Alumina: Catalyst and Support. XXV.[1] Aromatization of 2-Methylhexane-6-C^{14}, 3-Methylhexane-5-C^{14}, and 3-Methyl-C^{14}-hexane over Chromia–Alumina Catalyst. Contribution to the Mechanism of Aromatization[2,3]

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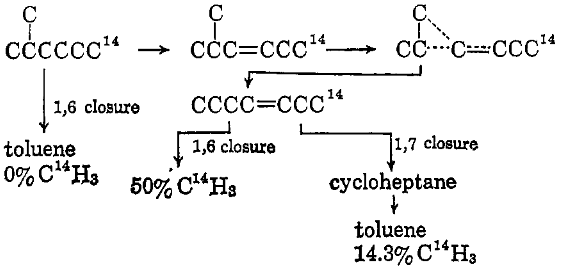
The aromatization of 2-methylhexane-6-C^{14}, 3-methylhexane-5-C^{14}, and 3-methyl-C^{14}-hexane over nonacidic chromia–alumina was studied. The main aromatic product was toluene. The radioactivity distribution in toluene supports 1,2- and 1,3-methyl-carbon insertion involving the previously proposed cyclopropane- and cyclobutane-type intermediates for the dehydroisomerization and aromatization of branched hydrocarbons. Higher sensitivity of the cyclobutane-type intermediate to the age of the catalyst has been reconfirmed. The study has also indicated that the noncarbonium ion type rearrangement (carbon insertions) is followed by the ring closure. There is evidence that one of the paths in aromatization of methylhexanes is formation of seven-membered-ring intermediates. Additional support has been obtained for the preferential involvement of primary carbon atoms. Rapid coke buildup and decline of conversion of 3-methylhexane indicated that the five-membered cyclic intermediates dehydrogenate and polymerize.

The main objective of this study was to determine the various paths by which methylhexanes can form toluene. For that reason 3-methyl-C^{14}-hexane, 3-methylhexane-5-C^{14}, and 2-methylhexane-6-C^{14} were synthesized and aromatized over nonacidic chromia–alumina catalyst under conditions similar to those described previously.[4] The aromatic product of the reaction was composed essentially of toluene.

The aromatization of 2-methylhexane-6-C^{14} through a direct 1,6 ring closure would produce toluene having all the radioactivity in the ring. The insertion of the 2-methyl group *via* a cyclopropane-type intermediate followed by 1,6 ring closure of the heptane would yield toluene in which 50% of C^{14} would be in the methyl group. 1,7 ring closure to a cycloheptane ring followed by ring contraction would produce toluene in which the radioactivity would be equally distributed between all of the carbon atoms, with the methyl group having 14.3% of C^{14} (Chart I). The distribution of radioactivity in toluene from 3-methyl-C^{14}-hexane and 3-methylhexane-5-C^{14} *via* three-, four-, six- and seven-membered-ring intermediates is presented in Chart II. Any radioactivity in the methyl group of toluene from 3-methylhexane-5-C^{14} would have to involve a seven-membered-ring intermediate.

Chart I

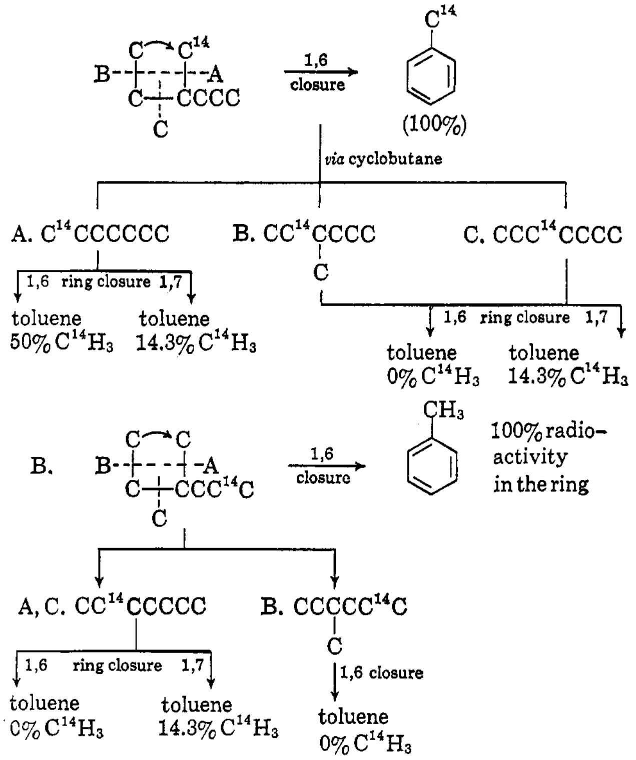
Aromatization of 2-Methylhexane-6-C^{14} *via* 1,2 Methyl-Carbon Insertion



