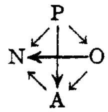
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF ILLINOIS INSTITUTE OF TECHNOLOGY]

Catalytic Aromatization of Branched Chain Aliphatic Hydrocarbons

BY V. I. KOMAREWSKY AND W. C. SHAND

The process of catalytic aromatization (dehydrocyclization) of aliphatic hydrocarbons discovered in 1936 already has found a wide industrial application.

However, the mechanism of the reaction presents many unsolved problems. Most important among these is a clarification of the path by which an aliphatic hydrocarbon is transformed into an aromatic, ring compound. This might best be illustrated according to a scheme (Fig. 1) presented by Hoog and co-workers.[1]



P, paraffin
O, olefin
N, naphthene
A, aromatic

Fig. 1.

This scheme indicates that the aromatic hydrocarbons can be formed from paraffin by four different mechanisms: POA, PNA, PONA and PA.

There are two distinct types of dehydrocyclization catalysts: 1, **metal catalysts** such as platinum[2] and nickel[3] on carriers which produce aromatization without deposition of carbon or any formation of unsaturated (olefin or diolefin) hydrocarbons—at a temperature of 300°, and 2, **oxide catalysts** such as oxides of chromium vanadium and molybdenum[4] on carriers, whose aromatizing action is accompanied by a formation of unsaturated hydrocarbons. The oxide catalysts require for their action, temperature of about 500°. The reaction with oxide catalysts is usually accompanied by carbon deposition. With the metal catalysts there is no indication of any intermediate formation of either olefin or naphthene hydrocarbons; and if they are formed, their dehydrogenation to aromatics is so fast that none are detected in the reaction products. With the oxide catalysts little evidence is available to determine whether the reaction goes through the olefin path (POA), naphthene path (PNA) or the combined olefin–naphthene mechanism (PONA).

Some kinetic studies[5] show indirectly that olefins are intermediate in this process.

It was thought that a direct indication of whether the aromatization of paraffins goes through the intermediate step of naphthene formation is possible from the following considerations: in previous investigations aromatization was accomplished only with aliphatic hydrocarbons whose structure allowed the formation of an aromatic ring.[6] In such case a necessary condition is that the original hydrocarbon must contain at least six carbon atoms in a straight chain; each of these carbons must possess at least one hydrogen. There are, however, aliphatic hydrocarbons whose structures prohibit the formation of aromatics but would allow the cyclization to a six-carbon naphthene ring. Aliphatic hydrocarbons with six (or seven) carbon atoms in a straight chain but containing quaternary carbon atom (or atoms) constitute an example of this structure (Fig. 2).

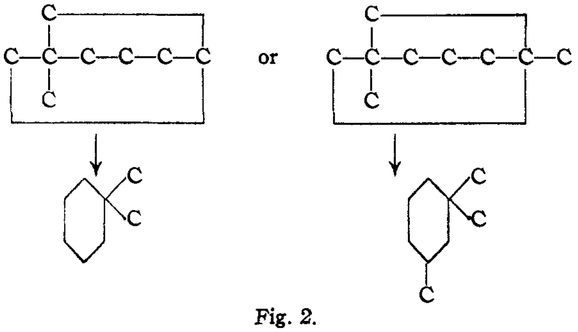


Fig. 2.

If the aromatization of paraffins goes through the intermediate step of naphthene formation (PNA or PONA of the scheme), the dehydrogenation of aliphatic hydrocarbon containing quaternary carbon would be expected to stop at this stage of cyclization (Fig. 2).

With this idea in mind the following aliphatic hydrocarbons were subjected to the action of chromia on alumina catalyst: **2,2-dimethylhexane, 2,2-dimethylhexene-3** and **2,2-dimethylheptane.**

There are also aliphatic hydrocarbons whose structure will allow them to cyclize in more than one way, depending upon which carbon atoms participate in the ring closure (Fig. 3).

