at a temperature of approximately 550°.[11] The product was collected in a 10% sodium carbonate solution to neutralize the acetate acid formed. The yield of **2,2-dimethyl-3-hexene** was 16 g. (70%), and its purity was 98% by gas chromatography. The 2,2-dimethyl-3-hexene was hydrogenated using 5% palladium on charcoal in a Parr hydrogenation apparatus at an initial hydrogen pressure of 42 p.s.i. The 2,2-dimethylhexane obtained had a purity of 99%.

3,3-Dimethylhexane.—The coupling reaction between the Grignard reagent prepared from 57.0 g. (0.53 mole) of *t*-amyl chloride and 14.0 g. (0.58 g.-atom) of magnesium turnings with 24.2 g. (0.20 mole) of allyl bromide gave a crude product weighing 23 g. Chromatographing the crude product through silica gel yielded 7.0 g. (31.3%) of **4,4-dimethyl-1-hexene** which had a purity of over 99%. Hydrogenation of 4,4-dimethyl-1-hexene in a Parr apparatus with platinum oxide catalyst and an initial hydrogen pressure of 45 p.s.i. yielded pure 3,3-dimethylhexane, $n^{18}\mathrm{D}$ 1.4028 (lit.[12] $n^{20}\mathrm{D}$ 1.4001).

2,3-Dimethylhexane.—The Grignard reaction of *n*-propylmagnesium bromide, prepared from 61.5 g. (0.50 mole) of 1-bromopropane and 13.2 g. (0.55 g.-atom) of magnesium turnings, with 34.4 g. (0.40 mole) of 3-methyl-2-butanone yielded a crude product weighing 43.5 g. Distillation yielded 33 g., 63%, of **2,3-dimethyl-3-hexanol**, b.p. 78° (45 mm.), $n^{29}\mathrm{D}$ 1.4280. A mixture of 20 g. (0.15 mole) of 2,3-dimethyl-3-hexanol, 5.0 g. (0.06 mole) of dry pyridine, and 23.4 g. (0.20 mole) of phenyl isocyanate were heated together at 140° for 2 hr., then allowed to distil with the bath temperature raised to 205°. The distillate was added to 5 ml. of water and shaken for 5 min. The solid material was filtered off, and the filtrate was washed with three 25-ml. portions of 10% aqueous acetic acid followed by 25 ml. of 10% aqueous sodium bicarbonate, and dried over anhydrous sodium carbonate. The **2,3-dimethylhexenes** were then chromatographed using alumina and pentane, yielding 12.8 g. (74%). The olefinic mixture was hydrogenated as before using platinum oxide catalyst. The title alkane was over 99.9% pure, according to v.p.c., $n^{29}\mathrm{D}$ 1.3983 (lit.[12] $n^{25}\mathrm{D}$ 1.3988).

3,4-Dimethylhexane.—A crude product of 22.1 g. of **3,4-dimethyl-3-hexanol** was obtained from the Grignard reaction of 1 mole of 2-butylmagnesium chloride with 1 mole of 2-butanone. The 22.1 g. (0.17 mole) of crude alcohol was dehydrated by the procedure described above using 4.86 g. of dry pyridine and 40.0 g. of phenyl isocyanate. The yield of **3,4-dimethylhexenes** was 11 g. (58%). Hydrogenation of the olefinic mixture using platinum oxide yielded the title alkane of over 99% purity by v.p.c.

2,4-Dimethylhexane.—The reaction of 185 g. (1.7 moles) of ethyl bromide and 43.3 g. (1.8 g.-atoms) of magnesium turnings followed by 150 g. (1.5 moles) of methyl isobutyl ketone yielded 138 g., 71%, of pure **2,4-dimethyl-4-hexanol**, b.p. 72° (38 mm.), $n^{27}\mathrm{D}$ 1.4241. The dehydration was accomplished as described before using 100 g. (0.77 mole) of 2,4-dimethyl-4-hexanol, 20 g. of dry pyridine, and 117 g. (0.98 mole) of phenyl isocyanate. The **2,4-dimethylhexenes** obtained amounted to 75.3 g., yield 87%. Hydrogenation of the olefins using 5% palladium on charcoal gave the title paraffin which, by v.p.c., was 99% pure.