Actual radioactivity distribution between the methyl group and the ring of the produced toluene gives solid support to the participation of various ring intermediates in the aromatization reaction (Table I).

Chart II

Aromatization of 3-Methyl-C^{14}-hexane and 3-Methyl-5-C^{14}-hexane *via* Cyclobutane Intermediates



An additional objective of the study was to gain more evidence to support the previously made observations[5] regarding preferential involvement of the primary carbon atoms in reactions over the nonacidic chromia–alumina. The data in Table II for aromatization of inactive 2- and 3-methylhexanes show a rapid catalyst deactivation in the case of 3-methylhexane. The skeletal structure of 3-methylhexane permitted closure to a five-membered ring between the primary carbon atoms, but the resultant adsorbed species probably underwent dehydrogenation and polymerization to form coke. The fact that five-membered-ring

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(1) For paper XXIV of this series, see H. Pines and C. T. Goetschel, *J. Org. Chem.*, **30**, 3530 (1965).

(2) Paper XIV of the series "Aromatization of Hydrocarbons"; for paper XIII, see ref. 1.

(3) This research was supported in part by the Atomic Energy Commission Contract AT (11-1)-1096.

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

(5) C. T. Chen, W. O. Haag, and H. Pines, *Chem. Ind.* (London), 1379 (1959).

TABLE I

DECARBOXYLATION OF BENZOIC ACID DERIVED FROM TOLUENE PRODUCED BY AROMATIZATION OF METHYLHEXANES

Methylhexane (cut)	10^{-2} μc./mmole Starting acid	BaCO$_3$	C$_6$H$_6$	Radioactivity distribution in toluene, % CH$_3$	Ring	Dif.[a]
$C\overset{C}{\overset{\vert}{C}}CCCC^{14}$						
(1)	677.4	16.1	658.0	2.4	97.2	−0.4
(2)	277.0	6.0	270.0	2.2	97.5	−0.3
(3)	123.1	2.5	...	2.0	...	...
$CC\overset{C^{14}}{\overset{\vert}{C}}CCC$						
(1)	137.6	128.9	10.3	93.7	7.5	+1.2
(2)	14.4	14.0	...	97.0	...	...
(3)	5.5	5.5	...	99.2	...	...
$CC\overset{C}{\overset{\vert}{C}}CC^{14}C$						
(1)	189.3	10.7	178.5	5.6	94.3	−0.1
(2)	156.9	4.1	152.6	2.6	97.3	−0.1
(3)	6.4	...	6.3	...	98.6	...

[a] Difference between the experimental value and 100% radioactivity recovery.

TABLE II

DEHYDROGENATION OF 2- AND 3-METHYLHEXANES OVER CHROMIA–ALUMINA CATALYST AT 510°

Conversion products	Composition, mole % 2-Methylhexane[a] Cut (length in min.)[b] 1 (9)	2 (10)	3 (12)	3-Methylhexane[a] Cut (length in min.)[c] 1 (6)	2 (7)	3 (8)
Methane	0.01	0.01	0.01	0.04	0.01	0.01
Ethane and ethylene	0.01	0.01	0.01	0.26	0.07	0.04
Propane and propylene	1.57	0.93	0.88	0.24	0.21	0.16
Isobutane	0.48	0.32	0.25	0.09	0.05	0.11
n-Butane	0.09	0.08	0.09	0.05	0.13	0.08
1-Butene	0.48	0.31	0.25	0.03	0.03	0.02
2-Butene (*trans*)	0.13	0.12	0.10	0.06	0.06	0.03
2-Butene (*cis*)	0.08	0.07	0.06	0.03	0.04	0.02
n-Pentane	0.02	0.02	0.02	0.06	0.05	0.04
Pentenes and hexenes	0.16	0.10	0.14	0.99	0.27	0.16
2-Methylhexene	7.55	7.00	5.65	...	...	...
3-Methylhexene	...	...	...	11.1	8.05	4.34
n-Heptane	1.96	1.74	1.08	0.51	0.33	0.23
Benzene	0.12	0.10	0.12	0.04	0.05	0.05
Toluene	18.03	16.54	15.94	6.18	5.21	0.56
Unidentified compounds	0.20	0.53	0.15	0.19	0.11	0.10
Carbonaceous material[a]	0.83	0.75	0.67	2.72	2.06	0.85
Total conversion of methylhexane	31.7	28.8	25.5	22.6	17.7	6.8