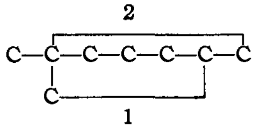


Fig. 3.

Aromatization will take place in case of the first mechanism (1) whereas naphthene formation will result in the second (2). Representative of such aliphatic hydrocarbons: **2-methylheptane,**

---

[1] Hoog, Verheus and Zuiderweg, *Trans. Faraday Soc.*, **35**, 993 (1939).

[2] Kazansky and Plate, *Ber.*, **69**, 1862 (1936).

[3] Komarewsky and Riesz, THIS JOURNAL, **61**, 2524 (1939).

[4] *E. g.*, Grosse, Morrell and Mattox, *Ind. Eng. Chem.*, **32**, 528 (1940); Turkevich and Young, THIS JOURNAL, **63**, 519 (1941).

[5] Pitkethly and Steiner, *Trans. Faraday Soc.*, **35**, 979 (1939).

[6] Traces of aromatics (1–3%) were obtained from 2,2,4-trimethylpentane in the presence of chromia[1] and molybdenum oxide[4] catalysts.

TABLE I

EXPERIMENTAL RESULTS

Catalyst (60 ml.); chromia (10%) on alumina; temperature 465°; space velocity 0.05

Hydrocarbon	Liquid recovery, weight % of charge	n^{20}D	Composition of the liquid, volume %			Gas formed in ml. per 1 ml. of charge	Gas composition, volume %	
			Paraffin	Olefin	Aromatic		Hydrogen	Paraffin
2,2-Dimethylhexane	60.0	1.4480	12	38	50[a]	200	77.0	23.0
2,2-Dimethylhexene-3	44.0	1.4655	5	30	65[a]	180	58.4	41.6
2,2-Dimethylheptane	38.0	1.4620	7	28	65[a]	200	51.0	49.0
2-Methylheptane	82.5	1.4825	4	16	80[a]	410	91.0	9.0
2-Methylheptene-6	76.0	1.4900	2	13	85[a]	370	88.0	12.0
2,3-Dimethylhexane	76.0	1.4720	6	24	70[b]	360	86.2	13.8

[a] *m*-Xylene. [b] *o*-Xylene.

and **2-methylheptene-6** were subjected to the action of chromia–alumina.

In addition the aromatization of **2,3-dimethylhexane** was carried out in the presence of the same catalyst.

Experimental Part

Apparatus and Procedure.—The hydrocarbons were passed at the rate of 3 ml. per hour through a glass tube of 14 mm. diameter over 60 ml. of catalyst (space velocity 0.05). The tube was placed in a horizontal electric furnace. The receiver end of the catalytic tube was supplied with a combination water and dry-ice condenser. The non-condensable gases were collected and measured in a gas-holder.

Catalysts. Chromia–Alumina (10% Cr_2O_3, 90% Al_2O_3 by weight) was prepared by impregnation of "activated alumina" grade A, Alcoa Co. (8–10 mesh size) with a chromium nitrate water solution. The mixture was dried on a steam-bath, calcined at 500° and activated with hydrogen, for one hour at 500°. This catalyst at 465° and a space velocity of 0.05 gave 85% of aromatization of pure *n*-heptane. **Activated Alumina** grade A, Alcoa Co. was used as alcohol dehydration catalyst. **Platinum (5% by weight) on alumina** was used as olefin hydrogenation catalyst. This catalyst was prepared by impregnation of activated alumina with platinum chloride, drying and reduction.

Synthesis of Aliphatic Hydrocarbons: 2,2-Dimethylhexene-3 was prepared by condensation of the Grignard complex, *t*-butylmagnesium bromide with butyraldehyde in ether solution.[7] The condensation product was hydrolysed to 2,2-dimethyl-3-hexanol. The alcohol was dehydrated over alumina catalyst at 350° to 2,2-dimethylhexene-3. The crude olefin was fractionated in a 100 theoretical plate Podbielniak column, with heligrid packing. The pure olefin has a boiling point of 99–100°; n^{20}D 1.4067.

