

Dehydrocyclization of Paraffins. Aromatic Distribution from Paraffins and Naphthenes Containing a Quaternary Carbon

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The aromatic product distribution from the dehydrocyclization of several paraffins that contain a quaternary carbon and at least one six-carbon chain are compared to the aromatics obtained from the conversion of the naphthenes corresponding to direct six-carbon ring formation from the paraffins. The distributions obtained using Pt and chromia supported on "nonacidic" alumina are compared. The *geminal*-dimethyl naphthenes gave similar results over chromia and a low isomerization Pt catalyst with demethylation at the quaternary carbon the predominate reaction pathway. Comparing the conversion of the paraffin with the corresponding naphthene shows that over Pt dehydrocyclization occurs by direct six-carbon ring formation. For chromia this comparison shows a different distribution for the paraffin and naphthene; this difference probably is due to an isomerization of the paraffin prior to cyclization. The aromatic distribution is very sensitive to the Pt-Al₂O₃ preparation; different preparations on the same alumina support gave very different aromatic distributions.

INTRODUCTION

The mechanism for the dehydrocyclization of paraffins has been widely studied and several reaction schemes have been proposed (1). Even today there is disagreement about the cyclization step for a particular catalyst system. For example, Kazanskii (2) proposed both five- and six-carbon ring intermediates over Pt catalysts at 300°C. Lester (3) reported that formation of five-carbon rings was important for the dehydrocyclization of trimethylpentanes at a higher temperature over Pt catalysts. Davis and co-workers (4) have reported evidence for the direct formation of six-carbon rings over both Pt and Cr₂O₃ catalysts. For chromia, Pines and Goetschel (5) have proposed a contribution to the dehydrocyclization pathway of all of the various carbon ring intermediates that can be formed from the paraffin and this is the one used to explain the dehydrocyclization mechanism in a recent book (6). The situation is even more confusing when one attempts to compare the dehydrocyclization

mechanism over different catalysts. Lester (3) claimed that different mechanisms are required for trimethylpentane aromatization over Pt and Cr₂O₃ catalysts. Pines and Chen (7) proposed that over chromia the mechanism was altered just by changing the preparation of the alumina support.

Part of the confusion may result from the facts that: (a) results have been obtained using paraffins with or without a six-carbon chain; and (b) some studies involved reactants containing quaternary carbons while others did not. Several examples of cyclization of paraffins with five-carbon chains capable of forming cyclic intermediates with a quaternary carbon have been reported (3, 8). However, little attention has been given to six or longer carbon chain paraffins containing a quaternary carbon. Kazanskii *et al.* (9) offered proof that cyclization of 3,3-dimethylhexane proceeded through the intermediate 1,1-dimethylcyclohexane. On the other hand, Balandin (10) favored five-carbon ring formation for the conversion of 2,2-

dimethylhexane. Komarewsky and Shand (11) found that C₈-paraffins with a quaternary carbon formed the thermodynamically most stable aromatic product, *m*-xylene. Much more work has been reported on the conversion of naphthenes with quaternary carbons (6) but an acceptable detailed mechanism has not evolved to date.

In the present study, we have compared the dehydrocyclization products from several C₈- and C₉-paraffins with quaternary carbon, which contain at least a six-carbon chain, to the aromatics from the naphthenes corresponding to direct six-carbon ring formation from the paraffins. In addition, these conversions were effected over both Pt and Cr₂O₃ catalysts on a "nonacidic" alumina support. This would provide data to compare quaternary carbon paraffins with a six-carbon chain to those without one. In addition, it would enable a comparison of Pt and chromia catalysts, on the same support, to be made under identical experimental conditions and using the same reactants. A valid comparison of these two widely studied catalyst systems can not be made at present.

EXPERIMENTAL METHODS

The dehydrocyclization apparatus consisted of a syringe pump, Vycor reactor, and liquid collector and has been described previously (4a). The catalysts were reduced in flowing hydrogen *in situ* at 550°C unless noted otherwise. The run conditions, unless noted otherwise, were: LHSV, 0.3; temperature, 500°C; no added hydrogen or carrier gas; and 5 ml of catalyst (8–14 mesh). Liquid samples were collected at intervals and analyzed by glc for conversion using a Carbowax column and for aromatic isomer distribution with a Bentone 34-diisodecyl phthalate column. The hydrocarbons were purchased from Chem-Samp-Co with the exception of 1,1,3-trimethyl-*x*-cyclohexene which was prepared by the pyrolysis of the acetate prepared from 3,3,5-trimethylcyclohexanol.

Catalysts. Pt–Al₂O₃–K (1): All nonacidic alumina used in this study was prepared by precipitation from potassium aluminate using CO₂ (7) and contained 0.4% K.

Alumina, dried at 120°C, was impregnated with sufficient chloroplatinic acid in just enough water to fill the alumina pore volume. The catalyst was dried at 120°C in air and reduced in flowing hydrogen at 482°C. The chlorine was reduced to less than 0.05 wt % by washing the reduced catalyst with 5% ammonium hydroxide, drying at 120°, and rewashing with 5% ammonium hydroxide containing 1 wt % KOH. Pt–Al₂O₃ (2) and (3) were repeat preparations of Pt–Al₂O₃–K (1) except the second ammonium hydroxide wash did not contain KOH and the alumina, after drying at 120°, was stored in a closed container for 3 years. Catalyst Pt–Al₂O₃–K (1) contained about 1 wt % K and 0.6 wt % Pt; (2) and (3) contained about 0.4 wt % K and 0.6 wt % Pt.

Rh- and Pd–Al₂O₃–K were prepared using the same procedure as for Pt–Al₂O₃–K (2) and (3) using alumina prepared by the same procedure. The metal content of the finished catalyst was 0.3 wt % for Rh and 0.55 wt % for Pd; both catalysts contained about 0.5 wt % K.

Cr₂O₃–Al₂O₃ was prepared by impregnating nonacidic alumina with chromic acid (4a). The final catalyst contained 13 wt % Cr.

RESULTS

The aromatic distribution from the conversion of 1,1-dimethylcyclohexane (DMCH) over chromia and Pt catalysts is shown in Fig. 1. Over both catalysts demethylation to form toluene is the major reaction pathway; suprisingly, demethylation occurs to a greater extent over chromia than over Pt. Also, the two catalysts yield a much different C₈-aromatic distribution. Over chromia, the total C₈-aromatic was about 10% of the total aromatics initially and *decreased* with time on stream; these aromatics were present in the order expected if a methyl group were to move from the 1,1-position by a simple 1,2-methyl migration: *ortho*- > *meta*- > *para*-xylene > ethylbenzene. For Pt, the C₈-aromatics comprise about 15% of the total; and their amount *increased* to about 35% after 100 min on stream. Likewise, the C₈-

