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^{14}C Tracer Study of the Dehydrocyclization of *n*-Heptane over Pt on Nonacidic Alumina

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The ^{14}C in the methyl position of toluene from the dehydrocyclization of *n*-heptane labeled in the 1 or 4 position was consistent with a mechanism including a direct six-carbon ring formation. The aromatic ring was degraded, and the ^{14}C distribution in the ring was also in agreement with 80% or more of the aromatic being formed by a direct six-carbon ring formation.

INTRODUCTION

The mechanism that received wide acceptance shortly after the dehydrocyclization of paraffins was discovered was one involving a direct six-carbon ring formation (*1*). The details of this mechanism were not confirmed experimentally, but it was postulated that olefins were formed as intermediates in the reaction mechanism and that the adsorbed species resembled the "half hydrogenated state" that was accepted as the intermediate in olefin hydrogenation and in deuterium–hydrogen exchange in paraffins. Wheatcroft (*2*) advanced a different mechanism in which the olefin intermediate was adsorbed at a position remote from the double bond and then this adsorbed position substituted at the double bond to give a six-carbon ring. In the 1960's, Pines and coworkers (*3*) obtained results which were inconsistent with a direct six-carbon ring formation mechanism. They proposed that various size rings were formed initially and these rings then underwent contraction or expansion to a six-carbon ring; rings other than six carbons were formed in largest amounts over chromia on a nonacidic alumina. Other investigators obtained ^{14}C tracer data that was in agreement with a direct six carbon ring mechanism over all chromia catalysts (*4*).

While most of the mechanism studies have been done with metal oxide catalysts, metal catalysts, especially platinum, are good dehydrocyclization catalysts. There is much less data in the literature for the metal catalysts, but, even so, there is some controversy as to the carbon number ring formed. Kazanskii (*5*) has proposed that both C_5 and C_6 cyclization occurs over Pt at 300°C; however, he has published papers in which he implied only a C_6-ring-formation mechanism for dehydrocyclization over chromia (*6*). Lester (*7*) proposed that different mechanisms are operating over the metal and the metal oxide catalysts for a trimethylpentane charge. Over Pt, Lester proposed a five-carbon ring intermediate which underwent ring expansion by a carbonium ion intermediate to a six-carbon ring. However, Davis (*8*) and Fogelberg and coworkers (*9*) obtained aromatic distributions over Pt catalysts which were consistent with a direct six-carbon ring formation.

We have studied the dehydrocyclization of *n*-[1-^{14}C]heptane and *n*-[4-^{14}C]heptane over Pt–Al_2O_3–K catalysts to obtain more information about the mechanism of the metal catalyzed dehydrocyclization mechanism. The toluene product was analyzed for ^{14}C content of the side chain and some of the ring positions to learn whether the

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^{14}C distribution was consistent with a direct six-carbon ring formation. At the same time, it would afford another opportunity to compare results from a metal catalyst to a metal oxide catalyst (*4*).

EXPERIMENTAL

The catalysts were prepared using "nonacidic" alumina obtained by precipitation from potassium aluminate by CO_2 (*8a*). Chloroplatinic acid was added to the amount of water sufficient to just fill the pore volume of the alumina and yield a finished catalyst containing 0.6 wt% Pt. The catalyst was dried at 120°C, reduced in flowing hydrogen at 482°C, and then washed with 5% ammonium hydroxide to reduce the chlorine level to less than 0.05 wt% (*8a*).

Procedure. The catalyst was reduced at 550°C *in situ* in flowing hydrogen. The liquid hydrocarbon was added by a syringe pump to a Vycor reactor with a 30-cc quartz chip preheater section and then to a 5-cc catalyst bed. After passing through a water cooled condenser, the liquid products were collected at intervals. The liquid samples were analyzed for conversion by gc using a Carbowax 20M column.

The ^{14}C-labeled hydrocarbons were prepared by the following schemes ($^{14}C = C^*$):

Scheme I

$$HC^*O_2H \xrightarrow{EtOH} HC^*O_2Et \xrightarrow{PrMgBr} PrC^*HOHPr \xrightarrow{HOAc} Pr\text{-}\underset{\displaystyle OAc}{\underset{|}{C^*H}}\text{-}Pr$$

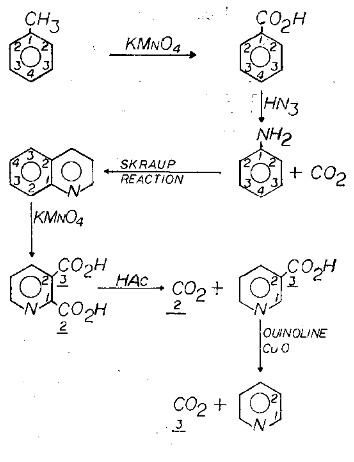
$$Pr\text{-}C^*H\text{-}Pr \xrightarrow{400^oC} C_3H_7C^*H{=}CHC_2H_5 \xrightarrow[H_2]{PtO_2} C_3H_7C^*H_2C_3H_7$$

