

Aromatization of [1-¹⁴C]Heptane over "Nonacidic" Platinum-Alumina Catalyst¹

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[1-¹⁴C]Heptane was aromatized under 5 atm pressure over a "nonacidic" 3% platinum on alumina catalyst maintained at 500°C. The reactant was pumped in at a HLSV of 0.88, and the hydrogen-to-heptane mole ratio was 5.1. The samples of product were collected (one during the first 90 min and another during the next 90 min), the toluene was separated from the respective samples, and the radioactivity in each position of the toluene was determined by a degradation sequence. The distribution of radioactivity in sample 1 was as follows: in position 1—2.6%, 2—38.6%; 3—14.5%; 4—4.2%, and in the methyl group—40.1%. Approximately similar distribution of radioactivity was found in sample 2. 1,6-Ring closure is the most important pathway leading to the formation of toluene from [1-¹⁴C]heptane; lesser amounts of repetitive, 1,5-ring closure and hydrogenolysis, and bond shift reactions followed by 1,6-ring closure and dehydration can explain the distribution of radioactivity. The participation of 1,7-ring closure in the reaction is also indicated.

The mechanism of aromatization of heptanes over a "nonacidic" platinum-alumina catalyst is complex and confusing (1). For that reason it was deemed advisable to investigate the aromatization of [1-¹⁴C]heptane and to determine the distribution of radioactivity in the produced toluene. The experiments were made using 3% Pt/Al₂O₃ catalyst and experimental conditions similar to the ones described in the preceding paper (1), with the exception that 2.0 g instead of the usual 0.4 g of catalyst was used.

EXPERIMENTAL PART

Synthesis of [1-¹⁴C]Heptane

The title hydrocarbon was synthesized in a 66% overall yield, based on the radioactive barium carbonate, by the following sequence of reactions (2):

a. [1-¹⁴C]Heptanoic acid was prepared by carbonation of 0.1 mole of hexylmagnesium bromide with carbon dioxide from barium [¹⁴C]carbonate.

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b. The acid was reduced with lithium aluminum hydride to [1-¹⁴C]heptanol.

c. The heptanol was hydrogenolyzed in the presence of nickel catalyst to which a small amount of thiophene was added to produce [1-¹⁴C]heptane.

Catalyst and Procedure

Platinum (3 wt%) on "nonacidic" alumina was employed as the catalyst (1). The experiments were conducted in a micro-pulse reactor (3). Modifications were made to adapt it to a continuous flow system reactor. Two grams of 16-20 mesh catalyst maintained at 500°C was used. [1-¹⁴C]Heptane was pumped in at a HLSV of 0.88 and at a hydrogen-to-heptane mole ratio of 5.1, and under pressure of 5 atm.

The sample of products collected during the first 90 min and the next 90 min were labeled cut 1 and cut 2. Toluene was separated from both cuts by chromatography on silica gel and the radioactivity present in each position of it was measured through a degradation sequence.

