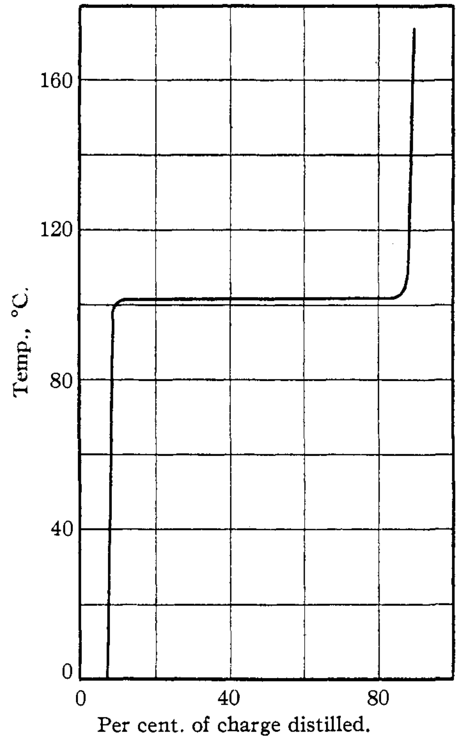

Fig. 8.—Fractionation of 2,4,4-trimethylpentene-1 subjected to a temperature of 350° for one hour.

may be due either to isomerization during the pyrolysis or to the possibility of some random structure (III) in the polymer. The material boiling at 110–115° on ozonization or chromic acid oxidation gave acetone, acetic acid and an odor of fatty acids. This may indicate the presence of 2,5-dimethyl-2-hexene.

The possibility of isomerization of the octenes after their liberation from the polymer was tested by heating diisobutene (b. p. 101.5–101.9°) at 350° for an hour. As shown in Fig. 8, cracking and polymerization took place but there was no noticeable degree of isomerization.

Acknowledgment.—The writers wish to acknowledge the active participation of many of their associates in obtaining the large amount of information from which this paper is abstracted.

Summary

The catalytic polymerization of isobutene at low temperatures to form a homologous series of polymers ranging to very high molecular weights is discussed in detail.

The structure of the polymers is partially established.

ELIZABETH, NEW JERSEY RECEIVED AUGUST 18, 1939

[CONTRIBUTION FROM THE UNIVERSITY OF MISSOURI]

The Action of Aluminum Chloride on Aromatic Hydrocarbons. II. The 1,3-Dimethyl-4-propylbenzenes

BY DOROTHY NIGHTINGALE AND BENOIST CARTON, JR.[1]

When the 1,3-dimethyl-4-butylbenzenes are warmed with aluminum chloride, the butyl group migrates to the 5 position.[2] During the rearrangement, the *n*- and *s*-butyl radicals are isomerized to *s*- and *t*-butyl radicals, respectively.

We have now completed a similar study of the 1,3-dimethyl-4-propylbenzenes. The results, showing that both the 4-*n*-propyl and the 4-isopropyl hydrocarbon rearrange to yield 1,3-dimethyl-5-isopropylbenzene, should be compared with those of Baddeley and Kenner,[3] who reported that 1,3,4-tri-*n*-propylbenzene when heated to 100° with aluminum chloride yielded 1,3,5-tri-*n*-propylbenzene. These authors, however, gave no evidence to support their statement that the migrating propyl group did not isomerize to an isopropyl group and, in view of our results, their conclusion is questionable. Similarly, Heise and Tohl's[4] conclusions that *n*-propylbenzene and aluminum chloride yielded *m*- and *p*-di-*n*-propylbenzene are also doubtful.

The present investigation has shown that the *n*-propyl radical in 1,3-dimethyl-4-*n*-propylbenzene does not readily shift to the 5 position but that its migration is accompanied by isomerization. At 55° the rearrangement is far from complete; at 85 and 100° the product appeared to consist largely of 1,3-dimethyl-5-isopropylbenzene along with some of the starting material.

Rearrangement of 1,3-dimethyl-4-isopropyl-

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[1] Abstract of a dissertation to be presented by Benoist Carton, Jr., in partial fulfilment of the requirement for the degree of Master of Arts at the University of Missouri.

[2] Nightingale and Smith, THIS JOURNAL, **61**, 101 (1939).

