Experiment 2.—The liquid product was separated in the following fractions: (1) 67–82°, 58.0 g.; (2) 152–153°, 10.0 g.; (3) 168–170°, 5.5 g.; (4) bottoms, 4.0 g. Fraction 2 was isopropylbenzene as shown by its analysis for carbon and hydrogen, molecular weight and conversion to benzoic acid by oxidation with permanganate.

Anal. Calcd. for C_9H_{12}: C, 90.00; H, 10.00. Found: C, 89.54; H, 10.33.

Fraction 3 was identified as butylbenzene.

Anal. Calcd. for $C_{10}H_{14}$: C, 89.56; H, 10.44. Found: C, 89.17; H, 10.56.

Experiment 3.—Liquid (92 g.) is completely stable toward permanganate, boiling from 79 to 100°.

Experiments 4 and 5.—The liquid product consisted of 2,2,4-trimethylpentane, b. p. 99–100°.

Experiments 6 and 7.—Liquids (48.0 g.) contain 12% of unsaturates due to the polymerization of the gaseous olefins formed during the reaction.

Experiments 8 and 9.—The product was identified as benzene; b. p. 79–81°.

Summary

1. It was shown that destructive alkylation of benzene with *n*-hexane and 2,2,4-trimethylpentane takes place in the presence of phosphoric acid as a catalyst. In the absence of phosphoric acid the reaction does not take place.

2. The products from this reaction were analyzed and identified.

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

Influence of Sulfuric Acid Concentration upon Reaction between Olefins and Benzene

BY V. N. IPATIEFF, B. B. CORSON AND HERMAN PINES

Direct alkylation of benzene with olefins, using sulfuric acid as catalyst, offers a convenient method for the preparation of alkylated benzenes. It is known from the work of Kraemer and Spilker[1] and Brochet[2] that sulfuric acid catalyzes the reaction between olefins and aromatic hydrocarbons. Brochet considered this reaction to be general for all olefins, but it is not applicable to the ethylation of benzene, either at atmospheric or superatmospheric pressure. Phosphoric acid, however, will bring about the ethylation of benzene.[3] Brochet alkylated benzene with hexene in the presence of sulfuric acid but was unsuccessful with pentene. Brochet's lack of success was due to the presence of amyl sulfates, which decomposed to tar when the crude product was distilled. It is a general precaution that esters of sulfuric acid should be removed before distillation, and this is readily accomplished by treatment with cold sulfuric acid.

The purpose of this investigation was to study the effect of varying the concentration of the sulfuric acid catalyst. Other conditions, temperature, pressure, and amount of benzene and olefin were kept constant.

Three competing reactions can take place in a mixture of benzene, sulfuric acid and olefin: (1) addition of olefin to benzene, (2) polymerization of olefin, (3) addition of olefin to acid to form ester.

The predominating reaction of propene in the presence of benzene and 96% sulfuric acid is alkylation (a little ester formation but no polymerization), whereas, with 80% acid, propene reacts about equally in two directions, ester formation and alkylation.

Three-fold competition for olefin is especially noticeable with isobutene. By suitable choice of acid concentration (temperature 4–20°), any one of three reactions can be made predominant. For example, in the presence of 96% acid, the main reaction is alkylation, together with a little ester formation. With 80% acid, the chief reaction is polymerization; there is a small amount of ester formation but no alkylation. With 70% acid, isobutene is converted into ester without polymerization or alkylation.

The mechanism of alkylation is assumed to be through the ester, the latter functioning as alkylating agent. The mechanism of polymerization is the same as that suggested for polymerization in the presence of phosphoric acid,[4] the ester being the intermediate. In the light of this explanation, it follows that 96% sulfuric acid catalyzes the alkylation of benzene by tertiary butyl sulfate, weaker acid catalyzes the formation of polymer from the same ester, and still weaker

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(1) Kraemer and Spilker, *Ber.*, **23**, 3169, 3269 (1890).

(2) Brochet, *Compt. rend.*, **117**, 115 (1893).

(3) Ipatieff, Pines and Komarewsky, *Ind. Eng. Chem.*, **28**, 222 (1936).

(4) Ipatieff, *ibid.*, **27**, 1067 (1935); Ipatieff and Pines, *ibid.*, **27**, 1364 (1935).

