Alumina. Catalyst and Support. XXI.[1] Aromatization of 2,4-Dimethyl-3-methyl-C^{14}-pentane over Chromia–Alumina Catalyst. Contribution to the Mechanism of Aromatization[2]

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The aromatization of 2,4-dimethyl-3-methyl-C^{14}-pentane over "nonacidic" chromia–alumina was studied. The main aromatic products were *o*-, *m*-, and *p*-xylene, with the production of *m*-xylene dropping rapidly with the time. The radioactivity distribution in the xylenes supports the previously proposed cyclopropane- and cyclobutane-type intermediates for the dehydroisomerization and aromatization of branched hydrocarbons. In addition, this study has indicated that C_7- and C_8-membered ring intermediates must play at least a minor role in the aromatization of branched chain hydrocarbons.

The aromatization of methylpentanes must be preceded by some rearrangement to at least a C_6-chain intermediate and such a rearrangement presents an interesting mechanistic problem. Studies in our laboratory have shown that alumina has intrinsic acidic properties and that the strength of the acidic sites depends upon the method employed for the preparation of the aluminas.[3] It was found that chromia–alumina catalyst containing alumina prepared from aluminum isopropoxide has relatively strong acidic sites and that this catalyst may cause skeletal isomerization of the hydrocarbon *via* a carbonium ion mechanism.[4,5] However, chromia–alumina catalyst containing alumina prepared from potassium aluminate ("nonacidic" chromia–alumina) has relatively weak acidic sites and such cationic skeletal isomerization does not occur. This observation has been subsequently confirmed by others.[6]

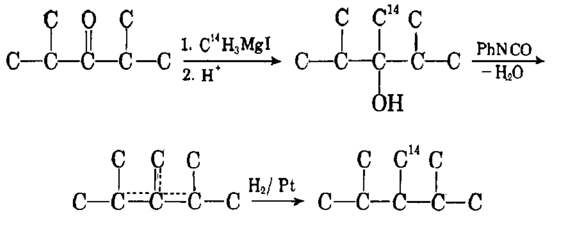
Large membered ring intermediates have been shown for the aromatization of *n*-heptane and *n*-octane[1,7,8] over "nonacidic" chromia–alumina catalyst. Further studies of the aromatization of branched C_6–C_8 hydrocarbons over "nonacidic" chromia–alumina catalyst have shown the existence of adsorbed cyclopropane intermediates and have indicated strongly the possibility of adsorbed cyclobutane intermediates prior to the aromatization reaction.[9,10]

In order to shed more light on the possible existence of cyclobutane intermediates, 2,4-dimethyl-3-methyl-C^{14}-pentane was synthesized and aromatized under conditions described previously.[9] The aromatic products of the reaction were mainly *o*-, *m*-, and *p*-xylene. The mechanism involving an adsorbed cyclopropane intermediate would produce *o*- and *p*-xylenes with 100% methyl-labeled *o*-xylene and 100% ring-labeled *p*-xylene (Scheme I). An adsorbed cyclobutane intermediate would give *m*-xylene with all the radioactivity in the ring (Scheme II). The production of *o*- and *p*-xylene are precluded by this mechanism.

The possibility of a combination of small and large membered ring intermediates cannot be excluded. Therefore, a mechanism combining an adsorbed cyclobutane intermediate followed by an adsorbed cycloheptane intermediate would predict 50–100% ring-labeled *o*- and *m*-xylene with 100% ring-labeled *p*-xylene (Scheme II, route b). However, a combination of cyclo-C_3, -C_4, and -C_8 adsorbed species would predict 75% ring-labeled *o*-, *m*-, and *p*-xylene (Scheme III). Therefore, ring label in *m*-xylene would give strong support for the existence of a cyclobutane intermediate.

Procedure

The 2,4-dimethyl-3-methyl-C^{14}-pentane was synthesized in greater than 99% purity by the following sequence of reactions.



The 2,4-dimethyl-3-methyl-C^{14}-pentane was dehydrogenated at 531° over "nonacidic" chromia–alumina catalyst by a previously described procedure.[8] Table I summarizes the reaction conditions and composition of the xylenes produced.

TABLE I

AROMATIZATION OF 2,4-DIMETHYL-3-METHYL-C^{14}-PENTANE OVER CHROMIA–ALUMINA CATALYST[a]

	Cut no.		
	1	2	3
Duration of experiment, min.	16	18	20
Total C_8H_{18} passed, ml.	3.9	4.5	5.0
Conversion of C_8H_{18} to xylenes, mole %	12	7.5	3.5
Conversion of C_8H_{18} to carbonaceous materials,[b] mole %.	←1.29%→		
Distribution of xylenes in the aromatic fraction, mole %			
o-Xylene	40.4	49.8	51.6
m-Xylene	33.0	21.5	18.8
p-Xylene	26.6	28.7	29.6

[a] The experiments were made at 531° and at an hourly liquid space velocity of 1.06. [b] The conversion to carbonaceous materials was determined at the end of the final experiment.