[a] It was assumed that the percentage of the methylhexane converted to carbonaceous material was the same in each of the three cuts. [b] Hourly liquid space velocity, 0.96. [c] Hourly liquid space velocity, 1.33.

species are coke precursors has been reported previously.[6]

Procedure.—The inactive 2-methylhexane was synthesized in greater than 99% purity by the sequence of reactions shown in Chart III.

The inactive 3-methylhexane was synthesized in greater than 99% purity by the steps shown in Chart IV.

The 2- and 3-methylhexanes were dehydrogenated over nonacidic chromia–alumina catalyst by a previously described procedure.[7] Table II summarizes the reaction conditions and product distribution.

CHART III

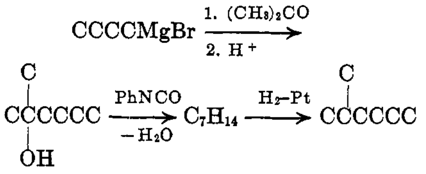
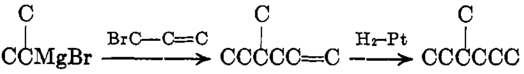
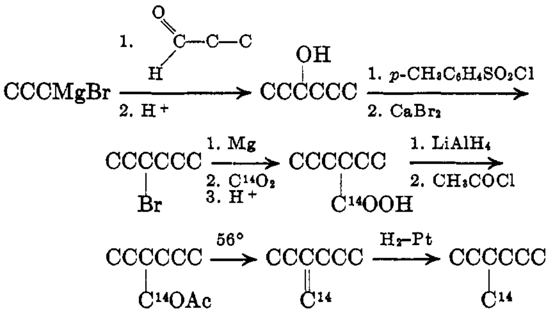


CHART IV



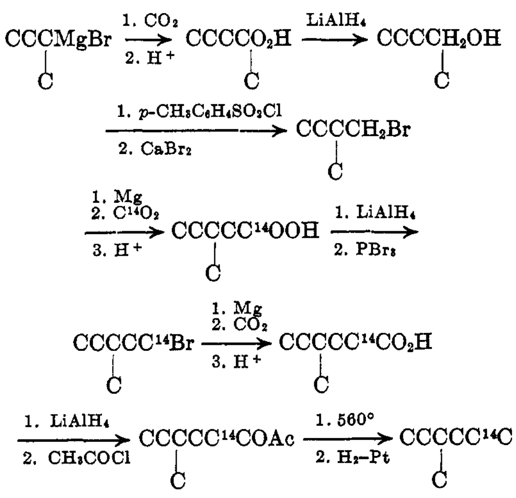
The 3-methyl-C^{14}-hexane was synthesized in above 99% purity by the sequence of reactions shown in Chart V.

CHART V



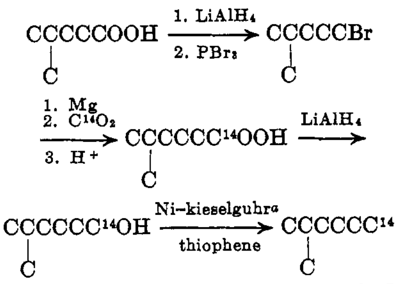
The 3-methylhexane-5-C^{14} was synthesized in more than 99% purity as shown in Chart VI.

CHART VI



The 2-methylhexane-6-C^{14} was synthesized as shown in Chart VII.

CHART VII



[a] H. Pines, M. Shamaiengar, and W. S. Postl, *J. Am. Chem. Soc.*, **77**, 5099 (1955).