2,5-Dimethylhexane.—Hydrogenation of 2,5-dimethyl-1,5-hexadiene (Eastman Organic Chemicals No. 8778), using 5% palladium-on-charcoal catalyst, gave the desired paraffin of over 99% purity.

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[11] C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

[12] F. D. Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, p. 103.

Alumina: Catalyst and Support. XXVII.[1] Aromatization of Methylcycloheptane and Methyl-C^{14}-cycloheptane over Chromia–Alumina Catalyst. Contribution to the Mechanism of Aromatization[2]

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The aromatization of methylcycloheptane and methyl-C^{14}-cycloheptane was studied. The fact that fairly large amounts of methylheptenes and *n*-octenes were found in the reaction product and that some of the carbon-14 was distributed in the ring of the aromatics suggests that at least part of the aromatization occurred through a cleavage of the methylcycloheptane ring. The acyclic compounds once formed do not just cyclize to the aromatics but may rearrange *via* methyl-carbon insertion reactions and/or cyclooctane species.

During the many studies given to the aromatization reaction both from this laboratory and others,[1,3-6] methylcycloheptane has been proposed as a possible intermediate prior to aromatization. It was assumed all possible aromatics, C_6–C_8, could be formed from such an intermediate. However, a complete product analysis was not reported. Such an analysis would be helpful and possibly indicate a pathway between methylcycloheptane and the aromatic compounds. One postulated mechanism[6] was a direct collapse of the methylcycloheptane to the aromatic compounds. Such a mechanism would yield little acyclic compounds. However, since cracking always accompanied the aromatization, the formation of acyclic compounds would not mean, necessarily, that the "collapse" mechanism is incorrect. Therefore, to examine more closely the mechanism of aromatic formation from methylcycloheptane, the methyl group was labeled with carbon-14. A direct collapse of the methylcycloheptane ring to the aromatic compounds would necessitate the carbon-14 to reside totally in the side chains. However, should the methylcycloheptane first open to acyclic compounds followed by closure to aromatics, the carbon-14 would be distributed partially in the ring (Chart I).[7]

Procedure. A. Methylcycloheptane.—This hydrocarbon was synthesized in over 99% purity and 69% over-all yield by dehydration of 1-methyl-1-cycloheptanol with phenylisocyanate and reducing the olefin with a platinum catalyst.

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[1] For paper XXVI of this series, see H. Pines, C. T. Goetschel, and J. W. Dembinski, *J. Org. Chem.*, **30**, 3540 (1965).

[2] (a) Paper XVI of the series "Aromatization of Hydrocarbons"; for paper XV, see ref. 1. (b) This research was supported by the Atomic Energy Commission Contract AT (11-1)-1096.

[3] F. R. Cannings, A. Fisher, J. F. Ford, P. D. Holmes, and R. S. Smith, "Radioisotopes in the Physical Sciences and Industry," International Atomic Energy Agency, Vienna, 1962, pp. 205–216.

[4] H. Pines, C. T. Goetschel, and S. M. Csicsery, *J. Org. Chem.*, **28**, 2713 (1963).

[5] C. T. Goetschel and H. Pines, *ibid.*, **29**, 399 (1964).

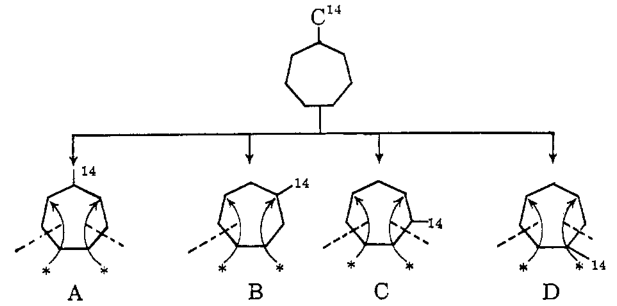
[6] H. Pines and C. T. Chen, *J. Am. Chem. Soc.*, **82**, 3562 (1960).

[7] The exact attachment of the hydrocarbon to the catalyst, denoted by an asterisk (Chart Ia), is purely for illustrative purposes. Although the hydrocarbon must be adsorbed on the catalyst before any reaction will occur, the attachment may be other than that indicated.