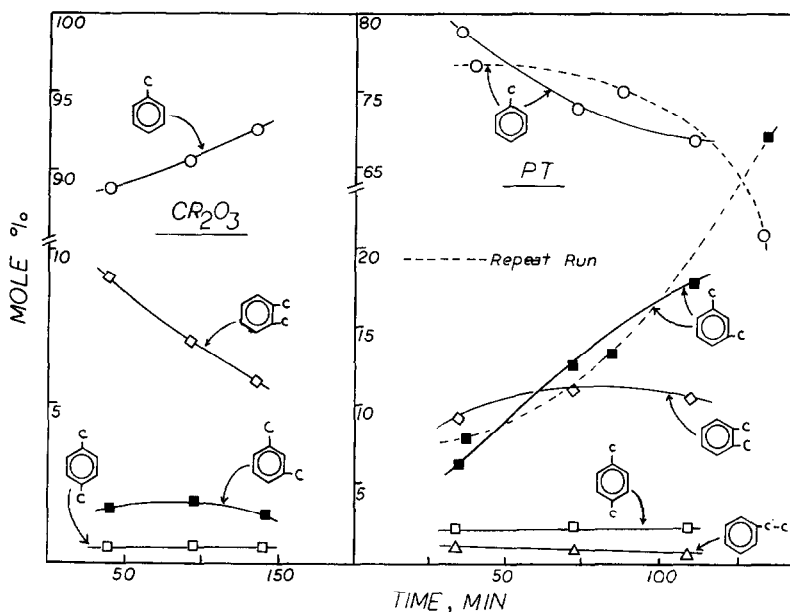


FIG. 1. Aromatic product distribution for the conversion of 1,1-dimethylcyclohexane over Pt (1) and chromia.

aromatics are present in a different order than expected for 1,2-methyl migration. About equal amounts of *o*- and *m*-xylene was formed initially and after 100 min the *m*-isomer was about twice the amount of *o*-xylene. Results of two identical runs are included for the Pt catalyst and they are in excellent agreement.

Direct six-carbon ring formation by 2,2-dimethylhexane (DMH) would lead to 1,1-DMCH. Thus the aromatic distribution from the *geminal*-DMH should be the same as with 1,1-DMCH if direct six-carbon ring formation is the major dehydrocyclization pathway. The aromatic distribution (Fig. 2) over the Pt catalyst is similar to that obtained with 1,1-DMCH except that there is slightly more C_8 -aromatics formed during the run and more *o*-xylene is formed relative to the *m*-xylene. But this difference is slight. Over the chromia catalyst the distribution from 2,2-DMH is much different than from 1,1-DMCH. Only about 20% of the aromatics is the demethylation product, toluene. The amount of *o*- and *m*-xylene is about equal and comprises about 90% of the C_8 -aromatics. Comparison of the C_8 -aromatic distribution for these two

reactants suggests that more "isomerization" occurs over the chromia than Pt.

Both 2,2- and 3,3-DMH (see Fig. 3) would yield the same intermediate provided six-carbon rings are formed directly. A similar distribution of aromatics* was obtained from the two isomers over the chromia catalyst since the major products are those from isomerization (80–85%) with little demethylation to form toluene (15–20%). The C_8 -aromatic distribution is different since the major products were about equal amounts of *m*- and *o*-xylene from the 2,2-isomer but *o*-xylene was the major product from the 3,3-isomer.

The conversion of both the 2,2- and 3,3-isomer was about the same over Pt- and $Cr_2O_3-Al_2O_3$. However, there was a considerable difference in the aromatic distribution for the 2,2- and 3,3-isomers over the Pt catalyst. First, toluene comprised about 50% of the aromatics from the 2,2-isomer

* The product distribution may be viewed as a distribution between demethylation and isomerization fractions, as well as the distribution within each of these fractions. In some cases, as for the 2,2- and 3,3-isomer, only one distribution may be similar for a particular catalyst.

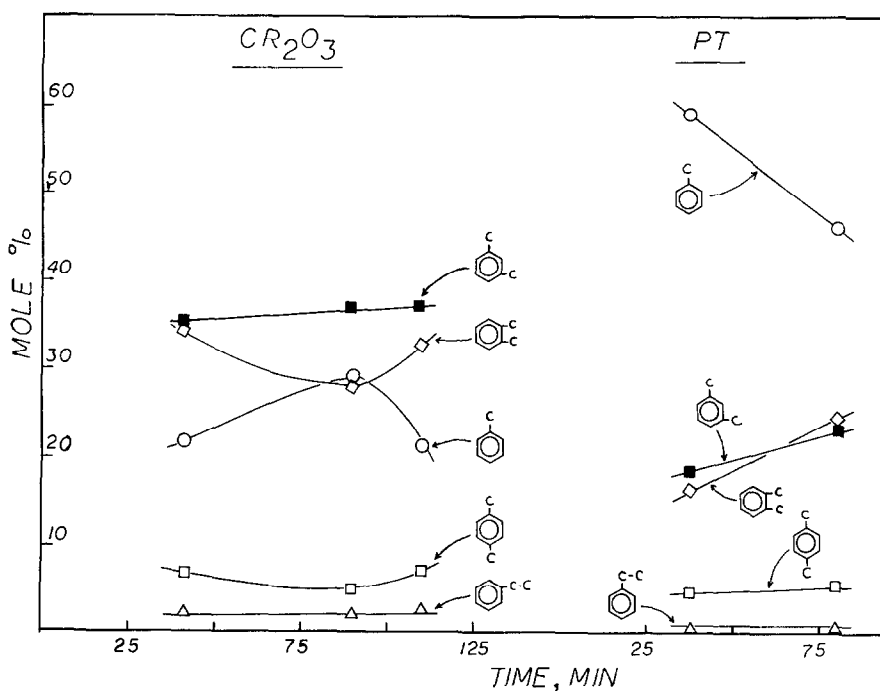


FIG. 2. Aromatic product distribution for the conversion of 2,2-dimethylhexane over Pt (1) and chromia.

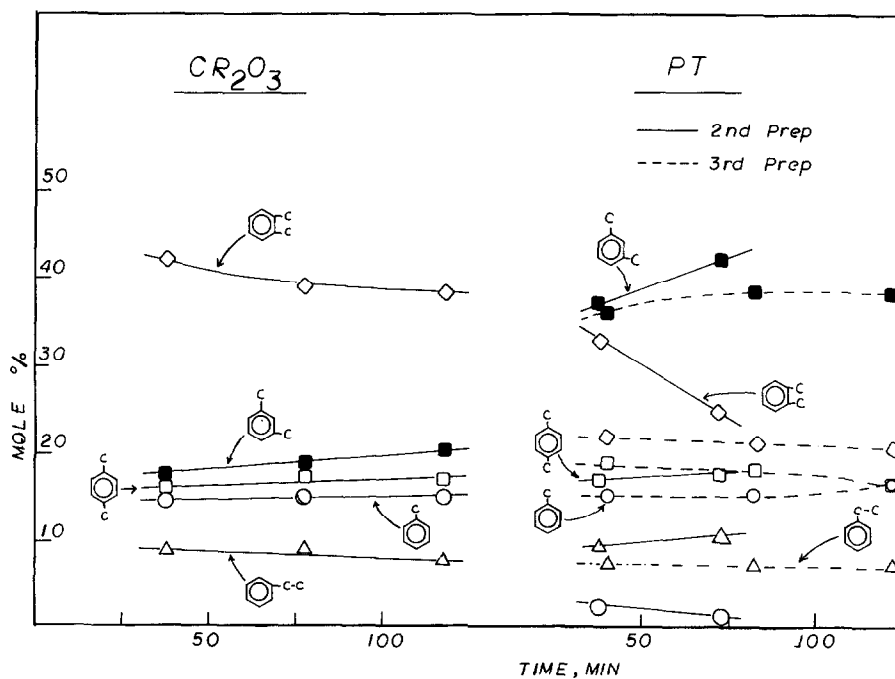


FIG. 3. Aromatic product distribution for the conversion of 3,3-dimethylhexane over Pt (3) and chromia.

