[Contribution from the Department of Chemistry at the
Ohio State University]

ALKYLBENZENES. I. SYNTHESES FROM ISOPHORONE[1]

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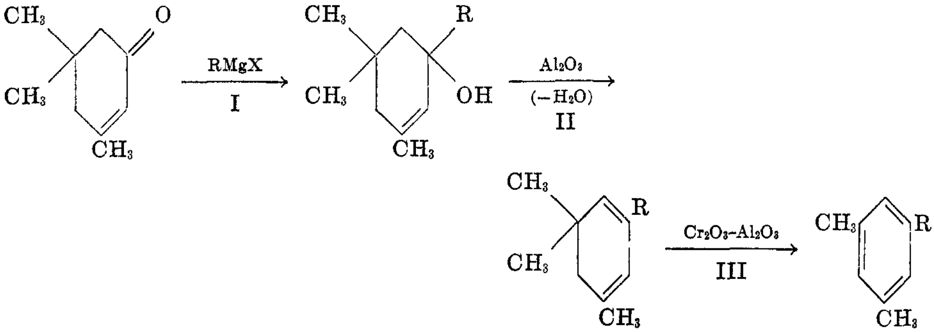
A number of polyalkylaromatic hydrocarbons can be synthesized by a novel method starting with the non-aromatic, commercially available isophorone (3,5,5-trimethyl-2-cyclohexene-1-one). The method appears to be general for 1,3-dimethyl-5-alkylbenzenes and with a simple modification can also be used for 1,3-dimethylbenzene (*m*-xylene); it is adaptable to the enlarged laboratory scale[2] and gives products which are amenable to a high degree of purification. This method involves the reaction of isophorone with an alkyl Grignard reagent to produce a 1,3,5,5-tetra-alkylcyclohexenol, dehydration of the formed carbinol, and "demethanation"[3] or aromatization of the resulting trimethylalkylcyclohexadiene. The aromatization process eliminates one of the *gem* methyl groups and a hydrogen atom from an adjacent carbon atom, giving the expected 1,3-dimethyl-5-alkylbenzene in acceptable yield. The method has been applied to the preparation of 1,3,5-trimethylbenzene, 1,3-dimethyl-5-ethylbenzene, and 1,3-dimethyl-5-*n*-propylbenzene. In step III the yield appears to decrease as the molecular weight of the "R group" is increased (Table I).



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[1] This material was abstracted from parts of the dissertations of J. P. Ferrin, T. B. Tom, and N. L. Koslin, presented to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in 1947, 1943, and 1942, respectively. Parts of this investigation were presented before the Organic Division of the American Chemical Society at its 107th Meeting, Cleveland, Ohio, 1944, and before the XIIth International Congress of Pure and Applied Chemistry (1951). Some of the work was sponsored by the American Petroleum Institute (Research Project 45) in cooperation with The Ohio State University Research Foundation.

[2] Using this method, the American Petroleum Institute Research Project 45 has prepared, in excellent purity, 7 liters of *m*-xylene, 4 liters of 1,3,5-trimethylbenzene, and 3 liters of 1,3-dimethyl-5-ethylbenzene.

[3] Mass spectral analysis of the "off gases" from this reaction on the tetramethyl derivative by Dr. Milton Orchin (U. S. Bureau of Mines) showed that in addition to methane, hydrogen, ethane, and higher hydrocarbons were present.

TABLE I

ALKYLBENZENES FROM ISOPHORONE

GRIGNARD REAGENT	HYDROCARBON OBTAINED	OVER-ALL YIELD, %
Methyl	1,3,5-Trimethylbenzene	65[a]
Ethyl	1,3-Dimethyl-5-ethylbenzene	36[a]
Propyl	1,3-Dimethyl-5-*n*-propylbenzene	32[a]
(Hydrogen)	1,3-Dimethylbenzene	64[b]

[a] Yield was calculated from the amount of hydrocarbon obtained by straight distillation of the crude aromatization product and is based on isophorone.

[b] As in *a*, but based on dihydro-isophorol.

