trichloride,[51b] fuming sulfuric acid[51b] and calcium and barium fluoride.[52] It was found that boron fluoride in benzene also produced an insoluble red precipitate. According to Kortüm,[53] all these reactions can be considered Lewis acid–base reactions.

There is a pronounced relationship between the sensitivity of the samples toward water and the strength of their Lewis acid sites. Silica–alumina gave crystal violet from I even after it was soaked with water, while alumina is rendered inactive by 5 minutes exposure to the humidity in the atmosphere. Similar observations were made by Kortüm.[53]

(3) **Conclusions.**—The present study shows that the intrinsic acidity of alumina, which manifests itself in certain catalytic reactions, can indeed be measured by chemical means. There is a good correlation between catalytic activity and the color formation. The leuco bases of crystal violet and malachite green are sensitive indicators of Lewis acid sites existing on the surface of alumina. However, their sensitivity toward oxidation requires some precaution. Test substances of the phenolphthalein type do not have this limitation. Catalysts which are not active for the isomerization of cyclohexene give no color with IV when freshly calcined (5 hours at 500°), even if they contain sizable amounts of alkali. The basic aluminas do give a red color with phenolphthalein when they contain larger amounts of water. The two types of color are readily distinguished: adding water to the colored sample causes a slow fading of color in the case of the truly acid catalysts, while the basic aluminas give an intense purplish red color in the water layer. Substituting the hydroxyl group in IV by methoxy groups should eliminate this difficulty altogether. It should certainly be possible to select from the rich resources of organic chemistry a series of indicators which combine sensitivity with specificity.

All the alumina samples gave a positive test for acidity with I, II and IV when crushed in the presence of the indicator solutions. This shows that the nascent surfaces contain Lewis acid sites.

Acknowledgment.—The authors extend their appreciation to the California Research Corporation for the analyses of aluminas, to Dr. R. A. Van Nordstrand for the advice given in the interpretation of the X-ray data and to Mr. Ed M. Lewicki for carrying out some of the experimental work.

EVANSTON, ILL.

[52] J. H. de Boer, *Z. Elektrochem.*, **44**, 488 (1938).

[53] G. Kortüm, J. Vogel and W. Braun, *Angew. Chem.*, **70**, 651 (1958).

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Alumina: Catalyts and Support. II.[1a] Hydroisomerization and Aromatization of Hydrocarbons in the Presence of Molybdena–Alumina Catalysts. Effect of Aluminas[1a,b]

BY HERMAN PINES AND GASTON BENOY[2]

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Extensive research has been reported on the catalytic action of molybdena–alumina hydrocarbons. In none of the reported investigations was there a mention made that alumina *per se* may have intrinsic acidic properties which may influence the hydroisomerization and aromatization properties of the molybdena–alumina catalyst. The object of this study was to determine the catalytic effect of molybdena–alumina catalysts having aluminas of increasing acid character. The catalytic activity was tested using as model hydrocarbons: *n*-octane, methylcyclopentane, cyclohexane, 1,2- and 1,4-dimethylcyclohexane and ethylcyclohexane. In each case it was noticed that with increasing acidity of the alumina the extent of hydroisomerization increases. The hydroisomerization of 1,2-dimethyl-C^{14}-cyclohexane was studied. Ethylcyclohexane upon hydroisomerization yielded *n*-propylcyclopentane as the principal single hydrocarbon. The mechanism of hydroisomerization is discussed.

Extensive research has been reported in the literature on the catalytic action of the oxides of transition metals supported on alumina. It has been shown that molybdena–alumina catalyst in the presence of hydrogen under pressure aromatizes and/or hydroisomerizes saturated hydrocarbons.[3–7] In none of the cited investigations was it indicated that alumina *per se* may have intrinsic acidic properties which might influence the hydroisomerization and aromatization properties of the molybdena catalyst. It was, however, recognized that the incorporation of small amounts of silica to alumina increased the hydroisomerization activities of the molybdena–alumina catalyst and this was attributed to the acidity of the support.[8,9]

Pines and Haag[1] have demonstrated that the catalytic behavior of alumina depends upon its method of preparation. Alumina prepared by the hydrolysis of aluminum isopropoxide showed

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[1] (a) For paper I see H. Pines and W. O. Haag, THIS JOURNAL, **82**, 2471 (1960). (b) Presented in part before the Gordon Research Conferences in Catalysis, June 23–27, 1958, New London, N. H.