Analysis

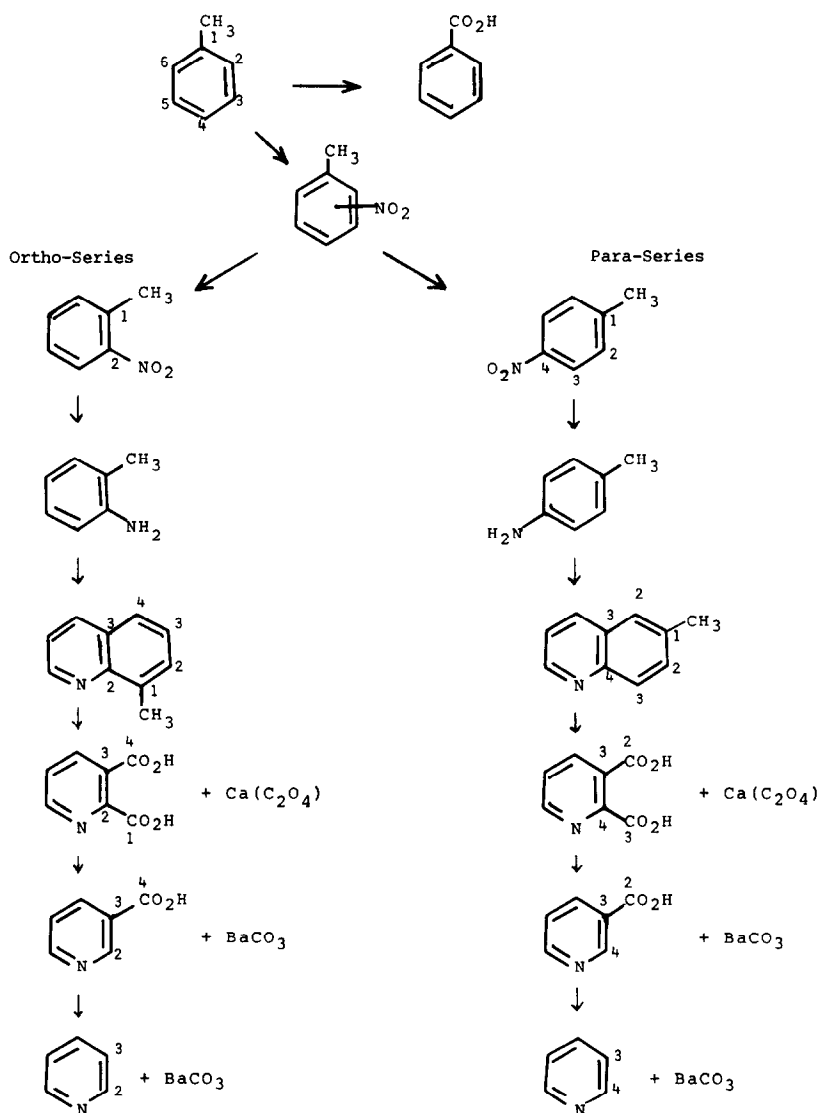
The general procedure of Steinberg and

Sixma (4) was used for the determination of the distribution of radioactivity in the toluene. The method was modified to omit the step where the nitrotoluenes are oxidized to nitrobenzoic acids and thus the cumbersome separation of the isomers of nitrobenzoic acid. Scheme 1 represents a convenient alternate degradation route. Separation and purification of the nitrotoluenes were achieved by preparative vpc.

The reduction of the nitrotoluenes to the toluidines was made with a yield of 92 to

94% by hydrogen transfer from cyclohexene in the presence of Pd/C catalyst (5).

Preparation of 6- and 8-methylquinolines from *o*- and *p*-toluidine, respectively, was accomplished by Skraup synthesis with a yield of 75 to 80%. Added to a mixture of 0.5 g of FeSO₄, 3.0 g of toluidine, and 1.17 g of *p*-nitrotoluene over a period of 15 min with vigorous stirring, was a solution of 0.89 g of boric acid dissolved in 5.36 g of glycerol. With continuous stirring 2.5 ml of 96% H₂SO₄ was added. The mixture was



SCHEME 1. Outline of degradation of [¹⁴C]toluene.

heated to boiling and left simmering at 150–160°C for 7 h (6, 7). The product was steam distilled to remove nitrotoluene. The residue was made alkaline with 8.7 ml of 50% NaOH and steam distilled. The distillate was acidified with 1.8 ml of 50% H₂SO₄, and steam distilled to expel volatile materials. The contents of the flask were made alkaline with 4.5 ml of 50% NaOH, and again steam distilled. The distillate was extracted with ether, dried, and the ether evaporated off. The methylquinolines thus produced were 99% pure.

Quinolinic acids were prepared by the potassium permanganate oxidation of the 6- and 8-methylquinoline; the respective yields of the acids were 62 and 32% (4).

The decarboxylation of quinolinic acid to nicotinic acid was made by boiling 350 mg of quinolinic acid and 50 ml of glacial acetic acid (4). The carbon dioxide produced was swept out by bubbling nitrogen through the solution, and adsorbed in sodium hydroxide solution, and thereafter converted to barium carbonate, and assayed (8).

Nicotinic acid was decarboxylated by boiling with copper oxide in quinoline. Almost quantitative yields of carbon dioxide in the form of BaCO₃ were obtained.

The activity in the ring and in the methyl group in toluene was obtained by direct oxidation of toluene. Toluene was oxidized to benzoic acid. The benzene resulting from the decarboxylation of benzoic acid was trapped at dry ice–acetone temperature while carbon dioxide was absorbed in aq NaOH, and precipitated as BaCO₃.

All liquid samples were assayed by a wet combustion method. Radioactivity measurements were made with the aid of an ionization chamber.