[3] Baddeley and Kenner, *J. Chem. Soc.*, 303 (1935).

[4] Heise and Tohl, *Ann.*, **270**, 155 (1892).

benzene to the 1,3,5 isomer took place more readily and was nearly complete at 55°.

In order to be certain of the structure of the rearrangement products, both 1,3-dimethyl-5-isopropylbenzene and 1,3-dimethyl-5-*n*-propylbenzene were synthesized. All of the synthetic hydrocarbons and the rearrangement products were identified by means of their diacetamino derivatives, and by oxidation to a tricarboxylic acid.

Smith and Perry[5] have suggested that during the alkylation of *m*-xylene in the presence of aluminum chloride, a 1,3,4-hydrocarbon is formed initially and is subsequently rearranged to yield finally a 1,3,5-hydrocarbon. If this is true, any alkylation in the presence of aluminum chloride which will lead to the formation of *n*-propylbenzene would be expected to yield a 1,3-dimethyl-5-isopropylbenzene when benzene is replaced by *m*-xylene. If the 1,3-dimethyl-5-propylbenzene is formed directly, such a procedure should yield a product containing a *n*-propyl radical in the 5 position.

There are two alkylating agents which yield *n*-propylbenzene with aluminum chloride as the catalyst: *n*-propyl formate[6] and cyclopropane.[7] *n*-Propyl formate and *m*-xylene yielded 1,3-dimethyl-5-*i*-propylbenzene. Cyclopropane and *m*-xylene yielded 1,3-dimethyl-4-*n*-propylbenzene. Both of these reactions may be interpreted as supporting the above view. It should be noted that the maximum temperatures during these alkylations were 60 and 15°, respectively, and with entirely different alkylating agents. There is considerable evidence in the literature to indicate that the temperature of the reaction as well as the size and type of alkyl group may be an important factor in governing the configuration of the polyalkylbenzenes formed.

Acknowledgments.—The authors wish to express their thanks to E. I. du Pont de Nemours and Company through Dr. Miles A. Dahlen for the *m*-xylene used in this investigation, and to the University Research Council for funds to purchase other necessary chemicals and apparatus to continue the study.

Experimental[8]

1,3-Dimethyl-4-*n*-propylbenzene.—The 4-propionyl-*m*-xylene was prepared by the usual Friedel–Crafts procedure from 60 g. of *m*-xylene, 46 g. of propionyl chloride, 66 g. of aluminum chloride, and 200 cc. of carbon disulfide. The yield of pure ketone was 57 g. (80%), b. p. 112° (10 mm.). The hydrocarbon was prepared from the ketone (50 g.) by the Clemmensen reduction in 50% yield; b. p. 95° (23 mm.); $n^{25}\text{D}$ 1.4995.

Anal. Calcd. for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.95; H, 10.95.

The hydrocarbon also was obtained from *m*-xylene, cyclopropane, and aluminum chloride by the procedure of Grosse and Ipatieff[7] for the preparation of *n*-propylbenzene from benzene and cyclopropane.[9] The cyclopropane (22 g.) was bubbled slowly through 120 g. of *m*-xylene and 4.4 g. of aluminum chloride at 0 to 5°. About half of the cyclopropane was absorbed during four and one-half hours. The temperature was allowed to rise to 15°, at which temperature the remainder of the cyclopropane was absorbed rapidly during thirty minutes while the flask was again cooled with ice. The product was decomposed in the usual manner, and distilled under reduced pressure; yield: 28 g. (40%); b. p. 95° (23 mm.).

The diacetamino derivative of this hydrocarbon melted at 284° and did not depress the melting point of the diacetamino derivative of the hydrocarbon prepared from 4-propionyl *m*-xylene. Oxidation of the hydrocarbon yielded trimellitic acid, m. p. 216°.

1,3-Dimethyl-4-isopropylbenzene.—The *m*-xylene (375 cc.) and isopropyl alcohol (47 cc.) were mixed and the flask placed in water cooled with ice. A mixture of 500 cc. of concd. sulfuric acid and 110 cc. of water was added during two hours while the solution was stirred mechanically. The stirring was continued at room temperature for fourteen hours. The xylene layer was separated and washed with dilute alkali and water, dried and vacuum distilled; yield 70 g. (75%), b. p. 77° (13 mm.); $n^{25}\text{D}$ 1.4998.