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

[2] (a) Paper XII of the series "Aromatization of Hydrocarbons"; for paper XI, see ref. 1; (b) this research was supported by the Atomic Energy Commission, Contract AT(11-1)-1046.

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

[4] H. Pines and C. T. Chen, *ibid.*, **82**, 3562 (1960).

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

[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).

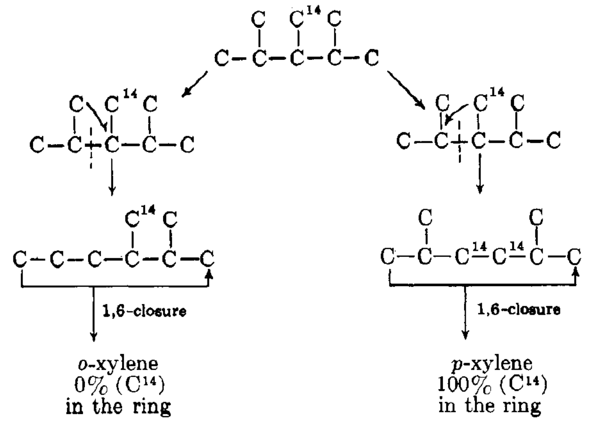
[8] H. Pines and C. T. Chen, *Actes Congr. Intern. Catalyse, 2e, Paris*, **I**, 367 (1960).

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

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

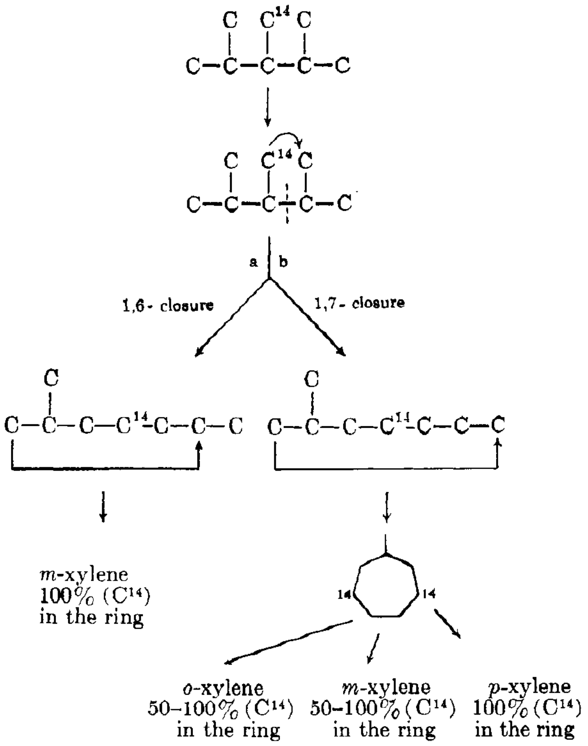
SCHEME I

AROMATIZATION OF 2,4-DIMETHYL-3-METHYL-C^{14}-PENTANE *via* CYCLOPROPANE INTERMEDIATES



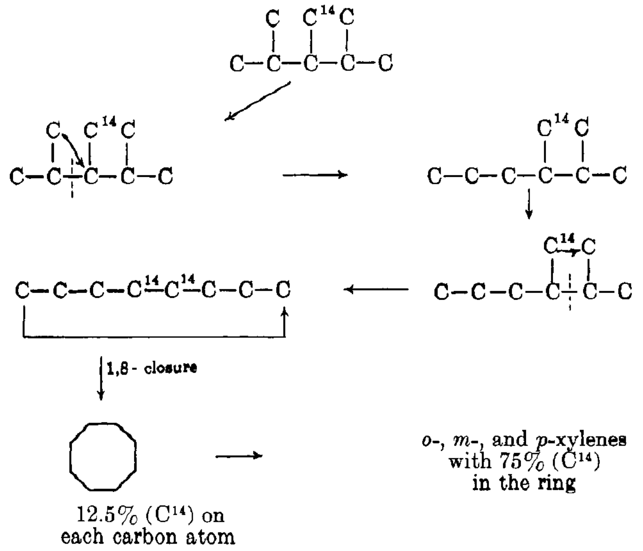
SCHEME II

AROMATIZATION OF 2,4-DIMETHYL-3-METHYL-C^{14}-PENTANE *via* A CYCLOBUTANE INTERMEDIATE FOLLOWED BY 1,6-CLOSURE (ROUTE a) OR 1,7-CLOSURE (ROUTE b)