Scheme II

$$C_6H_{13}C^*O_2H \xrightarrow{LiAlH_4} C_6H_{13}C^*H_2OH \xrightarrow{PBr_3} C_6H_{13}C^*H_2Br$$

$$C_6H_{13}C^*H_2Br \xrightarrow{Mg} C_6H_{13}C^*H_2MgBr \xrightarrow{H_2O} C_6H_{13}C^*H_3$$

The ^{14}C distribution in the toluene product was determined by the scheme we used in Ref. *4a* and is outlined below (the numbers in the ring refer to the ring position with respect to the methyl group of the original toluene):



The CO_2 was collected as $BaCO_3$, and the ^{14}C determined by liquid scintillation counting.

RESULTS

The methyl-^{14}C label for toluene from the dehydrocyclization of *n*-[1-^{14}C]heptane and *n*-[4-^{14}C]heptane over the same Pt–Al_2O_3–K catalyst used for the dehydrocyclization of a large number of C_7–C_9 paraffins (*8*) is shown in Table 1. For *n*-[1-^{14}C]heptane, the methyl position activity increases with time on stream from 36 to 44% of the total activity; this corresponds to 72–88% of the amount of the ^{14}C predicted for a direct six-carbon ring formation mechanism. For *n*-[4-^{14}C]heptane, the methyl activity decreases from 3.2 to 1.1% with time on stream. If all

TABLE 1

PERCENT ^{14}C IN THE METHYL POSITION OF TOLUENE FROM THE DEHYDROCYCLIZATION OF *n*-[1-^{14}C]-HEPTANE AND *n*-[4-^{14}C]HEPTANE AT 500°C

Sample	Time	Conversion to toluene	Methyl-^{14}C (%)
n-[4-^{14}C]Heptane			
1	42	33	3.22
2	95	19	1.32
3	143	13	1.07
n-[1-^{14}C]Heptane			
1	43	27	36
2	89	17	41
3	140	11	44

positions other than the C_3 ring position[1] have the same activity as the methyl position (an assumption that will be at least partially justified later in the results section), then 80–93% of the ^{14}C would be in the position expected for a direct C_6-ring formation. Thus, similar results are obtained for both n-[1-^{14}C]heptane and n-[4-^{14}C]heptane.

A defective hot plate caused our samples of nicotinic acid to overheat and decompose as the acetic acid was evaporated. Thus, we were unable to conclude the degradation scheme to obtain a ^{14}C activity for all ring positions. However, sufficient data was obtained to show that the ring activity is consistent with that expected for a direct C_6-ring formation and is consistent with the methyl activity in Table 1. If we assume that the toluene from n-[1-^{14}C]heptane was only formed by a direct C_6-ring intermediate, the degradation scheme in the experimental section shows that the CO_2 from the decarboxylation of quinolinic acid should have one-half the activity of the quinolinic acid (after correction for the dilution of the ^{14}C by six nonradioactive carbon atoms). The results in Table 2 show that the actual percentage of the activity in the CO_2 was 40 and 44%. This means that ring positions C_1 and C_3 have, at most, 20% as much activity as C_2 for sample 1 and 12% for sample 3. For direct C_6-ring formation, the quinoline, due to the carbon dilution, should have 7/9th of the activity of the quinolinic acid. For both samples 1 and 3, the experimental activity is only slightly greater than 7/9th that of quinolinic acid and would indicate that ring position C_4 has a low activity near to that of C_1 and C_3. Without question, ring position C_2 contains the predominate ^{14}C label ($\geq 80\%$).

TABLE 2

^{14}C DISTRIBUTION IN RING POSITIONS C_1, C_2, AND C_3

Sample	Activity[a] Quinoline	Activity[a] Quinolinic acid	$C_2/(C_1 + 2C_2 + C_3)$ Exptl	$C_2/(C_1 + 2C_2 + C_3)$ Calcd
n-[4-^{14}C]Heptane				
2	6320	3948	3.28	0
3	1932	1170	6.46	0
n-[1-^{14}C]Heptane				
1	528	643	40	50
3	1376	1829	44	50

[a] Activity expressed as cpm/100 mg $BaCO_3$.

Again, assuming a direct C_6-ring formation, toluene from n-[4-^{14}C]heptane would only have ^{14}C label in ring position C_3. The data in Table 2 shows that very little ^{14}C is present in C_2. Likewise, the calculated activity for quinoline, after correcting by a factor of 14/9 for carbon dilution and having both C_3 atoms rather than only one for quinolinic acid, is only slightly less than the measured value. Hence, C_4 has a low ^{14}C activity. Since the measured activity of positions C_2 and C_4 is low in comparison to the activity in C_3, it appears certain that C_1 also has a low activity.