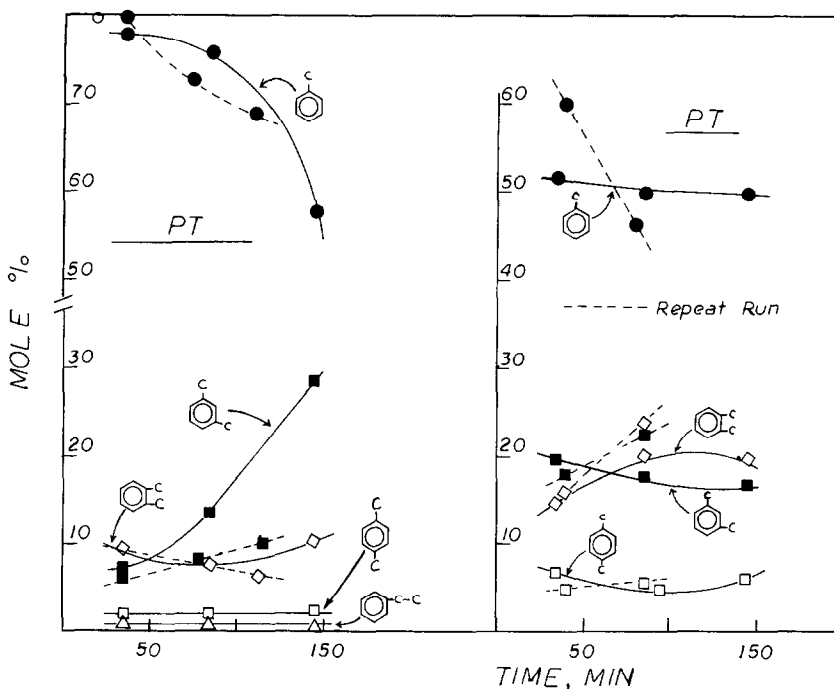


FIG. 4. Comparison of the aromatic products for repeat runs over Pt (1) with 1,1-dimethylcyclohexane (left); and 2,2-dimethylhexane (right).

but only about 10% from the 3,3-isomer. Also, the *meta:ortho* ratio was about 1:1 for 2,2-DMH but 2:1 for the 3,3-isomer; and more ethylbenzene and *p*-xylene were formed from the 3,3- than the 2,2-isomer. The results for repeat runs with the 1,1-DMCH and 3,3-DMH over Pt-Al₂O₃ are shown in Fig. 4 and the reproducibility is excellent. However, it must be kept in mind that most of these identifications are based on glc retention times and internal standards. But, for the runs in which selected peaks of the glc were trapped and submitted to mass spectral analysis, no indication of other components could be detected in the individual aromatic peak.

The aromatic distribution for the three isomeric trimethylcyclohexanes (1,1,2-; 1,1,3-; and 1,1,4-TMCH) are presented in Figs. 5, 6, and 7. The general aromatic distribution over the two catalysts is consistent for the three naphthenes—demethylation was the major pathway for chromia and isomerization to C₉-aromatics was the major reaction over Pt. Over chromia 85–90% of the conversion was demethylation

by loss of a *geminal*-methyl to yield the corresponding C₈-aromatic, e.g., 1,1,2-TMCH yielded *o*-xylene. The C₉-aromatics were the ones expected for isomerization by simple 1,2-methyl migration. In contrast, the naphthene conversion over Pt-Al₂O₃ produces mainly isomerization to form C₉-aromatics. The major C₉-aromatics from each of the three naphthene isomers are the ones that would result from 1,2-methyl migration in the reactant. The 1,1,2-TMCH forms primarily 1,2,3-trimethylbenzene; and 1,1,4-TMCH yields mostly 1,2,4-trimethylbenzene: the only aromatics possible by a 1,2-methyl migration. A single 1,2-methyl migration for 1,1,3-TMCH leads to two C₉-aromatics, 1,2,3- and 1,2,4-trimethylbenzene, with the 1,2,4-isomer being more probable because of less steric interaction of the methyl groups; the experimental results agree with this expectation. This isomerization must occur prior to the aromatic formation; the aromatics do not undergo significant isomerization after formation.

The aromatic product distribution from

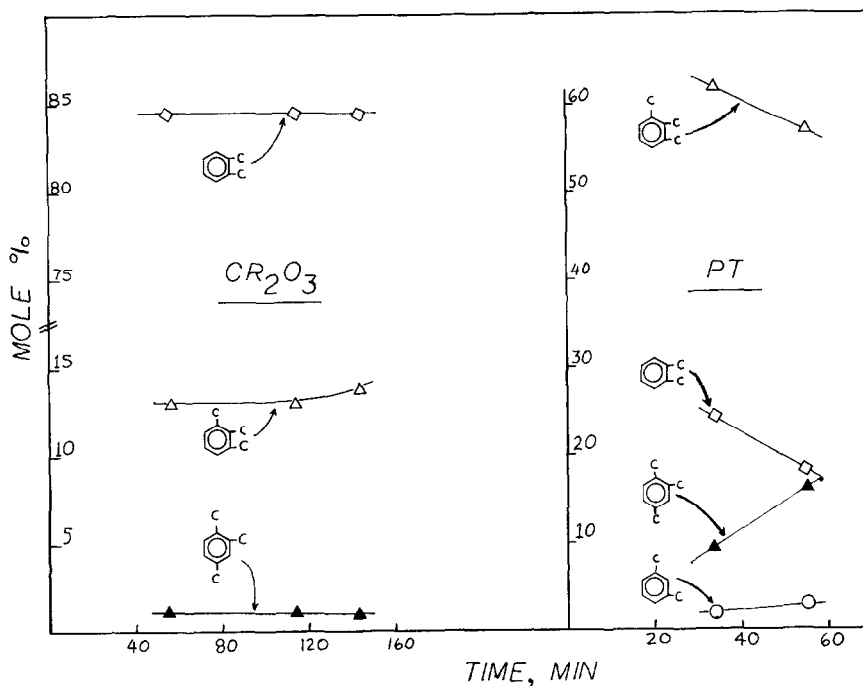


FIG. 5. Aromatic product distribution for the conversion of 1,1,2-trimethylcyclohexane over Pt (2) and chromia.