SCHEME III

AROMATIZATION OF 2,4-DIMETHYL-3-METHYL-C^{14}-PENTANE *via* A COMBINATION OF CYCLOPROPANE, CYCLOBUTANE, AND CYCLOOCTANE INTERMEDIATES



The reaction product was collected in three separate cuts. The xylenes in each cut were separated by preparative v.p.c.; the *m*- and *p*-xylene being collected together while the *o*-xylene was collected separately. The xylenes were diluted with their corresponding inactive compounds, then oxidized with alkaline potassium permanganate to their respective acids. The acids were then separated by the procedure described previously.[11]

The isophthalic and terephthalic acids thus produced were decarboxylated with boiling quinoline and copper oxide. The benzene and carbon dioxide produced were collected separately and analyzed for radioactivity. The *o*-xylene was decarboxylated by employing the Schmidt reaction and the products, anthranilic acid and carbon dioxide, collected separately and analyzed for radioactivity. Tables II and III summarize radioactivities of the aromatic acids and their decarboxylation products. The differences between the radioactivities of the acids and the sum of the radioactivities of their decarboxylation products were ±3% or less.

Discussion of Results

The radioactivity distribution of the xylenes produced from the aromatization of 2,4-dimethyl-3-methyl-C^{14}-pentane over "nonacidic" chromia-alumina catalyst is summarized in Table IV.

The fact that *m*- and *p*-xylene contain from 7-9% of their radioactivity in the side chain suggests that cyclopropane and cyclobutane intermediates cannot be the sole intermediate species participating in the aromatization reaction. This is substantiated further by the fact that *o*-xylene contains from 6-12% of the radioactivity in the ring. The inclusion of C_7- and/or C_8-membered intermediates appears necessary.

It cannot be determined from the present data whether cycloheptane or cyclooctane intermediate species are contributors or if, indeed, they both contribute. However, since over 90% of the radioactivity of *o*-xylene does, in fact, reside in the side chain, the contribution of such large membered ring intermediates is indicated to be only of minor importance. On the other hand, it can be seen that an adsorbed cyclobutane species must be involved in this aromatization process. The fact that *m*-xylene is formed at all suggests some sort of cyclobutane intermediate species, and also the fact that approximately 95% of the radioactivity of the *m*-xylene resides in the ring can be explained by assuming a cyclobutane intermediate. A strong support for the existence of a cyclobutane intermediate was the observation recorded before that 2,3-dimethylbutane isomerizes in the presence of a nonacidic chromia-alumina catalyst to 3-methylpentane.[9]

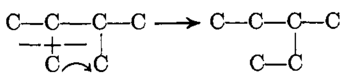


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Table II

Decarboxylations of Acids Derived from *p*-Xylene and *m*-Xylene Produced by the Aromatization of 2,4-Dimethyl-3-methyl-C^{14}-pentane

	p-Xylene, cut no.			*m*-Xylene, cut no.		
	1	2	3	1	2	3
Acid decarboxylated,[a] mmoles	0.48	0.47	0.58	0.57	0.48	0.43
Barium carbonate obtained, mmoles	0.92	0.84	0.47	1.06	0.87	0.79
Benzene obtained, mmoles	0.24	0.21	0.09	0.24	0.26	0.17
Barium carbonate yield, mole %	97	88	41	94	90	92
Benzene yield, mole %	49	43	16	43	54	39
Radioactivities 10^{-3} μc./mmole						
Starting acid[a]	144	10.3	25.3	24.1	1.96	23.5
Barium carbonate	5.1	0.36	1.2	1.1	0.08	
Benzene	138	9.8	23.5	22.6	1.86	

[a] For *p*-xylene, terephthalic acid, and for *m*-xylene, isophthalic acid.