DISCUSSION

A mechanism that includes a direct six-carbon ring formation as the major reaction pathway accounts for the major portion of the ^{14}C distribution in the toluene from the dehydrocyclization of n-heptane over $Pt–Al_2O_3$. This agrees with the conclusion of direct six-carbon ring formation based on the aromatic distribution from C_8 and C_9 paraffins over the same catalyst (*8*). The results with $Pt–Al_2O_3–K$ are similar to those obtained earlier with chromia and chromia–alumina catalysts and suggest a single mechanism for dehydrocyclization over both types of catalysts.

Lester proposed that dehydrocyclization of trimethylpentanes (*7*) occurred by the formation of a cyclopentane intermediate, which then underwent ring expansion on the Lewis acid metallic Pt. Since bulk Pt metal has 0.6 holes/atom, there can be no question about Pt being a Lewis acid; only

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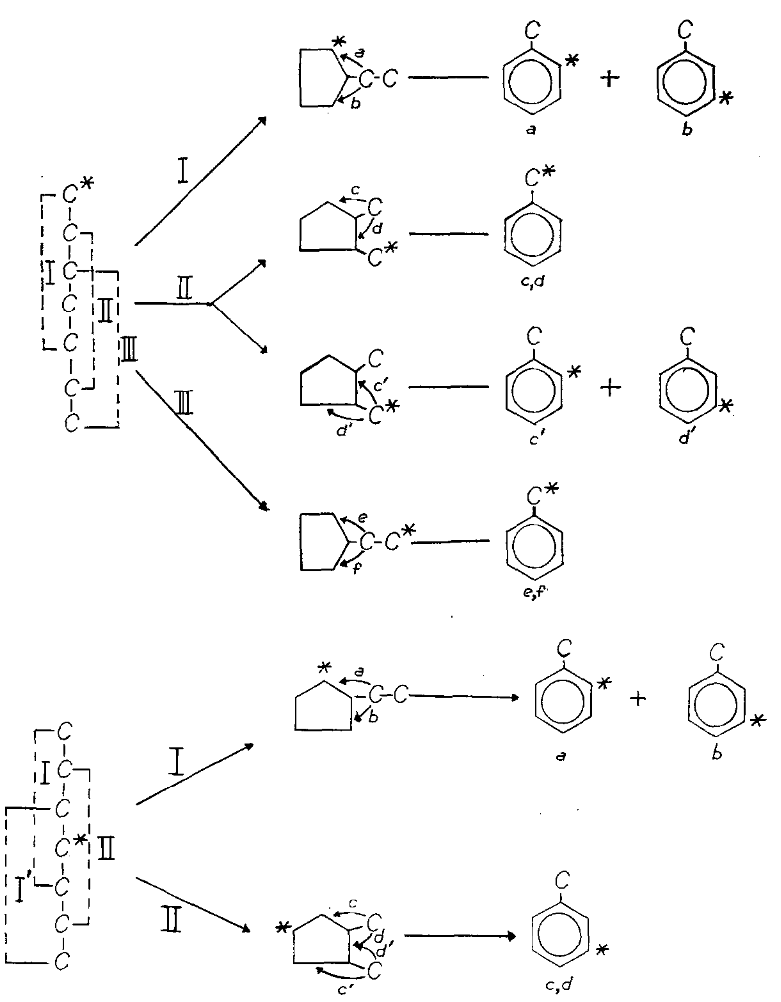
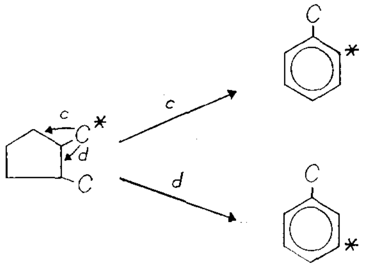
[1] C_n refers to the ring position location with respect to the methyl group; e.g., C_2 refers to the ring position ortho to the methyl position in the original toluene.

the relative strength may be debated. The contention of a cyclopentane intermediate can not be eliminated, but our results with heptane labeled in the 1 and 4 positions place very severe limitations on the cyclopentane intermediate. For *n*-heptane, the cyclopentane intermediate would provide the following possibilities:

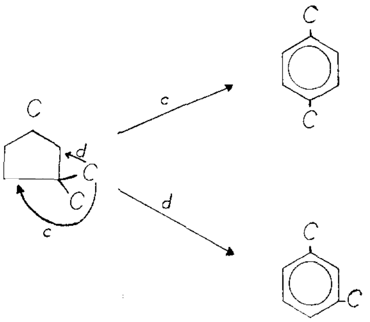


For *n*-[4-^{14}C]heptane the C_2 ring position label can arise only from pathways I and I′. From Table 2, we see that the label in C_2 for sample 2 is 3.3% of that in C_1, C_3, and $2C_2$ positions, and for sample 3 the C_2 label is 6.5% of the C_1, C_3 and $2C_2$ positions. The activity of the C_1 position can not be as large as C_3, so that even for the 6.5% C_2 label, $C_2/(C_2 + C_3)$ is less than 0.05. This means that pathway I, I′ contributes no more than 5% to the total reaction and that 95% of the toluene must be formed by ring expansion of the 1,2-dimethylcyclopentane intermediate.