2,2-Dimethylhexane was obtained by hydrogenation of 2,2-dimethylhexene-3 in the presence of platinum–alumina catalyst at 180°. The hydrocarbon has a b. p. of 107°, n^{20}D 1.3930, and was completely stable toward potassium permanganate solution.

2,2-Dimethylheptane was prepared by condensation of *t*-butylmagnesium chloride with *n*-valeraldehyde. The original product was hydrolyzed to 2,2-dimethyl-3-heptanol. The alcohol was dehydrated as before and the obtained olefin was hydrogenated. The boiling point of the pure hydrocarbon was 130–131°; n^{20}D 1.4024.

6-Methylheptene-1 was prepared by condensation of allyl chloride with isoamylmagnesium chloride in an anhydrous ether solution. After removal of ether and fractionation of crude olefin the material was obtained: b. p. 115–116°; n^{20}D 1.4122.

2-Methylheptane was obtained by hydrogenation of the preceding product. The material was obtained with b. p. 117°, n^{20}D 1.3945, completely stable toward potassium permanganate solution.

2,3-Dimethylhexane was prepared by condensation of isopropylmagnesium chloride with methyl *n*-propyl ketone in ether solution. The condensation product was hydrolyzed to 2,3-dimethyl-3-hexanol. The alcohol was dehydrated to olefin, the olefin hydrogenated to paraffin and fractionated; b. p. 115–115.5°; n^{20}D 1.4010.

***n*-Heptane** from California Chemical Co., b. p. 98°; n^{20}D 1.3876.

Analysis of the Products.—Liquid products were fractionated on a 100-plate Podbielniak column. The paraffin-olefin fraction was analyzed for olefin content by bromine titration. The aromatic fraction (olefin free) was identified by preparation of derivatives.[8] Gaseous products of the reaction were analyzed by the Goeckel method. Experimental results are represented in Table I.

Discussion of Results

Analyzing the results obtained it may be noted that the liquid products in all the experiments consisted only of olefin, aromatic and unreacted paraffin hydrocarbons. In no case was there any evidence of the presence of naphthene hydrocarbons. The conversion of hydrocarbons with a "prohibitive" structure to aromatics in comparatively high yields was quite unexpected and novel. In all cases the principal aromatic hydrocarbon produced was ***m*-xylene** which indicates that an isomerization takes place at some point in the dehydrocyclization reaction. In the case of 2,2-dimethylheptane the resulting aromatic was also *m*-xylene which indicates that besides cyclization a formation of a methyl radical took place. This can be seen from the high methane content of the reaction gases.

With hydrocarbons which can cyclize by either of two possible paths, one of which does not include a prohibitive naphthene structure, it may be noted that higher liquid recoveries and lower gaseous paraffin yields were found. Thus 2-methylheptane and 2-methylheptane-3 gave *m*-xylene as would be expected if the reaction proceeded through mechanism (2) Fig. 3.

With 2-3 dimethylhexane the expected formation of *o*-xylene took place.

Conclusions

1. Aliphatic hydrocarbons, containing a quaternary carbon atom, which does not permit direct aromatization, dehydrocyclize with the production of aromatics in the presence of chromia-alumina catalyst.
2. This indicates that isomerization takes place during dehydrocyclization.
3. Aliphatic hydrocarbons whose structure allows cyclization in more than one way, dehydrocyclize to aromatics by means of a mechanism which permits their direct formation.

CHICAGO, ILLINOIS RECEIVED MARCH 23, 1944

---

(7) Boord and Henne, Section of Petroleum Chemistry, Am. Chem. Soc. Meeting at Detroit, Sept. 11, 1940.

(8) 2,4,6-Trinitro-*m*-xylene, 1,2-dimethylbenzene-4-sulfonamide.