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A NEW METHOD FOR THE STUDY OF MOLECULAR REARRANGEMENTS WITH THE USE OF CARBON-13 DOUBLE RESONANCE NMR SPECTRA

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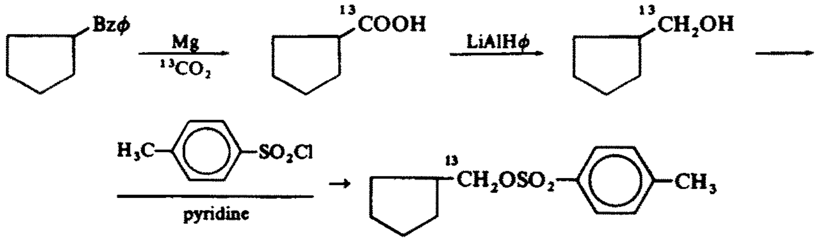
Abstract—Carbon-13 nuclear magnetic double resonance absorption spectra with complete decoupling of hydrogen nuclei has been used to establish the rearrangement by hydride ion shifts of the cyclohexyl cation in the formolysis reaction of cyclopentylcarbinyl-^{13}C *p*-toluenesulfonate.

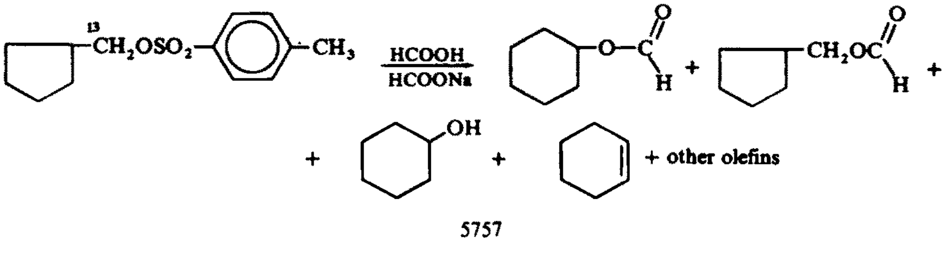
In previous papers[1-5] we published results on the cycloalkyl cation isomerization using radioactive ^{14}C or deuterium as a label. These methods involved very tedious and time-consuming (sometines several months) stepwise degradation of the molecule under investigation.

In the present paper we propose a new rapid method for the study of molecular rearrangements. Carbon-13 nuclear magnetic double resonance absorption spectra with complete decoupling of hydrogen nuclei were used first to establish the rearrangement by hydride ion shifts of the cyclohexyl cation formed as an intermediate in the formolysis reaction of cyclopentylcarbinyl *p*-toluenesulfonate, labelled in the side chain methylene group with ^{13}C (57% enrichment).

Labelled cyclopentylcarbinyl *p*-toluenesulfonate was synthesized as follows:



The formolysis of cyclopentylcarbinyl-^{13}C *p*-toleuensulfonate (0·02 M) was carried out in anhydrous HCOOH (50 ml) in presence of HCOONa (0·034 M), 30 hr at 50°.



Cyclohexanol, as separated from the reaction product after treatment withLiAlHy (with 4% cyclopentylcarbinol impurity by GLC) contained additional ^{13}C not only in position 2, as could be expected in the absence of cation rearrangement, but in all positions, viz. 10 ± 1% in position 1, 18 ± 2 total content in the two positions 2 and 6, 14 ± 2% total in the positions 2 and 5 and 7 ± 1% in position 4. The ratios of peak heights of two double resonance absorption spectra, one of unenriched material with the natural 1·08% content of ^{13}C and another of the same amount of the enriched rearrangement product, were taken to the equal to the ^{13}C content (Fig. 1, 2).

