benzene solution. In nitrobenzene and in dioxane the acids were found to be monomolecular. The *n*-butyl borate was monomolecular in all three solvents.

Normal butyl borate should, in the absence of steric effects, be able to polymerize according to formula II, but not according to formula I. That it does not polymerize suggests, but of course does not prove, that the association of the acids likewise does not involve the atom of boron. In that case, hydrogen bond formation would be the principal factor in that association.

The dissociating effect of both nitrobenzene and dioxane would be expected, since both possess the structures necessary for hydrogen bond formation with an hydroxyl containing solute, as well as for coördination with boron. Should either reaction take place between solvent and solute to any considerable extent, a monomolecular form of the acid would be indicated by the experimental results.

Summary

1. The molecular weights by freezing point depression of three organoboric acids and one ester have been determined in benzene, nitrobenzene, and in dioxane.

2. In benzene, the acids were found to be associated, and in the other solvents monomolecular. Normal butyl borate was found to be monomolecular in all three solvents.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Isomerization Accompanying Alkylation: Alkylation of Benzene with Isopropylethylene in the Presence of Sulfuric Acid[1]

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The shifting of the double bond in olefins under the influence of catalysts is well known. Butene-1 is isomerized completely to butene-2 at 249° in the presence of phosphoric acid.[2]

In the presence of phosphorus pentoxide on a silica gel at 300°, *unsym*-methylisopropylethylene, tetramethylethylene, and *t*-butylethylene each yields identical equilibrium mixtures of the three isomers in the ratio 31:61:3, respectively.[3]

Isopropylethylene is converted to trimethylethylene in about 80% yield[4] when passed over alumina at 525°; the same isomerization occurs in the presence of aluminum sulfate[5] and of phosphoric acid[5] at 450°. Norris and Reuter[5] also observed that the isomerization takes place to a very slight extent in the presence of 60% sulfuric acid at 38°.

In the present investigation it was found that complete isomerization of the isopropylethylene occurs at 0° during the alkylation of benzene, using 96% sulfuric acid as catalyst.

Due to the shifting of the double bond to form trimethylethylene, the alkylation product was *t*-amylbenzene and not 2-methyl-3-phenylbutane. The same product also was obtained by the alkylation of benzene with a mixture of trimethylethylene and *unsym*-methylethylethylene. That the two amylbenzenes were identical was shown by the fact that both yielded the same mono- and diacetamino derivatives.[6] Proof that these were derivatives of *t*-amylbenzene consisted in comparing them with the derivatives of a sample of *t*-amylbenzene obtained from *p*-*t*-amylphenol. Hydrogenation of the phenol with a nickel catalyst at 150° gave the cyclic alcohol. This was dehydrated over alumina at 427°. Hydrogenation then gave *t*-amylcyclohexane. Dehydrogenation by platinum at 250° gave the authentic specimen of *t*-amylbenzene. This was used because the commercial material was found to contain other amylbenzenes.

In order to compare the derivatives of 2-methyl-3-phenylbutane with those of *t*-amylbenzene, the former hydrocarbon[7] was synthesized by treating acetophenone with isopropylmagnesium bromide, dehydrating the resulting carbinol with oxalic acid, and hydrogenating the olefins with a nickel catalyst in the usual way.

The melting points of the derivatives of the amylbenzenes are given in the table.

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[1] Presented before the Division of Organic Chemistry of the American Chemical Society at Rochester, New York, September 6–10, 1937.

[2] Ipatieff, Pines and Schaad, THIS JOURNAL, **56**, 2696 (1934).

[3] Laughlin, Nash and Whitmore, *ibid.*, **56**, 1395 (1934).

[4] Ipatieff, *Ber.*, **36**, 2003 (1903).

[5] Norris and Reuter, THIS JOURNAL, **49**, 2624 (1927).

[6] Ipatieff and Schmerling, *ibid.*, **59**, 1056 (1937).

[7] Auwers and Eisenlohr, *J. prakt. Chem.*, [2] **82**, 93 (1910).

	Amylbenzene from benzene and			
	isopropylethylene	trimethylethylene and *unsym*-methylethylethylene	synthetic 2-phenyl-3-methylbutane	synthetic *t*-amylbenzene
Boiling point, °C.	188–189	189–190	184	187–188
Index of refraction, $n^{20}D$	1.4961	1.4922	1.4882	1.4869
M. p. of monoacetamino derivative, °C.	141–142[a]	141–142	147–148[b]	141
M. p. of diacetamino derivative,[c] °C.	180–181	180–181	193	180–181
M. p. of *p*-hydroxy derivative, °C.	95[d]	95[d]	.....	.....

[a] Anschütz and Beckerhoff [*Ann.*, **327**, 218 (1903)] report 138–139°; Hickinbottom [*J. Chem. Soc.*, 2396 (1932)], 140–141°. [b] Mixed m. p. (1:1) with 141–142° melting isomer: 130–134°. [c] These were also obtained in the form of hydrates having lower melting points (Ipatieff and Schmerling, unpublished results). [d] Mixed m. p. (1:1) with authentic sample, 95°.