RESULTS AND DISCUSSION

The experimental results obtained from the reaction of [1-¹⁴C]heptane (Table 1) are compared with the previously reported data received from the reaction of nonlabeled *n*-heptane in which the contact time was

TABLE 1

Dehydrocyclization of [1- ¹⁴ C]Heptane over Platinum–Alumina Catalyst ^a at 500°C ^b		
Time on stream (min):	Conversion products composition (mole%)	
	30	145
Conversion:	70.4	52.1
Ethane	6.4	5.3
Propane	6.8	6.8
Isobutane	0.6	0.3
<i>n</i> -Butane	6.5	7.2
Isopentane	1.4	1.0
<i>n</i> -Pentane	6.6	6.7
2-Methylpentane	5.1	4.1
3-Methylpentane	2.8	3.0
<i>n</i> -Hexane	5.6	6.3
2,4-Dimethylpentane	—	0.2 (0.2) ^c
2-Methylhexane	3.2 (5.5)	3.5 (5.8)
3-Methylhexane	15.4 (26.5)	18.7 (31.5)
3-Ethylpentane	3.3 (5.6)	2.6 (4.4)
1,2-Dimethylcyclopentane	1.9 (3.3)	1.5 (2.6)
Ethylcyclopentane	2.5 (4.3)	5.2 (8.9)
Toluene	29.3 (50.3)	24.7 (41.7)
Unidentified compounds	2.6 (4.5)	2.9 (4.9)

^a 2000 mg of 3 wt% platinum on alumina.

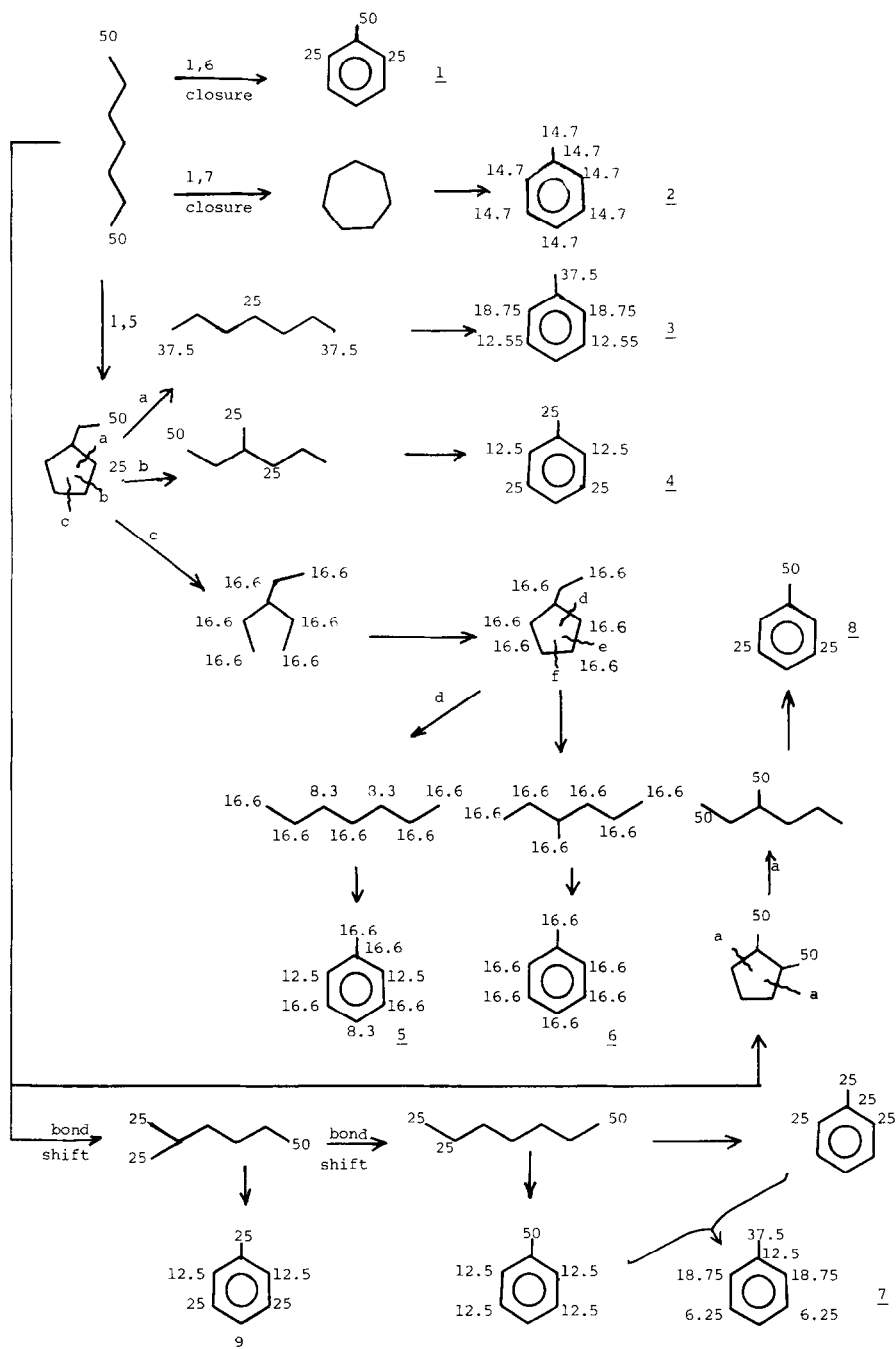
^b The experiment was made at an hourly liquid space velocity of 0.88. The liquid hydrocarbon flow rate was 2.3 ml/hr and that of hydrogen 30 cm³ (STP)/min. The hydrogen-to-hydrocarbon mole ratio is 5.1.

