

## Tritiations by HTO promoted aluminium chloride. IV\*. Cyclohexane and n-heptane

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### SUMMARY

*Tritium labelling of saturated hydrocarbons (n-heptane, cyclohexane) is conveniently performed on a small scale by isotopic exchange with tritiated water in the presence of aluminium chloride. The reaction involves hydride ion abstraction but is not accompanied by isomerization, unless the reaction conditions are rather severe. The activities of cyclohexane, and of the methylcyclopentane formed by its isomerization, were found to be comparable.*

### INTRODUCTION

In order to prepare *n*-heptane and cyclohexane labelled with tritium for the investigation of petroleum refining processes, recourse was had to isotopic exchange with tritiated water, in the presence of anhydrous aluminium chloride. This method has already been applied in our laboratory for the ring tritiation of aromatics<sup>(1)</sup>, heterocyclic compounds<sup>(1-3)</sup> and of other substances<sup>(3)</sup>.

The specific activities of the saturated hydrocarbons obtained by this method are expected to be lower than those obtained by the addition of tritium to olefins<sup>(4)</sup> or by isotopic exchange with gaseous tritium after Wilzbach. However, the method is very simple, rapid and convenient, and compares advantageously with the heterogeneous exchange between alkanes and tritiated water in the presence of platinum or oxidic catalysts<sup>(5)</sup>.

The tritiation of these saturated hydrocarbons by isotopic exchange in homogenous catalysis with Lewis acids has not previously been described. In the presence of  $\text{TH}_2\text{PO}_4\text{BF}_3$ , aromatics are tritiated very rapidly but saturated hydrocarbons without tertiary hydrogens are not affected<sup>(6)</sup>. Since aluminium chloride is one of the strongest Lewis acids known, we supposed it could be effective in catalyzing the isotopic exchange between tritium oxide and cyclohexane or *n*-heptane. This supposition was confirmed by experiment. In order to devise a useful method, the competing isomerization of the hydrocarbon must, however, be reduced to a minimum.

\* Preceding parts in the series are references 1-3.

There is evidence in the chemical literature that the isomerization and isotopic exchange are not proportional, although they involve similar or identical intermediates <sup>(7)</sup>.

Current theories as to the mechanism of isomerization, cracking and isotopic exchange of saturated hydrocarbons in the presence of Lewis acids <sup>(8-10)</sup> consider that the initial step involves abstraction of a hydride ion from the hydrocarbon. The co-catalyst (olefin, alkyl kalide or water) provides with the Lewis acid catalyst, a cation able to initiate the chain process of hydride abstraction. The co-catalytic effect of water, in the isomerization, first observed by Nenitzescu and Cantuniari <sup>(11)</sup> was confirmed by later authors <sup>(12-15)</sup>. Unlike the acid  $H[AlX_4]$  which cannot have independent existence, <sup>(16-18)</sup> the acids  $H[AlX_3OH]$  <sup>(19, 20)</sup> or  $H[X_2Al \langle \overset{X}{O} \rangle AlX_2]$  <sup>(15)</sup> exist (analogous oxygen-bridged structures have also been described in other cases <sup>(21, 22)</sup>). These substances with complex anions are extremely strong Brønsted acids, so that they can abstract hydride ions from alkanes evolving gaseous hydrogen <sup>(23)</sup>. The remaining organic cation undergoes competing isomerization and reversible proton elimination to an olefin, which by the reverse process leads to the isotopically labelled hydrocarbon. The relative rates of isomerization and labelling depend on the interaction between the carbonium ions and the anions or the solvent, hence on the reaction conditions.

