The 60-Mc. proton n.m.r. spectrum of a trifluoroacetic acid solution showed a phenyl complex extending from $\delta = 7.1$ to 8.3 p.p.m., as well as two other broad bands at $\delta = 4.5$ and 3.5 p.p.m. The latter were in the ratio of 1:2 and were assigned to the methinyl and methylene protons, respectively.

Reaction of Lithium Diphenylphosphide and *trans*-β-Styryldiphenylphosphine Oxide.—To a solution of lithium diphenylphosphide in tetrahydrofuran, made from 1.97 g. (0.0075 mole)[4] of triphenylphosphine, was added 2.0 g. (0.0066 mole) of *trans*-β-styryldiphenylphosphine oxide. After refluxing for 20 min., the solution had decolorized to a light yellow. Addition of 3% peroxide, followed by evaporation of the tetrahydrofuran, led to a precipitate. Filtration and drying of this precipitate gave 2.9 g. of phenylethylenebis(diphenylphosphine) dioxide, as shown by melting point, mixture melting point, infrared spectra, and proton magnetic resonance spectral comparison with authentic material. Acidification of the aqueous filtrate gave little diphenylphosphinic acid.

Reaction of Lithium Diphenylphosphide and *cis*-β-Styryldiphenylphosphine Oxide.—To a solution of lithium diphenylphosphide in tetrahydrofuran produced from 1.97 g. (0.0075 mole) of triphenylphosphine was added a solution of 2.0 g. (0.0066 mole) of *cis*-β-styryldiphenylphosphine oxide, and the reaction mixture was refluxed for 1 hr. The red color was slowly discharged. Addition of water, followed by evaporation of tetrahydrofuran, led to a precipitate which was filtered off. The aqueous filtrate was acidified with dilute hydrochloric acid. Little precipitate was obtained. The water-insoluble solid (2.5 g.) was recrystallized from ethanol and water and found to be phenylethylenebis(diphenylphosphine) dioxide by mixture melting point determination, infrared spectra, and proton magnetic resonance spectral comparison with authentic material.

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Alumina: Catalyst and Support. XXIV.[1] Discussion of the Mechanism of the Aromatization of Alkanes in the Presence of Chromia–Alumina Catalysts[2,3]

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The mechanism of aromatization of alkanes over chromia–alumina catalysts is reviewed. The experimental results reported by early investigators were re-examined in view of an inadequate description of the nature of alumina they used in the preparation of their catalysts and of the inadequacy of analytical tools. The importance of the nature of aluminas used in the preparation of the catalysts on the formation and the distribution of the reaction product is discussed. The use of C^{14}-labeled alkanes and the distribution of the C^{14} in the aromatics produced assisted in obtaining a clearer picture of the mechanism of aromatization. The participation of six-, seven-, and eight-membered-ring-adsorbed species in the aromatization of C_8 alkanes is discussed. A free-radical mechanism is postulated for methyl-carbon insertion accompanying the dehydrogenation of methylalkanes. The distribution of the cracking products accompanying the aromatization of alkanes is explained by a radical mechanism.

The catalytic aromatization of paraffins over chromia catalysts was discovered independently by Moldavsky and Kamuscher[4] and by Grosse, *et al.*[5,6] At about the same time Kazansky and Plate[7] reported that, at 350°, platinum catalysts are able to aromatize alkanes.

The catalytic aromatization of *n*-heptane over chromia at about 500° yielded large amounts of toluene. The obvious industrial importance of this reaction for converting low-octane-rated hydrocarbons into high-octane-rated aromatics, along with the possible synthesis of individual aromatic compounds, aroused considerable interest and study. Concerning the many aspects of this reaction, much study has been given to the mechanism of catalytic aromatization by a number of investigators. The complexity of the reaction will be shown in this and the following papers. However, in order to arrive at a common basis of understanding for this reaction, a condensed survey of the relevant previous work will be given.

The Catalysts. A. General.—The dehydrocyclization of paraffins is thermodynamically unfavorable at moderate temperatures. On the other hand, owing to the high stability of the aromatic ring, this unfavorable equilibrium can be displaced almost quantitatively in favor of the aromatic hydrocarbons at temperatures above 300° providing a suitable catalyst for ring closure is used. Such a catalyst must activate the carbon–hydrogen bond but not the carbon–carbon bond rupture. Taylor and Turkevich[8] have shown that metal dehydrogenation catalysts such as Fe, Ni, and Co would be of little utility owing to their tendency to break carbon–carbon bonds. However, the oxide catalysts, principally chromium oxide, are ideally suited as catalysts in aromatization. It has been shown[9,10] that acti-

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(1) For paper XXIII, see J. Manassen and H. Pines, Proceedings of the 3rd International Congress in Catalysis, Amsterdam, 1964, North-Holland Publishing Co., Amsterdam, 1965, pp. 845–856.

(2) Paper XIII of the series "Aromatization of Hydrocarbons"; for paper XII, see C. T. Goetschel and H. Pines, *J. Org. Chem.*, **29**, 399 (1964).

(3) This work was supported by Atomic Energy Commission Contract AT(11-1)-1096.

(4) B. L. Moldavsky and H. D. Kamuscher, *Compt. rend. Acad. Sci., USSR*, **1**, 355 (1936).

(5) A. V. Grosse and J. C. Morrell, U. S. Patents 2,124,566, 2,124,567, and 2,124,583–2,124,586 (July 1938), applied for Sept.–Oct. 1936.

(6) A. V. Grosse, J. C. Morrell, and W. J. Mattox, *Ind. Eng. Chem.*, **32**, 528 (1940).