TABLE I

CONSTANTS OF ISOPROPYLBENZENES

Isopropyl derivative of benzene	B. p., °C.	Mm.	M. p., °C.	d^{20}_4	n^{20}_D	Analyses, % Calcd. C	H	Found C	H
Mono-	151.9–152.2	758	....	0.861	1.4922	89.9	10.1	89.8	10.2
Di-	205.5–206.5	755	....	.858	1.4912	88.8	11.2	88.5	11.3
Tri-	240–242	753	....	.862	1.4929	87.9	12.1	88.2	11.9
Tetra-	....	...	119–119.4	...	....	87.7	12.3	87.3	12.4

acid exerts no catalytic effect, with the result that the ester is obtained as final product.

Besides reporting the effect of sulfuric acid concentration upon the reaction of propene and isobutene in the presence of benzene, this paper describes the alkylation of benzene with butene-1, pentene, octene, nonene and dodecene; also of toluene and naphthalene with propene. Nieuwland and co-workers[5] have described the propylation of benzene with a mixture of boron fluoride and concentrated sulfuric acid. They assumed that the latter functioned as "condensation accelerator." One of their experiments was repeated, omitting the boron fluoride, and the reaction was found to proceed in exactly the same manner as it had in the presence of boron fluoride and sulfuric acid. In other words, the small amount of sulfuric acid used supposedly as accelerator was sufficient, alone, to catalyze the reaction.

Experimental Part

96% Sulfuric Acid, Benzene and Propene.—Propene was passed into a cold, stirred mixture of 100 cc. of 96% sulfuric acid and 200 cc. of benzene until 110 g. had been absorbed. With 99% propene, the required weight was absorbed in two hours with the loss of only one liter of exit gas.

The apparatus consisted of a one-liter, three-necked flask, equipped with a mercury-sealed stirrer and immersed in an ice-bath. One of the side necks held a T-tube through which the olefin was introduced, and a thermometer which dipped into the liquid contents of the flask. The inlet tube did not dip into liquid; it was only necessary to maintain an atmosphere of propene within the flask. A propeller type of stirrer (with wide blades, 950 r. p. m.) was found to be effective, provided it was not too deep in the liquid. The temperature of the reaction mixture rose from 6 to 15° during the first thirty minutes and finally fell to 10°.

The reaction mixture was separated within thirty minutes and the acid layer (212 cc.) was worked up for the solid tetraisopropylbenzene which separated on standing. The cold hydrocarbon layer was shaken with three successive portions of cold 96% sulfuric acid. The purpose of the acid was to convert dipropyl sulfate into monopropyl sulfate which was subsequently washed out with water.

The yield of the crude isopropylbenzenes based on the propene absorbed was 32, 33, 12 and 2% for the mono, di, tri and tetra compounds, respectively. Tetra derivative crystallized from the distillation bottoms and also separated from the catalyst acid on standing.

The above procedure yielded 1.4 times as much mono- as diisopropylbenzene. Starting with twice as much benzene as specified, and adding the same amount of propene, yielded 3.9 times as much mono- as diisopropylbenzene. In another experiment, 300 g. of propene was passed into a mixture of 1000 cc. of benzene and 250 cc. of 96% sulfuric acid (temperature, 7–10°; time of addition, one and one-half hours). The alkylated product contained 663 g. of monoisopropylbenzene, 105 g. of diisopropylbenzene, and 12 g. of bottoms.

For the preparation of tri- and tetraisopropylbenzenes it is recommended to start with mono- or diisopropylbenzenes. Propene was passed into a mixture of 162 g. of diisopropylbenzene and 100 cc. of 96% sulfuric acid. The temperature was allowed to rise from 20 to 60°. At the end of one hour, 125 g. of propene had been absorbed and the mixture had become too thick to stir. The solid mass obtained on cooling was broken up in ice water. One hundred and fifty-two grams of tetraisopropylbenzene and 28 g. of triisopropylbenzene were obtained. Cyclohexane (100 cc.) was used as solvent for the diisopropylbenzene in a similar run made at 2 to 9°; 78 g. of propene was absorbed, but distillation showed that the diisopropylbenzene was unchanged.