[2] Vladimir N. Ipatieff Postdoctoral Fellow, 1957–1958. Present address: Gevaert Photo-Producten, Mortsel (Antwerpen), Belgium.

[3] A. S. Russell and J. J. Stokes, Jr., *Ind. Eng. Chem.*, **38**, 1071 (1946).

[4] A. S. Russell and J. J. Stokes, Jr., *ibid.*, **40**, 520 (1948).

[5] G. M. Webb, M. A. Smith and C. H. Ehrhardt, *Petrol. Processing*, **2**, 836 (1947).

[6] B. S. Greensfelder, R. C. Archibald and D. L. Fuller, *Ind. Eng. Chem.*, **43**, 561 (1945).

[7] B. S. Greensfelder and D. L. Fuller, THIS JOURNAL, **67**, 2171 (1945).

[8] A. Clark, M. P. Matuszak, N. C. Carter and J. C. Cromeans *Ind. Eng. Chem.*, **45**, 803 (1953).

[9] R. M. Dobres, D. S. Henderson, S. J. Lucki and B. W. Rope in "Catalysis," Vol. 6, edited by P. H. Emmett, Reinhold Publishing Corp., New York, N. Y., 1958, p. 513.

strongly acid catalytic properties and was able to catalyze the isomerization of cyclohexene to methylcyclopentenes. On the other hand, aluminas which were prepared by precipitation from sodium or potassium aluminate showed weak catalytic effect upon skeletal isomerization of olefins. Aluminas of intermediate catalytic activities were prepared or obtained from commercial sources.

The object of the present study was to determine the effect the various aluminas may have upon the hydroisomerization and aromatization of saturated hydrocarbons.

Catalysts.—The general procedure for the preparation of a molybdena–alumina catalyst consisted in the impregnation of 100 wt. equivalents of alumina in the form of $^1/_8$ inch pills with a solution of ammonium molybdate. To accomplish this 25 wt. equiv. of 85% molybdic acid was dissolved in 60 vol. equiv. of concentrated ammonium hydroxide, and the hot solution was poured onto the alumina pills. The catalyst contained 14% molybdenum (Mo/Al = 0.7); this concentration was reported to give the optimum activity.[3] The impregnated catalyst was dried for 5 hours at 110° and calcined at 500° for four hours in a stream of hydrogen. Just before each experiment the catalyst was treated for 30 minutes with a stream of air at the temperature of the experiment, and then flushed with nitrogen.

The preparation of the various aluminas is described in a preceding paper.[1] The relative catalytic acidic properties of the aluminas were determined by the effect they have upon the skeletal isomerization of *t*-butylethylene and cyclohexene.[1]

The catalysts used in the present investigation are listed in order of increasing acid character of the aluminas (Table I).

TABLE I

MOLYBDENA–ALUMINA CATALYSTS IN ORDER OF INCREASING ACID CHARACTER OF THE ALUMINAS

Catalyst	Source of alumina
1	From potassium aluminate
2	Commercial, A
3	Commercial, B
4	Commercial, molybdena alumina
5	From nitrate, impregnated to contain 0.3% of Na
6	From nitrate by pptn. with NH_4OH
7	From aluminum isopropoxide

Discussion of Results

In order to test the effect of molybdena–alumina catalysts having aluminas of various catalytic acidities upon the hydroisomerization of hydrocarbons, the following model compounds were chosen: *n*-octane, methylcyclopentane, cyclohexane, 1,2- and 1,4-dimethylcyclohexanes and ethylcyclohexane.