(7) B. A. Kazansky and A. F. Plate, *Ber.*, **69**, 1862 (1936).

(8) H. S. Taylor and J. Turkevich, *Trans. Faraday Soc.*, **35**, 921 (1939).

(9) J. Turkevich and H. S. Taylor, *J. Am. Chem. Soc.*, **56**, 2254 (1934).

(10) J. Howard and H. S. Taylor, *ibid.*, **56**, 2259 (1934).

vated adsorption of paraffins takes place readily on these surfaces above 300°, resulting in the rupture of the carbon–hydrogen bond. The oxide catalysts cause little cracking of the carbon–carbon bonds. Furthermore, at about 450°, in the case of chromium oxide, hydrogen is easily desorbed. The paraffin can therefore compete on an equal basis with hydrogen for the surface. Thus, the accumulation of hydrogen on the surface would not seriously poison the reaction. The above considerations lead logically to a study of aromatization using oxide catalysts, principally chromium oxide.

B. Chromia–Alumina Catalyst.—As discussed by Grosse, *et al.*,[6] chromium oxide catalysts not supported on carriers were found to produce cyclization at 450–500°, but at higher temperatures rapidly lost their activity as a result of crystallization. However, introduction of a suitable carrier, such as alumina, allowed the preparation of a catalyst which was active above 500° and with a useful life of over 1000 hr.

The use of chromia–alumina as a catalyst for aromatization has been studied extensively; yet, until recent years it has never been suggested that the alumina may exert an effect upon the catalytic properties of the catalyst. On the contrary, it was assumed that the alumina had no direct effect on the production of the various products.

Studies in our laboratory revealed that alumina has intrinsic acidic properties and that the strength of the acid sites depends upon its method of preparation.[11] For instance, alumina prepared from the hydrolysis of aluminum isopropoxide catalyzed the isomerization of cyclohexene to methylcyclopentenes. However, if this alumina was impregnated with sodium hydroxide or sodium chloride or if the alumina was prepared from potassium aluminate, there was no isomerization of cyclohexene. For future reference, the designation alumina-A has been given to the alumina prepared from aluminum isopropoxide, while alumina-B denotes alumina prepared from potassium aluminate.

It was shown[12,13] that chromia–alumina catalysts prepared separately from alumina-A and alumina-B gave quite different product distributions resulting from the aromatization reaction. This was demonstrated by passing 1,1-dimethylcyclohexane over chromia–alumina-A catalyst at 500°; the expected product, toluene, was obtained along with considerable amounts of xylenes and ethylbenzene. However, using chromia–alumina-B catalyst, only toluene and methane were produced.

It is obvious, therefore, that the alumina support does exert an effect upon the catalytic properties of the chromia–alumina catalyst, the effect being influenced by the method employed to prepare the alumina.

C. Catalyst Poisoning.—The activity of the aromatization catalysts decreases with time. This decrease in activity is due to carbonaceous material which accumulates on the surface and eventually covers it entirely. The carbonaceous material may be easily removed by burning it off with a mixture of air and nitrogen. Finally, reduction with hydrogen restores the catalyst to its original activity. The carbonaceous material is probably produced by condensation of olefinic or diolefinic compounds which are strongly adsorbed on the catalyst surface.[14]

It has also been suggested that the poisoning effects are due, in part, to the polymerization of fulvenes which are formed in small amounts as by-products in the cyclization reaction.[13–15]

Only recently has it been observed that the deactivation of the catalyst does not proceed in a homogeneous manner and that certain catalytic sites undergo deactivation more rapidly than others.[12,13,16,17] As a consequence the mechanism of the aromatization reaction can vary with time. For this reason it has been a standard practice, in our laboratory, to take individual cuts at various times during the aromatization reaction and to analyze them separately.

Studies Concerning the Mechanism. A. General.—The sequence of steps governing the conversion of a paraffin to an aromatic has been studied quite extensively. The careful examination of the products along with the determination of their relative rates of formation lead to a better understanding of the reaction.

For instance, Hoog, *et al.*,[18] showed that, when *n*-heptane was passed over chromium oxide catalyst, the products consisted mainly of toluene along with a small amount of *n*-heptenes. There were also some degradation products of the heptane. On the other hand, products such as methylcyclohexane and methylcyclohexene, which could be anticipated as intermediates in the cyclization reaction, were not detected. The fact that *n*-heptenes were found in the reaction product led to the problem of whether they were formed as by-products or as intermediates of the reaction.

As shown by Pitkethly and Steiner,[19] the concentration of *n*-heptenes in the reaction product does not correspond to the hydrogenation–dehydrogenation equilibrium of *n*-heptane. This conclusion was based on thermodynamic considerations of the reaction along with the fact that the addition of hydrogen did not reduce the concentration of *n*-heptenes. They also showed that the product distribution varied with contact time. For instance, at very short contact times the concentration of olefins rose much more rapidly than the concentration of aromatics. Actually, the concentration of aromatics approached zero at very short contact times. However, with increasing contact times the concentration of olefins reached a maximum then began to fall, while that of the aromatics continued to rise. These facts seemed to indicate that olefins are intermediates in the reaction.

Taylor and Fehrer,[20] by studying the comparative rates of reaction of *n*-heptene, 1-heptane, and methylcyclohexane, showed that the adsorption of olefins was markedly stronger than that of the corresponding

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[11] H. Pines and W. O. Haag, *J. Am. Chem. Soc.*, **82**, 2471 (1960).