Chart I

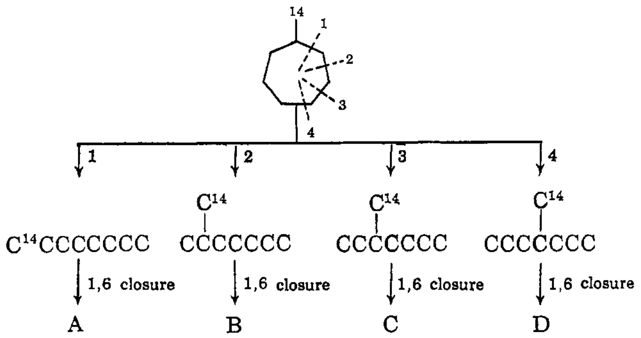
Aromatization of Methyl-C^{14}-cycloheptane *via* "Collapse" Mechanism (a) or Ring Cleavage (b)

a.



A, *o*-xylene, 100% (C^{14}) on the side chain
B, *m*-xylene and toluene, 100% (C^{14}) on the side chain
C, *p*-xylene and ethylbenzene, 100% (C^{14}) on the side chain
D, *m*-xylene and *o*-xylene, 100% (C^{14}) on the side chain

b.

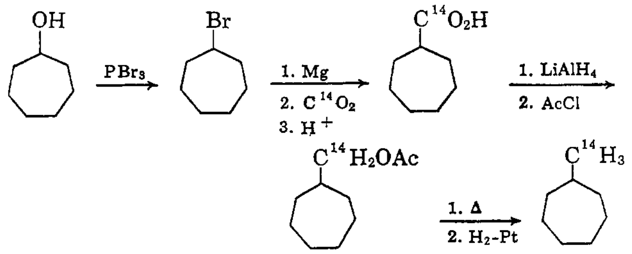


A, *o*-xylene, 100% (C^{14}) on the side chain; ethylbenzene, 50% (C^{14}) on the side chain
B, *m*-xylene, 50% (C^{14}) on the side chain; toluene, 100% (C^{14}) on the side chain
C, ethylbenzene, 0% (C^{14}) on the side chain; *o*-xylene, 100% (C^{14}) on the side chain; *p*-xylene, 100% (C^{14}) on the side chain
D, *m*-xylene, 100% (C^{14}) on the side chain

The methylcycloheptane was aromatized at 533° over nonacidic chromia–alumina catalyst, and the products were analyzed by gas chromatography, a procedure previously described[8] (Table I).

B. Methyl-C^{14}-cycloheptane.—The sequence of reactions shown in Chart II was used to synthesize the methyl-C^{14}-cycloheptane in greater than 99% purity.

Chart II



The dehydrogenation was carried out in the same manner as for the inactive methylcycloheptane. Table II summarizes the reaction conditions and composition of the C_8 aromatic fraction.

The reaction product was collected in three separate cuts. The aromatics were separated partially by preparative v.p.c. Three different fractions were collected: the first containing the nonaromatics and tolu-

Table I

Dehydrogenation and Dehydrocyclization of Methylcycloheptane over Chromia–Alumina-B at 533° and Contact Time of 3.0 Sec.[a]

	Composition, mole %[b]		
	Cut (length in min.)		
Conversion products	1 (10.0)	2 (8.0)	3 (6.5)
Methane	4.74	3.53	2.78
Ethane + ethylene	0.29	0.27	0.42
Propane	1.48	1.14	1.09
Propylene	0.86	1.02	1.03
Isobutane	0.15	0.11	0.15
n-Butane	0.37	0.30	0.39
1-Butene	0.46	0.46	0.52
Isobutylene	0.58	0.59	0.74
trans-2-Butene	0.73	0.75	0.85
Isopentane	0.23	0.15	0.20
cis-2-Butene	0.58	0.59	0.59
n-Pentane	0.26	0.18	0.20
Methylbutenes	1.39	1.59	1.60
1-Pentene	0.19	0.17	0.11
trans-2-Pentene	0.63	0.67	0.66
cis-2-Pentene	0.42	0.40	0.29
2-Methylpentane + olefins	0.41	0.32	0.55
Methylheptanes + olefins	2.00	2.80	1.93
n-Octane + olefins	1.50	2.39	2.98
1,1-Dimethylcyclohexane + olefins	0.44	0.52	0.66
Unknown	1.32	2.03	2.18
Methylcycloheptenes	2.94	3.61	3.43
Methylcycloheptane	55.87	63.06	65.33
Benzene	0.26	0.23	0.20
Toluene	2.46	2.17	1.97
Ethylbenzene	2.40	1.40	1.26
p-Xylene	3.48	1.87	1.59
m-Xylene	6.43	3.44	2.86
o-Xylene	7.00	4.10	3.35
Styrene	0.13	0.09	0.09
Total conversions of methylcycloheptane	44.13	36.94	34.77