***n*-Octane.**—The aromatization of *n*-octane was investigated using molybdena–alumina catalysts, which contained aluminas of various degrees of catalytic acidity. If the aromatization reaction proceeds by ring closure without being accompanied by an isomerization, the C_8-aromatics should then be composed of ethylbenzene and *o*-xylene only. It was found that the xylenes produced tend more and more to their equilibrium concentrations with increase in acid properties of the aluminas (Table II).

TABLE II

AROMATIZATION OF *n*-OCTANE

The experimental conditions used were: temperature 500°, pressure 20 atm., molar ratio of hydrogen/*n*-octane = 6, hourly liquid space velocity 0.5.

Catalyst	Hydrocarbons recovd., wt. %		Composition of aromatics, mole %						
	Satd.	Arom.	Benzene	Toluene	Ethylbenzene	Xylenes[b] o-	m-	p-	Ratio[c] o/m + p
2	90	10	9	30	7	38	12	4	2.4
3	83	17	8	32	5	31	18	7	1.2
4	86	14	3	15	7	23	35	17	0.44
7	82[a]	18	9	41	2	14	24	10	0.36

[a] The saturated hydrocarbons were composed of: propane and lower, 10%; *n*-butane, 20%; isobutane, 22%; *n*-pentane, 13%; isopentane, 6%; C_6–C_8, 29%. [b] Equilibrium between xylenes is given in Table VI. [c] Calculated equilibrium ratio: 0.34.

In the presence of catalysts 2, 3 and 4 the saturated hydrocarbons which were recovered showed that extensive skeletal isomerization had occurred. Owing to the complexity of the mixture, as determined by gas chromatography, no attempt was made to identify the individual hydrocarbons which were formed. In the presence of the most acidic catalyst (7) a considerable amount of cracking occurred.

Methylcyclopentane and Cyclohexane.—Ring expansion and contraction of five and six carbon atom rings usually occur by means of acid-catalyzed reactions. For that reason the conversion of methylcyclopentane to cyclohexane and benzene and that of cyclohexane to methylcyclopentane was tested as a function of the acidity of alumina in the molybdena–alumina catalyst. For a maximum conversion of methylcyclopentane to benzene the following experimental conditions were chosen: 10 atm. at 450° and 20 atm. at 500°. It was calculated that under these conditions theoretically 85% of benzene could be formed.[10] The experimental conditions and results obtained are summarized in Tables III and IV.

The nature of the alumina used exerts a considerable effect upon the reaction. Starting with methylcyclopentane the amount of benzene formed increases with the acidity of the alumina in the catalyst. Similarly, starting with cyclohexane the extent of skeletal isomerization, as indicated by the presence of methylcyclopentane, is also a function of the acidity of the alumina. The reaction is accompanied by the formation of lower boiling hydrocarbons which were most probably produced by the hydrogenolysis of methylcyclopentane. It is known that alkylcyclopentanes readily undergo hydrogenolysis in the presence of a hydrogenating catalyst.[11] This would also explain the larger yield of lower boiling hydrocarbons obtained when starting with methyl-

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(10) F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," published for the American Petroleum Institute by Carnegie Press, Pittsburgh, Pa., 1953.

(11) B. B. Corson, "Catalytic Hydrogenation of Hydrocarbons, in "Chemistry of Petroleum Hydrocarbons," Vol. 3, edited by B. T. Brooks, *et al.*, Reinhold Publishing Corp., New York, N. Y., 1955, pp 303–307.

TABLE III

ISOMERIZATION AND DEHYDROISOMERIZATION OF METHYLCYCLOPENTANE

The experimental conditions used were: molar ratio of hydrogen/methylcyclopentane = 6, hourly liquid space velocity (HLSV) 0.5; the catalyst, 40 ml., was in the form of $^1/_8$ inch pills.