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

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

[14] E. F. G. Herington and E. K. Rideal, *Proc. Roy. Soc.* (London), **A184**, 434, 447 (1945).

[15] J. M. Bridges, G. T. Rymer, and D. S. MacIver, *J. Phys. Chem.*, **66**, 871 (1962).

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

[17] H. Pines and C. T. Chen, Proceedings from the Second International Congress on Catalysis, Paris, 1960; Technip, Paris, 1961, pp. 367–387.

[18] H. Hoog, J. Verheus, and F. J. Zuiderweg, *Trans. Faraday Soc.*, **35**, 993 (1939).

[19] R. C. Pitkethly and A. H. Steiner, *ibid.*, **35**, 979 (1939).

[20] H. S. Taylor and H. Fehrer, *J. Am. Chem. Soc.*, **63**, 1387 (1941).

paraffins. In accord with this, they showed that the slow step in the conversion of *n*-heptane to toluene was the initial dehydrogenation of *n*-heptane. Further, the sequence of steps from 1-heptene to toluene were shown to be more rapid than the rehydrogenation of 1-heptene to *n*-heptane, with the dehydrogenation of methylcyclohexane the most rapid of all.

More recently Balandin, *et al.*,[21] using carbon-14 in the study of the catalytic dehydrogenation of a mixture of butane and 1-butene, have shown that 1-butene is the precursor of butadiene, while butane is transformed into 1-butene. It is, however, interesting to note that the dehydrogenation to olefins is much less sensitive to poisoning than is the aromatization step. This suggests that the catalytic sites for the dehydrogenation of the paraffins to olefins are different from those for the dehydrocyclization of the olefins to aromatics. Such a multiplicity of catalytic sites has also been suggested in the recent papers from our laboratory.

B. The Cyclization Step.—The rate of cyclization of an olefin has been shown to depend upon the position of its double bond.[18,22] For instance, 1-hexene cyclizes at about double the rate of 2-hexene, whereas 1-heptene and 2-heptene cyclize at about the same rate; however, 3-heptene cyclizes at a much reduced rate compared with 1- or 2-heptene.

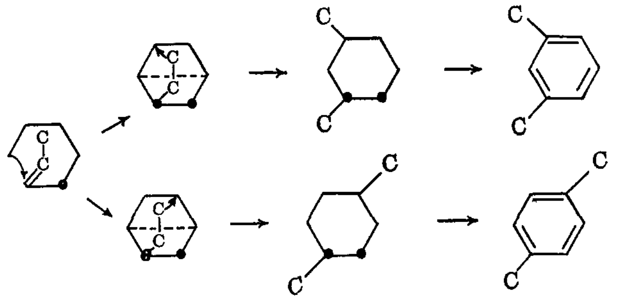
These results were explained by a mechanism of cyclization proposed by Twigg[23] and later elaborated upon by Herington and Rideal[14] for which cyclization must involve a carbon atom linked to the catalyst. So, in the case of *n*-heptane, cyclization would be possible only if the intermediate olefin were adsorbed at the 1,2 or 2,3 position corresponding to 1- and 2-heptene, respectively. Whereas 3-heptene must first isomerize to 1- or 2-heptene before cyclization can occur, the same could be said for 1- and 2-hexene since 1-hexene can cyclize directly, but 2-hexene must first isomerize to 1-hexene.

An important anomaly to this mechanism was that of *n*-octane. Should *n*-octane follow exactly this mechanism, then only ethylbenzene and *o*-xylene would be the aromatic products. However, *m*- and *p*-xylene were also produced. Obviously, there is an isomerization step occurring. Herington and Rideal[24] showed that the isomerization occurred neither after aromatization nor prior to the dehydrogenation of the paraffin. To account for the isomerization they proposed the formation of bicyclo[3.2.1]octane and bicyclo[2.2.2]-octane intermediates, which after bond cleavage give *m*- and *p*-xylenes, respectively (Chart I).

C. Carbon-14 Studies with *n*-Heptane and *n*-Octane.—An examination of the various proposed mechanisms for catalytic aromatization was done by Mitchell[25] using *n*-heptane-1-C^{14} and chromia–alumina as catalyst. The mechanisms of Pitkethly and Steiner,[19] Twigg,[23] Herington and Rideal,[14] and Wheatcroft[26] would all predict 50% methyl-labeled toluene from *n*-heptane-1-C^{14}. However, Mitchell found values of 27–29%. To account for the low value of methyl label, he postulated three possible mechanisms. These were formation of a transannular bridge,[24] rapid five- to six-membered-ring interconversion,[27] and possible formation of a cycloheptane species.

CHART I

ISOMERIZATION OF *n*-OCTANE DURING THE CYCLIZATION MECHANISM OF HERINGTON AND RIDEAL



As already mentioned, alumina does exert an effect upon the catalytic properties of chromia–alumina. Therefore, Pines and Chen[16] studied the effect of different chromia–alumina catalysts on the aromatization of *n*-heptane-1-C^{14}. They concluded that the formation of toluene may involve five-, six-, and seven-membered-ring intermediates, the relative contributions depending on the nature of the catalyst and change with time. For instance, using the acidic chromia–alumina-A they found that toluene formation dropped from 45 to 20% while at the same time the carbon-14 distribution rose from 39 to 42% methyl label. The intermediates postulated by Mitchell could be used to explain these results. However, remarkably different results were obtained with the less acidic chromia–alumina-B catalyst. The toluene formation dropped from 44 to 4% while the methyl label was rising from 18 to 32%. To explain the low 18% methyl label, they postulated the direct formation of a seven-membered-ring intermediate from heptene which, after equilibration and ring contraction, would yield 14.3% carbon-14 on each carbon atom of toluene. From this carbon-14 distribution they also suggested that the larger ring is more readily formed over chromia–alumina-B having low intrinsic acidity.