Diisopropylbenzene (b. p. 205.5–206.5° (755 mm.)) was shown to be the para derivative. A sample was oxidized by refluxing for five hours with nitric acid (1:3). The solid product was washed with water, alcohol and ether. It was identified by conversion into dimethyl terephthalate, which after crystallization from dilute methyl alcohol, melted at 138.5–139.5°. The tetrasubstituted derivative seemed to be identical with the 1,2,4,5-tetraisopropylbenzene described by Berry and Reid.[6]

80% Sulfuric Acid, Benzene and Propene.—Propene was passed into a mixture of 200 cc. of benzene and 100 cc. of 80% sulfuric acid. Absorption was slow at 0°, but fairly rapid at 60°; the temperature was maintained at 60° during the greater part of the experiment. Eighty-eight grams of propene was absorbed in one and eight-tenths hours. The hydrocarbon layer (178 g.) was distilled. The greater part was benzene, but there was 49 g. of material boiling above benzene. From the latter was isolated 23 cc. of monoisopropylbenzene (b. p. 145–160°; n^{21}_D 1.4910) and 10 cc. of diisopropylbenzene (b. p. 200–210°; n^{21}_D 1.4908). Propylation consumed about 45% of the absorbed propene. The acid layer was neutralized and distilled. The distillate contained 50.1 g. of isopropyl alcohol (55% of the theoretical).

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(5) Slanina, Sowa and Nieuwland, THIS JOURNAL, **57**, 1547 (1935).

(6) Berry and Reid, *ibid.*, **49**, 3142 (1927).

TABLE II

CONSTANTS OF TERTIARY BUTYLBENZENES

t-Butyl derivative of benzene	B. p.,		M. p., °C.	d^{20}_4	n^{20}_D	Analyses, %			
	°C.	Mm.				Calcd. C	Calcd. H	Found C	Found H
Mono-	168.5–170	760	.....	0.863	1.4912	89.5	10.5	89.4	11.0
Di-	....	...	78–78.5	..	....	88.4	11.6	88.6	11.7
Tri-	285–305	750	.....	..	1.4919^{30}	87.7	12.3	87.3	12.0

96% Sulfuric Acid, Benzene and Isobutene.—Isobutene was passed into a cold (4–21°) stirred mixture of 100 cc. of 96% sulfuric acid and 200 cc. of benzene until 150 g. of isobutene had been absorbed (1.2 hours). The solid di-*t*-butylbenzene was filtered and crystallized from methyl alcohol. The hydrocarbon layer (containing mono-, di- and tri- derivatives) was separated from the filtrate and distilled. Polymers were completely absent as evidenced by the permanganate stability of all the fractions. With 90% sulfuric acid as catalyst, the yields were about the same, but the product was contaminated with olefin polymer as shown by the permanganate test.

The yield of the crude *t*-butylbenzenes based on the isobutene absorbed was 7, 77 and 8% for the mono, di and tri compounds, respectively.

Di-*t*-butylbenzene (m. p. 78–78.5°) was shown to be the para derivative. A sample was nitrated by fuming nitric acid at room temperature,[7] and the product was crystallized twice from 95% alcohol. The nitro compound (2,6-dinitro-1,4-di-*t*-butylbenzene) melted at 191.5–192°.

80% Sulfuric Acid, Benzene and Isobutene.—Isobutene was passed into a mixture of 200 cc. of benzene and 100 cc. of 80% acid at 7–12°, 168 g. of olefin being absorbed in one and seven-tenths hours. The volume of the acid layer was 250 cc. at the end of the reaction, 107 cc. after two hours, and 100 cc. after sixteen hours. The hydrocarbon layer was washed with cold 80% acid before distillation.

Ninety-seven per cent. of the original benzene was recovered (b. p. 79–82°; d^{20}_4 0.860; n^{20}_D 1.4901). The constants of the material boiling above benzene were those of isobutene polymers.[8] No alkylated product was present. Of the 168 g. of olefin absorbed, 128 g. was recovered in the form of polymers, 72% of which was triisobutene. Fifty-two per cent. of the remaining 40 g. of isobutene was recovered from the acid layer as tertiary butyl alcohol (b. p. 81–84°; d^{20}_4 0.785). The identity of the triisobutene fraction (b. p. 176–178°; d^{20}_4 0.762; n^{20}_D 1.4334) was confirmed by hydrogenation with nickel oxide at 200–220° and 100 atmospheres initial hydrogen pressure, conditions under which cycloparaffins and aromatics are not affected. The original fraction analyzed for C_nH_{2n} (calcd. for $C_{12}H_{24}$: C, 85.6; H, 14.4. Found: C, 85.6; H, 14.4) and the hydrogenated product analyzed for C_nH_{2n+2} (calcd. for $C_{12}H_{26}$: C, 84.6; H, 15.4. Found: C, 84.5; H, 15.5.