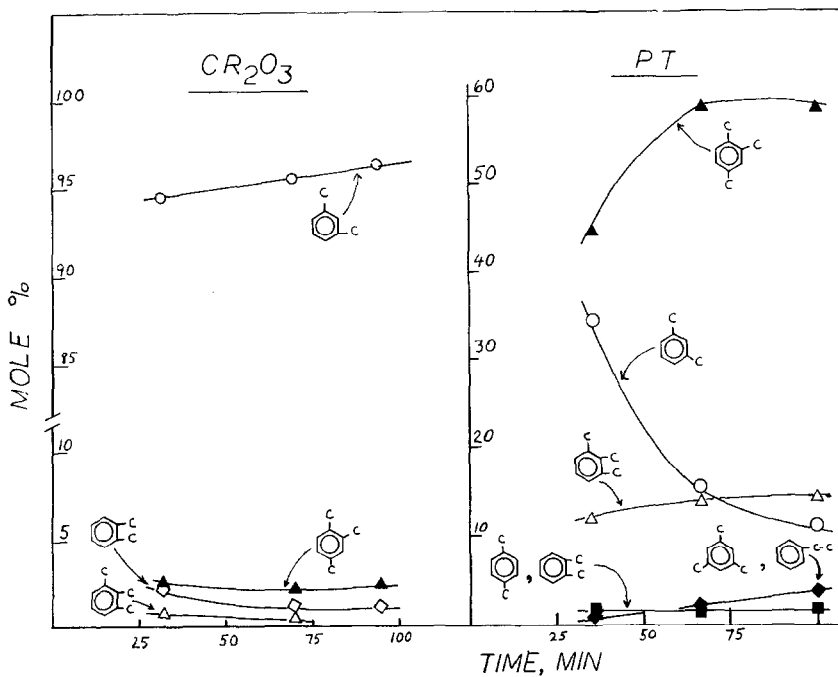


FIG. 6. Aromatic product distribution for the conversion of 1,1,3-trimethylcyclohexane over Pt (2) and chromia.

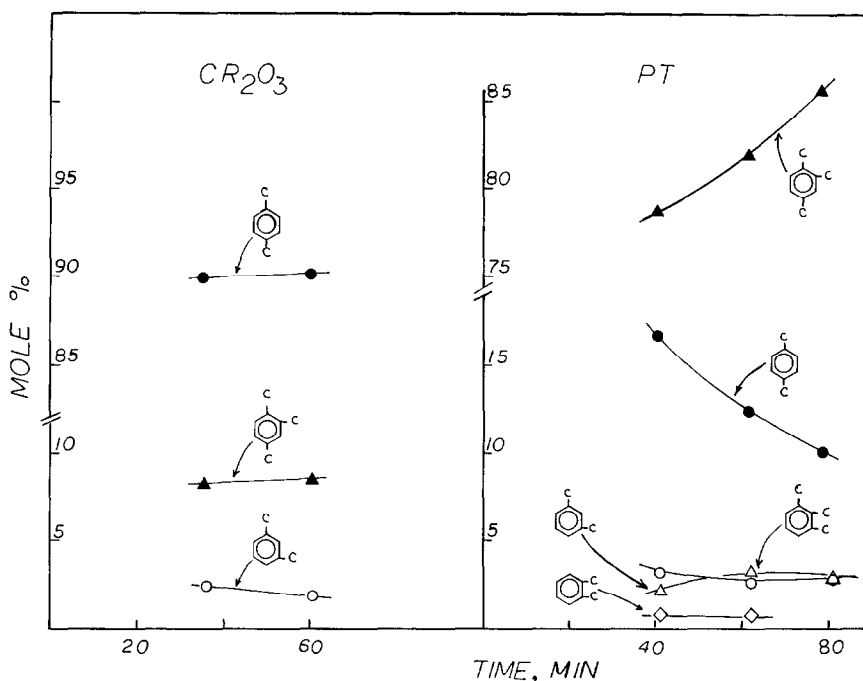


FIG. 7. Aromatic product distribution for the conversion of 1,1,4-trimethylcyclohexane over Pt (2) and chromia.

the dehydrocyclization of 2,2,4- and 2,2,5-trimethylhexane (TMH) are presented in Figs. 8 and 9. The conversion of both paraffins over chromia and Pt is similar in that the major aromatic product is the C_9 -aromatic, 1,2,4-trimethylbenzene: the product arising from an isomerization. Otherwise, there is little similarity for the products from the two paraffins. For both Cr_2O_3 and Pt, about 60% of the total aromatic from 2,2,5-TMH was 1,2,4-trimethylbenzene. The remaining C_8 - and C_9 -aromatic distributions were similar. *p*-Ethyltoluene and *m*-xylene were present in about the same amount as 1,2,3-trimethylbenzene and *p*-xylene (these latter two aromatics would be expected on the basis of 1,1,4-TMCH conversion). The other C_8 - and C_9 -aromatics are present in small amounts. For 2,2,4-TMH, 1,2,4-trimethylbenzene is again the major aromatic product but is only about 30% of the total aromatic compared to 60% for the 2,2,5-isomer. The other C_8 - and C_9 -aromatics are present in relative amounts that are quite different than expected from demethylation or simple 1,2-

methyl group migration. The major C_8 -aromatic over both catalysts is *m*-xylene but large amounts of the *o*- and *p*-isomers are also present. Likewise, the amount of *m*- and *p*-ethyltoluene is 20-30% of the total aromatics with more of the *p*-isomer formed over the chromia catalyst and more of the *m*-isomer over Pt. Also, about 15% of the C_8 - C_9 -aromatics over the Pt catalyst is 1,3,5-trimethylbenzene. Thus, the aromatic distribution is similar over both catalysts for a particular paraffin isomer and the aromatic isomer distribution for the 2,2,4-isomer apparently results from a more complicated isomerization than with the 2,2,5-isomer.

Direct six-carbon ring formation from 2,2,5- and 2,2,4-TMH would result in 1,1,4- and 1,1,3-TMCH, respectively. A comparison of the aromatic distribution from the C_9 -paraffins and the C_9 -naphthenes shows that over chromia very little (probably 15% or less based on the relative amount of *p*-xylene isomer) of the aromatic is formed from a common intermediate of adsorbed *geminal*-naphthene. Over the Pt