The isomerization of cyclohexane into methyl-cyclopentane first observed by Aschan <sup>(24)</sup> was subsequently studied by Zelinsky and Turova-Pollak <sup>(25)</sup>; it was, however, Nenitzescu and Cantuniari <sup>(11)</sup> who observed that the isomerization led to an equilibrium mixture of the two hydrocarbons, which could be reached from both sides. Subsequent workers <sup>(8-10, 14, 26-29)</sup> confirmed and refined these findings. The isomerization process is no longer pictured <sup>(30)</sup> as involving high energy primary carbonium ions, but dimeric structures <sup>(31, 32)</sup> or protonated cyclopropane intermediates <sup>(8, 10)</sup>.

#### EXPERIMENTAL PART AND RESULTS

In order to avoid isomerization, the influence of the temperature on the isomerization of *n*-heptane (literature cited in ref. 9) in the presence of aluminium chloride with ordinary water as co-catalyst was studied. In the absence of a solvent, 100 mmoles (14.4 ml) *n*-heptane were kept 24 hrs. at room temperature with 20 mmoles (2.66 g) anhydrous aluminium chloride and 10 mmoles (0.18 ml) water. After hydrolysis, gas-liquid chromatography showed the absence of isomerization. However, three hours' refluxing with the same amounts of reagents caused appreciable isomerization and cracking. Therefore the labelling was performed at room temperature, for 24 hrs. The same amounts of reagents were employed. A molar ratio 1:2 between tritiated water and aluminium chloride was selected after literature data <sup>(3, 7, 13-15, 23)</sup>; although aluminium halides  $AlX_2$  are active and do not evolve  $HX$  with up to 6 moles  $H_2O$  per mole  $AlX_3$ , the isomerization ceases at molar ratios higher than 3:1 <sup>(7)</sup>; the optimum

ratio for isomerization is 0.5<sup>(15, 23)</sup> or 0.8-1<sup>(14)</sup>. With a specific activity of the tritiated water equal to 0.56 Ci/ml the *n*-heptane had after hydrolysis and preparative gas-chromatographical purification a specific activity of 12 mCi/mole.

In the tritiation of cyclohexane a comparison was made between aluminium chloride and anhydrous perchloric acid as catalysts. A solution of anhydrous perchloric acid in dichloromethane<sup>(33)</sup> or anhydrous aluminium chloride without a solvent were employed as catalysts, and tritiated water in various molar ratios as co-catalyst. After hydrolysis and purification by preparative vapour phase chromatography, the cyclohexane and methylcyclopentane were collected and their activities were measured separately. Results are presented in the Table.

TABLE 1. Tritiation and isomerization of 1 mmole cyclohexane with HTO (0.56 Ci/ml) in the presence of sublimed AlCl<sub>3</sub>, or of anhydrous HClO<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>.

Catalyst		HTO mmole	CH <sub>2</sub> Cl <sub>2</sub> ml	Temp. °C	Time hrs	Specific activity mCi/mole		Ratio MeC <sub>5</sub> /C <sub>6</sub> after isom. %
AlCl <sub>3</sub> mmole	HClO <sub>4</sub> mmole					MeC <sub>5</sub>	C <sub>6</sub>	
—	0.5	0.5	8	40	1	2.0	2.0	1.0
—	0.5	2	8	40	1	—	0.17	1.0
—	0.5	3	8	40	1	—	0.20	1.0
0.5	—	0.5	—	70	3	1.3	3.2	9.0
0.2	—	0.1	—	20	24	—	3.0	1

It may be seen that in the presence of aluminium chloride at 20°C, or of anhydrous perchloric acid at 40°C, little or no isomerization is observed, although a fair amount of labelling is introduced into the cyclohexane. At 70°C, in the presence of aluminium chloride, extensive isomerization occurs, slowly approaching equilibrium. The specific activities of the resulting methylcyclopentane are of comparable magnitude to those of cyclohexane (equal with HClO<sub>4</sub>, half with AlCl<sub>3</sub>). The highest specific activity of cyclohexane was obtained with HClO<sub>4</sub> for a molar ratio hydrocarbon:HClO<sub>4</sub>:HTO equal to 1:0.5:0.5.