Aromatic conversion products	Distribution in the aromatic fraction, mole %		
Benzene	1.2	1.7	1.8
Toluene	11.1	16.3	17.4
Ethylbenzene	10.8	10.5	11.1
o-Xylene	31.6	30.8	29.6
m-Xylene	29.0	25.9	25.3
p-Xylene	15.7	14.1	14.0
Styrene	0.6	0.7	0.8

[a] The contact time was calculated according to the formula given in ref. 8. [b] Total carbonaceous materials: 1.39%.

Table II

Aromatization of Methyl-C^{14}-cycloheptane over Chromia–Alumina B Catalyst[a]

	Distribution in the aromatic fraction, mole %		
	Cut[b]		
C_8 aromatic conversion products	1 (3.0)[c]	2 (3.0)[c]	3 (2.9)[c]
Ethylbenzene	10.5	11.2	11.1
o-Xylene	36.3	36.6	37.9
m-Xylene	34.1	33.6	32.2
p-Xylene	19.1	18.6	18.8
Total conversion of C_8H_{16} to aromatics	22	13	11

[a] The experiment was made at 532° and an hourly liquid space velocity of 1.58. [b] Length of cuts: 8.0 min. [c] Total C_8H_{16} passed, ml.

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(8) H. Pines and S. M. Csicsery, *J. Catalysis*, **1**, 313 (1962).

TABLE III

RADIOCHEMICAL ASSAY DATA. DECARBOXYLATION OF ACID DERIVED FROM AROMATICS PRODUCED FROM METHYL-C^{14}-CYCLOHEPTANE

Aromatic assayed	Toluene		Ethylbenzene			*o*-Xylene			*m*-Xylene			*p*-Xylene		
Acid decarboxylated	Benzoic		Benzoic			Phthalic			Isophthalic			Terephthalic		
Cut number	1	2	1	2	3	1	2	3	1	2	3	1	2	3
Acid decarboxylated, mmoles	2.37	1.13	1.07	0.59	0.66	1.00	0.76	0.38	0.75	0.50	0.37	0.90	0.97	0.42
Barium carbonate obtained, mmoles	2.12	0.32	0.89	0.53	0.62	1.65	0.58	0.20	1.44	0.89	0.64	1.42	1.67	0.74
Barium carbonate yield, mole %	90	28	83	90	94	82	38	26	96	89	86	79	86	88
Benzene obtained, mmole	0.61	0.10	0.14	0.30	0.13	0.42	0.24	0.04	0.09	0.05	0.09	0.10	0.39	...
Benzene yield, mole %	26	9	13	50	19	42	32	10	10	10	25	11	40	...
Radioactivity 10^{-3} μc./mmole														
Acid	339	1150	611	685	42	1158	2080	579	95.6	5460	735	8790	4970	812
Barium carbonate	274	1005	28	43	4.4	974	2012	560	69.6	3936	612	7780	4770	784
Benzene	55	157	567	619	37.4	149	90	24	27.1	1500	118	960	277	...

ene, the second composed of ethylbenzene and *m*- and *p*-xylene, and the third fraction containing *o*-xylene. The second and third fractions were diluted with their corresponding inactive aromatic compounds and oxidized with alkaline potassium permanganate to their respective acids. These acids were then separated by the procedure described previously.[9] The first preparative fraction was selectively hydrogenated with palladium-on-charcoal catalyst to eliminate olefins, diluted with inactive toluene, and oxidized to benzoic acid with alkaline permanganate. Purification of the benzoic acid was *via* sublimation followed by crystallization from water.