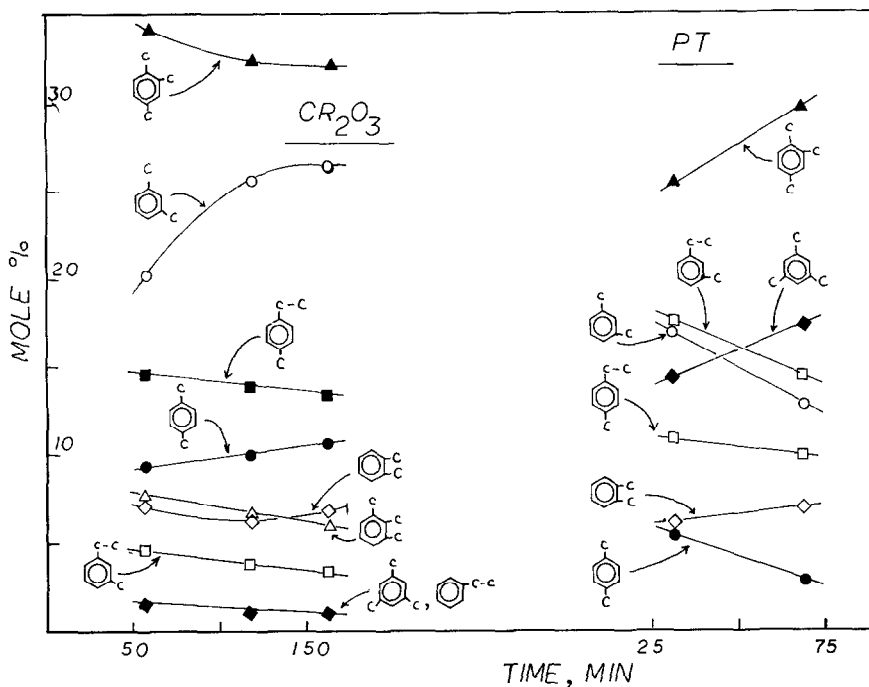


FIG. 8. Aromatic product distribution for the conversion of 2,2,4-trimethylhexane over Pt (2) and chromia.

As a catalyst, a common intermediate could be involved, but is not required, to a much greater extent since isomerization to yield 1,2,4-trimethylbenzene is the major pathway for both the paraffin and naphthene.

In general, the major conversion of the trimethylcyclohexanes over chromia was dealkylation to C_8 -aromatics, but over Pt it was isomerization; thus the catalyst was the major factor in determining the aro-

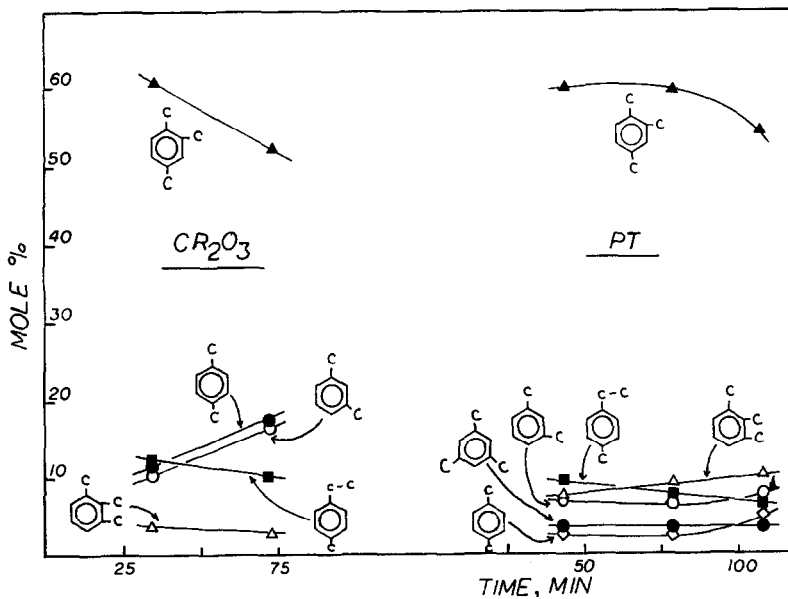


FIG. 9. Aromatic product distribution for the conversion of 2,2,5-trimethylhexane over Pt (2) and chromia.

matic distribution. In contrast, the distribution for the 2,2,4- and 2,2,5-TMH is nearly the same over both catalysts but depends on the reactant.

Three Pt-Al₂O₃ catalyst preparations—intended to be identical—were used in this study. The same “nonacidic” alumina preparation was used for each catalyst but the first preparation contained about twice as much K as the other two after the impregnation and washing. The first and third preparations are compared for the conversion of *n*-octane in Table 1. It is observed that there is little difference between the two catalysts for this reactant except that the first preparation was more active. In contrast, the Pt-Al₂O₃ catalysts are quite different for the conversion of 1,1-DMCH over the first and second preparations (Fig. 10). It is obvious that the major reaction pathway over the first preparation was demethylation but over the second preparation it was isomerization.

This difference in the Pt catalysts is also apparent when we compare the conversion of 1,1-DMCH over the first preparation with the three TMCH isomers over the third preparation. Over the first prepara-

TABLE 1
COMPARISON OF *n*-OCTANE CONVERSION OVER DIFFERENT PREPARATIONS OF Pt-Al₂O₃ CATALYSTS^a

Time on stream (min)	Ethylbenzene <i>m</i> - and <i>p</i> -xylene	<i>o</i> -Xylene	Total C ₈ -aromatic (%)
Pt (1)			
36	26	25	51
78	18	17	35
120	10	13	23
160	11	10	21
201	9	9	18
Pt (3)			
37	18	17	35
88	8	7	15
142	5	5	10

^a Run at 482°C; LHSV 0.3; and no carrier gas.

tion, the major conversion products were from the demethylation pathway but over the third preparation the major aromatics must result from an isomerization rather than demethylation. A comparison of the conversion products from 1,1,3-TMCH over the second preparation and the olefin 1,1,3-trimethyl- α -cyclohexene over the first

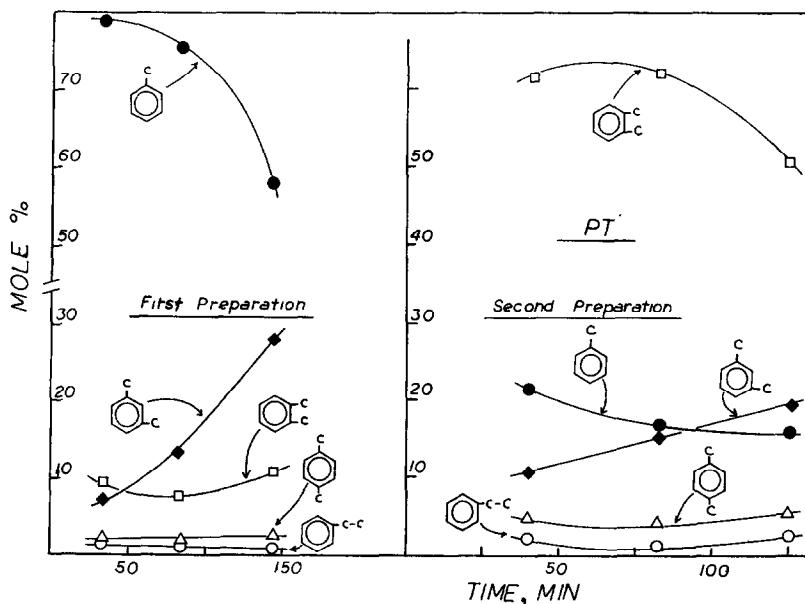


FIG. 10. Comparison of the aromatic products from 1,1-dimethylcyclohexane over Pt (1) and Pt (2).