From the tritium atoms present in the tritiated water introduced into the reaction, 1.2% are incorporated into *n*-heptane and 0.3% into cyclohexane. Despite this low tritium uptake and the low specific activity, there are cases when the present method offers considerable advantages owing to its simplicity and rapidity.

Manipulations were effected in the absence of atmospheric moisture. The exchange was carried out in double-walled flasks with thermostated water under magnetic stirring, as described previously<sup>(1-3)</sup>. After hydrolysis the organic layer was shaken with acidified water until a constant activity was obtained.

Measurements were performed in compensated Geiger-Müller counters, using the hydrocarbon as quencher<sup>(34)</sup>. Gas-liquid chromatographic determinations were effected with a CARLO-ERBA apparatus PAID/f type with flame ionization detector, and VPC separations were made with a WILLY GIEDE chromatograph with catharometer on a 2 m column packed with APIEZON L 25% on cellite C22; the temperature was 60°C and the hydrogen flow 100 ml/min.

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#### REFERENCES

1. MĂNTEȘCU, C. and BALABAN, A.T. — *Canad. J. Chem.*, **41** : 2120 (1963).
2. MĂNTEȘCU, C., GENUNCHE, A. and BALABAN, A.T. — *J. Labelled Comp.*, **1** : 178 (1965).
3. MĂNTEȘCU, C., GENUNCHE, A. and BALABAN, A.T. — *Ibid.*
4. RABE, J.G., GUARINO, A. and RABE, B. — *Internal J. Appl. Radiation Isotopes*, **14** : 571 (1963).
5. GARNETT, J.L., HENDERSON, L. and SOLLICH, W.A. — “Symposium on the Detection and Use of Tritium in the Physical and Biological Sciences”, I.A.E.A., Vienna 1962, vol. II, p. 47; GORDON, B.E. and KLAVEREN, J.A. van — *Internal. J. Appl. Radiation Isotopes*, **13** : 103 (1962).
6. YAVORSKI, D.M. and GORIN, E. — *J. Am. Chem. Soc.*, **84** : 1071 (1962).
7. WACKLER, R.C. and PINES, H. — *Ibid.*, **68** : 1642 (1946); PINES, H. and WACKLER, R.C. — *Ibid.*, **68** : 2518 (1946); OTVOS, J.W., STEVENSON, D.P., WAGNER, C.D. and BEECK, O. — *Ibid.*, **73** : 5741 (1951); *J. Chem. Phys.*, **16**, 745 (1948); STEVENSON, D.P., WAGNER, C.D., BEECK, O. and OTVOS, J.W. — *J. Am. Chem. Soc.*, **74** : 3269 (1952).
8. NENITZESCU, C.D. — *Usp. Khim.*, **26** : 390 (1957); “Carbonium Ions”, edited by Olah, G.A., Wiley-Interscience, New York, in press.
9. PINES, H. — “Advances in Catalysis”, edited by Frankenburg, W.G., Komarewsky, V.I. and Rideal, E.K., Academic Press, New York, 1948, vol. I, pp. 201, 252.  
PINES, H. and HOFFMAN, N.E. — “Friedel-Crafts and Related Reactions”, edited by Olah, G.A., Wiley-Interscience, New York, 1964, vol. II, p. 1121.
10. CONDON, F.E. — “Catalysis”, edited by Emmett, P.H., Reinhold, New York, 1958, vol. VI, p. 43.
11. NENITZESCU, C.D. and CANTUNIARI, I.P. — *Ber. dtsh. Chem. Ges.*, **65** : 1449 (1932); **66** : 1097 (1933).
12. GLASEBROCK, A.L. and LAVELL, W.G. — *J. Am. Chem. Soc.*, **61** : 1717 (1939).
13. STEVENSON, D.P. and BEECK, O. — *Ibid.*, **70** : 2890 (1948); STEVENSON, D.P. and MORGAN, J.H. — *Ibid.*, **70** : 2890 (1948).
14. GAWALEK, G., SCHNEIDER, G. and KONNECKE, H.G. — *Z. Physik. Chem.*, (Leipzig), **223** : 269 (1963).
15. KRAMER, G.M., SKOMORSKI, R.M. and HINLICKY, J.A. — *J. Org. Chem.*, **28** : 2085 (1963).
16. PINES, H. and WACKLER, R.C. — *J. Am. Soc.*, **68** : 595, 599 (1946).
17. BROWN, H.C. and PEARSALL, H.W. — *Ibid.*, **73** : 4681 (1951); **74** : 191 (1952).
18. RICHARDSON, R.L. and BENSON, S.W. — *Ibid.*, **73** : 5096 (1951); WIBERG, E., SCHMIDT, M. and GALINOS, A.G. — *Angew. Chem.*, **66** : 443 (1954)
19. FAIRBROTHER, F. and FRITH, W.C. — *J. Chem. Soc.*, **1953**, 2975.