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(6) J. M. Bridges, C. T. Rymer, and D. S. MacIver, *J. Phys. Chem.*, **66**, 871 (1962).

(7) H. Pines and C. T. Chen, *J. Org. Chem.*, **26**, 1057 (1961).

All the three radioactive compounds and the corresponding inactive compounds were dehydrogenated at identical conditions. In all cases the product was collected in three separate cuts. When radioactive compounds were used, the toluene in each cut was separated by preparative vapor phase chromatography, diluted with inactive toluene, and oxidized with alkaline potassium permanganate to benzoic acid. This technique has been described previously.[8,9] The benzoic acid was then decarboxylated with boiling quinoline and copper dioxide. The benzene and carbon dioxide produced were collected separately and analyzed for radioactivity.

Discussion of Results

The radioactivity distribution in toluene produced from aromatization of 2-methylhexane-6-C^{14} (**1**), 3-methylhexane-5-C^{14} (**2**), and 3-methyl-C^{14}-hexane (**3**) (Table I) indicates that simple 1,6 ring closure is not the exclusive path of dehydrocyclization of these three compounds, because it would result in 100% radioactivity in the methyl group of toluene in the case of compounds **1** and **2** and 0% radioactivity in the methyl group of toluene in the case of **3**.

The observed radioactivity distribution in toluene can be explained by an insertion mechanism involving cyclopropane and cyclobutane intermediates. Rupture of the cyclobutane species in various positions produces branched- and straight-chain heptanes which then undergo either 1,6 or 1,7 ring closure. In the latter case toluene would result from ring contraction and dehydrogenation.

Lower than 100% radioactivity in the ring of toluene from 2-methylhexane-6-C^{14} can be explained in terms of 1,6 and 1,7 ring closure after the initial isomerization step involving a cyclopropane-type intermediate (Chart I). Little variation with time in the radioactivity distribution in toluene from cuts 1–3 is consistent with the previously made observation[10,11] that cyclopropane-type intermediates are practically time independent. At this point there is not sufficient data for determining the relative contribution of 1,6 and 1,7 closures after the initial isomerization step.

Similarly, lower than 100% radioactivity in the methyl group of toluene from 3-methyl-C^{14}-hexane can be explained in terms of 1,6 and 1,7 ring closure which follow the initial isomerization step proceeding *via* the cyclobutane-type intermediate (Chart II). A strong support for the existence of the cyclobutane intermediate was the observation recorded before that 2,3-dimethylbutane isomerizes in the presence of nonacidic chromia–alumina catalyst to 3-methylpentane.[11] Further support for the cyclobutane-type isomerization stems from the fact that the structure of the 3-methylhexane resembles that of 2,3-dimethylbutane and that the radioactivity distribution was changing considerably with the time. Substantially higher sensitivity of the cyclobutane intermediate to the age of the catalyst than that of the cyclopropane-type intermediate has been also noticed previously.[10,11] Also in this case no distinction could be made between 1,6 or 1,7 closure after the initial isomerization step.

Such a distinction between the two types of closures can be made by aromatizing of 3-methylhexane-5-C^{14}. If the above reasoning regarding the mechanism of aromatization is correct, then higher than 0% radioactivity in the methyl group of toluene could be accounted for only by dehydrocyclization *via* a seven-membered-ring intermediate. The results showed that 38% of the first cut and 17% of the second cut aromatized *via* a seven-membered-ring intermediate. Substantially higher coke formation has been found from the aromatization of 3-methylhexane than from 2-methylhexane. These results suggest that under favorable structural conditions five-membered cyclic species do form but undergo dehydrogenation and polymerization resulting in coke buildup rather than expand to a six-membered ring and dehydrogenate to aromatics.

Conclusion.—This study has contributed and added support for the noncarbonium ion type isomerization over nonacidic chromia–alumina catalyst. This isomerization involves methyl-carbon insertions resulting in the formation of cyclopropane- and cyclobutane-type intermediates. The latter declines rapidly with time. Radioactivity distribution showed that isomerization of 3-methylhexane-5-C^{14} proceeded *via* cyclobutane-type intermediate. The resulting isomers undergo dehydrocyclization by 1,6 and 1,7 ring closure. Deviation from 0% radioactivity in the methyl group of toluene is a direct measure of participation of the seven-membered-ring intermediates. Five-membered-ring intermediates probably do not participate in aromatization over nonacidic chromia–alumina catalyst. However, they do form, but end up in coke.