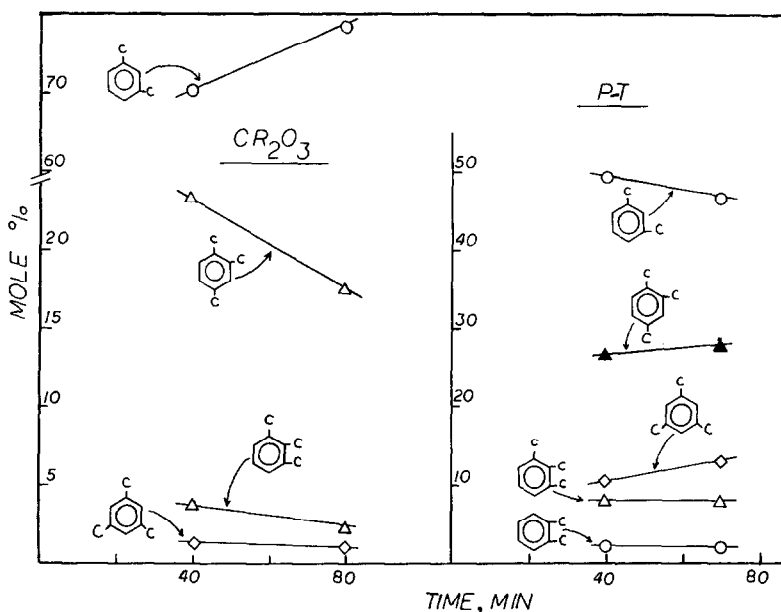


Fig. 11. Aromatic product distribution for the conversion of 1,1,3-trimethyl- α -cyclohexene over Pt (1) and chromia.

preparation (Figs. 6 and 11) shows that it is the catalyst preparation which determines the product distribution. The major reaction product from the cyclic olefin was the demethylation product, *m*-xylene. This would mean that the major reaction path-

way for the three TMCH isomers should be demethylation over the first catalyst preparation. The data shown in Fig. 12 for the conversion of 1,1,3-TMCH over the first and third Pt preparations confirm this, since demethylation is practically the only

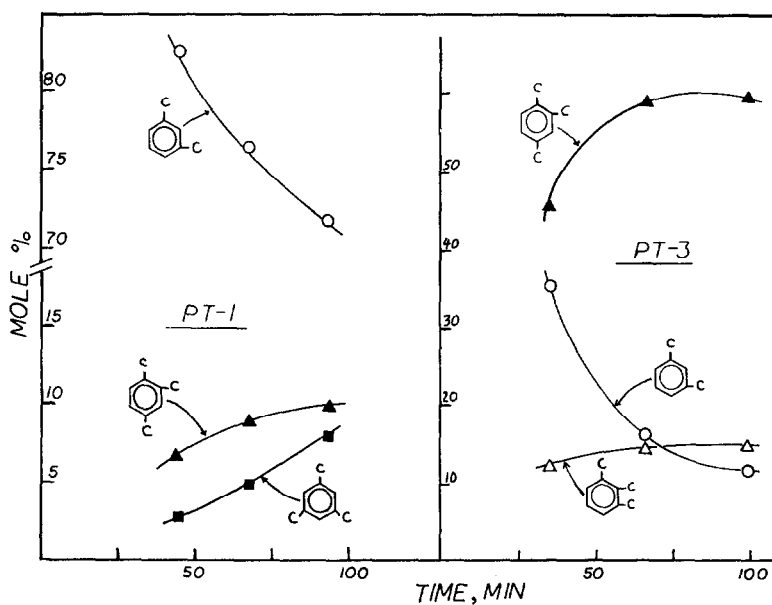


Fig. 12. Aromatic product distribution for the conversion of 1,1,3-trimethylcyclohexane over Pt (1) and Pt (3).

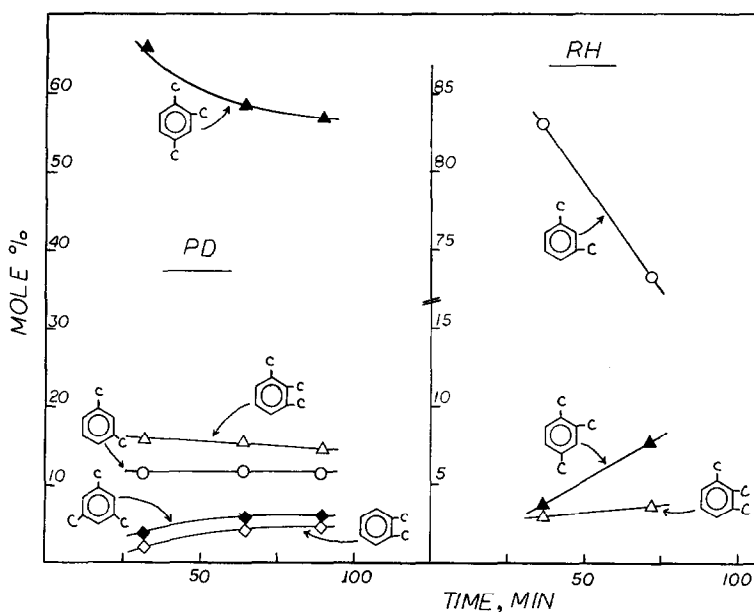


FIG. 13. Aromatic product distribution for the conversion of 1,1,3-trimethylcyclohexane over Pd- and Rh- Al_2O_3 .

reaction pathway over Pt (1), while the third preparation produces mostly isomerization products.

The aromatic products from 1,1,3-TMCH were obtained using a Pd- and Rh- Al_2O_3 catalyst (Fig. 13). The major

reaction pathway over the Rh catalyst was demethylation ($\approx 80\%$) but over the Pd catalyst it was isomerization ($\approx 90\%$). It has been concluded from hydrogenation studies (12) that the order of decreasing metal isomerization ability is Pd > Pt >

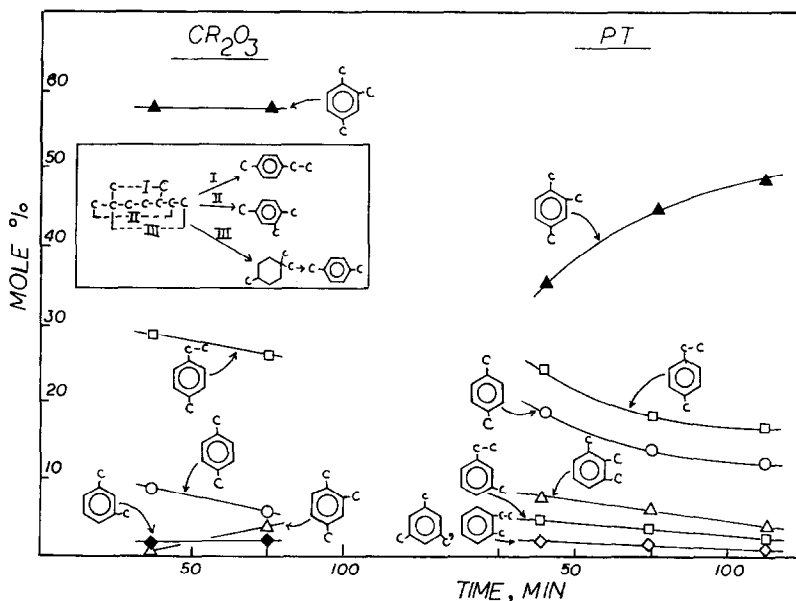


Fig. 14. Aromatic product distribution from the dehydrocyclization of 2,5-dimethylheptane over Pt (1) and chromia.