Catalyst	Temp., °C.	Pressure, atm.	Mecyclopentane recovd., %	Composition based on reacted methylcyclopentane, wt. % Low boiling	Cyclohexane	Benzene	Toluene
3	450	10	90	63	25	12	
5	450[a]	10	85	35	15	50	
7	450	10	49	42[b]	7	49	2
3	500	20	33	81	2	17	
5	500	20	52	60	4	35	
7	500	20	5	42	<1	54	4

[a] HLSV 0.25. [b] Analyzed by vapor phase chromatography: *n*-butane, 1.2%; isopentane, 3.9; *n*-C_5 and C_6 (?), 5.6; 2-methylpentane, 31.2; 3-methylpentane, 20.8, cyclopentane and *n*-hexane, 37.4.

TABLE IV

ISOMERIZATION OF CYCLOHEXANE

The experimental conditions used were: molar ratio of hydrogen/cyclohexane = 6, hourly liquid space velocity 0.5; the catalyst, 40 ml., was in the form of $^1/_8$ inch pills.

Catalyst	Temp., °C.	Pressure, atm.	Composition of hydrocarbons, wt. % Cyclohexane	Benzene	Low boiling	Methylcyclopentane	Toluene
5	450	10	38	50	3	9	
7	450	10	36	25	7	32	
5	500	20	2	86	6	5	1
7	500	20	2	59	23	14	2

cyclopentane (Table III) as compared with cyclohexane (Table IV).

The main reactions which occur in the presence of the molybdena–alumina catalysts are: hydrogenolysis of methylcyclopentane, isomerization of methylcyclopentane to cyclohexane and dehydrogenation of the latter to benzene. With the less acidic aluminas hydrogenolysis seems to be the preferred reaction as indicated by the high yield of the low boiling hydrocarbons produced. The more acidic aluminas increase the rate of isomerization and at the same time increase the effect of dehydrogenation of cyclohexane to benzene even more strikingly.

1,2- and 1,4-Dimethylcyclohexanes.—The effect of acidic properties of aluminas upon the catalytic action of molybdena–alumina catalysts is clearly illustrated in the case of 1,2-dimethylcyclohexanes (Table V). The extent of dehydroisomerization, based on the xylenes produced, increases with the relative catalytic acidity of the aluminas. The ratio of *m*- to *p*-xylene decreases and approaches a thermodynamic equilibrium ratio[12] (Table VI) with increase in the acidity of the aluminas. The non-equilibration between *m*- and *p*-xylene would seem to indicate that the isomerization proceeds by a stepwise migration of a methyl group of either 1,2-dimethylcyclohexanes or of their product of dehydrogenation, namely *o*-xylene. Such stepwise migration of a methyl group in xylenes[13a,b] and dimethylcyclohexanes[14] has been reported previously.

TABLE V

DEHYDROISOMERIZATION OF DIMETHYLCYCLOHEXANES[a]

The experiments were made at 450°, 60 atm., 0.5 hourly liquid space velocity (HLSV) and with a molar ratio of hydrogen to hydrocarbons equal to 6.

Catalyst	DMCH[a]	Composition of products, wt. Satd.	Toluene	Ethylbenzene	Xylenes $p+m$-	o-	m/p	Isomerization, wt. %[b]
1	1,2	79	0.8			20.5		
2	1,2	60	1.5	0.1	1.8	37.0	7	4.6
3	1,2	70	1.7		2.9	25.3	6.5	10.2
4	1,2	62	4.9	0.5	8	24.8	4	24.4
5	1,2	68	1.8	.8	12.1	17.9	2.9	40.5
6	1,2	71	1	.8	13	13.7	2.4	48.5
7	1,2	70	3.1	1.7	18.4	6.2	2.0	75
							m/o	
4	1,4	53	16.1	0.8	24	3.5	3.6	58[c]
7	1,4	53	0.9	2.5	32.3	10.6	2.0	79[c]

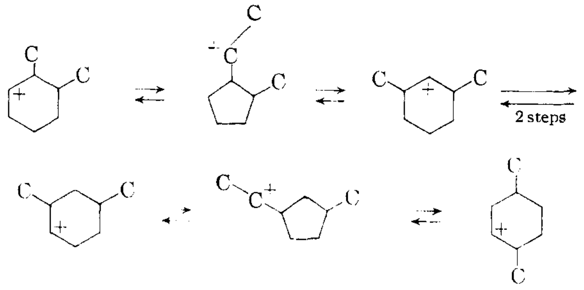
[a] DMCH = dimethylcyclohexane; the 1,2-dimethylcyclohexane consisted of 38% *trans* and 62% *cis* isomers. [b] Based on $(m + p)/(m + p + o) \times 100$. [c] Based on $(o + m)/(o + m + p) \times 100$.

