(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.	B. p., Mm.	Analyses, % Calcd. C	Analyses, % Calcd. H	Analyses, % Found C	Analyses, % Found 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).

Ethylbenzene yielded benzene, toluene, methane, ethane, hydrogen and naphthalene. Thus, the side chain was split in two ways: (1) completely, to form benzene and ethane, and (2) partially, to form toluene and methane. The hydrogen resulted from the naphthalene formation. Ethylcyclohexane, under the same conditions, yielded benzene, toluene, methane and hydrogen. Therefore, either ethylbenzene or ethylcyclohexane could have served as intermediate in the proposed mechanism.

It is interesting to note a similar dual action of another catalyst of wholly different type. Aluminum chloride, a typical alkylation catalyst, is also able to bring about hydrogenation-dehydrogenation phenomena.[4]

The alkylating action of the nickel oxide-alumina catalyst must be attributed to the alumina. No alkylation was observed with platinum-charcoal and palladium-asbestos catalysts. The alkylating action of the alumina can be explained by the intermediate formation of ester,[5] as follows.

$$Al_2O_3 + H_2O \longrightarrow 2AlO(OH) \tag{1}$$

$$AlO(OH) + C_2H_4 \longrightarrow AlO(OC_2H_5) \tag{2}$$

$$AlO(OC_2H_5) + C_6H_6 \longrightarrow C_6H_5C_2H_5 + AlO(OH) \tag{3}$$

Experimental Part

Apparatus and Procedure.—The hydrocarbon was passed at the rate of 10 cc. per hour through a glass tube filled with 30 g. of catalyst. The tube was heated in a constant temperature electric furnace. The liquid product was fractionated through a micro-Podbielniak column. The gas was analyzed by the Göckel combustion method.

Material.—The cyclohexane (m. p. 3.5–4.5°; n^{20}_{D} 1.4270) and the ethylbenzene (b. p. 134–136°; n^{25}_{D} 1.4931) were Eastman products. The ethylcyclohexene was prepared by hydrogenation under pressure of ethylbenzene at 250° with a nickel oxide catalyst. The product boiled at 129–130° and was completely stable to nitrating mixture. The nickel oxide-alumina catalyst was prepared according to Zelinsky and Komarewsky.[2]

Dehydrogenation of Cyclohexane.—Seventy cc. of cyclohexane yielded 67 cc. of liquid and 29 liters of gas containing 71% of methane and 29% of hydrogen. The liquid (n^{25}_{D} 1.4890) was separated into two fractions. The first fraction (60 cc.; b. p. 79–82°; n^{25}_{D} 1.4740) was completely stable toward permanganate. Treatment with fuming sulfuric acid (15% SO_3) left a 25% residue of unreacted cyclohexane (n^{24}_{D} 1.4240). The second fraction (5 cc.; b. p. 110–112°; n^{24}_{D} 1.4935) was completely soluble in fuming sulfuric acid (15% SO_3). Nitration yielded 2,4-dinitrotoluene, m. p. 70°. Bromination in the presence of aluminum bromide gave toluene pentabromide, m. p. 283–285°.

Dehydrogenation of Ethylbenzene.—Thirty-seven cc. of ethylbenzene yielded 30 cc. of liquid and 5.66 liters of gas containing 22.8% of hydrogen, 38.0% of methane and 38.0% of ethane. The liquid (n^{25}_{D} 1.4945) was separated into four fractions: (1) b. p. 79–82°, 5 cc.; (2) b. p. 108–113°, 6.0 cc.; (3) b. p. 113–133°, 14.9 cc.; (4) above 133°, 3 g. The second fraction (n^{25}_{D} 1.4920) was identified as toluene.

Anal. Calcd. for C_7H_8: C, 91.3; H, 8.7. Found: C, 91.2; H, 8.8.

Nitration of this fraction gave 2,4-dinitrotoluene. Fraction No. 4 consisted of naphthalene, m. p. 80°.

Dehydrogenation of Ethylcyclohexane.—Fifty-nine and four-tenths cc. of ethylcyclohexane yielded 45 cc. of liquid and 20.4 liters of gas consisting of 55.5% of methane, and 44.5% of hydrogen. The liquid (n^{25}_{D} 1.4725) was separated into five fractions: (1) b. p. 80–82°, 10.5 cc.; (2) b. p. 82–105°, 1.5 cc.; (3) b. p. 108–112°, 5.0 cc.; (4) b. p. 115–131°, 10.5 cc.; (5) above 131°, 0.1 g. The third fraction (n^{25}_{D} 1.4875) was toluene.

Anal. Calcd. for C_7H_8: C, 91.3; H, 8.7. Found: C, 91.0; H, 9.0.

Nitration of this fraction gave 2,4-dinitrotoluene.

Summary

1. Destructive alkylation was observed in the presence of a hydrogenating-dehydrogenating (nickel oxide-alumina) catalyst.

2. Cyclohexane and ethylcyclohexane formed benzene, toluene, methane and hydrogen. Ethylbenzene formed benzene, toluene, methane, ethane, hydrogen and naphthalene.

3. A mechanism for this reaction is proposed.

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(5) V. N. Ipatieff, "Catalytic Reactions at High Temperatures and Pressures," chapter on polymerization (in publication).