The benzoic, phthalic, isophthalic, and terephthalic acids were decarboxylated in boiling quinoline with copper oxide. The benzene and carbon dioxide products were analyzed for radioactivity. Table III summarizes the radioactivities of the aromatic acids and their decarboxylation products. The differences between the radioactivities of the acids and the sum of the radioactivities of their decarboxylation products were ±3% or less.

TABLE IV

RADIOACTIVITY DISTRIBUTION FROM THE AROMATIZATION OF METHYL-C^{14}-CYCLOHEPTANE

Aromatic compd. (cut)	% side chain	% ring	Dif.[a]
Toluene			
(1)	80.8	16.2	−3.0
(2)	87.4	13.6	1.0
(3)	...	...	
Ethylbenzene[b]			
(1)	α, 3.3; β, 30.9	64.3	−1.5
(2)	α, 3.5; β, 44.3	50.5	−1.7
(3)	*c*	*c*	
o-Xylene			
(1)	84.2	12.9	−2.9
(2)	96.6	4.5	1.1
(3)	96.7	4.1	0.8
m-Xylene			
(1)	72.7	28.3	1.0
(2)	72.0	27.5	−0.5
(3)	83.2	16.1	−0.7
p-Xylene			
(1)	88.6	10.9	−0.5
(2)	96.0	5.6	1.6
(3)	96.4	...	...

[a] The difference between the experimental value and 100% radioactivity. [b] The activity on the α- and β-carbon atoms was calculated using the v.p.c. data to determine the weight of ethylbenzene produced. Knowing the amount of inactive ethylbenzene added and the specific activity of the ethylbenzene, the loss in activity going from ethylbenzene can be calculated. This corresponds to the β-carbon activity. [c] Distribution in benzoic acid derived from ethylbenzene: side chain, 10.5%; ring, 89.0%.

Discussion of Results

Methylcycloheptane.—This reaction is accompanied by the usual amount of cracking as shown in Table I. Also prominent is the large amount of methylheptenes and *n*-octenes produced. Their presence may serve as an indication that they may be intermediates between the methylcycloheptane and aromatic compounds. If such is the case, the ring cleavage mechanism (Chart Ib) would be attractive. However, examination of the distribution of the aromatic products shows ethylbenzene and toluene to be about one-half that of *o*- and *m*-xylene. Such would be the case if the collapse mechanism (Chart Ia) were operating in a statistical manner. The C^{14} tracer technique was used to distinguish between the two paths for the formation of aromatics.

Methyl-C^{14}-cycloheptane.—The radioactivity distribution of the aromatics produced is summarized in Table IV. The fact that some of the radioactivity has become distributed in the ring of the aromatic compounds, indicates that the collapse mechanism, if operating, is not the sole mechanism. The cleavage mechanism would explain the radioactivity in the rings of *m*-xylene and ethylbenzene (Chart Ib). However, neither of the above mechanisms explains the distribution of the radioactivity in *o*- and *p*-xylene nor do they explain the activity on the α-carbon of the side chain in ethylbenzene. It is obvious, therefore, that a mechanism must be proposed which could distribute the carbon-14 between the side chain and ring of each aromatic produced. A possible explanation could be that the cleavage mechanism does occur, but, the acyclic compounds produced would not necessarily cyclize to aromatic compounds but would undergo methyl insertion reactions similar to those described previously[1,5,10] to afford new acyclic intermediates. Cyclization to aromatic compounds would explain the distribution of the carbon-14 in the aromatic compounds (Chart III). The radioactivity in the ring of *p*-xylene and on the α-carbon of ethylbenzene can be explained by assuming a cyclooctane-type intermediate from the *n*-octane species, and/or a 1,3 methyl insertion with the 3-methylheptane species. A methyl-carbon insertion of methylcycloheptene to cyclooctene is also a possibility. The variation with time of the radioactivity distributions is in keeping with these postulates.