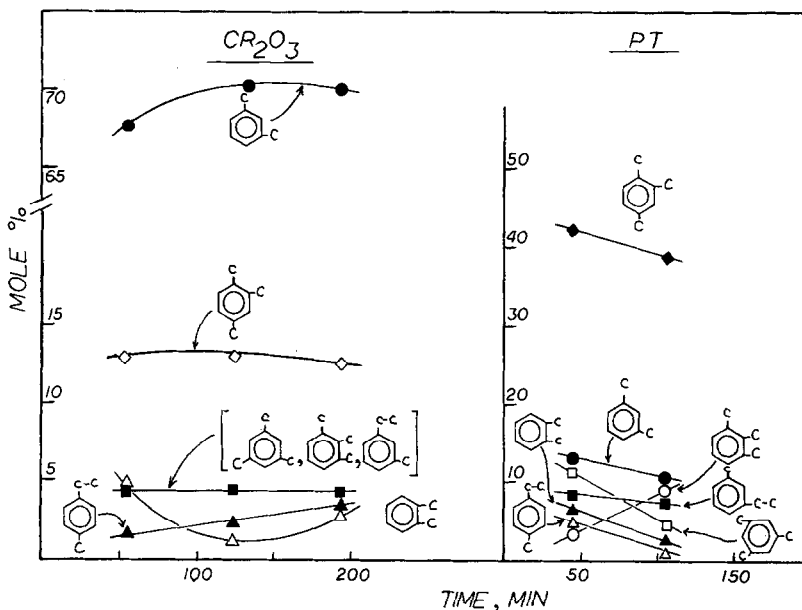


Fig. 15. Aromatic product distribution from the dehydrocyclization of 2,6-dimethyl-3-heptene over Pt (2) and chromia.

Rh—the same order as obtained for the 1,1,3-TMCH conversion. However, in view of the sensitivity of the demethylation selectivity to catalyst preparation, the ranking of the metals for isomerization for the above reactant must be accepted with caution.

The aromatics from the conversion of 2,5-dimethylheptane (DMHT) over chromia and Pt (1) are presented in Fig. 14. Products possible by direct six-carbon ring formation are shown in the insert. It is obvious that only those products from direct six-carbon rings are formed in significant amounts.

Figure 15 shows the distribution of aro-

matics from 2,6-dimethyl-3-heptene (DMHTE) over chromia and Pt (2). With this reactant, the only reaction pathway by direct six-carbon ring closure leads to the *geminal*-dimethyl naphthalene 1,1,3-TMCH. Over chromia the distribution is very similar to that obtained from 1,1,3-TMCH showing that the major aromatics are explained by direct six-carbon ring formation. Pt (2) yields a distribution rather similar to that from 1,1,3-TMCH over Pt (3). Comparing the data in Table 2 and Fig. 15, it is seen that much more demethylation occurred over Pt (1) than over Pt (2); also the addition of hydrogen did not increase the amount of demethylation.

TABLE 2
C₈- AND C₉-AROMATIC PRODUCTS IN THE FIRST LIQUID SAMPLE FROM DEHYDROCYCLIZATION OF 2,6-DIMETHYL-3-HEPTENE OVER Pt-Al₂O₃^a

	Aromatic distribution (% total C ₈ and C ₉)								
	Xylenes			Ethyltoluenes			Trimethylbenzene		
	<i>o</i>	<i>m</i>	<i>p</i>	<i>o</i>	<i>m</i>	<i>p</i>	135	124	123
Without H ₂	2	49	10		Traces		18	15	2
With added H ₂	6	41	2		Traces		18	18	7

^a Run at 482°C, LHSV 0.3.

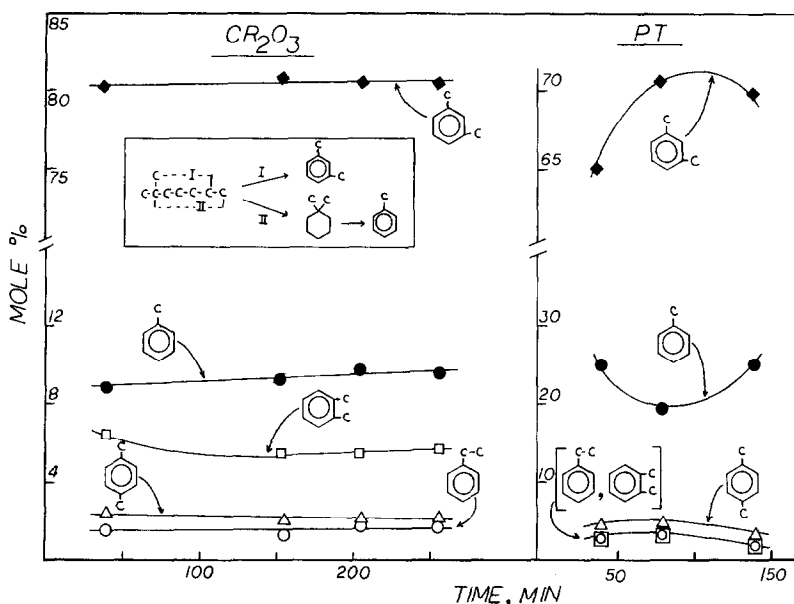


Fig. 16. Aromatic product distribution from the dehydrocyclization of 2-methylheptane over Pt (1) and chromia.

2-Methylheptane is another paraffin that can lead to a *geminal*-dimethyl naphthene, 1,1-DMCH. The amount of toluene in the aromatic products (Fig. 16) over both Pt (1) and chromia show that the *geminal*-dimethyl naphthene contributes significantly to the cyclization and, together with the amount of *m*-xylene formed, show that C_6 -ring formation is the major reaction pathway.

DISCUSSION

A comparison of the conversion of the *geminal* methylcyclohexanes over the Pt and chromia catalysts shows two groupings: (a) chromia and Pt (1) which give nearly identical aromatic distributions with demethylation the major reaction pathway; and (b) Pt (2) and (3) where the major pathway is one involving isomerization with little demethylation. Furthermore, comparing the aromatic distributions from the *geminal*-DMCH and -TMCH with the paraffins that would form these *geminal*-naphthenes by direct six-carbon ring closure yields three groupings: (a) those over Pt (1) where the distribution for the paraffin and corresponding naphthene are very similar with demethylation

the predominate reaction pathway; (b) those over Pt (2) and (3) where the distribution from the paraffin and the corresponding naphthene is similar but isomerization is the predominate reaction pathway; and (c) those over chromia where the distribution from the paraffin and the naphthene are much different.