Anal. Calcd. for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.34; H, 11.12.

1,3-Dimethyl-5-isopropylbenzene.—This hydrocarbon is the principal product from three different alkylating agents: isopropyl chloride, *n*-propyl chloride, and *n*-propyl formate.

A mixture of 53 g. of *m*-xylene and 15 g. of aluminum chloride was stirred mechanically while 20 g. of isopropyl chloride was added during an hour. The stirring was continued for an additional three hours. The mixture was decomposed in the usual way, washed, dried and distilled: yield 19 g. (48%), b. p. 83–85° (17 mm.); $n^{25}\text{D}$ 1.4930.

Anal. Calcd. for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.91; H, 10.95.

Oxidation of this hydrocarbon yielded trimesic acid, m. p. 365°, and its diacetamino derivative melted at 295°.

The alkylation was repeated, using *n*-propyl chloride in place of the isopropyl chloride: yield of hydrocarbon, 17 g. (46%), b. p. 83–85° (17 mm.); $n^{25}\text{D}$ 1.4935. The diacetamino derivative of this product melted at 276° and when mixed with the diacetamino derivative of the hydrocarbon from isopropyl chloride, the melting point was 283°. The trimesic acid formed by oxidation melted at

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[5] Smith and Perry, This Journal, **61**, 1411 (1939).

[6] Bowden, *ibid.*, **60**, 645 (1938).

[7] Grosse and Ipatieff, *J. Org. Chem.*, **2**, 447 (1939).

[8] Semimicroanalyses for C and H by B. Carton; for nitrogen by R. G. Taylor.

[9] The cyclopropane was obtained from Mallinckrodt Chemical Works, St. Louis, Mo.

355°. These melting points would indicate that the hydrocarbon was largely 1,3-dimethyl-5-isopropylbenzene, containing perhaps some 1,3,4-isomer.

The procedure of Bowden[6] for the preparation of *n*-propylbenzene from benzene and *n*-propyl formate was followed in detail, with 320 cc. of *m*-xylene in place of benzene: yield of hydrocarbon from 22 g. of ester, 18 g. (50%), b. p. 90° (23 mm.); $n^{25}D$ 1.4930.

Oxidation of this product yielded trimesic acid, m. p. 360°. Its diacetamino derivative melted at 295° and did not depress the melting point of the diacetamino derivative of the hydrocarbon from isopropyl chloride.

1,3-Dimethyl-5-*n*-propylbenzene.—This hydrocarbon was obtained from the reaction of methyl *n*-propyl ketone and acetone in the presence of concd. sulfuric acid, following the procedure for the preparation of mesitylene from acetone and sulfuric acid.[10]

The sulfuric acid (1363 cc.) was added to 1060 cc. of methyl *n*-propyl ketone (tech.) and 1406 cc. of acetone at 0–10°. The material distilling at 150–240° was purified by treatment with sodium, and fractionated at 20 mm.: (I) 50 g. 67–92°; (II) 35 g. 92–94°; (III) 10 g. 94–96°; (IV) 16 g. above 96°. Fraction II was carefully refractionated to yield finally 19 g. of hydrocarbon, b. p. 90–91° (18 mm.); $n^{25}D$ 1.4913.

This product, when oxidized, yielded trimesic acid, m. p. 360°, and its diacetamino derivative melted at 239°.

The procedure of Morton and Fallwell[11] for the preparation of ethylbenzene from benzyl sodium and methyl iodide was followed in detail, substituting 80 cc. of mesitylene for 75 cc. of toluene, and with 78 g. of ethyl iodide. The yield of trialkylbenzene was 5.5 g., b. p. 92–93° (18 mm.); $n^{25}D$ 1.4900.

The diacetamino derivative of this hydrocarbon melted at 239° and did not depress the melting point of the derivative of the hydrocarbon from the ketone synthesis.

The diacetamino derivatives of the hydrocarbons were prepared by the procedure of Ipatieff and Schmerling[12] from 1 cc. of hydrocarbon. Purification was tedious, and the yield of pure product was small.