The fact that isomerization may accompany alkylation in the presence of sulfuric acid indicates that there is a limitation in the use of the alkylation method for the synthesis of hydrocarbons. In all cases it will be necessary to prove the structure of the product by means of suitable derivatives.

Experimental

Preparation of Isopropylethylene.—Isoamyl alcohol was dehydrated by passing it through activated alumina at 400.[8] A mixture of isopropylethylene and trimethylethylene was formed. The product was treated at 0° with 75% sulfuric acid which "dissolves" trimethylethylene and does not affect isopropylethylene.[9] The latter was carefully fractionated in a precision still. The major portion boiled at 20.8–21.7°. The boiling point of trimethylethylene is 38.6°; of *unsym*-methylethylethylene, 31.2°.

Reaction of Isopropylethylethylene with Benzene.—The method used was essentially the same as that described in a previous paper.[10] To a mixture of 375. g. of benzene and 105 cc. of 96% sulfuric acid at 5°, there was added during a period of two hours 146 g. of isopropylethylene. The alkylated benzene consisted of monoamylbenzene, 20%, and diamylbenzene, 56%.

Reaction of Trimethylethylene and *unsym*-Methylethylethylene with Benzene.—One hundred and seventy-five grams of amylenes (b. p. 34–35°), obtained from the dehydration of *t*-amyl alcohol,[8] was treated with 390 g. of benzene in the presence of 100 cc. of 96% sulfuric acid.[10] The hydrocarbon layer, 539 g., was washed and distilled. The alkylated product consisted of mono-*t*-amylbenzene, 18%, and di-*t*-amylbenzene, 50%.

Synthesis of 2-Methyl-3-phenylbutane.—Fifteen grams of trimethylphenylethylene prepared according to the method of Auwers and Eisenlohr[7] was dissolved in 20 g. of isopentane and hydrogenated in a 125-cc. stainless steel high pressure bomb in the presence of 3 g. of precipitated nickel. The hydrogenation was carried out at 50° under 100 atmospheres of initial hydrogen pressure; the duration of hydrogenation was six hours.

The 2-methyl-3-phenylbutane prepared distilled at 184°, $n^{20}D$ 1.4882, d^{20}_4 0.8795.

Anal. Calcd. for $C_{11}H_{16}$: C, 89.19; H, 10.81. Found: C, 89.12; H, 10.95; mol. wt., 142.

Synthesis of *t*-Amylbenzene.—Twenty-five grams of *p*-*t*-amylphenol, m. p. 95°, was dissolved in 100 cc. of *n*-pentane and hydrogenated in the stainless steel bomb in the presence of 3 g. of precipitated nickel. The reaction temperature was 200°. The initial hydrogen pressure was 100 atmospheres. After removal of the nickel by filtration and the pentane by distillation there remained 25 g. of a viscous liquid, 4-*t*-amylcyclohexanol. This was dissolved in 100 cc. of *n*-pentane and dehydrated by passing over an alumina catalyst at 427° at a rate of 30 cc./hr. *t*-Amylcyclohexene of b. p. 193–197° was thus obtained.

Fourteen grams of the *t*-amylcyclohexene was dissolved in 50 cc. of *n*-pentane and hydrogenated at 150° in the presence of 100 atmospheres initial pressure of hydrogen and 3 g. of the nickel catalyst. Distillation of the product yielded *t*-amylcyclohexane, b. p. 192–193°.

This compound was dehydrogenated by passing it over an aluminum oxide catalyst containing 7% of precipitated platinum at 250° at a rate of 5 cc./hr. The yield of the hydrogen formed indicated that the dehydrogenation was 95% complete. The *t*-amylbenzene boiled at 187–188°. Its refractive index, $n^{20}D$ 1.4869, was somewhat low due to the presence of the unreacted *t*-amylcyclohexane.

The yield in each step of the preparation was about 90–95% of the theoretical.

Characterization of the Amylbenzenes.—The amylbenzenes were characterized by means of their mono- and diacetamino derivatives,[6] the melting points of which are given in the table.

As further proof that the alkylbenzene obtained from the reaction of benzene with the amylenes was *t*-amylbenzene, the *p*-amino derivative was isolated by way of the ether-soluble tin salt[6] and diazotized. Warming the acidic diazonium sulfate solution yielded an oil from which *p*-*t*-amylphenol, m. p. 95°, was isolated by means of an alkali extraction of the ether extract. There was no depression of the melting point when the compound was mixed with an authentic sample of *p*-*t*-amylphenol.

Summary

The reaction between isopropylethylene and benzene using sulfuric acid as a catalyst yields *t*-amylbenzene and not 2-methyl-3-phenylbutane.

The two amylbenzenes were characterized by preparing the mono- and diacetamino derivatives.

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[8] Ipatieff, *Ber.*, **36**, 2001 (1903); Pines, THIS JOURNAL, **55**, 3892 (1933).

[9] Wischnegradsky, *Ann.*, **190**, 354 (1878).

[10] Ipatieff, Corson and Pines, THIS JOURNAL, **58**, 919 (1936).