Thus, over Pt (1) there seems to be little question about the dehydrocyclization pathway—it proceeds by direct six-carbon ring formation. A comparison of Pt (1) and chromia for naphthene conversion shows that both catalysts have the same action: mainly demethylation. Thus, it appears that, in those cases where a different distribution is obtained for the naphthene and paraffin, dehydrocyclization still occurs by a six-carbon ring intermediate and the distribution differs due to an isomerization of the reactant prior to the cyclization. Furthermore, this isomerization could be a dual-function metal-acid isomerization or it may only occur on the dehydrogenation site. It is even possible for this isomerization to occur by a dual-function pathway without the formation of appreciable amounts of the isomerized reactant in the final products (4a).

The distribution of the products from the *geminal*-dimethyl paraffins over Pt-Al₂O₃ catalysts is extremely sensitive to the preparation variables. Pt catalysts prepared by the same procedure and using the same "nonacidic" alumina support had very different demethylation activity relative to the isomerization activity. The more selective demethylation catalyst was almost twice as active for the dehydrocyclization of *n*-octane. There seems to be two possible explanations for the different demethylation-isomerization selectivity. On the one hand, the inclusion of KOH in the second wash would suggest that the lower isomerization activity of the first preparation may be due to the more complete neutralization of the alumina acidity which would decrease the dual functional metal-acid isomerization. On the other hand, the lower dehydrocyclization activity for *n*-octane of the second and third preparations would suggest a lower metal function activity. The most likely reason for this lower activity would be a lower metal surface area even though all three catalysts contain metal crystallites below the limits of X-ray determination. This lower activity could also explain the greater relative amount of isomerization provided the metal-catalyzed demethylation was also lower but the dual-functional isomerization activity remained near the same level for all three catalysts.

It is of interest to compare the present results with some from earlier studies. The aromatic distribution for the first sample from 1,1,3-TMCH over three of our catalysts is compared with that obtained by Maurel and Germain (13) in Fig. 17. Pt (1) gave a distribution nearly identical to Maurel and Germain's distribution from a higher loading Pt catalyst at 300°C but the distribution from Pt (3) contains much more of the aromatics from an isomerization. The distribution for Pt (1) is also similar to that obtained by Pines *et al.* (14) who reported only *m*-xylene as the product from 1,1,3-TMCH over a 7% Pt-Al₂O₃ catalyst at 330°. The distribution from 1,1-DMCH does not vary significantly from that obtained by Pines and Chen

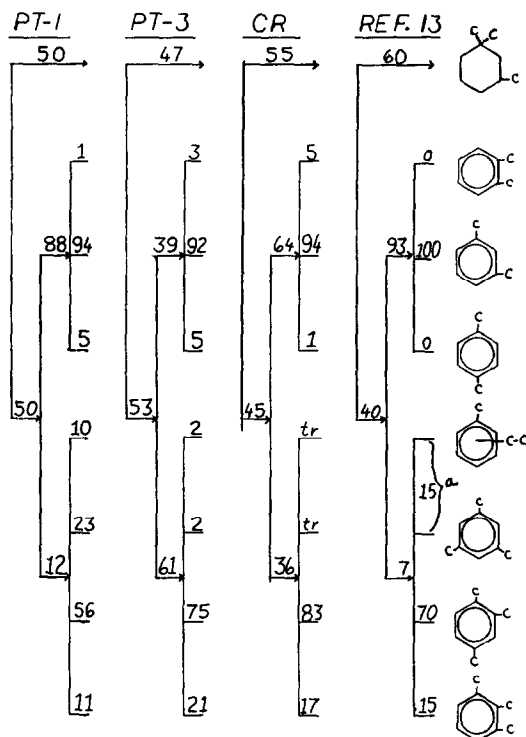
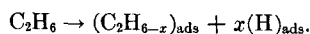


FIG. 17. Comparison of the aromatic distribution from 1,1,3-trimethylcyclohexane (first liquid sample) over Pt (1), Pt (3), and chromia with those from Ref. (13). ^aEthyltoluenes and 1,3,5-trimethylbenzene are combined from Ref. (13).

(15) for this reactant over a similar catalyst.

The conversion of both 1,1-DMCH and the three TMCH over chromia and Pt (1) proceeds mainly by demethylation. This reaction pathway presumably involves hydrogenolysis. For ethane, the kinetics of hydrogenolysis suggests a mechanism in which dehydrogenation determines the kinetics (12):



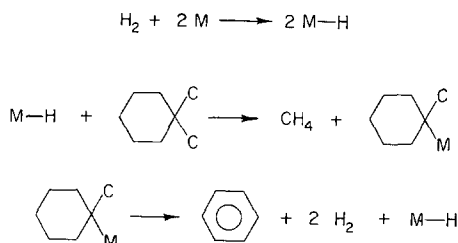
One could expect a similar demethylation mechanism for the geminal DMCH. However, the addition of hydrogen to the reactant charge increased the amount of demethylation (see Table 3) contrary to the expectation for a hydrogen pressure dependence with a negative order larger than one for the above mechanism. This suggests the following mechanism may be

TABLE 3
INFLUENCE OF ADDED HYDROGEN ON THE
AMOUNT OF DEMETHYLATION OCCURRING
DURING CONVERSION OF 1,1,3-TRI-
METHYLCYCLOHEXANE OVER $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3^a$

No added hydrogen		Hydrogen: hydro- carbon, 1:2.5	
Time on stream (min)	<i>m</i> -Xylene/ total aromatic (%)	Time on stream (min)	<i>m</i> -Xylene/ total aromatic (%)
33	59	33	98
72	66	70	98
94	67	94	98

^a Run at 482°C; LHSV 0.3; catalyst reduced at 550°C in flowing H_2 .

more applicable for the demethylation of the quaternary carbon naphthenes:



For strong acid solutions, the addition of a proton to a hydrocarbon resulting in the formation of methane has been reported. The M-H bond could be expected to behave similarly provided M was a sufficiently strong electron acceptor. Kinetic studies of hydrogenolysis over wider hydrogen pressures and over metal catalysts with varying electron deficiencies are clearly needed; a start in this direction has been made by Sinfelt (16).

The hydrogen pressure dependence for the quaternary carbon paraffins must be different from that observed at atmospheric pressure for ethane because conversion of 2,2,5-TMH over Pt (1) at 400 psig (10:1, hydrogen:hydrocarbon ratio) resulted in only C_8 and lower carbon aromatics (17). At the same time there was a larger conversion of 2,2,5-TMH to $<\text{C}_8$ paraffins and naphthenes than to aromatics. This suggests that hydrogenolysis of a geminal-methyl group was the initial reaction in 2,2,5-TMH conversion.

In summary, we conclude that this study has demonstrated that the major dehydrocyclization pathway for paraffins containing a quaternary carbon and those which can form a quaternary carbon in naphthene is by direct formation of six-carbon rings. The catalytic character of chromia and Pt is similar for these reactants with the exception that chromia may have more isomerization activity than a properly prepared Pt-alumina catalyst.

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