

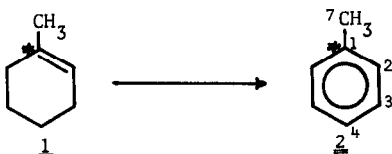
SCRAMBLING OF THE 1-CARBON DURING THE CATALYTIC DEHYDROGENATION
of 1-METHYLCYCLOHEXENE

James L. Marshall*, Denis E. Miiller, and Arthur M. Ihrig

Department of Chemistry, North Texas State University, Denton, Texas 76203

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One of the synthetic sequences employed to incorporate a carbon label (^{13}C or ^{14}C) in a mononuclear aromatic compound involves as one of its steps the catalytic dehydrogenation of 1-methylcyclohexene-1- ^{13}C [or ^{14}C] (1) to toluene-1- ^{13}C [or ^{14}C] (2)¹⁻⁵:



It is generally assumed that during this conversion the isotopic integrity of the C-1 carbon atom is preserved. In connection with our carbon nmr studies, we had occasion⁶ to synthesize >90% ^{13}C -1-toluene (2) by this published procedure. In studying the carbon and proton nmr spectra of this product, we observed that there was not complete retention of the label at C-1, but instead there was a *considerable amount of scrambling throughout the aromatic ring*.⁷ This observation has serious implications not only for those workers who deal with the ^{14}C -isotope and who cannot easily check the isotopic integrity of the dehydrogenated product, but also for those dealing with the ^{13}C -isotope with isotopic purities considerably below 90% wherein a routine check by nmr may be misleading.

The procedure we used for the conversion 1 \rightarrow 2 was that used previously,¹⁻⁵ with the choice of catalyst 0.5% platinum on alumina⁸ (as was used previously³). Yields of 60% were routinely obtained of >95% toluene by passing the reaction mixture three times over the catalyst at 350-400°.

By studying the methyl region of the proton nmr of 2, we could determine the amount of ^{13}C label at C-1, at C-2,3,4 (the other aromatic positions), and at C-7 (the methyl group).⁹ The amount of scrambling varied from about 13% to 32%, with the label moving to the other aromatic positions (C-2,3,4) but not to the methyl position (C-7). It was not possible to assess the amount of label at each of the aromatic positions by proton nmr,¹⁰ but carbon nmr gave an approximate¹¹ measure: perhaps 90% of the scrambled label was distributed fairly evenly between C-2 and C-3 with the remaining 10% at C-4.

Since the scrambling does not take place within the methyl group, it is safe to assume

that the scrambling takes place by the methyl group migrating about the ring, as opposed to some "tropylium-type" process.¹² Wondering if the scrambling might take place in the 1-methylcyclohexene in an alumina-catalyzed carbonium ion process before the toluene was produced, we subjected cyclohexene to the same conditions; but only benzene, and no cyclopentane products (that would be expected from carbonium ion rearrangements on alumina¹³), were observed. Therefore, it seems reasonable that the methyl group migrates after the toluene is produced. We consider it likely that the migration occurs by alumina-catalyzed aronium ion intermediates with the requisite methyl and hydride shifts.

Although scrambling always occurred to a greater or lesser extent, it was not clear from the inconsistent results precisely what conditions were conducive to scrambling, but it appeared that the scrambling could perhaps be held to a minimum by using lower catalyst temperatures (around 350°) and by carefully excluding atmospheric moisture from the catalyst during the initial heating period and during the dehydrogenation process.

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7. A careful study of the starting material 1-methylcyclohexene-1-¹³C showed it possessed its label cleanly at C-1.
8. We wish to thank R. Slimp of American Cyanamid of Houston, Texas, and C. R. Dick of The Dow Chemical Company of Freeport, Texas, for generous gifts of platinum-alumina catalyst.
9. The methyl proton signal would be split into a doublet of 125.8 Hz with the label at C-7 and into a doublet of 6.0 Hz at C-1 [J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N.Y., 1972, pp 340, 358] and would be an unresolved singlet with the label at C-2,3,4.
10. The chemical shifts of the aromatic protons of toluene are the same and accordingly one cannot differentiate among them.
11. A quantitative assessment cannot be made using carbon nmr because of the NOE rendering integration only approximate [J. H. Noggle and R. E. Schirmer, "The Nuclear Overhauser Effect," Academic Press, New York, N.Y., 1971, p 72.
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