For *n*-[1-^{14}C]heptane, if we assume that the ^{14}C isotope effect is negligible at 500°C, we must get the same amount of ethyl- and dimethylcyclopentane intermediates as with *n*-[4-^{14}C]heptane. We find that C_2 contains greater than 80% of the ^{14}C activity of ring positions C_1, C_2, and C_3. Hence, the ring expansion for the dimethylcyclopentane must be very selective; i.e.,



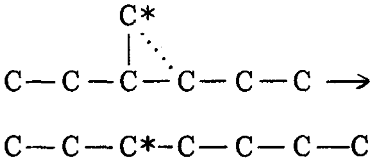
must occur so that more than 80% of the toluene is formed by pathway c. This would require the rate of methyl insertion adjacent to the other methyl group to be at least four times faster than at the bond removed from the methyl group. There does not seem to be a compelling reason for this to occur. In fact, Lester (*7*) would propose the opposite for 1,1,3-trimethylcyclopentane,



where about 2 times as much of the meta-isomer was formed by pathway d as the para-isomer by pathway c.

In order to explain our ^{14}C results by a cyclopentane intermediate, we are required to propose a very restrictive isomerization. In addition, the required specific isomerization will lead to the same ring label as a direct six-carbon ring formation and is, in fact, a direct six-carbon ring formation mechanism that is carried out in two steps. Furthermore, the cyclopentane intermediate mechanism proposed by Lester requires 50% ^{14}C label in the methyl position for toluene from n-[1-^{14}C]heptane. Thus, this mechanism, in addition to being more complicated than direct six-carbon ring formation, can not account for the low methyl-^{14}C label.

In this study with n-[1-^{14}C]heptane, as well as in all others reported to date, less than 50% of the ^{14}C activity is found in the position predicted for C_6-ring formation. Pines and coworkers (*3*) proposed that the low activity they obtained with n-[1-^{14}C]heptane and n-[1-^{14}C]octane was the result of (a) the formation of various size carbon rings which, after rolling around on the surface to acquire carbon equivalency at each position, formed aromatics by ring contraction(s) and dehydrogenation of the resulting C_6-naphthene, and (b) by an isomerization by a methyl insertion reaction such as



$$\mathrm{C{-}C{-}\overset{\overset{C^*}{|}}{C}{-}C{-}C{-}C \longrightarrow}$$
$$\mathrm{C{-}C{-}C^*{-}C{-}C{-}C{-}C}$$

prior to the C_6-ring formation. Additional data for the conversion of other hydrocarbons over chromia on nonacidic alumina were obtained, which they interpreted to support a methyl-insertion-type reaction over the catalyst. Over unsupported chromia and chromia on acidic alumina, Pines and coworkers obtained results consistent with nearly all of the aromatic being formed by a direct six-carbon ring closure. On the other hand, Davis and coworkers (*4*) proposed that isomerization of the normal structure to methylhexane structures prior to or during cyclization could account for the low activity they found using chromia and chromia supported on acidic and nonacidic alumina. If the isomerization reaction involved only a classical carbonium ion, it should be possible to distinguish between these two mechanisms since n-[1-^{14}C]heptane should isomerize to a methylhexane labeled in the terminal carbon. The various methylhexanes should yield toluene without ^{14}C in the C_1 position, whereas the cycloheptane intermediate would have equal labeling in all ring positions. Unfortunately, Pines and coworkers did not measure the distribution of ^{14}C in the aromatic ring. Davis and coworkers measured the ^{14}C distribution in the aromatic ring of toluene from the dehydrocyclization of *n*-heptane over chromia; however, the data was not accurate enough to distinguish between the two mechanisms. The ^{14}C distribution in the ring in the present study also suffers from the limitation of not being able to distinguish between the possible isomerization reactions.

In summary, we believe our ^{14}C distribution over Pt and over chromia (*4*) can be explained by a mechanism involving direct six-carbon ring formation. The small (20% or less) amount of ^{14}C in positions unallowed by direct six-carbon ring formation would be considered to arise by a side reaction. Several side reactions can be advanced; we prefer the simple one involving the isomerization to a methylhexane structure prior to or during cyclization.

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