In a similar manner, Pines and Chen[12,17] studied the aromatization of *n*-octane-1-C^{14} over the two chromia–alumina catalysts. From their results they showed that no combination of mechanisms which contain the bicyclic intermediates of Herington and Rideal[24] would fit their data. They explained their data by a combination of mechanisms involving six-, seven-, and eight-membered-ring intermediates. In order to demonstrate that a cyclooctane intermediate does participate in this aromatization reaction, *n*-octane-4-C^{14} was aromatized over chromia–alumina-B.[28] The presence of carbon-14 on the α- and β-carbon atoms of the ethylbenzene side chain indicated that an eight-membered ring was, indeed, an intermediate with its contributions dropping from 31 to 20% with time.

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[21] A. A. Balandin, M. B. Neiman, O. K. Bogdanova, G. V. Isagulyants, A. P. Shcheglova, and E. I. Popov, *Probl. Kinetiki i Kataliza, Akad. Nauk. SSSR, Inst. Fiz. Khim., Soveshch., Moscow*, **9**, 45 (1956).

[22] A. F. Plate and G. A. Tarasova, *J. Gen. Chem. USSR*, **20**, 1193 (1950).

[23] G. H. Twigg, *Trans. Faraday Soc.*, **35**, 1006 (1939).

[24] E. F. G. Herington and E. K. Rideal, *Proc. Roy. Soc.* (London), **A184**, 447 (1945).

[25] J. J. Mitchell, *J. Am. Chem. Soc.*, **80**, 5848 (1958).

[26] R. W. Wheatcroft, dissertation, University of California, 1949.

[27] H. Pines and R. W. Myerholtz, *J. Am. Chem. Soc.*, **77**, 5392 (1955).

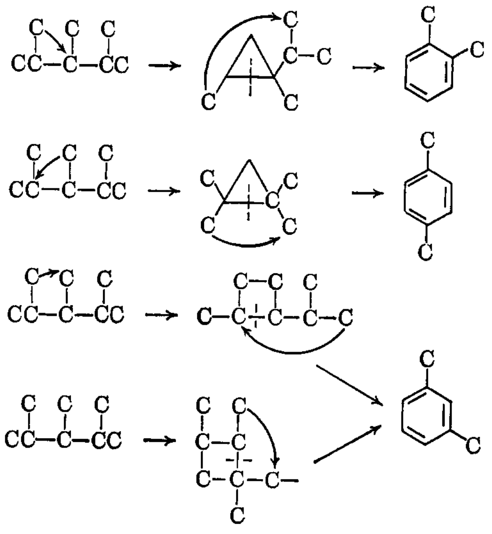
[28] H. Pines, C. T. Goetschel, and S. M. Csicsery, *J. Org. Chem.*, **28**, 2713 (1963).

D. Dehydrocyclization of Methylpentanes.—The aromatization of trimethylpentanes has been known for some time. Obviously prior to the aromatization, an isomerization must occur to extend the chain length. Cannings and co-workers,[29] studying the aromatization of 2,2-dimethyl-4-methyl-C^{14}-pentane over potassium- and cerium-promoted chromia–alumina, proposed a mechanism which involved the insertion of a methyl group between the quaternary carbon to which the methyl group was attached and the adjacent secondary carbon atom.

Pines and Csicsery[30-32] extended this work to various other trimethylpentanes and found that the above mechanism did not explain many of the products produced. The aromatization of 2,3,4-trimethylpentane compelled them to propose the existence of adsorbed cyclopropane- and cyclobutane-type intermediates in order to explain the formation of the products. Cannings mechanism would only explain the formation of *o*- and *p*-xylene; however much *m*-xylene and some ethylbenzene were also produced. To explain the formation of *m*-xylene, a cyclobutane-type intermediate was proposed (Chart II).

Chart II

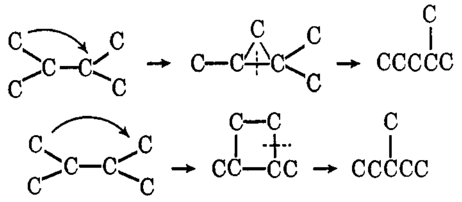
Aromatization of 2,3,4-Trimethylpentane. Isomerization *via* Cyclopropane- and Cyclobutane-Type Intermediates



Further evidence for a cyclobutane-type intermediate was the fact that 2,3-dimethylbutane gave both 2- and 3-methylpentenes. A cyclopropane-type intermediate would explain the formation of 2-methylpentenes, whereas only an adsorbed cyclobutane species would give 3-methylpentenes (Chart III).

It was also shown that the isomerization involving cyclobutane-type intermediates decreases considerably during the dehydrogenation cycle, while the isomerization involving cyclopropane-type intermediates remains much more constant. Apparently the active sites responsible for the cyclic C_4 species deactivate very rapidly, while those sites contributing to the cyclic C_3 species deactivate more slowly.

Chart III



In recent years several papers have appeared describing the dehydrogenation of methylhexanes and methylpentanes.[33-35] The results indicated considerable carbon skeleton isomerization.

The isomerization and aromatic products from methylpentanes can be explained by assuming intermediate formation of three- and/or four-membered rings. However, recent studies of the carbon-14 distribution of the aromatic products following the dehydrocyclization of 2,4-dimethyl-3-methyl-C^{14}-pentane could not be explained solely by assuming small-ring intermediates.[36] It was postulated that, following the initial isomerization reaction, C_7- and/or C_8-membered-ring intermediates were participating to a minor extent prior to aromatic formation.