TABLE I

Hydrocarbon 1,3-Dimethyl-	M. p., °C.[c]	Diacetamino derivative[a] % nitrogen found
A 4-*n*-Propylbenzene	284	10.81
B 4-Isopropylbenzene	292	10.96
C 5-Isopropylbenzene (isopropyl chloride)	295	10.76[b]
D 5-*n*-Propylbenzene (ketones)	239	10.78
E 5-*n*-Propylbenzene (organo alkali)	239	

[a] Calcd. for $C_{11}H_{22}N_2O_2$: C, 68.70; H, 8.39; N, 10.68. [b] Found: C, 68.80; H, 8.21. [c] Mixed melting points: A + B, 263°; B + C, 255°; A + C, 250°.

Rearrangements with Aluminum Chloride.—The aluminum chloride was added directly to the hydrocarbon, and the mixture warmed in a water-bath. A thermometer was placed in the reaction mixture and during the heating the flask was shaken frequently. After heating, the mixture was poured onto ice, extracted with ether, washed, dried and vacuum distilled. Fraction I contained some *m*-xylene and fraction II the trialkylbenzenes.

1,3-Dimethyl-4-isopropylbenzene.—The hydrocarbon (32 g.) was warmed with aluminum chloride (7 g.) at 55–60° for three hours. The reaction products were distilled at 20 mm. and yielded only two fractions: (I) 1.4 g. up to 85°; (II) 29 g. 85–86°. The boiling point of II was unchanged on redistillation. The diacetamino derivative of II melted at 295°, and did not depress the melting point of the derivative of 1,3-dimethyl-5-isopropylbenzene. This rearrangement product is therefore 1,3-dimethyl-5-isopropylbenzene.

1,3-Dimethyl-4-*n*-propylbenzene.—The hydrocarbon (35 g.) was warmed with aluminum chloride (8 g.) for three hours at 55°. The reaction products were fractionated at 30 mm.; (I) 3.6 g. 45–95°; (II) 14.9 g. 95–105°; (III) 6 g. 132°; residue 2 g.

Fraction II on slow distillation came over at 105° (38 mm.). The diacetamino derivative of this fraction melted at 279° and did not depress the melting point of the derivative of 1,3-dimethyl-4-*n*-propylbenzene. This fraction is therefore mainly unchanged 4-*n*-propyl hydrocarbon.

The reaction was repeated with 28 g. of hydrocarbon and 7 g. of aluminum chloride at 85–90° for four hours. The following fractions were obtained at 15 mm.: (I) 8.7 g. 45–89°; (II) 7.2 g. 89–94°; (III) 5.1 g. 105–110°.

Fraction II formed a diacetamino derivative which melted at 240–250°, and depressed the melting point of the derivatives of both the 4-*n*-propyl and 5-isopropyl hydrocarbons some 20°. The fraction is probably a mixture of unchanged 4-*n*-propyl hydrocarbon and 5-isopropyl hydrocarbon.

To determine whether or not longer heating and a higher temperature would improve the yield and quality of the trialkyl fraction, the rearrangement was carried out with the same amounts of materials at a temperature of 100° for four hours. These are the experimental conditions of Baddeley and Kenner[3] for 1,3,4-tri-*n*-propylbenzene.

The following fractions were obtained at 15 mm.: (I) 6.8 g. 45–92°; (II) 6.7 g. 89–92°; (III) 3 g. 95–97°; (IV) 2.6 g. 97–110°.

The diacetamino derivative of II melted at 280–285°. Mixed with the derivative of the 4-*n*-propyl hydrocarbon, the melting point was 260–265°, and with the derivative of the 5-isopropyl hydrocarbon the melting point was 285°. The trimesic acid obtained from the oxidation of II melted at 330°.

These data indicate that the 1,3-dimethyl-4-*n*-propylbenzene is largely rearranged to 1,3-dimethyl-5-isopropylbenzene and other hydrocarbons in the presence of aluminum chloride at 100°.

Summary

The 1,3-dimethyl-4-isopropylbenzene undergoes rearrangement on warming with aluminum chloride at 55° for three hours to yield 1,3-dimethyl-5-isopropylbenzene as the principal trialkylbenzene.

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[10] "Organic Syntheses," Coll. Vol. I, p. 334.

[11] Morton and Fallwell, THIS JOURNAL, **60**, 1429 (1938).