TABLE VI

EQUILIBRIA BETWEEN XYLENES AND BETWEEN DIMETHYLCYCLOHEXANES

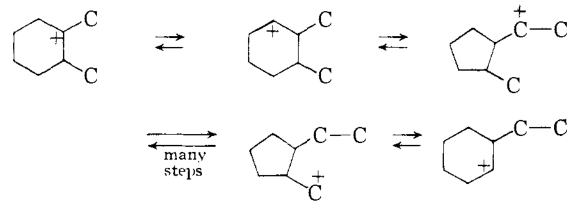
Temp., °C.	Xylenes m/p	m/o	p/o	Dimethylcyclohexanes $\frac{1,3}{1,4}$	$\frac{1,3}{1,2}$	$\frac{1,4}{1,2}$
450	2.23	2.12	0.95	1.91	2.11	1.1
500	2.21	2.04	.92			

It is not, however, excluded that part of the dimethylcyclohexanes might have been produced through ring contractions and expansions



The dehydroisomerization of 1,2-dimethylcyclohexane is also accompanied by the formation of ethylbenzene, the extent of which increases with the acidity of the aluminas used for the preparation of the catalyst.

The formation of ethylbenzene can best be explained by means of ring contraction and expansion of cycloalkylcarbonium ions followed by a dehydrogenation reaction. In its simplified form it can be written as



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[12] J. E. Kilpatrick, H. G. Werner, C. W. Beckett and F. D. Rossini, *J. Research Natl. Bur. Standards*, **39**, 523 (1947).

[13] (a) H. C. Brown and H. Jungk, THIS JOURNAL, **77**, 5579 (1955); (b) R. H. Allen and L. D. Yats, *ibid.*, **81**, 5289 (1959).

[14] A. K. Roebuck and B. L. Evering, *ibid.*, **75**, 1631 (1953).

A more detailed mechanism of this type of reaction has been described previously.[15,16]

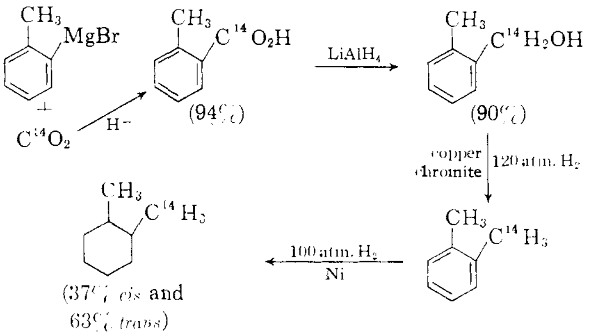
The saturated hydrocarbons obtained from the experiment in which catalyst 5 was used (Table V), were composed of 35% dimethylcyclohexanes, as determined by means of selective dehydrogenation to xylenes using platinum–alumina catalyst.[17] The ratio of 1,3- to 1,4-dimethylcyclohexanes was the same as that of *m*- and *p*-xylene in the original reaction mixture.

The non-dehydrogenable hydrocarbons were fractionally distilled on a spinning band column.[18] The index of refraction of the various cuts 1.4063–1.4225 and the absorption bands at 10.1 and 10.4 μ[19] indicated the presence of alkylcyclopentanes.

The behavior of 1,4 - dimethylcyclohexanes toward the hydroisomerization reaction also was studied (Table V). In the case of 1,4-isomer the ratio of *m*- to *o*-xylene was determined as an index of equilibration. The results obtained were similar to that carried out with 1,2-dimethylcyclohexanes. The non-equilibration between 1,3- and 1,2-dimethylcyclohexanes in the presence of the least acidic catalyst is in agreement with reasons discussed above.