TABLE II

TETRA-ALKYLCYCLOHEXENOLS

GRIGNARD REAGENT	CYCLOHEXENOL	B.P., °C.	MM.	d_4^{20}	n_D^{20}	YIELD, %
Methyl	1,3,5,5-Tetramethyl-2-cyclohexene-1-ol	61	5	0.9070	1.4689	83
	[Literature (1)]	(59–60)	5	(0.9075$_{20}^{20}$)	(1.4690)	—
Ethyl	1-Ethyl-3,5,5-trimethyl-2-cyclohexene-1-ol	46	8	.9061	1.4713	88
n-Propyl	1-*n*-Propyl-3,5,5-trimethyl-2-cyclohexene-1-ol	77	14	.9032	1.4718	76

By reducing isophorone directly with hydrogen (or by starting with dihydroisophorol, the commercial "trimethylcyclohexanol") and then carrying out steps II and III, 1,3-dimethylbenzene is produced; in step III the trimethylcyclohexene loses two atoms of hydrogen as well as the usual elements of methane.

EXPERIMENTAL

Tetra-alkylcyclohexenols. The Grignard reagents from 12.0 moles of methyl, ethyl, and *n*-propyl chlorides were prepared separately, each in 4 liters of dried ether in a glass flask equipped with reflux condenser, iron Hershberg stirrer, and dropping-funnel. To each of the prepared Grignard reagents was added 10.0 moles of commercial isophorone (Carbide and Carbon Chemical Corp.). The reaction mixtures were allowed to stand several hours, or overnight, after which they were hydrolyzed with saturated ammonium chloride solution and were washed thoroughly with water. The crude products were dried over sodium sulfate and were fractionated at about 20-plate efficiency (see Table II). Kharasch and Tawney (1) prepared 1,3,5,5-tetramethyl-2-cyclohexene-1-ol by the same reaction and found that the Grignard reagent reacted with isophorone entirely by 1,2-addition in the absence of metallic halides.

Trimethylcyclohexanol. 3,3,5-Trimethylcyclohexanol-1 (dihydroisophorol) was purchased from Carbide and Carbon Chemicals Corp.

Tetra-alkylcyclohexadienes. The distilled cyclohexenols were dehydrated in the vapor phase by passing them at a rate of about 50 ml. (liquid) per hour through a 1.9 × 100 cm. Pyrex tube filled with 8–14 mesh activated alumina and maintained at 275°. The organic material resulting from the dehydration was in each case distilled at about 20-plate efficiency. Table III lists the physical properties of the products obtained; the yield in each case was about 90% of theory.

TABLE III

TETRA-ALKYLCYCLOHEXADIENES

DIENE	B.P., °C.	MM.	d^{20}_{4}	n^{20}_{D}
1,3,5,5-Tetramethyl-1,3-cyclohexadiene.........	47	13	0.8178	1.4700
[Literature (1)].............................	(24–25)	7	(0.8152^{20}_{20})	(1.4698)
3-Ethyl-1,5,5-trimethyl-1,3-cyclohexadiene......	69	15	.8474	1.4878
3-*n*-Propyl-1,5,5-trimethyl-1,3-cyclohexadiene...	84	15	.8478	1.4765

Trimethylcyclohexenes. The 3,3,5-trimethylcyclohexanol (dihydroisophorol) was dehydrated at 325° in the same way as were the cyclohexenols, to obtain a mixture of 3,3,5- and 3,5,5-trimethylcyclohexene[4] (b.p. 131.2 to 133.6°/760 mm., d^{20}_{4} 0.7921 to 0.7942, n^{20}_{D} 1.4396 to 1.4406) in 85% yield, after distillation at about 25-plate efficiency.

Aromatization. The "demethanation" catalyst was prepared as follows: Activated Al_2O_3 (alumina) (8–14 mesh, 500 g.) was impregnated with sufficient $Cr(NO_3)_3 \cdot 9H_2O$ to give a 10 mole-% Cr_2O_3-90 mole-% Al_2O_3 catalyst. The nitrate-coated material was dried overnight in an oven at 110°, after the suggestion of Grosse and Ipatieff (2). The catalyst was then re-impregnated with enough nitrate to make 20 mole-% Cr_2O_3 on 80 mole-% Al_2O_3. This was dried, as before, and a vertical 1.9 × 100 cm. pyrolysis tube (Pyrex or Vycor) was filled with the material. To complete the drying of the catalyst and to activate it, the tube was heated at 400° for 4 hours, after which air was passed through it overnight at this temperature; then the air in the tube was displaced by nitrogen, and hydrogen was passed over the catalyst for 1–4 hours (the 400° temperature being maintained). Similarly prepared catalysts with as little as 5 mole-% chromia were found useful though producing somewhat lower conversions.

