[Contribution from the Research Laboratories of Universal Oil Products Company]

Reaction of Aromatics in the Presence of Dehydrogenation Catalysts. I. Action of Chromia–Alumina on Benzene, Toluene, Butylbenzenes and Bibenzyl

By William J. Mattox and Aristid V. Grosse

Recent investigations in the conversion of various types of hydrocarbons to aromatics by the action of dehydrogenation or aromatization catalyst have in a number of instances necessarily involved the question of what action such catalysts exert on the aromatics formed. A number of other alkyl aromatics, or compounds which in the presence of hydrogen are converted to these alkyl aromatics, capable of yielding polycyclic aromatics, have also been subjected to the action of these catalysts. The present series of papers summarizes typical data obtained in these investigations on benzene and substituted benzenes containing up to eight carbon atoms in two or more alkyl groups.

The catalytic treatment of benzene with metals having dehydrogenating properties has been reported by a number of investigators.[1] With iron, platinum, copper, nickel and nickel–chromium, biphenyl has been the main reaction product accompanied by diphenylbenzene, triphenylene, and other polycyclic aromatics and, especially with platinum, iron and nickel, varying amounts of hydrogen, methane and carbon. Benzene vapor when passed through lead at 750° has been reported to yield high percentages of biphenyl.[2] Oxide catalysts have been investigated only to a minor extent. Molybdena–alumina at 550° had little effect[3] while nickel oxide and manganous oxide[4] resulted primarily in carbon and hydrogen formation. Oxides of barium, zinc, aluminum, lead and silicon[5,6,7] were effective only at temperatures above 600°.

Toluene when subjected to the action of lead oxide[8] and platinum[9] at red heat yielded a variety of products including benzene, biphenyl, phenanthrene, anthracene, bitolyl, stilbene and probably *p*-methyldiphenylmethane. The formation of any of these products was not observed when using molybdena–alumina,[3] silica,[10] or iron and copper catalysts.[11]

Moldavski and co-workers[12] passed *n*-butylbenzene over chromic oxide gel at 472° and received a product containing 12% of naphthalene.

Meyer and Hoffman[9] by passing bibenzyl over a platinum wire at red heat obtained anthracene as the chief product with lesser amounts of stilbene and toluene. Dreher and Otto[13] decomposed bibenzyl by passage over pumice at red heat and reported the products as toluene and stilbene with small amounts of phenanthrene.

The conditions employed in this investigation were not the most favorable for any particular hydrocarbon but were chosen so that a reasonable conversion could be expected. Chromia–alumina catalysts were selected as being generally suitable for hydrocarbons and of a type in present commercial use.

Although benzene and toluene gave, under the conditions employed, comparatively low yields of biphenyl and anthracene, respectively, the absence of other aromatics in the reaction products is significant in view of the work of previous investigators.

The naphthalene yields of 51–55% per pass obtained from *n*-butylbenzene show a considerably increased efficiency over the yield of less than 12% reported by Moldavski and associates for a chromic oxide gel catalyst.

The direct conversion of phenyl *n*-propyl ketone to naphthalene was of interest since in the dehydrogenation more than sufficient hydrogen should be made available for the reduction of the ketone to butylbenzene. However, in the absence of extraneous hydrogen the naphthalene yields were low and the rapid accumulation of carbonaceous deposits soon deactivated the catalyst. The simultaneous formation of water and its known poisoning effects on chromia–alumina[14] probably accounts for the fact that even in the presence of added hydrogen no appreciable quantities of naphthalene were obtained at temperatures below about 550°.

Of the two apparently equally possible polynuclear aromatics to be obtained from *p*-di-*n*-butylbenzene, phenanthrene was the only one formed in any appreciable amount. No trace of anthracene was observed.

The dehydrogenation of bibenzyl to stilbene without phenanthrene formation appears unique

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(1) G. Egloff, "Reactions of Pure Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1937, pp. 504, 526.

(2) K. G. Andrianov, F. Kuitner and V. Titova, *Org. Chem. Ind.* (U. S. S. R.), **4**, 161–164 (1937).

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(6) V. N. Ipatieff, This Journal, **55**, 3696 (1933).

(7) Y. Kosaka, *J. Fuel Soc.* (Japan), **7**, 892 (1928).