1,2-Dimethyl-1-C^{14}-cyclohexane.—The isomerization of 1,2-dimethylcyclohexane to 1,3- and 1,4-dimethylcyclohexane may proceed by either migration of methyl groups or by repeated ring expansions and contraction. Since ring expansion and contraction may involve the formation of a primary carbonium ion, it was thought that such an involvement should be relatively small when a catalyst of a medium catalytic acidity is used. To test this hypothesis 1,2-dimethyl-C^{14}-cyclohexane was hydroisomerized using molybdena–alumina catalyst 6.

1,2-Dimethyl-C^{14}-cyclohexane was synthesized by the sequence of reactions



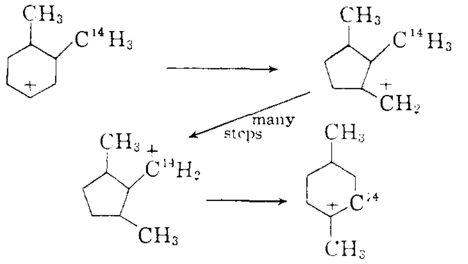
The hydroisomerization reaction of the 1,2-dimethyl-C^{14}-cyclohexane was carried out at HLSV of 1.0, pressure of 46 atm., and at hydrogen to hydrocarbon ratio of 5. The reaction product consisted of 75% saturated hydrocarbons and 25% aromatics. The composition of the aromatic fraction and the relative distribution between the radioactivity in the ring and the side chain is given in Table VII.

The analytical procedure used was similar to the one described previously.[15,16] Toluene and ethylbenzene were not analyzed for their isotopical distribution because of their relatively small concentration. The relative radioactivity distribution between side chain and ring in xylenes (Table VII) indicates that skeletal isomerization through ring contraction and expansion involving primary carbonium ion proceeds to a small extent only as indicated by the scheme

TABLE VII

THE COMPOSITION AND RADIOACTIVITY DISTRIBUTION OF THE AROMATIC REACTION OBTAINED FROM 1,2-DIMETHYL-1-C^{14}-CYCLOHEXANE

	Toluene	Ethylbenzene	Xylenes		
			o-	*m*-	*p*-
Composition, %	0.8	1.8	69	21	7
Radioactivity					
ring, %			2.4	5.1	9.8
side chain, %			97.7	91.8	82.7



It was found that in *p*-xylene 10% of the radioactive carbon was in the ring. If we assume, according to previous observations,[15] that the extent of isotopic equilibration was 70% of the theoretical 75% for the fraction which underwent a ring expansion and contraction *via* a primary carbonium ion, it could be concluded that $9.7/(0.7 \times 75) \times 100$ or about 20% of the *p*-xylene was formed through such rearrangement.

The fact that *m*-xylene contained only 5% of the radioactivity in the ring as compared with 10% in the case of *p*-xylene is an indication that the isomerization involving methyl shift is a stepwise reaction and that ring contraction and expansion *via* a primary carbonium occurs to a small extent only.

Ethylcyclohexane.—The mechanism of the skeletal hydroisomerization of ethylcyclohexane to isomeric dimethylcyclohexanes in the presence of a nickel–silica–alumina catalyst had been studied applying radioactive tracer technique.[15] It was concluded that the isomerization proceeds through a repeated ring contraction and expansion involving the intermediate formation of primary carbonium ions. This type of isomerization was attributed to silica–alumina which is known to be a relatively strong acid.[20]

The isomerization of ethylcyclohexane was presently carried out in the presence of weakly acidic molybdena–alumina catalyst 3. The experimental conditions and results obtained are summarized in Table VIII. About 51% of the ethylcyclohexane underwent demethanation, skeletal isomerization and dehydroisomerization. The isomerized product was composed of 18% dimethylcyclohexanes and xylenes, 36% *n*-propylcyclopentane and 14% 1-methyl-3-ethylcyclopentane.

The formation of *n*-propylcyclopentane as the major component could be attributed to the relatively weakly acidic

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(15) H. Pines and A. W. Shaw, THIS JOURNAL, **79**, 1474 (1957).