Conclusion.—The present study has shown the complexity of the aromatization of methylcycloheptane

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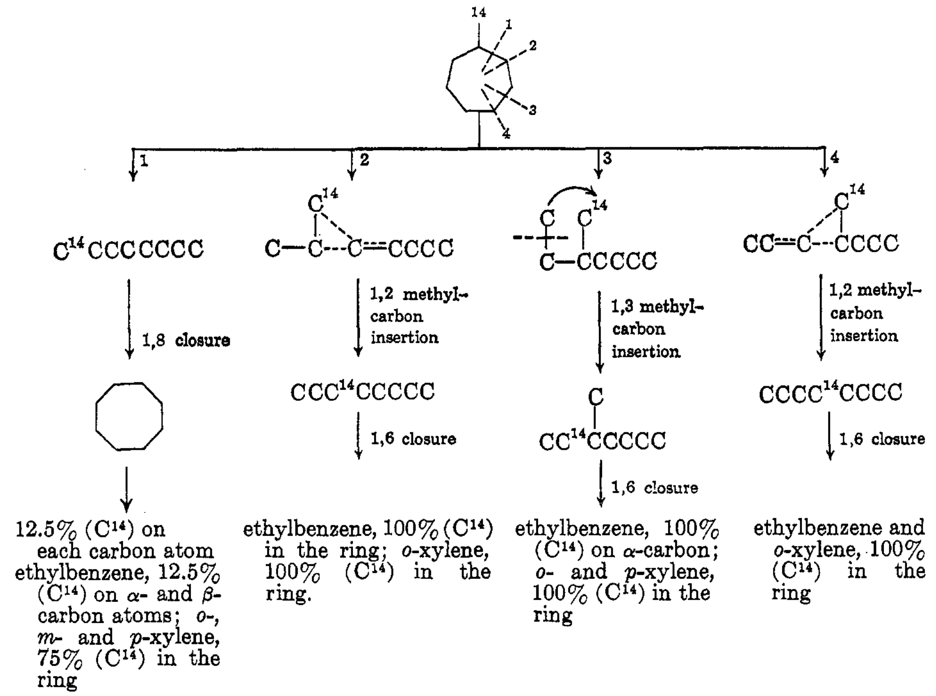
(9) H. Pines and A. Shaw, *J. Am. Chem. Soc.*, **79**, 1474 (1957).

(10) H. Pines and C. T. Goetschel, *J. Org. Chem.*, **30**, 3530 (1965).

Chart III



over chromia–alumina catalyst. The mechanism involving ring cleavage appears to be most attractive as a route to the aromatic compounds. However, the acyclic compounds once formed do not just cyclize to the aromatics but may rearrange *via* methyl-carbon insertion reactions and/or a cyclooctane intermediate. Methyl-carbon insertion of methylheptenes to cyclooctene as well as a collapse of C_7 and C_8 ring systems to aromatics may also contribute to the aromatization reaction.

Experimental Section

Methylcycloheptane.—The reaction between 0.60 mole of methylmagnesium iodide and 0.50 mole of cycloheptanone yielded 54.4 g. (85%) of **1-hydroxy-1-methylcycloheptane**, b.p. 91° (35 mm.), $n^{25.5}\text{D}$ 1.4703, over 99% pure. The above alcohol, 51 g. (0.40 mole), was dehydrated with 79.0 g. (0.66 mole) of phenylisocyanate and 9.6 g. (0.12 mole) of dry pyridine according to a procedure described previously.[1] The yield of **methylcycloheptenes** was 36.6 g. (82%) and the purity was over 99%. Hydrogenation of the olefins, using platinum oxide catalyst in a Parr hydrogenation apparatus, gave methylcycloheptane.

