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THE LABELLING VIA SATURATION OF A SPIN SYSTEM IN STUDY OF MECHANISMS OF MODERATELY RAPID REVERSIBLE REACTIONS - AN EXAMPLE

B.G. Derendyaev, V.I. Mamatyuk, V.A. Koptyug

Institute of Organic Chemistry, USSR Academy of Sciences, Siberian Division,

Novosibirsk, USSR

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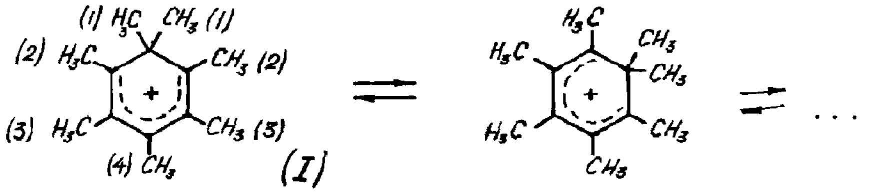
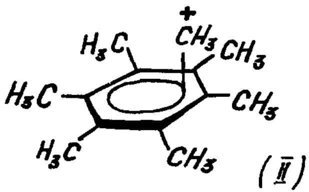
Some years ago (1,2) the rearrangement of heptamethylbenzenonium ion (I) to the ion of the same structure (an "automerization" reaction, ref. 3) was revealed in our laboratory. The analysis (4) of temperature dependence of proton magnetic resonance spectra of this ion in HSO_3Cl carried out over the range - 10°C to + 113°C has made it possible to estimate the frequency factor and the activation energy ($A = 10^{13.5 \pm 0.4}$ sec.$^{-1}$; $E_a = 18.2 \pm 0.6$ kcal·mole^{-1}) and to conclude that this rearrangement is due to the intramolecular 1,2-shift of CH_3-group (mechanism A).



(A)

Recently (5) M. Saunders has published the results of kinetic study of the same rearrangement for temperature ranging from + 25.5°C to + 75.5°C (in 9.4M H_2SO_4). The reported rate constants are in agreement with published ones (4), but the parameters A and E_a are somewhat different ($10^{12.3}$; 15.2). According to results of this author, the most plausible mechanism of the rearrangement under consideration is one mentioned above (A). At the same time Saunders does not rule out the possibility of simultaneous operating the mechanism (B) via "unlocalized" (6) σ-complex (II). The main feature of this mechanism lies in "random" migration of CH_3-group.



(II)

We would like to draw attention to the fact, that in this case (and in other similar cases) the relative contributions of the two alternative mechanisms can be easily estimated by nuclear magnetic multiple resonance method. This method makes it possible (cf. 7) to "introduce" the sui generis label (the labelling via saturation of a spin system) in the certain positions of ions or molecules and to observe the subsequent transfer of this label into other positions.

If the rearrangement of ion I proceeds solely by mechanism A CH_3-groups from sites 3 and 4 will be transferred into site 1 via site 2. By contrast mechanism B implies the possibility of direct transfer of CH_3-groups into site 1 not only from site 2 but also from sites 3 and 4. In both cases saturation with strong irradiation at the frequency corresponding to the resonance of 2-CH_3--groups will reduce 1-CH_3-group signal intensity. The subsequent complete saturation of 3-CH_3- (or 4-CH_3)-group signal will result in further reduction of this signal intensity in the case of mechanism B; on the other hand the intensity of 1-CH_3-group signal will be unchanged if only mechanism A is realized.

The single resonance spectrum (a) of heptamethylbenzenonium trifluoroacetate in CF_3COOH at 28°C and the double resonance spectrum (b) obtained for the same system by saturation of 2-CH_3-group signal are depicted in Fig. One can see from the figure that transfer of CH_3-groups from site 2 into site 1 causes under these conditions the reduction of 1-CH_3-group signal intensity in double resonance experiment by the factor of 2.5. In this case according to quantative consideration (all the details will be published separetely) the further reduction of 1-CH_3-group signal intensity at complete saturation of 3-CH_3-group signal must amount to 22%, if the rearrangement proceeds by mechanism B. No changes ($\leq 1\%$) in 1-CH_3-group signal intensity were observed,

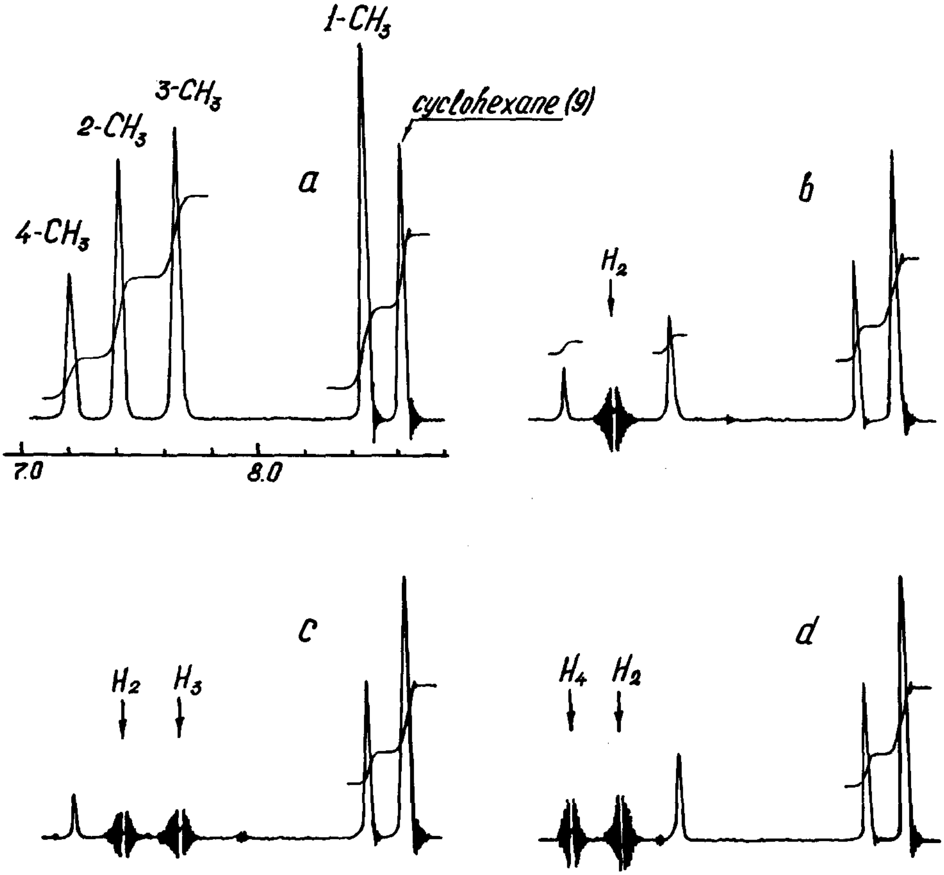


Fig.

NMR spectra of heptamethylbenzenonium trifluoroacetate in CF_3COOH at 28°C, 100 Mc/s (Varian HA-100).

however, in the triple resonance experiments with simultaneous saturation of $2-CH_3$- and $3-CH_3$-group (spectrum c) or $2-CH_3$- and $4-CH_3$-group (spectrum d) signals.

These results show that mechanisms with "random" migration of CH_3-group do not play any significant role in the rearrangement of ion I, which proceeds therefore solely (or almost solely) by the intramolecular 1,2-shift of CH_3-group (cf. the isomerization of methylsubstituted aromatic compounds, ref. 8).

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