70% Sulfuric Acid, Benzene and Isobutene.—Isobutene was passed into a mixture of 200 cc. of benzene and 100 cc. of 70% sulfuric acid at about 4°, 143 g. of isobutene being absorbed in two and eight-tenths hours. The hydrocarbon layer consisted of benzene, 98% of the original benzene being recovered unchanged. A portion was distilled over sodium: b. p. 80°; d^{20}_4 0.873; n^{20}_D 1.4992. Therefore, no alkylation or polymerization took place in this reaction. Tertiary butyl alcohol (f. p. about 23°; b. p. 82–83°; d^{20}_4 0.787) was obtained from the neutralized acid. The yield was 76% of the theoretical amount.

96% Sulfuric Acid, Toluene and Propene.—Two products were obtained, one boiling at 177°, and the other at 221–223°. The former was the main product and was identified as *p*-isopropyltoluene; the latter, presumably diisopropyltoluene, was not investigated. The fraction boiling at 177° was refluxed for eight hours with nitric acid (1:3). The crude solid was a mixture of *p*-toluic and terephthalic acids. Ether extraction left a residue which was identified as terephthalic acid. A portion of the solid obtained by evaporating the ether extract was recrystallized from water to yield *p*-toluic acid (m. p. 176–178°). A portion of the *p*-toluic acid was oxidized to terephthalic acid by alkaline permanganate.

96% Sulfuric Acid, Naphthalene and Propene.—Propene was passed into a mixture of naphthalene, carbon tetrachloride and sulfuric acid. The olefin was rapidly absorbed. A liquid product was isolated which boiled at 260–265° and whose carbon–hydrogen ratio was that of isopropylnaphthalene.

Alkylation of Benzene with Butene-1, Pentene, Octene, Nonene and Dodecene.—Benzene was alkylated with the above olefins, using 96% sulfuric acid as catalyst. The effect of different acid concentrations was not studied. Mono- and di- derivatives were obtained whose boiling points agreed with those previously reported and whose carbon–hydrogen ratios checked the calculated values. In the case of amylene, two isomeric tri-substituted derivatives were also obtained. The triamyl-, dioctyl-, dinonyl- and didodecylbenzenes are new.

The initial olefins were mixtures except butene-1. The latter was prepared by the Ipatieff method[9] by catalytic dehydration of *n*-butyl alcohol over activated alumina; the pentene was a 34–38° cut (presumably a mixture of 2-methylbutene-2 and pentene-2), and the octene was a 124–126° cut from Eastman products; the nonene was a 130–137° fraction, and the dodecene was a 175–186° fraction from material made by the polymerization of propene with phosphoric acid.[10]

The structure and position of the side chains in these alkylated products were determined only with mono-*s*-butylbenzene and *p*-di-*s*-butylbenzene. The mono compound (n^{20}_D 1.4902) was nitrated with cold nitric acid, the nitro compound was reduced with tin and hydrochloric acid, and the amine was converted into its acetanilide

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(7) Boedtker, *Bull. soc. chim.*, [3] **31**, 969 (1904); [3] **35**, 825 (1906).

(8) Whitmore and Church, THIS JOURNAL, **54**, 3710 (1932); Ipatieff and Corson, *Ind. Eng. Chem.*, **27**, 1069 (1935). The result was the same when three times as much acid was used as catalyst.

(9) Ipatieff, *Ber.*, **36**, 1990 (1903); Pines, THIS JOURNAL, **55**, 3892 (1933).

(10) Ipatieff, *Ind. Eng. Chem.*, **27**, 1067 (1935).

(m. p. 125–126°).[11] The di- derivative (n^{20}_D 1.4884) was oxidized with alkaline permanganate to terephthalic acid which was identified in the form of its dimethyl ester.