The Present Study. A. General.—The foregoing survey has revealed the numerous mechanisms proposed for the aromatization reaction. However, recent observations that alumina does effect the catalytic properties of chromia–alumina has allowed a more concise mechanism study. That is, chromia–alumina-A has relatively strong acidic sites and may cause skeletal isomerization of the hydrocarbon *via* a carbonium ion mechanism, whereas chromia–alumina-B has relatively weak acidic sites and such cationic skeletal isomerization was not observed. The fact that skeletal isomerization does occur during aromatization over chromia–alumina-B has led to the observation that C_3- and/or C_4-ring intermediates and C_7- and/or C_8-ring intermediates participate in the dehydrocyclization of methylpentanes and *n*-paraffins, respectively. It was also suggested that all four intermediates may, at times, be participating concurrently. That these intermediates may occur during the aromatization of higher homologs of the branched paraffins is the basis of the present investigation. The general findings will be summarized in this paper, while the details will be presented in the papers which follow.

B. 2- and 3-Methylhexane.—The aromatization of 2- and 3-methylhexane over chromia–alumina-B catalyst was studied. From 2-methylhexane, toluene formation varied from 18–16% during the period of the reaction. With 3-methylhexane, under similar conditions, toluene initially was formed to only 6% while falling to 0.5%. This drastic difference in toluene formation was probably due to the greater deposition on the catalyst of carbonaceous materials from 3-methylhexane than from 2-methylhexane, thus reducing the activity of the catalyst. This difference

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(29) F. R. Cannings, A. Fisher, J. F. Ford, P. D. Holmes, and R. S. Smith, *Chem. Ind.* (London), 228 (1960).

(30) S. M. Csicsery and H. Pines, *ibid.*, 1398 (1961).

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

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

(33) N. I. Shuikin, E. A. Timofeeva, T. P. Dobrynina, Yu N. Plotnikov, G. S. Petryaeva, and G. K. Gaivoronskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1457 (1960).

(34) C.-L. Chang, K. P. Lavrovskii, and A. A. Rozental, *Kinetika i Kataliz*, **1**, 583 (1960).

(35) B. A. Kazanskii, A. Z. Dorogochinskii, M. I. Rozengart, N. I. Iyun'kina, I. M. Kuzentsoca, A. V. Lyuter, and M. G. Mitrofanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1308 (1962).

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

most likely arises from the fact that 3-methylhexane can easily form cyclopentane derivatives, *via* ring closure between two primary carbon atoms. The cyclopentanes can produce fulvenes, which are responsible, in a great part, for the carbonaceous material.[15]

n-Heptane was found in the reaction products from 2- and 3-methylhexane, thus indicating a methyl-carbon insertion into the hexane chain. This suggests that the small-ring intermediates proposed for the aromatization of methylpentanes probably operate during the aromatization of methylhexanes. To explore this more fully Pines and Dembinski[37] have synthesized and aromatized 2-methylhexane-6-C^{14} and 3-methyl-C^{14}-hexane. Any carbon-14 incorporated in the side chain of toluene from 2-methylhexane-6-C^{14} could arrive only through a methyl-carbon insertion *via* a cyclopropane intermediate. At the same time, any carbon-14 in the ring of toluene from 3-methyl-C^{14}-hexane could be due to a methyl-C^{14} insertion either *via* a cyclopropane- or/and cyclobutane-adsorbed species.

Indeed, carbon-14 was found distributed both in the side chain and in the ring in each case. The 2-methylhexane-6-C^{14} gave 2% methyl-labeled toluene and changed very little with time. This only slight variation of methyl label is in accord with the relative time independence of the cyclopropane intermediate. However, the carbon-14 distribution in toluene obtained from 3-methyl-C^{14}-hexane showed a definite time dependence, with the ring label varying from 6 to 1%. This supports the involvement, in part, of a cyclobutane-adsorbed species prior to aromatization.

To examine the possibility of a C_7-ring intermediate intervening between the initial methyl-carbon insertion process and the aromatization reaction, 3-methylhexane-5-C^{14} was synthesized and aromatized over chromia–alumina-B.[37] Any carbon-14 in the methyl group of toluene would show the participation of a cyclic C_7 intermediate prior to aromatization.

The fact that carbon-14 was found in the methyl group of toluene to the extent of 5.6–1.4% shows that a cyclic C_7 species is participating and to a considerable extent. The time dependent character of the methyl label is in agreement with previous studies showing that participation of large-ring intermediates diminishes with time.

C. Aromatization of Dimethylhexanes.—Since direct 1,6 ring closure is not the only mechanism occurring during the aromatization of 2- and 3-methylhexane, it seems reasonable that such would be the case for the dimethylhexanes. Reports in the literature indicate that 1,6 ring closure is the prevailing mechanism.[38] It was felt that the dimethylhexanes should be reexamined using chromia–alumina-B catalyst.[39] As was expected, the aromatics formed were not only those of direct 1,6 ring closure but also others arising from some prior methyl-carbon insertion reactions. These products could be explained by assuming contributions of small- and/or large-membered-ring intermediates as discussed previously.

D. Methylcycloheptane and Methyl-C^{14}-cycloheptane.—Since a methylcycloheptane-adsorbed species may be involved as an intermediate in the aromatization of C_8 hydrocarbons it was considered necessary to study the behavior of methylcycloheptane under the aromatization conditions.[40] It was found that methylcycloheptane gave high yields of aromatics in about a statistical distribution.

