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Synthesis of Durene from Pseudocumene

DURENE is increasingly used for making polybasic acids (*2, 11*) for use in plastics and alkyds. However, most durene is recovered from petroleum fractions having such low content that expensive combinations of distillation and crystallization (*4*) are needed.

In contrast, pseudocumene from petroleum sources can be recovered in 90 to 95% purity by fractional distillation. Pseudocumene has three of the required four methyl groups in proper position, and a two-step process has been developed by introducing another methyl group to produce durene in an over-all yield of 84 mole %.

Literature Background

Subject	Ref.
Direct methylation of aromatics yields mixtures requiring complex methods for separating durene	(*15*)
Alkylation yields wide spectrum compounds and isomers	(*16*)
Conversion of chlorodurene to durene prohibitively expensive	(*14*)
Chlorodurene treated with sodium methoxide gives a methyl ether which catalytically reduces to durene	(*3*)

Description of the Synthesis

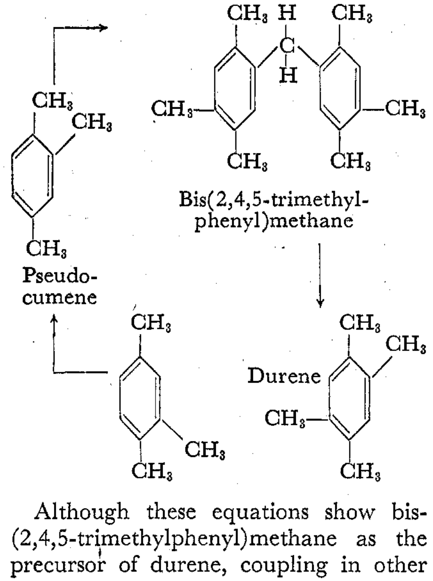
In the condensation step, 2 or more moles of pseudocumene per mole of formaldehyde (paraformaldehyde) and anhydrous toluenesulfonic acid (10 weight % based on aromatic) are stirred vigorously under reflux for 2 hours at 90° to 100° C. The aqueous phase, containing toluenesulfonic acid and traces of formaldehyde, is removed and the hydrocarbon layer, containing such products as unreacted pseudocumene, dipseudocumylmethane, polycondensation products, and traces of acidic oxygenated compounds. This material is then passed through a bed of Attapulgus clay to increase life of the catalyst in the second or hydrocracking step.

Bis(trimethylphenyl)methane is the major product of this condensation; a typical yield of 87% of substituted diphenylmethanes is obtained per pass, all of which can be used in the second step.

In the second or hydrocracking step, a 160-ml. stainless steel reactor is loaded with silicon carbide, 100 ml. of molybdenum oxide-alumina catalyst and, 35 ml. of silicon carbide in the order mentioned. The catalyst is pretreated for 30 minutes with hydrogen at a flow of 125 liters per hour at atmospheric pressure and 625° C. Then, the temperature is decreased and the system brought to equilibrium by pumping the charge stock through the reactor at the desired temperature, pressure, and flow rate for 30 minutes before sampling.

A known weight of C.P. paraffins (*n*-hexane, *n*-nonane, *n*-decane, *n*-dodecane, and *n*-tetradecane) are added as fillers to the product and the resulting solution is then fractionally distilled—boiling points of pseudocumene and durene differ by about 27.5° C.—using a 3-foot Hypercal distillation column at 10 to 1 reflux ratio. Boiling points of the fillers are used as cut-point temperatures for collecting fractions and the compounds present are determined by a Perkins-Elmer Model 21 infrared spectrophotometer (*4*). The pseudocumene recovered can be recycled to produce additional dipseudocumylmethane.

Discussion of Results



Although these equations show bis-(2,4,5-trimethylphenyl)methane as the precursor of durene, coupling in other positions in one of the rings would also permit durene to be formed. Cleavage of such unsymmetrical compounds to produce durene would require selective scission in which the methylene group is retained on the ring having methyl groups in the 2,4,5 positions. However, with bis(2,4,5trimethylphenyl)methane, only durene and pseudocumene are obtainable by hydrocracking. Because the total condensation product is hydrocracked, the charge stock is referred to as dipseudocumylmethane which includes all isomers produced.