(16) H. Pines, C. T. Chen and A. W. Shaw, *ibid.*, **80**, 1930 (1958).

(17) H. Pines, R. C. Olberg and V. N. Ipatieff, *ibid.*, **70**, 533 (1948).

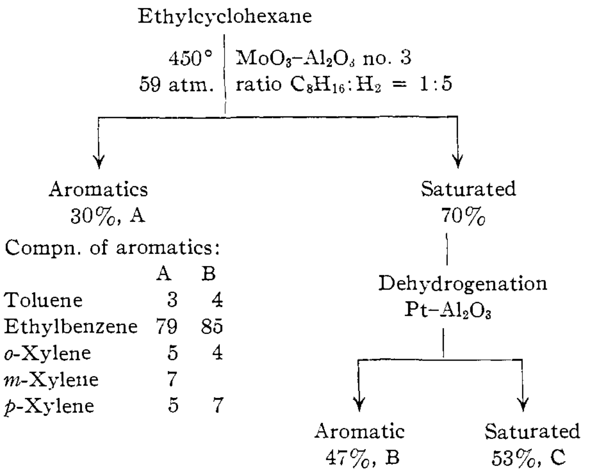
(18) Podbielniak, Inc., Chicago, Ill.

(19) J. Marisson, *J. Chem. Soc.*, 1614 (1951).

(20) H. A. Benesi, THIS JOURNAL, **78**, 5490 (1956).

TABLE VIII

HYDROISOMERIZATION OF ETHYLCYCLOHEXANE

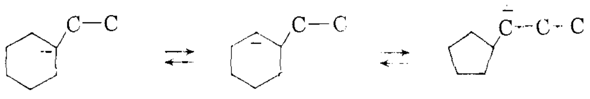


Compn. of aromatics:

	A	B
Toluene	3	4
Ethylbenzene	79	85
o-Xylene	5	4
m-Xylene	7	
p-Xylene	5	7

(C) Composition of satd. hydrocarbons: 1-methyl-*trans*-3-ethylcyclopentane (?), b.p. 119–120°, 20%; *n*-propylcyclopentane, 50%; other alkylcyclopentones 7–10%.

molybdena–alumina catalyst used in this reaction; the isomerization was kinetically rather than thermodynamically controlled, in the sense that it does not result in an equilibrium mixture. This is not too unexpected since in the presence of weak acids the participation of primary carbonium ions in the reaction is curtailed. The formation of *n*-propylcyclopentane involves the participation in the reaction of secondary and tertiary carbonium ions only while any other product formed would involve the participation of a primary carbonium ion.



Experimental Part

The apparatus and procedure used were similar to those reported previously.[15]

The analytical procedure used involving chromatographic separation of aromatics from saturated hydrocarbons and selective dehydrogenation was the same as described previously.[12] The composition of xylenes was determined by a combination of gas chromatography and infrared spectroscopy.

Preparation of 1,2-Dimethyl-C^{14}-cyclohexane. a. ***o*-Toluic acid-carboxyl C^{14}** was obtained in 94% yield by treating 35 mmoles of tolylmagnesium bromide with carbon dioxide generated from 30.7 mmoles of radioactive barium carbonate.

b. ***o*-Tolylcarbinol-C^{14}** was prepared by dissolving in ether the radioactive *o*-toluic acid, obtained above, diluted with 15 mmoles of inactive acid and reducing it with lithium aluminum hydride; yield 90%.

c. ***o*-Xylene-methyl-C^{14}** was obtained by reductive dehydroxylation of the radioactive *o*-tolylcarbinol, diluted with 42.5 mmoles of inactive carbinol; the hydrogenolysis was carried out at 225°, 200 atm. of hydrogen and in the presence of copper chromite catalyst. The *o*-xylene was 99.6% pure according to gas chromatographic analysis.

d. **1,2-Dimethylcyclohexane-methyl C^{14}** was obtained by hydrogenating the radioactive *o*-xylene in the presence of a nickel–kieselguhr catalyst at 150° and 100 atm. of hydrogen. The reaction product consisted of 37% *trans*- and 63% *cis*-1,2-dimethylcyclohexane.