The mode of collapse of the C_7 ring to aromatics was still in doubt. It could collapse directly to a C_6 ring followed by aromatization; yet again, the methylcycloheptane could open to *n*-octane and to the various methylheptanes followed by 1,6 closure to give the aromatics. To distinguish between these two possibilities, Goetschel and Pines[40] aromatized methyl-C^{14}-cycloheptane over chromia–alumina-B. If the methylcycloheptane collapsed directly to a C_6 ring, all of the carbon-14 would reside in the side chain of the aromatics produced. However, if the ring were first opened to the acyclic compounds, then closed to form the aromatics, the carbon-14 would be distributed in the ring of ethylbenzene and *m*-xylene.

Carbon-14 was found in the rings of ethylbenzene and of xylenes. Thus, methylcycloheptane does not collapse directly to a C_6 ring but rather opens to give the acyclic compounds which then undergo dehydrocyclization.

E. 3- and 4-Methylheptane.—Previous studies concerning the aromatization of 3-methylheptane indicated that practically no *m*-xylene was produced while ethylbenzene and *o*- and *p*-xylene were the major aromatics formed.[14] Since ethylbenzene and *o*- and *p*-xylene can be produced by direct 1,6 ring closure while *m*-xylene cannot, it appeared that this was the predominant process for aromatic formation. However, re-examination of the aromatization of 3-methylheptane over chromia–alumina-B catalyst showed that *m*-xylene formed in amounts varying from 12–8% during the course of the reaction.[41]

Aromatization of 4-methylheptane gave similar results. That is, only *m*-xylene could be formed from direct 1,6 ring closure; however, ethylbenzene and *o*- and *p*-xylene were also produced.

To more fully understand the various paths operating in the isomerization reactions, the aromatization of 4-methyl-C^{14}-heptane and 3-methyl-C^{14}-heptane were studied.[41] If the isomerization were *via* cycloheptane-adsorbed species, the carbon-14 distribution in those aromatics which cannot be formed by direct 1,6 ring closure should be similar to the distribution in the corresponding aromatics from the methyl-C^{14}-heptanes. However, it is possible for 4- and 3-methylheptane to isomerize to a *n*-octane-adsorbed species through methyl-C^{14}-carbon insertion *via* cyclo C_3 and cyclo C_4 intermediates, respectively. If such were the case, the carbon-14 would be distributed to a greater extent in the ring than if only a cycloheptane species were involved. The carbon-C^{14} distribution in the aromatic compounds indicates that besides 1,2 and/or 1,3 methyl-C^{14}-carbon insertion, the 1,7 ring closure is a major contribution to the aromatization reactions.

Mechanism of Methyl–Carbon Insertion.—Kinetic studies have revealed that the aromatization of alkanes is preceded by the formation of alkenes.[38] The methyl-carbon insertion over chromia–alumina-B requires

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[37] H. Pines and J. W. Dembinski, *J. Org. Chem.*, **30**, 3537 (1965).

[38] A. H. Steiner, "Catalysis," Vol. IV, P. H. Emmett, Ed., Reinhold Publishing Corp., New York, N. Y., 1956, Table I, p. 531.

[39] H. Pines, C. T. Goetschel, and J. W. Dembinski, *J. Org. Chem.*, **30**, 3540 (1965).

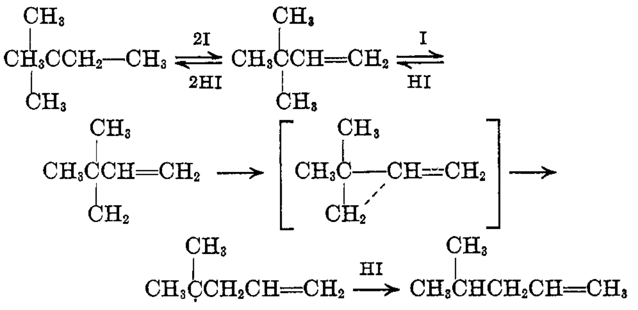
[40] C. T. Goetschel and H. Pines, *ibid.*, **30**, 3544 (1965).

[41] H. Pines and C. T. Goetschel, *ibid.*, **30**, 3548 (1965).

also a dehydrogenation step because neopentane[31] or 2,2,3,3-tetramethylbutane[42] does not undergo skeletal rearrangement or aromatization. When the rate of aromatization is slow, the products of methyl-carbon insertions consist of olefins only. From 2,2-dimethylbutane the main products of insertion consisted of 2-methylpentenes and 2-methylpentadienes, while 2,3-dimethylbutane produced 2- and 3-methylpentenes and the corresponding methylpentadienes with a ratio of the 2 to 3 isomer of about 2.

Methyl-carbon insertion, *via* 1,2 vinyl migration, had been recently reported by Raley and co-workers[43–45] in the dehydrogenation and aromatization of hydrocarbons by iodine at 500°, and a free-radical mechanism was proposed for this reaction. These authors also reported the formation of 2-methylpentenes and 2-methylpentadienes from 2,2-dimethylbutane and *p*-xylene from a mixture of 2,4,4-trimethyl-1- and -2-pentene. They have found, as in the case of chromia–alumina catalyst,[31] that neopentane does not rearrange to 2-methylbutane or 2-methylbutenes. To explain the free-radical rearrangement in the presence of iodine, Slaugh and co-workers[45] proposed 1,2 vinyl group migration, which in the case of 2,2-dimethylbutane can be illustrated as shown in Chart IV.