The 3-alkyl-1,5,5-trimethyl-1,3-cyclohexadienes were separately introduced at a rate of 35–40 ml. per hour into the top of the catalyst tube, the temperature of which was maintained at 450 to 500°. In each case the evolution of a combustible gas was noted. The liquid product, which was collected in a flask surrounded by an ice-bath, was dried over silica gel and distilled at about 20-plate efficiency. It was necessary to re-activate the catalyst or replace it after 500 to 1000 ml. had been passed over it. Passing air through the hot (450–500°) catalyst bed for several hours burned away carbonaceous deposits and oxidized the surface chromia to CrO_3. Hydrogen, passed through at the same temperature restored the catalyst to its original form and virtually its original activity.

In the preparation of 1,3-dimethylbenzene a commercial coprecipitated chromia-alumina catalyst (12% chromia) was used in the form of ⅛ inch pellets and the trimethylcyclohexene mixture was passed over it at 500°. This catalyst became de-activated rapidly, and could not be re-activated satisfactorily. It caused the formation of higher-boiling products which were isolated from the aromatization mixture by distillation and were identified as 1,3,5-, 1,2,4-, and 1,2,3-trimethylbenzenes in the approximate ratio of 5:5:1. After 2 to 3 liters of the trimethylcyclohexenes had been passed over the catalyst, the yield of higher-boiling material rose from 11% to about 35%. The formation of the trialkylbenzenes was rather surprising since chromia-alumina catalyst reputedly does not promote migration of methyl groups. The fact that no benzene or toluene was found indicates that the alkylation was effected by methyl groups split from the *gem* carbon atoms and normally appearing as methane or ethane in the off-gases.

Purification of aromatics. Upon distillation of the crude 1,3,5-trimethylbenzene (96% yield) at about 30-plate efficiency, 92% of it was recovered as a product of constant boiling point and refractive index and 99.5% purity; another 6% was suitable for recycling over he catalyst. Physical properties of the constant boiling material are listed in Table IV.

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[4] These cyclo-olefins have since been separated and identified in this laboratory. George Slomp, K. W. Greenlee, J. M. Derfer, and C. E. Boord, paper in preparation.

For 1,3-dimethyl-5-ethylbenzene the yield of crude product (after two passages over the catalyst) was 83%, and the subsequent distillation at about 20-plate efficiency separated it into headings (28% of charge), 1,3-dimethyl-5-ethylbenzene, b.p. 183.5–183.8°, n_D^{20} 1.4980 to 1.4982 (54%), and tailings (8%). The headings consisted chiefly of 1,3,5-trimethylbenzene, and the tailings (unsaturated) probably contained 3,5-dimethylstyrene and higher polyalkylbenzenes. The semi-pure 1,3-dimethyl-5-ethylbenzene was then distilled azeotropically with ethylene glycol monobutyl ether at better than 100-plate efficiency, and the fractions were individually washed and dried. About 8% of the charge was rejected as headings (low refractive index), the rest of the distillate being good 1,3-dimethyl-5-ethylbenzene (0.02° boiling range); the residue amounted to 11% of the charge. It was noted that the washed headings actually boiled slightly higher than did the washed 1,3-dimethyl-5-ethylbenzene, probably because of the presence of 1,1,3-trimethyl-5-ethylcyclohexane. The composite of the good 1,3-dimethyl-5-ethylbenzene fractions was 99.4 mole-% pure as indicated by cryoscopy, but showed unsaturation. Exhaustive treatment with cold, aqueous permanganate solution increased the purity to 99.8% and removed the last traces of unsaturation. From the once-distilled 1,3-dimethyl-5-ethylbenzene to the final product the eliminations and losses were 40%. The physical properties listed in Table IV were determined on the highly purified material.

On distillation of the crude 1,3-dimethyl-5-*n*-propylbenzene at about 20-plate efficiency, an initial boiling point of 153° was noted; temperature rose quickly to 195° and then gradually to a flat at about 202°; the distillation was stopped at 205°, leaving only a small residue. The best product, a center fraction, had the following properties: b.p. 202.3°, f.p. −59.79°, n_D^{20} 1.4955; treating it with permanganate solution considerably raised its melting point and purity (Table IV). All of the other distillate (except the center fraction) was recycled over the aromatization catalyst, then redistilled. This time small amounts of 1,3,5-trimethylbenzene and 1,3-dimethyl-5-ethylbenzene were found, and the final fifth of the distillate was in the high-boiling range of 211–226°. The center fractions, which boiled in the range of 1,3-dimethyl-5-*n*-propylbenzene, had higher refractive indices (n_D^{20} 1.4961 to 1.4981) than before and showed unsaturation to bromine. These fractions were bulked, treated exhaustively with permanganate, washed, dried and distilled, thus yielding more 1,3-dimethyl-5-*n*-propylbenzene. It was of fair purity as indicated by its physical properties (b.p. 202.20°, f.p. −60.0°, n_D^{20} 1.4954), and, taken with the center fraction from the first distillation, constituted a 32% yield of the aromatic from the diene. The high-boiling by-product separated in the second distillation was unsaturated and of rather high refractive index (n_D^{20} 1.5259 to 1.5307). The most likely compounds of this boiling range to be obtained