[12] Ipatieff and Schmerling, *ibid.*, **60**, 1476 (1938).

The 1,3-dimethyl-4-*n*-propylbenzene is largely rearranged by aluminum chloride at 100° for four hours to yield 1,3-dimethyl-5-isopropylbenzene. After heating at 85–90°, the trialkyl fraction is a mixture, and at 55° the trialkyl fraction is mainly unchanged 1,3,4 hydrocarbon.

The 1,3-dimethyl-4-*n*-propylbenzene was prepared from *m*-xylene and cyclopropane with aluminum chloride as the catalyst, and by the reduction of 4-propionyl-*m*-xylene.

The 1,3-dimethyl-5-isopropylbenzene was obtained from *m*-xylene and isopropyl chloride, *n*-propyl formate, and *n*-propyl chloride with aluminum chloride as the catalyst.

The formation of the 4-*n*-propyl hydrocarbon from *m*-xylene and cyclopropane and the 5-isopropyl hydrocarbon from *m*-xylene and *n*-propyl formate support the view of Smith and Perry that a 1,3,4 hydrocarbon is the initial product of the reaction when *m*-xylene is alkylated in the presence of aluminum chloride.

COLUMBIA, MISSOURI RECEIVED OCTOBER 5, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

The Hydrogenation of Coumarin and Related Compounds

BY PETER L. DE BENNEVILLE AND RALPH CONNOR

γ-Valerolactone at 250° and 100–200 atmospheres of hydrogen over a copper chromite catalyst has been reported[1] to give pentanediol-1,4, the product expected from an ester under these conditions, and a small amount of hydrogenolysis product, pentanol-1. Over nickel, however, γ-butyrolactone and γ-valerolactone gave[2] 9% of tetrahydrofuran and 17% of α-methyltetrahydrofuran, respectively. These seem to be the only known examples, except in cases where other functional groups complicate the reactions, of the formation of ethers and also of the attack of an ester group in the presence of a nickel catalyst. Apparently no other γ-lactones and no δ-lactones have been investigated under these conditions.

The products obtained by the hydrogenation of coumarin and certain related compounds are shown in the flow sheet (Table I). Over copper chromite, the behavior of coumarin was like that of any α,β-unsaturated ester. The formation of dihydrocoumarin (II) at 140–160° was shown by the pressure drop but the hydrogenation was not interrupted to permit its isolation. At 250° there was obtained a good yield of the product expected from a normal ester hydrogenation, γ-(*o*-hydroxyphenyl)-propyl alcohol (V).

Dihydrocoumarin (II) was isolated from the hydrogenation of coumarin over Raney nickel at 100°. In hydrogenations at higher temperatures dihydrocoumarin was not isolated but was formed quantitatively, as shown by the hydrogen absorption, before any subsequent reaction occurred. At 200–250° the main reactions which occurred over Raney nickel were saturation of the benzenoid ring, giving octahydrocoumarin (III), and conversion of the lactone to the cyclic ether, hexahydrochroman (IV). Pure octahydrocoumarin was obtained in 50–55% yields by carrying out the hydrogenation at 200° and interrupting the reaction before the absorption of hydrogen had ceased.[3] Under these conditions 10–15% of hexahydrochroman was formed. Higher yields (up to 35%) of the latter product were obtained by using a relatively long reaction period at 250°.

Since the formation of ethers from esters over nickel is by no means a common reaction, it is of some interest to determine the intermediates in the formation of hexahydrochroman from coumarin. Three possible mechanisms are shown by broken lines in Table I and none of these may be definitely eliminated on the basis of the facts now available. Path (c) agrees with the observation that IV is the sole product obtained by the hydrogenation of III under these conditions. This also agrees with the results previously mentioned with γ-butyrolactone and γ-valerolactone except that the yield of ether from coumarin was

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(1) Adkins, "Reactions of Hydrogen, etc.," University of Wisconsin Press, Madison, Wisconsin, 1937, p. 105.

(2) Ref. 1, p. 77.

(3) A plot of time against pressure showed a definite change in slope which seemed to mark the best time to interrupt the reaction. At 250° this point was not observed readily and, while good yields (60–70%) of the octahydrocoumarin fraction were obtained, the refractive index of the product showed that it contained unreacted dihydrocoumarin.