Table III

Radiochemical Assay Data

(Schmidt reaction on phthalic acid derived from *o*-xylene produced by aromatization of 2,4-dimethyl-3-methyl-C^{14}-pentane)

	Cut no.		
	1	2	3
Phthalic acid decarboxylated, mmoles	2.18	0.87	2.96
Barium carbonate obtained, mmoles	2.08	0.78	2.77
Anthranilic acid obtained, mmoles	0.33	0.04	0.08
Barium carbonate yield, mole %	96	90	94
Anthranilic acid yield, mole %	15	4	2.5
Radioactivities, 10^{-3} μc./mmole			
Phthalic acid	95.7	0.745	25.8
Barium carbonate	45.1	0.353	11.8
Anthranilic acid	50.8		14.8

Table IV

Radioactivity Distribution from the Aromatization of 2,4-Dimethyl-3-methyl-C^{14}-pentane

Compound and C^{14} location	Distribution in		
	Cut no. 1	Cut no. 2	Cut no. 3
o-Xylene			
% side chain	94.2	96.1	91.4
% ring	6.0		11.6
Difference[a]	+0.2		+3.0
m-Xylene			
% side chain	9.1	8.1	
% ring	93.7	95.0	
Difference[a]	+2.8	+3.1	
p-Xylene			
% side chain	7.1	7.0	9.5
% ring	95.7	94.7	93.0
Difference[a]	+2.8	+1.7	+2.5

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

As of now, no mention has been made of the possibility of aromatization to occur from two simultaneous methyl injections *via* cyclopropane-type intermediates followed by either 1,6-closure to give *m*-xylene or 1,7-closure which yields *o*-, *m*-, and *p*-xylene. This mechanistic route would eliminate the need of a cyclobutane intermediate and still explain the production of *m*-xylene with the observed radioactivity distribution. However, it has been shown[9,10] that cyclopropane-type intermediates vary but little with time. Therefore, the fact that the *m*-xylene production is definitely a "time-dependent" reaction rules out the possibility of *m*-xylene formation by such a path.

Finally, since there is very little variation in the radioactivity distribution of the xylenes from cuts 1–3, little can be said about the possible change, with time, in the contributions of the various probable mechanisms for the formation of the xylenes.

Conclusion

This study has contributed and added support for the participation of cyclobutane-type intermediates in the aromatization of 2,3,4-trimethylpentane over chromia–alumina catalyst. Indeed, a cyclobutane-type intermediate must be involved to account for the *m*-xylene produced. As was to be expected, cyclopropane-type intermediates were also contributors. However, the participation of cyclopropane- and cyclobutane-type intermediates cannot be the only intermediate species in this reaction. It appears that C_7- and/or C_8-membered ring intermediates are participating to a minor extent.

Experimental

Synthesis of 2,4-Dimethyl-3-methyl-C^{14}-pentane. A. 2,4-Dimethyl-3-methyl-C^{14}-3-pentanol.—To a rapidly stirred mixture of 4.62 g. (0.19 g.-atom) of magnesium turnings in 80 ml. of absolute ether was added dropwise a solution of 24.2 g. (0.17 mol., 4.0 mc. C^{14}) of methyl iodide-C^{14} in 40 ml. of absolute ether over a period of 1.5–2.0 hr. Following the addition, the reaction mixture was stirred an additional hour at room temperature. Then a solution of 19.4 g. (0.17 mole) of 2,4-dimethyl-3-pentanone in 40 ml. of absolute ether was added dropwise over a 1.5–2.0-hr. period. Rapid stirring was continued at room temperature for 15 hr. after completion of the ketone addition. The reaction mixture was then poured over *ca.* 100 ml. of crushed ice and most of the precipitated hydroxide dissolved with 10% aqueous sulfuric acid (the pH always being kept on the basic side). The layers were separated and the water layer extracted with ether. The ether extracts and original organic layer were combined and washed with water, then 10% aqueous sodium bicarbonate, and finally dried with anhydrous sodium sulfate. The ether was removed by distilling from a small amount of anhydrous sodium carbonate. The residue (24 g.) contained 19.2 g. of 2,4-dimethyl-3-methyl-C^{14}-3-pentanol; yield, 87%.

B. 2,4-Dimethyl-3-methyl-C^{14}-pentenes.—The crude alcohol, prepared above, was dehydrated with 4.86 g. (0.06 mole) of dry pyridine and 40.0 g. (0.34 mole) of phenyl isocyanate, according to the procedure described in a previous paper.[9]

C. 2,4-Dimethyl-3-methyl-C^{14}-pentane.—The olefin (13.0 g.) was hydrogenated in a low-pressure shaking hydrogenation apparatus with platinum oxide catalyst. The product was chromatographed over 43 ml. of alumina (Merck, reagent grade). The 2,4-dimethyl-3-methyl-C^{14}-pentane thus obtained, 9.64 g., was 99.5% pure. Its radioactivity was 4.28 μc./mmole. Overall yield based on $C^{14}H_3I$ used was 9.0%.