Methyl-C^{14}-cycloheptane.—To a solution of 36.0 g. (0.32 mole) of cycloheptanol and 5.0 ml. of absolute ether, cooled in an ice–salt bath, was added 97.0 g. (0.35 mole) of phosphorus tribromide over a 0.5-hr. period. The reaction mixture was warmed to room temperature and stirred for 20 hr. After decomposing in *ca.* 500 ml. of crushed ice, the water layer was extracted with ether. The combined organic layer and ether extracts were washed with 10% aqueous sodium bicarbonate and dried over anhydrous calcium chloride. After removing the ether, the residue was vacuum distilled; the yield of **bromocycloheptane** was 50.4 g. (90%): b.p. 85–86° (18 mm.), $n^{28}\text{D}$ 1.5018; lit. b.p. 83° (15 mm.)[11] and 64.3–64.5° (7 mm.),[12] $n^{20}\text{D}$ 1.5049.[12] **Cycloheptanoic acid-1-C^{14}** was prepared using 0.05 mole of cycloheptylmagnesium bromide and 0.036 mole of sodium carbonate containing *ca.* 15 mc. of barium carbonate-C^{14} according to the published procedure.[13] The ethereal solution of the product was diluted with *ca.* 0.03 mole of inactive cycloheptanoic acid and dried over anhydrous magnesium sulfate. The ethereal solution of acid was treated with 7.6 g. (0.2 mole) of lithium aluminum hydride according to a previously published procedure.[14] The ether was removed and the residue, **hydroxymethyl-C^{14}-cycloheptane** (16 g.), was directly acetylated with 12.4 g. (0.16 mole) of acetyl chloride in 60 ml. of pyridine, according to the described procedure.[14] **Hydroxymethyl-C^{14}-cycloheptane acetate** after distillation weighed 11.0 g., b.p. 100° (12 mm.), $n^{25}\text{D}$ 1.4549. The activity of the acetate was 0.126 mc./mmole or a total activity of 8.15 mc.; yield was 54% based on barium carbonate-C^{14}. A solution of 7.7 g. (0.045 mole) of the acetate in 7.0 ml. of methylcycloheptane was pyrolyzed at 555° as described previously, yielding **methyl-C^{14}-cycloheptene**. The infrared spectra of the product showed no acetate band but an olefin band at 6.1 μ. Hydrogenation of the olefin with platinum oxide catalyst gave methyl-C^{14}-cycloheptane of over 99% purity by v.p.c. The over-all yield based on starting barium carbonate activity was 22.4%.

Catalyst.—The chromia–alumina catalyst was prepared according to the procedure described previously.[6] The alumina was precipitated from sodium aluminate and impregnated with chromic acid. The catalyst contained 13.8 wt. % of Cr_2O_3, its surface area was 89 m.²/g., and the average pellet weight was 0.022 g.

Apparatus and Procedure.—The apparatus and procedure were the same as those described earlier.[8]

Separation of Aromatic Hydrocarbons from the Dehydrogenation Product.—The separation was accomplished using an F & M Model 300 programmed-temperature gas chromatograph[15] with an 11 mm. × 2.5 m. preparative v.p.c. column filled with 5% 7,8-benzoquinoline on 30–60-mesh Chromosorb. The column temperature was 75° with a helium flow rate of 105–114 cc./min. Sample sizes injected were up to 1.3 ml. The sample recovery was the same as described previously.[4]

Oxidation of the Aromatics.—After separation, the aromatics were diluted from 3 to 15 times with their corresponding inactive aromatic compounds and oxidized to benzoic and phthalic acids with hot alkaline potassium permanganate as described previously.[4]

Separation of the Aromatic Acids.—The benzoic, isophthalic, and terephthalic acids obtained from the mixture containing

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[11] L. Ruzicka, P. Barman, and V. Prelog, *Helv. Chim. Acta*, **34**, 401 (1951).

[12] P. J. C. Fierens and P. Verschelden, *Bull. soc. chim. Belges*, **61**, 427 (1952).

[13] M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert, and P. E. Yankwich, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 178–179.

[14] W. R. Vaughan, C. T. Goetschel, M. H. Goodrow, and C. L. Warren, *J. Am. Chem. Soc.*, **85**, 2282 (1963).

[15] F & M Scientific Corp., Avondale, Pa.

ethylbenzene and *m*- and *p*-xylene were separated by a procedure described previously.[9] The benzoic acid from the toluene was purified by sublimation at 100° followed by recrystallization from boiling water. Purification of the phthalic acid from *o*-xylene was made as described previously.[9]

Radiochemical Assay.—The radiochemical assay of the resulting aromatic acids and their decarboxylation products was the same as that reported previously[16] (Table IV).

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(16) H. Pines and G. Benoy, *J. Am. Chem. Soc.*, **82**, 2483 (1960).