Chart IV



Owing to the similarity of reactions of hydrocarbons in the presence of chromia catalysts and in the presence of iodine, it can be assumed that their mechanistic interpretation may also be similar. The removal of two hydrogen atoms from 2,2-dimethylbutane to form the olefins can be explained by a mechanism which was proposed by Burwell and co-workers.[46] They suggested that a chromium(II) atom and an adjacent oxygen atom form a pair of sites and that monoadsorbed alkane is adsorbed to chromium. At high temperature the monoadsorbed alkane can desorb as an olefin (Chart V). The chromium and oxygen sites can then remove a hydrogen atom from the methyl group of 3,3-dimethyl-1-butene. The methyl-hydrogen bond in this olefin is probably weakened owing to the participation of the vinyl group. The monoadsorbed alkenyl group can then dissociate into a radical, which can undergo a skeletal rearrangement (Chart VI).

Chart V

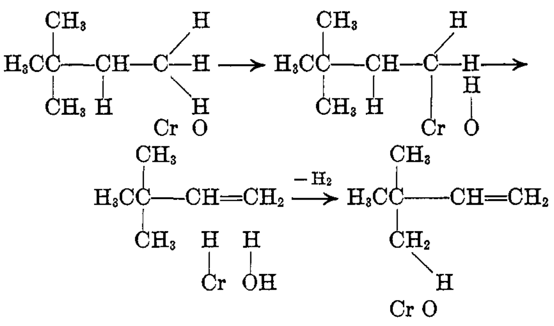
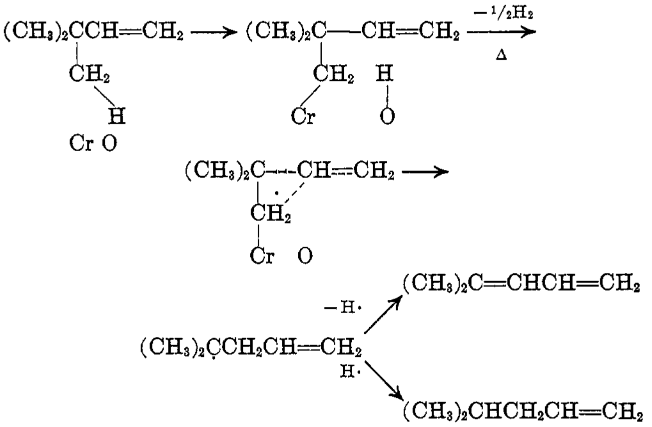


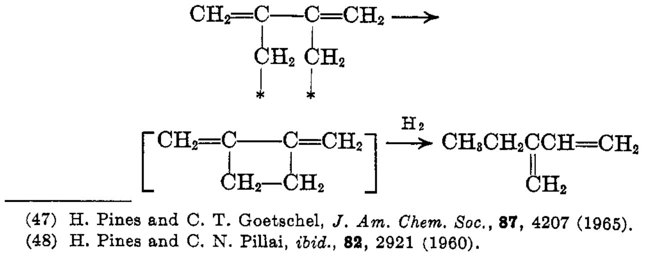
Chart VI



Skeletal rearrangement accompanying dehydrogenation is not limited to alkanes only. Pines and Goetschel[47] have found that *t*-butylbenzene rearranges when passed over chromia–alumina catalyst. This is a convincing diagnostic test that a radical intermediate participates in the reaction. The rearrangement of *t*-butylbenzene to isobutylbenzene induced by organic peroxides was previously studied by Pines and Pillai.[48]

Both phenyl migration and methyl-carbon insertion contributed equally to the rearrangement of *sec*-butylbenzene to *n*-butylbenzene. It was found by the use of 2-phenylbutane-2-C^{14} that the *n*-butylbenzenes produced were comprised of about equal amounts of $C_6H_5C^{14}H_2C_3H_7$ and $C_6H_5CH_2C^{14}H_2C_2H_5$.[48]

The 1,2 methyl-carbon insertion, which apparently occurs through 1,2 vinyl migration, is not the only type of insertion observed on chromia–alumina. The rearrangement of 2,3-dimethylbutane to 3-methylpentenes can best be explained through 1,3 methyl-carbon insertion. The first steps in the reaction may involve the formation of 2,3-dimethylbutadiene which through a dimonoadsorbed species involving 1,4 carbon atoms, followed by a four-carbon ring rupture, would give the 1,3 methyl-carbon insertion. Such 1,3 methyl-



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[42] H. Pines and C. T. Goetschel, unpublished results.

[43] J. H. Raley, R. D. Mullineaux, and C. W. Bittner, *J. Am. Chem. Soc.*, **85**, 3174 (1963).

[44] R. D. Mullineaux and J. H. Raley, *ibid.*, **85**, 3178 (1963).

[45] L. H. Slaugh, R. D. Mullineaux, and J. H. Raley, *ibid.*, **85**, 3180 (1963).

[46] R. L. Burwell, Jr., A. B. Littlewood, M. Cardew, G. Pass, and C. T. H. Stoddart, *ibid.*, **82**, 6272 (1960).

[47] H. Pines and C. T. Goetschel, *J. Am. Chem. Soc.*, **87**, 4207 (1965).