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(10) Y. Kosaka, *J. Soc. Chem. Ind.*, Japan, Supplement, **32**, 298B, 299B (1929).

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(12) B. L. Moldavski, G. D. Kamusher and M. V. Kobyl'skaya, *J. Gen. Chem.* (U. S. S. R.), **7**, 169–178 (1937); *Refiner and Natural Gasoline Mfg.*, **18**, 118–122 (1939).

(13) E. Dreher and R. Otto, *Ann.*, **154**, 176 (1870).

(14) H. S. Taylor and J. Turkevich, *Trans. Faraday Soc.*, **35**, 921 (1939); D. J. Salley, H. Fehrer and H. S. Taylor, This Journal, **63**, 1131 (1941); W. J. Mattox, *ibid.*, **66**, 2059 (1944).

in view of Zelinsky and Titz's[15] quantitative conversion of stilbene to phenanthrene by dehydrogenation over platinized charcoal at 300°. However, the further conversion of stilbene to phenanthrene by the chromia–alumina may be retarded by the stilbene in a manner similar to the retardation of aromatization observed in the presence of aliphatic olefins.[3,16]

Experimental

Apparatus and Procedure.—The apparatus and the procedure by which the dehydrogenations were carried out were essentially the same as those described previously.[17] All tests were made at atmospheric pressure. Space velocity refers to volumes of liquid charge per hour per volume of catalyst space. The analysis of the products of the dehydrogenations will be described for the individual hydrocarbons.

Materials.—Merck C. P. benzene and toluene were used without further purification. Bibenzyl was obtained from Eastman Kodak Company and had a melting point of 50–51°. *n*-Butylbenzene prepared by reduction of phenyl *n*-propyl ketone with amalgamated zinc and hydrochloric acid had a boiling point of 181–183°, n^{20}_D 1.4987, d^{20}_4 0.873.

Di-*n*-butylbenzene was prepared by the reduction of *p*-*n*-butyl-N-butyrophenone (b. p. 136° [3.5 mm.]; m. p −13.5°; d^{20}_4 0.9461; n^{20}_D 1.5139), the ketone being obtained in 44% yield by the action of *n*-butyryl chloride on *n*-butylbenzene in carbon disulfide solution with aluminum chloride as catalyst. The reduction yielded 68% of dibutylbenzene having the following properties: b. p. 100° (2.5 mm.); m. p. −31°; d^{20}_4 0.8555; n^{20}_D 1.4883.

The catalysts used were chromium oxide-alumina composites, prepared by the general method described by Grosse, Morrell and Mattox,[17] calcined in air and reduced for ten to fifteen minutes with hydrogen at the temperature employed in the dehydrogenation. A fresh portion of catalyst was used for each test. Catalyst A contained 4 wt. % chromium oxide and Catalyst B 10 wt. % of the oxide.

Reaction of Benzene.—Dehydrogenation of benzene at 550° and 0.06 space velocity gave a 2.6 wt. % yield of biphenyl per pass. At 600° the once-through yield was increased to 4.4%. The calculated recycle yields amounted to 15–20%. The unreacted benzene, removed from the reaction products by distillation at atmospheric pressure, solidified at 0°, contained no olefinic hydrocarbons, and had a refractive index of 1.5011 (20°). The biphenyl residue was crystallized from hot alcohol: m. p., 69°, mixed m. p., 69°. A summary of these tests is shown in Table I.

TABLE I

DEHYDROGENATION OF BENZENE, CATALYST A

Temperature, °C.	550	600
Space velocity	0.06	0.06
Yields, wt. % of charge		
Benzene	86.5	69.8
Biphenyl	2.6	4.4
Gas	1.7	3.4
Carbon	5.7	17.4
Unaccounted	−3.5	−5.0
Biphenyl yield, % of benzene converted	20.0	14.8
Analysis of gas, mole %		
H_2	89.0	91.4
CO	2.6	1.4
Hydrocarbons	8.4	7.2

Reaction of Toluene.—The passage of toluene at a space velocity of 0.19 over catalyst A at 550°, resulted in the formation of anthracene amounting to 1% by weight of the total charge per pass (unreacted toluene, 93.2%, gas, 1.9%, catalyst carbon, 3.3%, unaccounted, 0.6%) or to 16% of the toluene decomposed. The recovered anthracene, separated from the unreacted toluene by distillation, had a melting point of 208°, and a mixed melting point of 205° with pure anthracene. The anthracene was further identified by oxidation to anthraquinone, melting point 270°.