Dipseudocumylmethane Production. Toluenesulfonic acid is a preferred catalyst for coupling pseudocumene with formaldehyde. This is in contrast to reports that this acid is unsatisfactory for condensing aromatic hydrocarbons with formaldehyde (*18*). Also, no reference was found for preparing dipseudocumylmethane (*6, 7, 9, 10, 13, 17*).

Toluenesulfonic acid has many advantages as a catalyst for condensing formaldehyde with aromatic hydrocarbons. It is less prone to sulfonate or oxidize than sulfuric acid and is more stable than catalysts such as formic acid. No solvent recovery problem is encountered, and toluenesulfonic acid can be removed from the condensate as an aqueous phase and dehydrated for re-use—e.g., about 95% of the acid charged can be recovered in anhydrous form by either gas stripping or by trapping water from the condensate of a refluxing solution containing a suitable aromatic. To avoid degradation of the acid, the temperature should not exceed 110° C.

Toluenesulfonic acid concentrations of 8, 10, and 19 weight %, based on pseudocumene, yielded 78, 86, and 89 mole % of dipseudocumylmethane, respectively, based on aromatics charged. These yields, determined gravimetrically by evaporating the unreacted hydrocarbon, include both the alkylated diphenylmethanes and small quantities of polymers. Determining bis(2,4,5, trimethylphenyl)methane by infrared was unsatisfactory because of interference from accompanying isomers. Reaction times in excess of 2 hours increase polymer yields and shorter times yield oxygenated compounds which cause a rapid activity decline of the hydrocracking catalyst. Typically, the polymer content is 10 to 20% when a 2 to 1 molar ratio of pseudocumene reactants is used.

A number of other catalysts were studied. Benzenesulfonic acid was more reactive than toluenesulfonic acid, and hydrogenolysis of the resulting product gave durene in high purity and yield. Toluenesulfonic acid dihydrate produced an 81% yield of dipseudocumylmethane, compared with 17% from toluenesulfonic acid diluted with an equal weight of water. Methanesulfonic acid produced an 88% yield; but decomposition of the sulfonic acid was observed.

Bis(2,4,5-trimethylphenyl)methane was purified also by distillation and crystallization from the reaction mix. The resulting crystals had a boiling point (10 mm. of mercury) of 200° C., melting point of 98° C., and molecular weight [Menzies-Wright method (*7*)] of 252. They contained 90.50% carbon compared to 90.42% theoretical, and 9.40% hydrogen compared to 9.58% theoretical. Their infrared spectrum showed doublet peaks near 11.24 and 11.49 microns.

Hydrocracking Catalysts for Diphenylmethane

(H_2 press., 100 p.s.i.g.)

Catalyst Agent	Catalyst Support	Temp., ° C.	Toluene, Mole %
Cr_2O_3	**Al_2O_3**	**550**	**12**
Co	**Charcoal**	**575**	**63**
FeO	**None**	**525**	**0**
MoO_3	**Al_2O_3**	**525**	**100**
Ni	**Kieselguhr**	**525**	**45**

Catalysts for Durene Production

(Temp. 450° C.; H_2 press., 100 p.s.i.g.)

	Durene		Pseudocumene, Mole %	
Catalyst	Yield, mole %	Purity, wt. %	Isomerized	Demethylated
Mo	**81**	**98**	**0**	**0**
Pt	**67**	**84**	**0**	**1**
Ti	**63**	**95**	**7**	**0**
Co	**49**	**91**	**3**	**22**
Al_2O_3-6% SiO_2	**46**	**71**	**6**	**0**
Al_2O_3	**3.7**	**94**	**0**	**0**
Ni	**27**	**50**	**17**	**5**
Co	**5.6**	**94**	**2**	**12**
Ni	**2.6**	**92**	**3**	**1**
Cr[a]	**11.0**	**94**	**0**	**0**

[a] Reaction temp., 525° C.