Analysis of the Reaction Products from 1,2-Dimethyl-C^{14}-cyclohexane.—The aromatic fraction obtained from the reaction was oxidized with potassium permanganate and the resulting acids were separated according to the procedure outlined previously.[15]

The radioactivity assay of the resulting pure phthalic acids and of their decarboxylation products was performed in a 250-ml. ionization chamber, connected with a vibrating Reed type electrometer. The commercial equipment used was a Dynacon model 6000,[21] equipped with a 10-millivolt variable chart speed recorder.

All the samples to be assayed were converted to gaseous carbon dioxide. The organic samples were burned by wet combustion according to the procedure of Van Slyke,[22a,b] in which the yield of carbon dioxide produced was 100 ± 0.5% for all substances to be assayed. The barium carbonate resulting from the decarboxylation of the side chain was converted to carbon dioxide by means of concentrated sulfuric acid. After the first violent reaction the sulfuric acid was heated in order to expel the dissolved carbon dioxide and to dissolve the precipitated barium sulfate which could include some barium carbonate.

The pure phthalic acids, which were subjected to decarboxylation were found to have the following activities expressed in millicuries per milligram of carbon: orthophthalic acid, 6.72×10^{-3}; isophthalic acid, 1.24×10^{-2}; terephthalic acid, 1.72×10^{-3} mc./mg.

The tere- and isophthalic acids were decarboxylated in the presence of copper oxide and quinoline and the Schmidt reaction was performed on orthophthalic acid, giving carbon dioxide and anthranilic acid. The activities of the decarboxylation products were in millicuries per mg. carbon: orthophthalic acid: $BaCO_3$, 2.63×10^{-2} mc./mg., anthranilic acid, 3.93×10^{-3}; isophthalic acid: $BaCO_3$, 4.55×10^{-2}, benzene, 8.35×10^{-4}; terephthalic acid: $BaCO_3$, 5.69×10^{-3}, benzene, 2.22×10^{-4}.

The distribution of the C^{14} in the ring and the side of the various xylenes was calculated.

Calculations. ***o*-Xylene.**—Anthranilic acid has 7 carbon atoms, the total activity therefore is: $7 \times 3.93 \times 10^{-3} = 27.6 \times 10^{-3}$ mc./mg. carbon. The activity of the side CO_2 is 2.63×10^{-2}. So the total activity of the ring is: $27.6 \times 10^{-3} - 26.3 \times 10^{-3} = 1.3 \times 10^{-3}$. The percentage activity in the ring

$$\frac{1.3 \times 10^{-3} \times 10^2}{8 \times 6.72 \times 10^{-3}} = 2.4\%$$

The percentage activity in the side chain

$$\frac{2.63 \times 10^{-2} \times 2 \times 10^2}{8 \times 6.72 \times 10^{-3}} = 97.7\%$$

m-Xylene:

$$\text{ring: } \frac{6 \times 83.5 \times 10^{-5} \times 10^2}{8 \times 1.24 \times 10^{-2}} = 5.1\%$$

$$\text{side chain: } \frac{2 \times 4.55 \times 10^{-2} \times 10^2}{8 \times 1.24 \times 10^{-2}} = 91.8\%$$

p-Xylene:

$$\text{ring: } \frac{6 \times 2.22 \times 10^{-4}}{8 \times 1.72 \times 10^{-3}} = 9.8\%$$

$$\text{side chain: } \frac{2 \times 5.69 \times 10^{-3} \times 10^2}{8 \times 1.72 \times 10^{-3}} = 82.7\%$$

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(21) Nuclear-Chicago Corporation.

(22) (a) D. D. Van Slyke and J. Folch, *J. Biol. Chem.*, **136**, 509 (1940); (b) D. D. Van Slyke, J. Plazin and T. R. Weisiger, *ibid.*, **191**, 299 (1951).