^c The numbers in parentheses indicate the composition of seven-carbon hydrocarbons.

much shorter, Table 1 (1). With the longer contact time the conversion was 70.4% in comparison with 20.3% after 30 min. on stream, and 52.1% as compared with 14.3% during a period on stream of 30–150 min. The main difference in the composition of seven-carbon hydrocarbons formed in the reaction is that with the higher conversion the concentration of toluene increased from 30.9 to 50.3% at the expense of ethylcyclopentane, which decreased from 29.8 to 4.3%. The concentration of 3-methylhexane, on the other hand, increased from 17.8 to 26.5%, and from 16.4 to 70.4% and from 14.3 to 31.6% when the conversion of *n*-heptane increased from 20.3 to 70.4%, and from 14.3 to 52.1%, respectively.

The comparative data of the present and previously reported investigation (1) show that ethylcyclopentane was produced parallel to toluene, and that with longer contact

time and higher conversion part of the ethylcyclopentane undergoes hydrogenolysis to 3-methylhexane and conversion to toluene.



SCHEME 2. Calculated distribution of radioactivity in toluene derived from various intermediates.

The distribution of radioactivity in each carbon of the toluene produced in the two respective cuts, after the first and second 90 min on stream, is given in Fig. 1. From the results obtained it is obvious that several intermediate steps must be invoked, each contributing to different extents, in order to obtain the final distribution of radioactivity. The steps which might be involved and the distribution of radioactivity in each carbon of the toluene produced are presented in Scheme 2.

1,6-Ring closure of heptane would yield toluene 1 with 50% radioactivity in the methyl group and with the remaining radioactivity equally distributed between carbons 2 and 6 of the toluene. Although such closure could probably be responsible for the major part of toluene, it would certainly not account for the radioactivity in the remaining positions of the toluene produced.

In order to account for radioactivity in carbon 1, steps leading to toluenes 2, 5, and 7 should be considered. Toluene 2 would be obtained by a prior formation of cycloheptane, followed by ring contraction. This would lead to an equal distribution of radioactivity in each of the carbon atoms in toluene.

Cycloheptane in small amounts has been found in the product from the reaction of ethylcyclopentane, and its structure has been confirmed by a combination of mass spectroscopy and gas chromatography (1). The lack of detection of any sizable amounts of cycloheptane in the reaction product might be due either to the difficulty of 1,7-ring closure or to the ease with which cycloheptane undergoes aromatization (1).

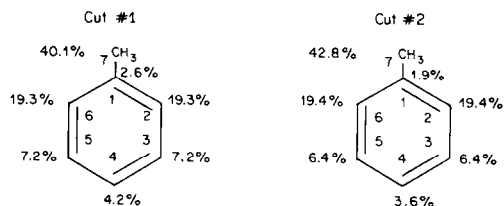


FIG. 1. Activity distribution in toluene produced by the aromatization of $[1-^{14}\text{C}]$ heptane.

Bond shift mechanism would produce toluene 9 with radioactivity equally divided between carbons 3, 5, and 7. Repetitive 1,5-ring closures followed by hydrogenolysis and an eventual 1,6-ring closure would lead to toluene 5 having radioactivity distributed between all the carbon atoms. The experimentally obtained ratio of radioactivity between carbons 1 and 4 amounting to about 0.5 is an indication that toluene 6 in conjunction with toluenes 2, 5, and 7 must have contributed to this particular ratio of radioactivity.

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