Experimental Section

2-Methylhexane-5-C^{14}.—To 150 ml. of absolute ether was added carefully under stirring 7.6 g. (0.2 mole) of lithium aluminum hydride. Then an ethereal solution of 0.126 mole of 4-methylpentanoic acid was added dropwise with rapid stirring. The addition was followed by stirring for 2 hr. and then was added dropwise 12.2 ml. of 10% aqueous sodium hydroxide and 15.2 ml. of water, followed by additional stirring at room temperature for 5 hr. Finally the ether was removed by distillation; the yield of **4-methyl-1-pentanol** was *ca.* 95%. **4-Methyl-1-bromopentane** was prepared from the above alcohol and phosphorus tribromide by the standard procedure. 5-Methylhexanoic acid-1-C^{14} was synthesized in 70% yield by carbonation of the 4-methylpentylmagnesium bromide with carbon-C^{14} dioxide and reduced with lithium aluminum hydride to **5-methylhexanol-1-C^{14}**. A synthetic sequence of this type was described previously.[8] The alcohol was dehydrated over alumina at 400° and hydrogenated with platinum black to form the title hydrocarbon.

3-Methylhexane-5-C^{14}.—**2-Methyl-1-butanol** was prepared in 55% yield by carbonation of *sec*-butylmagnesium bromide[12] followed by lithium aluminum hydride reduction as described above. **3-Methylpentyl-1-C^{14} bromide** was prepared in 35% yield from 2-methyl-1-butanol *via* tosylate and calcium bromide displacement,[13,14] followed by carbonation with carbon-C^{14} dioxide of the 2-methyl-1-butylmagnesium bromide, lithium aluminum hydride reduction, and bromination of resulting alcohol with phosphorus tribromide. **4-Methylhexyl-2-C^{14} 1-acetate** was prepared in 40% yield by carbonation of 3-methylpentyl-1-C^{14} bromide, reduction with lithium aluminum hydride of the

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[8] H. Pines and A. W. Shaw, *J. Am. Chem. Soc.*, **79**, 1474 (1957).

[9] S. M. Csicsery and H. Pines, *ibid.*, **84**, 3939 (1962).

[10] H. Pines and S. M. Csicsery, *ibid.*, **84**, 292 (1962).

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

[12] H. S. Hussey, *J. Am. Chem. Soc.*, **73**, 1364 (1951).

[13] A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *ibid.*, **80**, 2326 (1958).

[14] G. L. Jenkins and J. C. Kellet, Jr., *J. Org. Chem.*, **27**, 624 (1962).

resulting alcohol, and acetylation with acetyl chloride. 3-Methylhexane-5-C^{14} was prepared in 94% yield by pyrolysis of 4-methylhexyl-2-C^{14} 1-acetate at 560° and hydrogenation of the resulting olefin.

3-Methyl-C^{14}-hexane was prepared in 16% over-all yield from propylmagnesium bromide by the procedure outlined in the text.

Catalyst.—The chromia–alumina catalyst was prepared according to the procedure described.[4] 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. A. Aromatization.—The apparatus and procedure for the aromatization were the same as those described earlier.[11]

B. Separation of Aromatic Hydrocarbons from Reaction Product.—The separation was accomplished using an F & M Model 300 programmed-temperature gas chromatograph[15] with an 11 mm. × 2.4 m. preparative v.p.c. column filled with 5% 7,8-benzoquinoline on 30–60-mesh Chromosorb. The column temperature used was 75° with a helium flow rate of 105–114 cc./min. The liquid products obtained from radioactive compounds were before separation diluted with inactive toluene.

C. Oxidation of Toluene.—Toluene was oxidized to benzoic acid with alkaline potassium permanganate decarboxylated by heating in quinoline with copper oxide at 265° for 3 hr., and then both carbon dioxide and benzene were assayed for C^{14} to obtain the isotope distribution.[8]

D. Radiochemical Assay.—The radiochemical assay of the benzoic acids and the decarboxylation products was the same that as previously described.[16]

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(15) F & M Scientific Corp., Avondale, Pa.