TABLE IV

PHYSICAL PROPERTIES OF ALKYLBENZENES

HYDROCARBON	F.P., °C.	B.P. °C.	d_4^{20}	n_D^{20}	PURITY (Mole—%)	LITERATURE (ref. no.)
1,3,5-Trimethylbenzene	−51.94	164.74	0.8650	1.4992	99.5[a]	(4)
1,3-Dimethyl-5-ethylbenzene	−84.41	183.58	.8645	1.4982	99.8[b]	(5)
1,3-Dimethyl-5-*n*-propylbenzene	−59.26	202.23	.8608	1.4952	99.3[c]	(6)
1,3-Dimethylbenzene	−47.99	139.11	.8641	1.4972	99.7[a]	(7)

[a] Calculated from the m.p.'s together with cryoscopic constants found in *Selected Values of Properties of Hydrocarbons*, F. D. Rossini, et al., N.B.S. Circular C461, U. S. Govt. Printing Office, Washington, D. C., 1947. [b] Cryoscopic constants for 1,3-dimethyl-5-ethylbenzene were obtained by private communication with Dr. F. D. Rossini, Dept. of Chemistry, Carnegie Institute of Technology. [c] The m.p. and cryoscopic constants for 1,3-dimethyl-5-*n*-propylbenzene were determined by Mr. V. G. Wiley of this laboratory: $t_{f_0} = -59.07°$, $A = 0.035$.

by dehydrogenation involving the *n*-propyl side chain are 4,7-dimethylindane, 4,7-dimethylindene, and 1,3-dimethyl-5-propenylbenzene. The indene derivative was ruled out on the basis of its high refractive index (estimated n_D^{20}, 1.57 to 1.58). Of the other two, only the styrene-type hydrocarbon (1,3-dimethyl-5-*n*-propenylbenzene) would be expected to react with sodium in liquid ammonia (3). The high-boiling by-product was treated with sodium in liquid ammonia, reaction taking place readily, and some 1,3-dimethyl-5-*n*-propylbenzene was obtained (b.p. 201–203° and n_D^{20} 1.4950–1.4957, after distillation).

The *meta*-xylene (75% yield from cyclo-olefin) prepared by the present method with fresh catalyst and isolated from the crude aromatization mixture by distillation at about 20-plate efficiency contained 1 to 2% of impurity, presumably *para*-xylene. The impurity was found to be best removed by sulfonation of the distilled product and recrystallization of the *meta*-xylenesulfonic acid before subsequent desulfonation by superheated steam (recovery, 85%). Distillation of the regenerated *m*-xylene, done to remove traces of fragmentation, oxidation, and condensation products, lowered the recovery from the purification to 71% of *meta*-xylene, 99.7 mole-% pure.

SUMMARY

A novel method has been developed whereby a number of 1,3-dimethyl-5-alkylbenzenes and 1,3-dimethylbenzene (*m*-xylene) can be synthesized in three steps from the readily available isophorone. It involves the splitting of hydrogen and a *gem* methyl group from a cyclohexadiene or a cyclohexene intermediate in the vapor phase over chromia-alumina catalyst. The hydrocarbon products are amenable to a high degree of purification, and the process is suitable for both small and large scale laboratory use.

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REFERENCES

(1) KHARASCH AND TAWNEY, *J. Am. Chem. Soc.*, **63**, 2312 (1941).
(2) GROSSE AND IPATIEFF, *Ind. Eng. Chem.*, **32**, 268 (1940).
(3) WOOSTER AND RYAN, *J. Am. Chem. Soc.*, **56**, 1133 (1934).
(4) MAIR AND SCHICKTANZ, *J. Research Nat. Bur. Standrds*, **11**, 665 (1933).
(5) BIRCH, DEAN, FIDLER, AND LOWRY, *J. Am. Chem. Soc.*, **71**, 1362 (1949).
(6) NIGHTINGALE AND CARTON, JR., *J. Am. Chem. Soc.*, **62**, 280 (1940).
(7) WHITE AND ROSE, JR., *J. Research Nat. Bur. Standards*, **9**, 711 (1932).