

³H N.M.R. DEMONSTRATION OF THE PATTERN OF TRITIATION OF ALKANES BY
ETHYLALUMINIUM DICHLORIDE/TRITIATED WATER

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Recently developed catalytic methods¹ make the labelling of organic compounds with deuterium or tritium very easy. As regards rapidity of labelling, selectivity for aromatic ring positions, and freedom from steric hindrance, ethylaluminium dichloride²⁻⁴ is one of the most promising catalysts, although with polysubstituted benzenes there may be some accompanying isomerisation.⁵ Aliphatic compounds such as alkanes and alkenes can also be labelled provided they contain a tertiary hydrogen atom,⁶ but whether just that position becomes labelled was not ascertained.

In previous work² the extent and pattern of deuterium incorporation (which was high) was found by a combination of mass spectrometry and ¹H n.m.r. spectroscopy. For tritium incorporation (necessarily low) radio-gas chromatography was employed³ to measure the extent of labelling. This method, however, cannot determine the distribution of label within a product. We have therefore used ³H n.m.r. spectroscopy.⁷ Our results confirm that the ethylaluminium method⁶ tritiates appropriate alkanes efficiently: they show that the label is not confined to the tertiary positions but is distributed.

TABLE. Position and Extent of Tritium Labelling in some Alkanes

Compound*	³ H Chemical shift (p.p.m.)	Position labelled	Relative incorporation (%)	Relative incorporation per site
2,3-Dimethylbutane ^a	1.27	CH	17	8.5
	0.84	CH ₃	83	6.9
3-Methylpentane ^b	1.28	CH	21	21
	1.10	CH ₂	29	7.2
	0.84	CH ₃	50	5.6
Methylcyclohexane ^c	1.63	CH	28	28
	ca. 1.26	CH ₂	32	3.2
	0.84	CH ₃	40	13.3

*Duration of exchange a, 4 days; b, 1 day; c, 19 days

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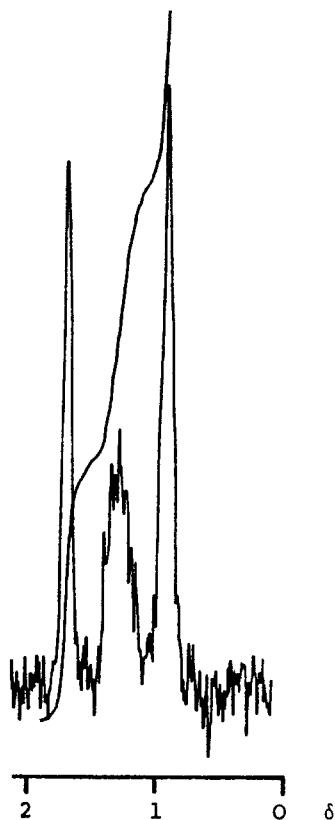


Figure. ^3H N.m.r. spectrum (^1H decoupled) of tritiated methylcyclohexane.

Alkanes (0.1 ml) were treated at 85°C with ethylaluminium dichloride and then a trace of high specific activity tritiated water ($10\ \mu\text{l}, 50\ \text{Ci ml}^{-1}$) to hydrolyse the complex.² Extraction of the labelled product, removal of remaining tritiated water, and ^3H n.m.r. analysis⁷ provided the results shown in the Table.

All three compounds were thus found to be generally labelled. Although most of the label appears in the methyl groups, allowance for statistical factors shows that the tertiary positions are labelled preferentially (last column of Table). The fact that the label is not confined to tertiary positions has implications for a reaction mechanism. Presumably the alkane is induced by association with the catalyst to form, through the weakest C-H bond at a tertiary position, an incipient or a full carbonium ion in which charge can be redistributed by proton migration or exchange. General labelling of the alkane after contact of the complex with the trace of tritiated water may thus be explained. Under the experimental conditions, little or no rearrangement of the carbon skeleton occurred, as shown by the n.m.r. spectra. The ^3H n.m.r. spectrum of the tritiated methylcyclohexane (Figure) showed single methyl and CH-group chemical shifts for the equatorially substituted molecule and at least seven distinct shifts from the ten non-equivalent CH_2 -group tritons.

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