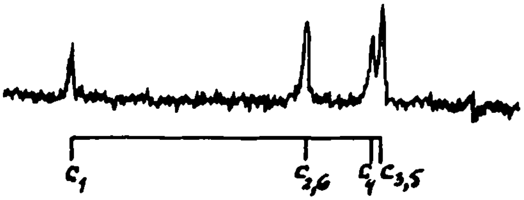


FIG. 1

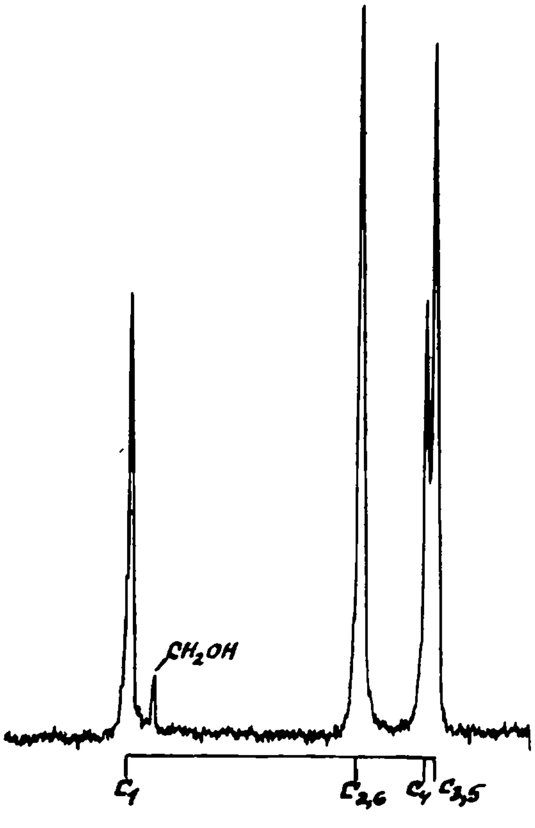


FIG. 2

The necessary very high sensitivity, quantitative precision of measurement, and base line stability were achieved by the use of time sharing with a high (4 kc/s) pulse repetition rate[6] and virtually total decoupling of all hydrogen nuclei with a very strong ($\gamma H_2 > 1000$ c/s) perturbing radiofrequency field[7-9] which provides a 4-to 6-fold signal increase through the nuclear Overhauser effect and multiplet collapse. Only absorption spectra can be used for line intensity determinations, the usual rapid passage dispersion signals can provide only qualitative data. The spectra of both samples were registered 5 to 10 times at 15·1 Mc frequency under strictly identical conditions without saturation of the signals by measuring the R_f field. The necessary sample size must be 0·01 to 0·015 mole (1 to 2 grammes of neat liquid) for the unenriched compound while it is possible to use a smaller sample of the enriched compound. The necessary amount is in this case inversely proportional to the ^{13}C content of the least enriched carbon position under investigation. ^{13}C relaxation times,[10] and accordingly the sample composition (solvents, even main impurities, etc.) must be the same for both samples. At present the relative error of measurement does not exceed ±10% for the absolute ^{13}C content as determined by comparing the spectra of the two above-mentioned samples, but relative contents, proportional to peak heights in one spectrum, can be compared with a 2 to 3 times higher precision.

The ^{13}C absorption spectra were also used to measure the ^{13}C content of the side chain methylene groups in the intermediate compounds, cyclopentylcarbinol tosylate (51 ± 5%) and cyclopentylcarbinol (55 ± 5% and 54 ± 5%). The last value was measured by comparing the peak heights of side chain and cycle methylene carbon spectral lines. The good agreement of both values is indicative of a close similarity in the relaxation δ behaviour of these methylene groups.

The ^{13}C chemical shifts $_{CS_2}$ of the two cyclic alcohols and n-hexanol are given in Table 1:

TABLE 1

Compound	C_1	C_2	C_3	C_4	C_5	C_6
Cyclohexanol	124·8	158·9	169·9	168·6	169·9	158·9
Cyclopentylcarbinol	128·3	152	169	165	165	169
n-Hexanol	131·5	161·3	167·7	161·9	171·1	179·6
n-Hexyl chloride	148·5	160·2	166·1	162·0	170·2	179·1

The diamagnetic shift of γ-C atoms relative to the same atom in hydrocarbons or β- and δ-C shifts in alcohols is specific to alcohols (and alkyl chlorides) and cannot be due to the inductive effect of the substituent. Hyperconjugation of σ-bonds and the corresponding electron delocalization in long saturated chains of methylene groups, which also accounts for the contact spin-spin coupling J_{HH} between adjacent hydrogen nuclei is the most likely cause for this effect. This very general phenomenon is well illustrated by the methylene chemical shifts of n-hexanol.

The distribution of additional ^{13}C over the whole cyclohexanol molecule is indicative of a considerable rearrangement of the cyclohexyl cation by hydride ion migration. It follows from the above-mentioned ^{13}C contents and the spectra in Fig. 1, 2 that the overall degree of isomerization is 77% and hydride ion migration from the positions 2 and 6, 3 and 5, and 4 (or by stepwise 1,2 hydride ion shifts) contribute [2.(10–1).100]/43 = 42%, 28% and 7% respectively (Fig. 2).

Corresponding data which we have obtained from the study of the same reaction using ^{14}C label are as follows: the overall degree of isomerization is ~80% and hydride ions migration from the positions 2 and 6, (3 and 5 + 4) (or by stepwise 1,2 hydride ions shifts) contribute 48% and 32% respectively.

It is clear that ^{13}C double resonance absorption spectra are most useful for the study of molecular rearrangement and at present, as a very fast and non-destructive method, has many advantages over the use of radioactive ^{14}C, which involves the very tedious and time-consuming controlled stepwise destruction of the molecule under investigation.

REFERENCES

[1] O. A. Reutov and T. N. Shatkina, *Dokl. Akad. Nauk SSSR* **142**, 835 (1962); *Tetrahedron* **18**, 237 (1962).

[2] T. N. Shatkina, E. V. Leontieva and O. A. Reutov, *Dokl. Akad. Nauk SSSR* **173**, 113 (1967).

[3] T. N. Shatkina, E. V. Leontieva and O. A. Reutov, *Ibid.* **177**, 143 (1967).

[4] T. N. Shatkina, E. V. Leontieva and O. A. Reutov, *Ibid.* **177**, 343 (1967).

[5] Ju. G. Bundel, V. A. Savin and O. A. Reutov, *Ibid.* **165**, 1078 (1965).

[6] E. Lippmaa, J. Past, A. Olivson and T. Saluvere, *Eesti NSV Tead. Akad. Toimetised, füüs.-matem.* **15**, 58 (1966).

[7] E. Lippmaa, T. Pehk and J. Past, *Ibid.* **16**, 345 (1967).

[8] S. Rang, T. Pehk, E. Lippmaa and O. Eisen, *E. NSV Tead. Akad. Toimetised, keemia-geol.* **16**, 346 (1967).

[9] E. Lippmaa and T. Pehk, *Kemian Teollisuus, Finland* **24**, N12, 1 (1967).

[10] A. Olivson, E. Lippmaa and J. Past, *Eesti NSV Tead. Akad. Toimetised, füüs.-matem.* **16**, 390 (1967).