Alumina: Catalyst and Support. XXVIII.[1] Aromatization and Dehydroisomerization of 3- and 4-Methylheptane and 3- and 4-Methyl-C^{14}-heptane. Contribution to the Mechanism of Aromatization[2]

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The aromatization of 3- and 4-methylheptane along with their corresponding methyl-C^{14} compounds was investigated. The usual skeletal rearrangements observed in other such studies were also observed in the present study. The carbon-14 distribution in the aromatic compounds indicates that not only 1,2 and/or 1,3 methyl-carbon insertion reactions participate, but also 1,7 ring closure is a major contributor to the skeletal rearrangement of the methylheptanes prior to aromatization. The present study has also suggested a reasonable correlation between the various "closure" mechanisms and the catalytic sites responsible for such closures.

The studies in the preceeding papers have left little doubt that the aromatization of hydrocarbons over chromia–alumina catalysts is anything but simple. *n*-Heptane[3-5] and *n*-octane[6,7] have been shown to form cycloheptane and cyclooctane intermediates over this catalyst. The methylpentanes[8-10] and the methylhexanes[11] undergo skeletal rearrangements partially *via* 1,2 and/or 1,3 methyl-carbon insertion reactions.[12] Finally, at any particular time one or all of these reactions may be occurring. Although all these data appear to make the reaction mechanism very complex, a closer examination shows a surprising consistency from a wide variety of different compounds. For example, *n*-heptane[4,5] and *n*-octane[7] aromatize not only *via* 1,6 ring closure but aso *via* cycloheptane- and cyclooctane-type species, respectively. Apparently, closure at the terminal methyl groups is a desired path. This seems to hold true in branched hydrocarbons as well. An earlier discussion[11] on carbonaceous material formation indicated the ease of five-membered ring formation in cases where two methyl groups were separated by three methylene carbon atoms. Fulvene compounds have actually been isolated in some cases.[13] Further, the methyl-carbon insertion mechanism seems to be common with the branched hydrocarbons. That is, the aromatic products from the methylpentanes and methylhexanes can be explained by the same 1,2 and in some cases by 1,3 methyl-carbon insertion reactions, and, unifying even more, the 1,3 methyl insertion may be the closure *via* two adjacent methyl groups followed by ring cleavage. The 1,2 methyl insertion may be a 1,2 vinyl group shift.[12,14] In the present case, 3- and 4-methylheptanes were studied to show that the next higher homologous series follows this same pattern.

4-Methylheptane can cyclize *via* 1,6 closure to only *m*-xylene. If other aromatics are produced, skeletal rearrangements by possibly 1,2 methyl-carbon insertion and/or 1,7 ring closure would be necessary. 3-Methylheptane can directly yield ethylbenzene and *o*- and *p*-xylene. However, *m*-xylene is precluded. Skeletal rearrangements by either 1,2 and, in this case, 1,3 methyl-carbon insertion and/or 1,7 ring closure would allow *m*-xylene to be formed. Therefore, the formation of any aromatics other than *m*-xylene in the former case and *m*-xylene formation in the latter case would indicate skeletal rearrangements prior to aromatization.

Carbon-14 tracer studies on 3- and 4-methylheptane also appear necessary. Assuming skeletal rearrangement does occur, then the question arises as to whether it is a methyl-carbon insertion or 1,7 ring closure which is occurring. If skeletal rearrangement follows 1,7 ring closure, then the carbon-14 distribution in aromatics not produced by direct ring closure should be similar to that found in the corresponding aromatic compounds from the aromatization of methyl-C^{14}-cycloheptane.[1]

In the case of 4-methyl-C^{14}-heptane, a 1,2 methyl-carbon insertion would give *n*-octane-4-C^{14}-adsorbed species. Therefore, if this were the sole process for skeletal rearrangement, the carbon-14 distribution in the *o*-xylene isolated should be similar to that found in the *o*-xylene produced when *n*-octane-4-C^{14} was passed over this catalyst.[7] The carbon-14 distribution in the *m*-xylene would be more difficult to decipher since the possible methyl-carbon insertion reactions would leave the rearranged products labeled with carbon-14 in several different positions.

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(1) For paper XXVII, see C. T. Goetschel and H. Pines, **30**, 3544 (1965).

(2) (a) Paper XVII of the series "Aromatization of Hydrocarbons"; for paper XVI, see ref. 1. (b) This research was supported by the Atomic Energy Commission Contract AT (11-1)-1196.

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