Dehydrogenation of *n*-Butylbenzene.—The dehydrogenation of *n*-butylbenzene with Catalyst A was investigated at 500° and space velocities of 0.21, 0.38 and 0.80. The recovered liquid products were filtered to separate naphthalene which solidified on cooling to room temperature. The filtrates were then distilled to 190° to separate unreacted butylbenzene and lower boiling hydrocarbons from dissolved naphthalene. The naphthalene fractions remaining in the distillation flasks solidified on cooling and were combined with the naphthalene separated by filtration and crystallized from hot alcohol. The melting point of the recrystallized naphthalene from each of the tests was 80°. These tests are summarized in Table II.

TABLE II

DEHYDROGENATION OF *n*-BUTYLBENZENE

Catalyst A; temperature, 500°

Space velocity	0.80	0.38	0.21
Yields, wt. % of charge			
Liquid fraction	73.4	70.7	66.7
Gas	16.2	15.7	17.0
Carbon	13.7	11.8	12.9
Unaccounted	+3.3	−1.8	−3.4
Wt. % naphthalene in liquid fraction	69.8	77.8	79.7
Naphthalene yield, wt. %/pass	51.2	55.0	53.2
Analysis of gas, mole %			
H_2	75.5	72.4	71.7
CO	2.7	3.3	3.1
CH_4	11.0	7.6	7.5
C_2H_6		7.9	9.4
C_3H_8	4.8	6.0	6.1
C_2H_4	0.6	0.2	0.2
C_3H_6	2.6	1.3	.9
C_4	2.0	0.3	1.1
C_5	0.8	1.0	0.0

Recycle yields could not be calculated accurately from the data obtained in these tests because of the difficulty of determining quantitatively the *n*-butylbenzene in the hydrocarbon recovery.

Dehydrogenation of Phenyl *n*-Propyl Ketone.—The ketone was vaporized, mixed with seven moles of hydrogen, and passed over Catalyst B at 600°. The space velocity of the ketone was 0.23 and the reaction period one hour. The following yields were obtained as weight per cent. of the ketone charged: total liquid, 52.6%; water, 8.0%; gas, 21.4%; and catalyst deposit, 18.0%. After removing 35.6 wt. % of a fraction boiling below the naphthalene range, a crude naphthalene fraction was obtained which solidified on cooling to room temperature and which amounted to 34 wt. % of the charge. Removal of a small amount of brownish oil from the crude fraction by means of a porous tile dish followed by sublimation yielded naphthalene melting sharply at 80°.

Dehydrogenation of *p*-Di-*n*-butylbenzene.—The dehydrogenation of *p*-di-*n*-butylbenzene with Catalyst A was investigated at 500° and space velocities of 0.20 and 0.38. These tests are summarized in Table III. The recovered

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[15] N. D. Zelinsky and J. N. Titz, *Ber.*, **62B**, 2869–2873 (1929).

[16] H. S. Taylor and H. Fehrer, THIS JOURNAL, **63**, 1387 (1941).

[17] A. V. Grosse, J. C. Morrell and W. J. Mattox, *Ind. Eng. Chem.*, **32**, 528 (1940); Reprinted in Universal Oil Products Company Booklet No. 241.

liquid products from each of the above tests were distilled to 260° to separate unconverted di-butylbenzene and lower boiling fractions. The residual fraction boiling above 260° solidified on cooling to room temperature and was extracted with hot 80% alcohol to separate phenanthrene (solubility 5 g. per 100 cc.) from any anthracene present which is comparatively insoluble in dilute alcohol. After one recrystallization from the hot, dilute alcohol the phenanthrene had a melting point of 100° which was not lowered when mixed with an authentic sample.

The residue from the extraction with dilute alcohol was a dark gummy oil in which no anthracene could be detected.