Catalyst.—The chromia–alumina catalyst was prepared according to a described procedure.[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 was the same as described earlier.[9]

B. Separation of Aromatic Hydrocarbons from Reaction Product.—The separation was accomplished using an F & M Model 300 programmed temperature gas chromatograph[12] 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 ml./min. The sample recovery was the same as described previously.[1]

C. Oxidation of the Xylenes.—The xylenes which were separated and collected from the preparative v.p.c. column were diluted from five–fifty times with their inactive xylenes and oxidized to the corresponding phthalic acids with hot alkaline potassium permanganate as described previously.[1]

D. Separation of the Phthalic Acids.—The separation and purification of the phthalic acids produced before was accomplished as described earlier.[11]

E. Radiochemical Assay.—The radiochemical assay of the resulting phthalic acids and their decarboxylation products was the same as previously described.[13]

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Kinetics of the Reaction of 2-Nitropropane with Methylenebisamines. A Study of the Mannich Reaction

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The Mannich reactions of 2-nitropropane with methylenebispiperidine and with methylenebismorpholine exhibit second-order kinetics, first order in each component. The 2-nitropropane reacts through the *aci* form. The rate increases with increasing dielectric constant, and decreases in basic media. Methylenebispiperidine exhibits a faster rate than methylenebismorpholine. The greater reactivity of the piperidine derivative is attributed to its greater base strength. Mechanisms are presented for media of low and high dielectric constant.

The Mannich reaction has been reviewed by Blicke[2] and Hellman,[3] and two excellent kinetic studies have been reported.[4,5] Alexander and Underhill studied the reaction of ethylmalonic acid as active hydrogen compound and dimethylamine as amine component. Cummings and Shelton used cyclohexanone and dimethylamine. Both of these studies employed aqueous solvents and both involved the over-all Mannich reaction of active hydrogen compound, formaldehyde, and amine.

$$\text{Z}-\overset{|}{\underset{|}{\text{C}}}-\text{H} + \text{HCHO} + \text{HNR}_2 \longrightarrow \text{Z}-\overset{|}{\underset{|}{\text{C}}}-\text{CH}_2\text{NR}_2 + \text{H}_2\text{O} \quad (1)$$

The present kinetic study was undertaken to investigate (1) the effect of amine basicity and (2) the effect of solvent dielectric constant.

Attempts to follow the rate of reaction of the mixture of reactants shown in eq. 1 necessarily leads to complex results because of the known initial reaction of amine and formaldehyde to form any of several intermediate species, *e.g.*, aminomethylol, methylenebisamine, and methyleneimmonium ion. The complexities of this reaction have been reviewed by Wagner.[6] The above mechanisms[4,5] are thus complicated by this initial reaction and further by the participation of water in the amine–formaldehyde equilibrium.[6]

$$\text{R}_2\text{NH} + \text{HCHO} \rightleftarrows \text{R}_2\text{NCH}_2\text{OH} \xrightleftharpoons{\text{R}_2\text{NH}} \text{R}_2\text{NCH}_2\text{NR}_2 + \text{H}_2\text{O}$$

For these reasons, deductions about the intermediates (aminomethylol *vs.* methylenebisamine) and deductions based on activation parameters were prevented.

In the present work we studied the reaction of 2-nitropropane with two methylenebisamines. It is well-known that nitro alkanes react to form Mannich bases. Senkus[7] and Johnson[8] reported that the Mannich reaction of nitro alkanes proceeds through an intermediate formed by the condensation of the amine with formaldehyde. Butler[9] found that methylenebisamines react with 2-methyl-2-nitro-1-propanol (formed by the reaction of 2-nitropropane with formaldehyde) to form the usual Mannich bases. Another interesting feature of 2-nitropropane is its acidity which is intermediate between those of the active hydrogen compounds used in the kinetics studies discussed.[4,5]

The use of methylenebisamines in the present study can be explained on the following basis. Aminomethylols are not generally isolable,[6] thus they are difficult to study. It is known that methylenebisamines react with active hydrogen compounds to produce normal Mannich bases.[9–11] Fernandez and Butler[12] have demonstrated recently that the reaction of formaldehyde with secondary aliphatic amines produces primarily the methylenebisamine and only small proportions, if any, of the aminomethylol. While aminomethylols are not excluded as intermediates, evidence offered for their reactivity as intermediates is indirect and only recently was inferred[11] through a study of the reaction of α-amino ethers with β-naphthol to produce normal Mannich bases.

We have thus attempted to simplify the system at the risk of narrowing the scope of the results. Anhydrous solvents were employed in all runs to avoid formation of aminomethylol by hydrolysis of the methylenebisamines. We employed the methylenebisamines of piperidine and morpholine because of the rather large

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[1] Student participant sponsored by National Science Foundation Undergraduate Science Education Grants No. G-21888 and GE-1210.

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