20. MILIOTIS, J. — *Compt. Rend.*, **245** : 1314 (1957).
21. SCHMIDBAUR, H. and SCHMIDT, M. — *J. Am. Chem. Soc.*, **84** : 1069 (1962).
22. BREWSTER, J.H. and BAYER, H.O. — *J. Org. Chem.*, **29** : 105 (1964).
23. NENITZESCU, C.D., AVRAM, M. and SLIAM, E. — *Bull. Soc. Chem. Fr.*, **1955**, 1266.
24. ASCHAN, O. — *Liebigs Ann. Chem.*, **324** : 1 (1902).
25. ZELINSKY, N. and TUROVA-POLIAK, M. — *Ber. dtsh. chem. Ges.*, **58** : 1292 (1925); **62** : 1658 (1929); **65** : 1299 (1932); *Zh. Obsh. Khim.*, **2** : 666 (1932); TUROVA-POLLAK, M.B. and coworkers — *Ibid.*, **9** : 233, 2179 (1939); **10** : 172, 1435 (1940); **11** : 821 (1941); **16** : 825 (1946); KUZNETSOV, V.I. — “Razvitie kataliticheskogo organicheskogo sinteza”, Izd. Nauka, Moscow 1964, p. 101.
26. STEVENSON, D.P. and MORGAN, J.H. — *J. Am. Chem. Soc.*, **70** : 2773 (1948); RUSSEL, G.A. — *Ibid.*, **81** : 4834 (1959).
27. KÖNNECKE, H.G., GAWALEK, G. and SCHMIERS, H. — *Z. Physik. Chem.*, (Leipzig), **218** : 233 (1961).
28. SHNIKIN, N.I., NARYSHKINA, T.I., RASHCHYUPKINA, Z.A. and GERSHTEIN, N.A. — *Neftekhimia*, **1** : 756 (1961).
29. TURNER, H.S. and WARNE, R.J. — *J. Chem. Soc.*, 789 (1953); KILNER, A.E.H., TURNER, H.S. and WARNE, R.J. — “Radioisotope Conference, Oxford 1964”, edited by Johnston, J.E. — Butterworths, London, 1954, vol. II, p. 23.
30. PINES, H., ABRAHAM, B.M. and IPATIEV, V.N. — *J. Am. Chem. Soc.* **70** : 1742 (1948).
31. KARABATSOS, G.J. and VANE, F.M. — *Ibid.*, **85** : 729 (1963); KARABATSOS, G.J., VANE, F.M. and MEYERSON, S. — *Ibid.*, **85**, 733 (1963).
32. SPERLING, R. — *J. Chem. Soc.*, **1949**, 1928.
33. KLAGES, F. and HEGENBERG, P. — *Angew. Chem.*, **74** : 902 (1962).
34. MĂNTESCU, C. and GENUNCHE, A. — *Studii și Cercetări Chim. Acad. R.S.R.*, **13** : 1101 (1965).