TABLE III

DEHYDROGENATION OF *p*-DI-*n*-BUTYLBENZENE

Catalyst A; temperature, 500°

Space velocity	0.38	0.20
Yields, wt. % of charge		
Total liquid fraction	70.2	53.8
Toluene	0.5	0.3
Paraffins 110–120°	1.4	1.0
Aromatics 120–150°	4.6	3.3
Aromatics 150–175°	6.1	4.6
Aromatics 175–200°	8.6	6.5
Aromatics 200–260°	27.6	20.7
Phenanthrene	17.6	14.3
Residue	3.8	3.1
Gas	11.0	20.0
Carbon	18.8	26.2
Wt. % phenanthrene in liq. frac.	25.1	26.6

The composition of the gas from the 0.2 space velocity test in mole % was: H_2, 74.4%; CH_4, 7.0%; C_2H_4, 0.5%; C_2H_6, 7.0%; C_3H_6, 1.1%; C_3H_8, 7.1%; and C_4, 2.9%.

Dehydrogenation of Bibenzyl.—A 25 wt. % bibenzyl–75% benzene solution was passed over Catalyst B at 550°, atmospheric pressure, and 1 space velocity during a reaction period of one hour. The recovered liquid products amounted to 95.4 wt. % of the total charge from which a mixture of stilbene and isostilbene was separated by distillation. Stilbene was identified as α-stilbene dibromide, melting point 237°. Toluene was identified as symmetrical trinitrotoluene, melting point 80°. The gas contained 92.3 mole % hydrogen and 7.7% paraffins having a carbon index of 1.21. The following yields were obtained as weight per cent. of the bibenzyl charged: stilbene, 43.1%; benzene, 9.1%; toluene, 26.8% unreacted bibenzyl and unidentified lower boiling hydrocarbons, 2.5%; gas, 4.0%; and catalyst deposit, 14.5%. No detectable quantity of phenanthrene was found in the reaction products.

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Summary

The action of chromia–alumina on benzene, toluene, *n*-butylbenzene, *p*-di-*n*-butylbenzene, phenyl *n*-propyl ketone and bibenzyl at 500–600° has been investigated.

Biphenyl and anthracene were formed from benzene and toluene, respectively, without the formation of detectable amounts of other aromatics.

Naphthalene yields of 51–55 wt. % per pass were obtained from *n*-butylbenzene.

Similar dehydrogenations with *p*-di-*n*-butylbenzene gave phenanthrene yields of 14–18 wt. % per pass. Anthracene was not formed in any appreciable amount.

Dehydrogenation of phenyl *n*-propyl ketone resulted in the formation of napththalene which at 600° amounted to 34 wt. % per pass.

Dehydrogenation of bibenzyl resulted in the formation of stilbene without the formation of phenanthrene or anthracene.

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The Preparation of 4-Methylquinolines

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In the course of other work in progress in this Laboratory, large amounts of quininic acid were needed. The methods described in the literature[3] for the preparation of this substance are both expensive and laborious, and involve a large number of steps. It seemed to us that if 6-methoxylepidine could be obtained in good yields in one step from *p*-anisidine by the Doebner–Miller reaction, and then oxidized to quininic acid, a great saving in time and materials would be effected.

Many workers have used the Doebner–Miller reaction to prepare 4-alkylquinolines, but the yields have, in general, been low. In some cases the required α,β-unsaturated ketone has been used directly,[4] but as these substances are not readily available they are frequently generated in the reaction mixture. Thus a mixture of a methyl ketone and an aldehyde may be used,[5] but the results are not satisfactory; the yield of lepidine by this procedure was around 4%.[5b]

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(1) This paper is abstracted from the dissertation submitted by Mr. Schaffner in partial fulfillment of the requirements for the Ph.D. degree, June, 1944. This paper was presented before the Organic Division of the American Chemical Society at the New York meeting, September, 1944.

(2) Present address, Metallurgical Laboratory, University of Chicago.

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(4) (a) Blaise and Maire, *Bull. soc. chim.*, (4) **3**, 658, 667 (1908); (b) Prill and Walter, U. S. Patent 1,806,564 (1931); *C. A.*, **25**, 3668 (1931).

(5) (a) Beyer, *J. prakt. Chem.*, (2) **33**, 393 (1886); (b) Mikeska, Stewart and Wise, *Ind. Eng. Chem.*, **11**, 456 (1919); Mikeska, THIS JOURNAL, **42**, 2396 (1920); (c) Palkin and Harris, *Ind. Eng. Chem.*, **14**, 704 (1922).