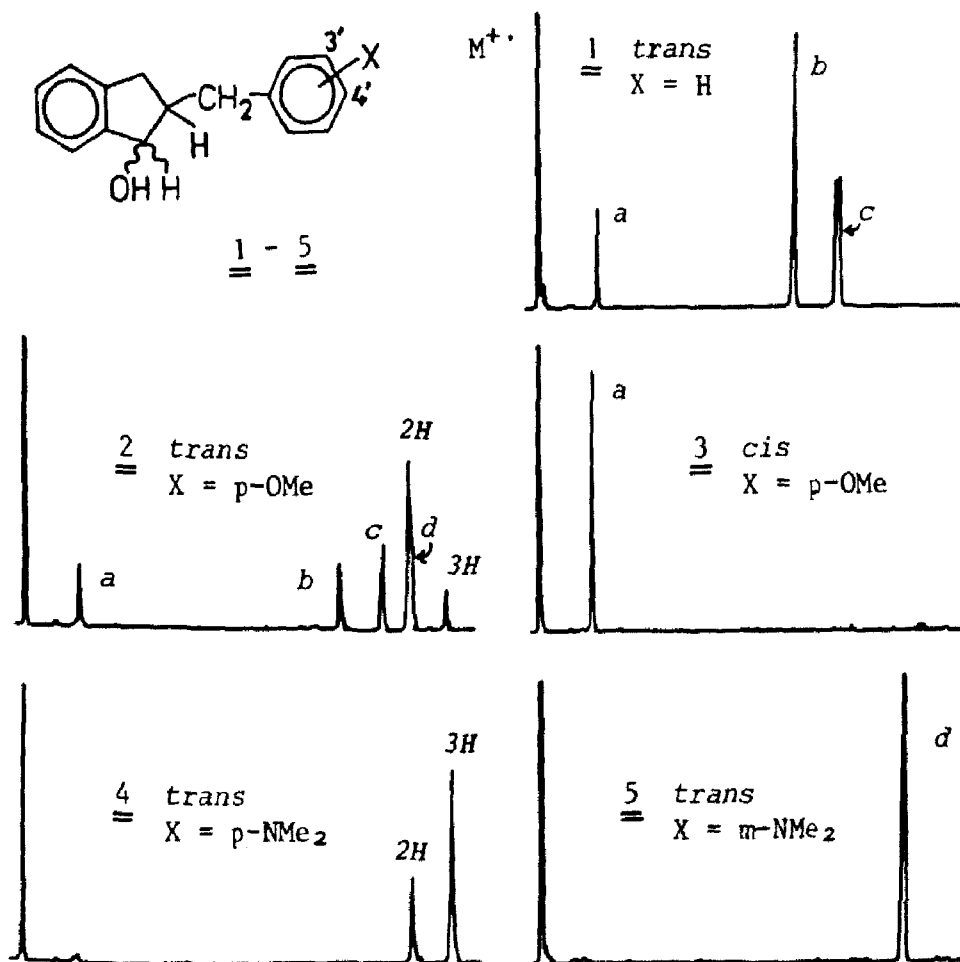
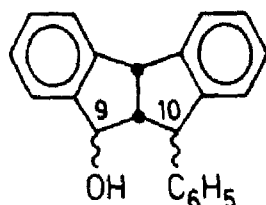


Fig 1. MIKE spectra of the $M^{+\bullet}$ ions of 2-benzyl-1-indanols (ZAB-2F, 70 eV, 200 °C). Single hydrogen rearrangements: a $[M-\text{H}_2\text{O}]^{+\bullet}$, b $[M-\text{C}_6\text{H}_5\text{X}]^{+\bullet}$, c $[M-\text{C}_7\text{H}_7\text{X}]^{+\bullet}$, d $[\text{C}_7\text{H}_7\text{X}]^{+\bullet}$; double hydrogen rearrangements: 2H $[\text{C}_7\text{H}_9\text{X}]^{+\bullet}$; triple hydrogen rearrangements: 3H $[\text{C}_6\text{H}_7\text{X}]^{+\bullet}$.

It is inferred from the results that the novel $2H$ and $3H$ rearrangements occur specifically with *trans*-indanols bearing a strongly electron-donating substituent in the *para* position of the benzyl group (e.g., 2 and 4). In turn, exclusive loss of water or the well-known (single) γ -hydrogen rearrangement indicate *cis* orientation and *meta* substitution, respectively (e.g., 3 and 5).

The $3H$ rearrangement has been found also in the MIKE spectra of acyclic γ -aryl alkanols, e.g., $(4'\text{-Me}_2\text{NC}_6\text{H}_4)\text{CH}_2\text{CH}_2\text{CH}(\text{Me})\text{OH}$. Thus, its occurrence is not limited to cyclic alcohols or even to indanols.

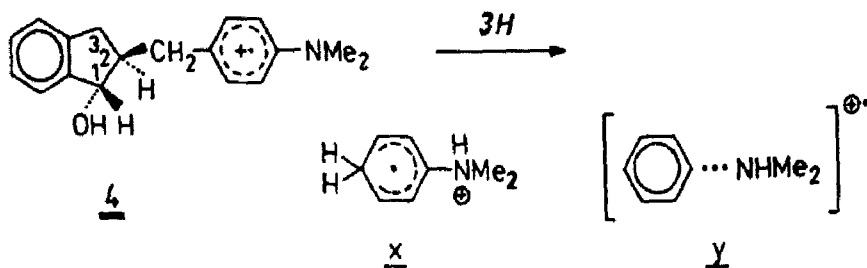
On the basis of these results, the stereochemistry of 1-indanols which are relevant to the synthesis of centropolyquinanes [1] can be determined. For example, the isomers "A" and "B" of hitherto unspecified stereochemistry [2] have been identified by their mass spectrometric fragmentation as follows:



Isomer	m.p. [2]	Stereochemistry
"A"	176-8 °C	9- <i>syn</i> , 10- <i>anti</i>
"B"	148 °C	9- <i>anti</i> , 10- <i>anti</i>

In this case, mass spectrometry has been found to be superior to nuclear magnetic resonance spectroscopy.

Various deuterium labelled analogues of 4 (Fig 1) have been studied. The three H atoms transferred in the $3H$ rearrangement reaction are H^1 (100%), H^{OH} (100%), and H^2 ($\sim 95\%$), without any preceding hydrogen exchange. The $2H$ rearrangement reaction is less specific, H^{OH} (100%), H^2 ($\sim 35\%$), and H^3 ($\sim 65\%$) being transferred. As deduced from primary isotope effects, the rate-determining steps are the migration of H^2 ($3H$ rearrangement) and of H^1 and H^3 ($2H$ rearrangement). The product ion of the $3H$ rearrangement is suggested to be a distonic ion, x, or an ion-molecule complex, y. The latter has been proposed to be an intermediate during the homolytic amination of alkyl benzenes in the liquid phase [3].



1. D. Kuck, *Angew.Chem.Int.Ed.Engl.* **23**, 508 (1984).
2. W. Baker, J.F.W. McOmie, S.D. Parfitt, and D.A.M. Watkins, *J.Chem.Soc.* 4026 (1957).
3. A. Clerici, F. Minisci, M. Perchinunno, and O. Porta, *J.Chem.Soc., Perkin Trans. II* 416 (1974).