TABLE III

BUTYL-, AMYL-, OCTYL-, NONYL- AND DODECYLBENZENES

Compound	B. p., °C.	Mm.	Analyses, % Calcd. C	H	Found C	H
Mono-*s*-butylbenzene	170–171		89.5	10.5	89.4	10.6
p-Di-*s*-butylbenzene	233–237		88.4	11.6	88.1	11.7
Triamylbenzene	282–288		87.4	12.6	87.3	12.5
Triamylbenzene	312–318		87.4	12.6	86.9	12.8
Dioctylbenzene	338–343		87.3	12.7	86.8	12.9
Dinonylbenzene	153–163	5	87.2	12.8	87.3	12.9
Didodecylbenzene	197–211	5	86.9	13.1	86.7	13.1

Boron Fluoride–Sulfuric Acid as Alkylation Catalyst.—One of the experiments of Slanina, Sowa and Nieuwland[5] was repeated, omitting the boron fluoride catalyst. The pressure was 750 mm. of mercury as compared with 970 mm. in Nieuwland's experiment. Propene was passed into a stirred (950 r. p. m.) mixture of 150 g. of benzene and 17 g. of sulfuric acid for one hour, the temperature rising from 20° to a maximum of 82° of its own accord, until 68 g. of propene had been absorbed; 50 g. of benzene; 108 g. of monoisopropylbenzene; 34 g. of diisopropylbenzene; and 5 g. of bottoms were recovered. It is therefore evident that the boron fluoride was unnecessary and that the sulfuric acid, the so-called condensation acceleration, was quite sufficient to catalyse the reaction.

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Summary

A study has been made of the effect of sulfuric acid concentration upon the reactions of propene and isobutene in the presence of benzene.

With 96% sulfuric acid, propene alkylates benzene, but with 80% acid, half of the propene alkylates benzene and the other half forms propyl sulfate which can be hydrolyzed to isopropyl alcohol.

The main reaction of isobutene in the presence of 90 and 96% acids is alkylation. With 80% acid it is polymerized, chiefly to triisobutene, and with 70% acid isobutene reacts only to form ester from which tertiary butyl alcohol can be obtained by hydrolysis.

Benzene has been alkylated, in the presence of sulfuric acid as catalyst, by butene-1, pentene, octene, nonene and dodecene. Toluene and naphthalene were also propylated.

Boron fluoride, presumably promoted by sulfuric acid, has been described elsewhere as a catalyst for alkylation of benzene by propene. However, in the presence of sulfuric acid, boron fluoride is unnecessary.

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[11] Reilly and Hickenbottom, *J. Chem. Soc.*, **117**, 120 (1920); Harrison, Kenyon and Shepherd, *ibid.*, 659 (1926).

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

Destructive Alkylation with a Hydrogenating Catalyst

BY V. N. IPATIEFF AND V. I. KOMAREWSKY

In the dehydrogenation of cyclohexane over palladium, platinum, or nickel oxide–alumina catalyst at 300°, traces of a crystalline material are always found in the cool end of the tube or in the distillation bottoms. This material has been identified as *diphenyl.* Its formation is due to a further dehydrogenation of benzene, the main product of the reaction.

In an attempt to increase the yield of this secondary product, the dehydrogenation temperature was raised to 350°. The catalyst was a mixed nickel oxide–alumina catalyst, first introduced by Ipatieff[1] in 1910–1912, and later (1924) used by Zelinsky and Komarewsky[2] in dehydrogenation.

The reaction product consisted of (1) a gas containing 29% of hydrogen and 71% of methane and (2) a liquid containing 21.5% of unchanged cyclohexane, 71.4% of benzene and 7.1% of toluene.[3] The appearance of toluene showed that destructive alkylation[4] accompanied the dehydrogenation of cyclohexane to benzene, ethylbenzene and ethylcyclohexane being possible intermediates.

We examined the behavior of ethylbenzene and ethylcyclohexane in the presence of the nickel oxide–alumina catalyst at 350°.

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[1] Ipatieff and Matov, *Ber.*, **45**, 4305 (1912).

[2] Zelinsky and Komarewsky, *ibid.*, **57**, 667 (1924).

[3] Zelinsky and Shuikin [*Compt. rend. de l'académie des Sciences de U. S. S. R.*, **3**, 255 (1934)] had previously noticed the formation of toluene in the dehydrogenation of cyclohexane over a similar catalyst.

[4] Ipatieff and Komarewsky, THIS JOURNAL, **56**, 1926 (1934); Ipatieff, Komarewsky and Grosse, *ibid.*, **57**, 1722 (1935).