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

Alumina: Catalyst and Support. XXVI.[1] Aromatization and Dehydroisomerization of Dimethylhexanes over Chromia–Alumina Catalyst. Contribution to the Mechanism of Aromatization[2]

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The aromatization and dehydroisomerization of the dimethylhexanes over nonacidic chromia–alumina-B catalyst was studied. Contrary to previous reports, the aromatization is preceded, to some degree, by skeletal isomerization. The isomerization reactions can be explained by assuming 1,2 and/or 1,3 methyl-carbon insertion reactions. However, in some cases it appears necessary to include cycloheptane- and/or cyclooctane-adsorbed species prior to aromatization. When cyclization to alkylcyclopentane derivatives is possible, the catalyst is deactivated more rapidly than when cyclopentane species cannot be formed. Formation of fulvene derivatives from the cyclopentanes followed by their facile polymerization would explain these results.

Studies on various trimethylpentanes in this and other laboratories[3,5] over nonacidic chromia–alumina catalyst have shown that considerable amounts of aromatic compounds have been formed, necessitating the involvement of skeletal isomerizations prior to ring closure. Since it has been shown that cationic isomerization cannot be involved over this catalyst,[6] it was proposed that 1,2 and 1,3 methyl-carbon insertions were involved during the isomerization steps. Later the picture was made even more complex when it was shown that C_7 and/or C_8 rings were formed from 2- and 3-methylhexane and 2,3,4-trimethylpentane prior to aromatization.[1,7]

It has been reported that the C_8 aromatics formed from 2,5-dimethylhexane consisted of 80% *p*-xylene and from 2,3-dimethylhexane, 90% *o*-xylene and 10% *p*-xylene.[8] Owing to the above described results it was felt that a reinvestigation of the aromatization of the various dimethylhexanes was necessary. Therefore 2,2-dimethylhexane (I), 3,3-dimethylhexane (II), 2,3-dimethylhexane (III), 3,4-dimethylhexane (IV), 2,4-dimethylhexane (V), and 2,5-dimethylhexane (VI) were synthesized and aromatized over nonacidic chromia–alumina-B catalyst. If only 1,6 ring closure were operating to give the aromatic compounds, then each dimethylhexane would yield only one aromatic compound: namely, I and II, toluene; III and IV, *o*-xylene; V, *m*-xylene; and VI, *p*-xylene. If however, methyl-carbon insertion, *via* free-radical vinyl migration, occurs prior to ring closure, a combination of many of the aromatic compounds should be formed from each dimethylhexane.

Procedure. A. Apparatus and Technique.—The same apparatus was used as described previously.[4] The temperature of the catalyst was kept constant by an automatic temperature controller, while measured with thermocouples held inside and outside the catalyst bed. The amount of catalyst was 14.1 ml. (10.3 g.) mixed with 38.6 g. of glass beads of approximately the same dimension. All experiments were made at atmospheric pressure. The products were collected at Dry Ice–acetone temperature. In this manner, all the liquid and gaseous products were trapped with the exception of hydrogen and a small amount of methane; the latter was collected in a liquid nitrogen trap while the hydrogen was measured with a wet-test meter. Collecting the product at this low temperature simplified the analytical procedure since practically all of the gaseous products were dissolved in the liquid.

B. Analytical Procedure.—The products were analyzed by gas chromatography using an F & M Model 300 programmed-temperature gas chromatograph by a procedure previously described.[4]

C. Catalyst.—Nonacidic chromia–alumina catalyst was prepared as described previously.[6] The alumina was precipitated from potassium aluminate and im-

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(1) For paper XXV of this series, see H. Pines and J. W. Dembinski, *J. Org. Chem.*, **30**, 3537 (1965).

(2) (a) Paper XV of the series "Aromatization of Hydrocarbons"; for paper XIV, 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, *Chem. Ind.* (London), 228 (1960).

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

(5) S. M. Csicsery and H. Pines, *J. Am. Chem. Soc.*, **84**, 3939 (1962).

(6) H. Pines and C. T. Chen, *ibid.*, **82**, 3562 (1960).

(7) C. T. Goetschel and H. Pines, *J. Org. Chem.*, **29**, 399 (1964).

(8) A. H. Steiner in "Catalysis," Vol. IV, P. H. Emmett, Ed., Reinhold Publishing Corp., New York, N. Y., 1956, pp. 529–560.