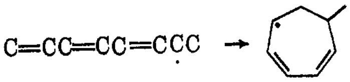
[48] H. Pines and C. N. Pillai, *ibid.*, **82**, 2921 (1960).

carbon insertion was also observed in the aromatization of 2,4-dimethyl-3-methyl-C^{14}-pentane.[36]

Mechanism of Aromatization.—Studies of aromatization of C^{14}-labeled alkanes, such as *n*-heptane-1-C^{14},[16] and *n*-octane-1-C^{14},[17] and -4-C^{14},[28] over nonacidic chromia–alumina have revealed that the cyclization occurs *via* C_8-, C_7-, and C_6-ring intermediates. The contribution of each ring toward aromatization is time dependent. At the beginning of the experiment the contribution of the larger rings is greater. The change in the course of the reaction with time may be attributed to the heterogeneity of the active sites of the catalyst and to the nonuniformity of their deactivation. It cannot, however, be ruled out that the actual cyclization may occur in the gas phase. The octatetraenes produced from *n*-octane could undergo thermal cyclization to the cyclooctatrienes.

The aromatization reaction is always accompanied by the deposition of carbonaceous material on the surface of the catalyst. It might therefore be possible that the rate of the desorption of the dehydrogenated alkanes depends on their depth of dehydrogenation and on the condition of the surface of the catalyst. The desorption of octatrienes to the gas phase would produce by thermal cyclization C_6-ring intermediates.[49]

The formation of C_7-ring intermediates may be the result of an alkatriene free-radical cyclization reaction in the gas phase.



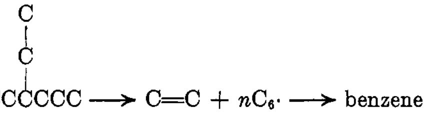
The free radicals could be produced by a mechanism proposed for the methyl-carbon insertion reaction. More detailed experimental facts are however required to differentiate between the cyclization reactions which may occur in the gas phase and on the surface of the catalyst.

Mechanism of Cracking Reaction.—The aromatization of alkanes is accompanied by an extensive cracking which in the case of nonacidic chromia–alumina-B catalyst was correlated with the types of carbon–carbon bonds cleaved.[50] In alkanes bond cleavage was preferred between the most substituted carbon atoms and in olefins bond breakage occurred β to the double bond. The cleavage pattern over the nonacidic catalyst favors a radical mechanism.

The difference in the distribution of reaction products from 3-ethylhexane and 3-ethylhexenes is most revealing.[50] In the case of the olefins it can be assumed that the addition of hydrogen atom from the catalyst to the olefin would produce an alkyl radical. Since in the presence of the chromia–alumina catalyst there is a rapid equilibration of the olefins, the addition of hydrogen atom to the most stable olefins, namely 3-ethyl-2-hexene (I) and 3-ethyl-3-hexene (II), would yield 3-ethyl-3-hexyl radical as the principal product. This addition would occur *via* the preferred Markovnikov addition. The less favored anti-Markovnikov addition would produce $C\underset{\cdot}{C}C(C_2)CCC$ and $CCC(C_2)\underset{\cdot}{C}CC$ radicals, respectively. The three isomeric alkyl radicals can then undergo carbon–carbon cleavage, according to the mechanism suggested by Kossiakoff and Rice.[51] The principal products of the reaction conform to the radical mechanism applied to the most favored radical.[52]

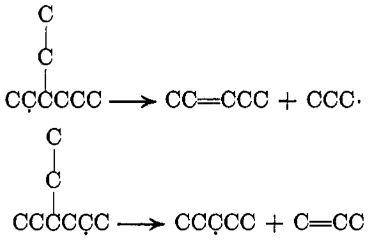
The cracking of alkanes can be explained also by a radical mechanism. The method of the generation of radicals by chromia was discussed earlier in this paper as occurring through the rupture of the carbon–chromium bond. It was pointed out by Burwell and coworkers[46] from the deuterium–hydrocarbon exchange study that primary hydrogen atoms exchange faster than secondary hydrogen atoms.

There is a great difference in the product distribution formed from the cracking of 3-ethylhexenes and 3-ethylhexane. In the former case hydrocarbons having the skeletons of 3-methylhexane and 3-methylpentane are the predominant cleavage products, while with 3-ethylhexane the major products are *n*-pentane, *n*-hexane, and benzene. The latter results are not unexpected since the attachment of the chromium to the primary carbon atom produces a primary radical, which through a β scission could yield C_6 and C_2 groups.



$$\underset{\cdot}{C}C\overset{\substack{C\\|\\C\\|}}{C}CCC \longrightarrow C{=}C + n\mathrm{C}_6\cdot \longrightarrow \text{benzene}$$

The formation of *n*-pentane as the cleavage product can be explained through the intermediate formation of secondary alkyl radicals.



$$C\underset{\cdot}{C}\overset{\substack{C\\|\\C\\|}}{C}CCC \longrightarrow CC{=}CCC + CCC\cdot$$

$$CC\overset{\substack{C\\|\\C\\|}}{C}C\underset{\cdot}{C}C \longrightarrow CC\underset{\cdot}{C}CC + C{=}CC$$

In a similar way it is possible to explain the distribution of the products from the cleavage of other alkanes over the nonacidic chromia–alumina-B catalyst.

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(49) E. J. Hawkins and H. G. Hunt, *J. Am. Chem. Soc.*, **73**, 5379 (1951).

(50) S. M. Csicsery and H. Pines, *J. Org. Chem.*, **1**, 329 (1962).

(51) A. Kossiakoff and F. O. Rice, *J. Am. Chem. Soc.*, **65**, 590 (1943).

(52) B. S. Greensfelder, Stanford Research Institute, in a private communication to the senior author also pointed out the similarity of the distribution of cracking product obtained from 3-ethylhexenes from chromia–alumina and that predicted from a free-radical mechanism.