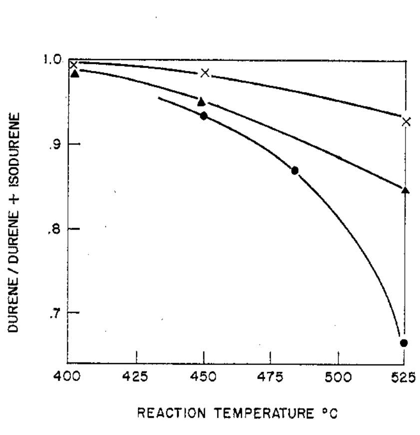


Figure 1. Effect of hydrogen pressure and activation of molybdenum-alumina catalyst on durene-isodurene ratio

× Activated at 100 p.s.i

● Activated at 250 p.s.i.

▲ Unactivated

Hydrocracking Dipseudocumylmethane. No literature is available on cleavage of alkylated diphenylmethanes with hydrogen; the nearest related work deals with hydrocracking diphenylmethane to produce benzene and toluene (*8, 12*) using a molybdenum catalyst. Fluorene is formed from diphenylmethane in the absence of hydrogen at 300° C. in the presence of a platinum on charcoal catalyst (*19*). Also, substituted diphenylmethanes with at least one methyl group ortho to the methylene bridge can be cyclized in the vapor phase to anthracene or its derivatives (*12*).

To find a catalyst to promote dehydrocracking of diphenylmethane but not demethylation or other side reactions, runs made with six common catalysts showed that molybdenum oxide is preferred.

Durene of 90 to 92% purity can be obtained in 81 to 84 mole % yield. The durene content of the C_{10} fraction can be increased to as much as 98% by fractionating out the prehnitene which distills 6° C. higher than isodurene and 7° C. above durene.

The C_9 fraction is essentially unchanged pseudocumene which can be further condensed with formaldehyde. Therefore, it is concluded that pseudocumene does not isomerize in either step of the synthesis. Trace amounts of toluene in the product also prove that demethylation is minor.

Only traces of prehnitene are present in the C_{10} fraction and the ratio of durene to durene-isodurene is a measure of durene purity obtainable by distillation (Figure 1). Pretreating the molybdenum oxide catalyst with hydrogen at 625° C. for 30 minutes increases durene and decreases isodurene yields.

Neither the dipseudocumylmethane conversion nor the durene purity are functions of the weight hourly space velocities. At rates above 1, conversion decreases rapidly. The minimum ratio of hydrogen to dipseudocumylmethane required for hydrocracking is 1 to 1; ratios as high at 10 to 1 cause little change in the products.

Durene yield and purity depend on composition of the pseudocumene employed in the condensation step. Isomers in the charge stock produce C_{10} aromatics other than durene in the hydrocracking step. The pseudocumene used in this study contained about 1% hemimellitene and 4% *tert*-butylbenzene. Paraffins up to 10 volume % in the charge stock gave no serious problems.

Hydrocracking of Dipseudocumylmethane[a]

(MoO_3 on Al_2O_3; data for 2 runs)

Reactor press., p.s.i.	**100**	**Atm.**
Temp., ° C.	**400**	**450**
Recovered, wt. %	**92.1**	**91.9**
Product analysis, wt. %		
Toluene	**0.1**	**0.1**
Pseudocumene	**47.7**	**47.1**
Durene	**31.1**	**34.2**
Isodurene	**0.4**	**0.4**
Prehnitene	**2.5**	**2.5**
Durene in C_{10} fraction	**91**	**92**
Durene[b], mole %	**75**	**82**

[a] Charge compn., wt. %: dipseudocumylmethane from 95% pseudocumene, 39.3; pseudocumene 9; benzene (solvent) 50; hydrocarbon flow, 0.8 g./min., LSHV, 0.6; H_2 flow, 1.0 l./min.

[b] Based on hexamethyldiphenylmethane plus polycondensate product.

Conclusions

The general technique of condensing aromatics with aldehydes to produce intermediate diarylparaffins which are subsequently hydrocracked to alkylated aromatics is applicable to the preparation of a wide selection of compounds. This technique is particularly applicable for producing polyalkylated aromatics which cannot be satisfactorily produced in high purity by conventional alkylation techniques.

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