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Phosphoric Acid as a Catalyst for the Destructive Alkylation of Hydrocarbons

BY V. N. IPATIEFF, V. I. KOMAREWSKY AND HERMAN PINES

In previous work[1] it was shown that under the action of a catalyst (aluminum chloride) the hydrocarbons might undergo decomposition and the fragments combine with each other or with some other hydrocarbon present, giving rise to the formation of higher boiling alkylated hydrocarbons. This reaction was defined as "destructive alkylation." The present paper deals with the destructive alkylation of 2,2,4-trimethylpentane and benzene and *n*-hexane and benzene in the presence of phosphoric acid as catalyst.

The reactions take place according to the equations

$$(CH_3)_3CCH_2CH(CH_3)_2 + C_6H_6 \xrightarrow{H_3PO_4} (CH_3)_3CH + C_6H_5C(CH_3)_3$$

$$2n\text{-}C_6H_{14} + 2C_6H_5 \xrightarrow{H_3PO_4} C_3H_8 + C_2H_6 + C_6H_5CH(CH_3)_2 + C_6H_5C_4H_9$$

These reactions do not take place in the absence of phosphoric acid. Under our experimental conditions benzene alone remains unchanged, but the paraffinic hydrocarbons decompose to a slight degree into olefins and paraffins. The olefins formed, under the influence of phosphoric acid, as it was shown before by us,[2] react with benzene to give alkylated benzenes.

Experimental Part

Experiments were carried on in an Ipatieff's rotating autoclave of 850-cc. capacity. The autoclave was provided with a glass tube in which the reagents were placed. The air from the apparatus was replaced by nitrogen in order to avoid oxidation.

The liquid products obtained from the reaction were fractionated by means of a Podbielniak high temperature column.[3] The results are summarized in the table.

TABLE I

THE DESTRUCTIVE ALKYLATION OF HYDROCARBONS

Experiment[a]	1	2	3	4	5	6	7	8	9
Paraffin: Name	2,2,4-Trimethylpentane	*n*-Hexane	2,2,4-Trimethylpentane			*n*-Hexane			
Paraffin: Grams	52.0	48.0	50.0	60.0	60.0	30.0	30.0	..	..
Benzene, grams	51.5	47.5	50.0	..	..	..	..	50.0	50.0
100% H_3PO_4, grams	15.0	21.0	..	17.0	..	10.0	..	15.0	..
Reaction time, hours	6	10	6	6	6	6	6	6	6
Final press., atm., at 21°	18	19	4	5	4.5	3.0	3.0	0	0
Gases on N-free basis, cc.	7000	6200	1270	2500	2200	1400	1000	100	100
Compn. of gas on N-free basis, %: i-C_4H_{10}	63.2		65.0	33.5	32.0	..	..	..	..
	C_3H_8	C_2H_6	i-C_4H_8	n-C_4H_{10}	n-C_4H_{10}	Paraffin	Paraffin		
	4.7	54.0	24.0	12.0	13.0	75.0[b]	74.0[c]	Not analyzed	
	CH_4	C_3H_8		CH_4	CH_4	Olefins	Olefins		
	24.0	18.0		21.0	20.0	2.5	3.0		
Hydrogen	8.1	28.0	10.0	33.5	35.0	22.5	21.7		
Liq. prod. from H_3PO_4	85.0	80.0	92.0	44.0	47.0	26.5	27.0	48.0	48.0

[a] The capacity of the autoclave was 850 cc. The experiments were carried out at 450°. [b] Average molecular weight of the paraffins 30. [c] Average molecular weight of the paraffins 34.

Investigation of the Liquid Products

Experiment 1.—The product (85.0 g.) was distilled and the following fractions were obtained: (1) 80–81°, 41 g.; (2) 99–100°, 12 g.; (3) 169–170°, 11.5 g.; (4) bottoms 3.0 g. Fraction 1 was the unreacted benzene. Fraction 2 consisted of 2,2,4-trimethylpentane. Fraction 3 was tertiary butylbenzene as shown by its analysis for carbon and hydrogen, molecular weight and conversion to tertiary butylphenol, m. p. 98.5°.

Anal. Calcd. for $C_{10}H_{14}$: C, 89.56; H, 10.44. Found: C, 89.05; H, 10.73.

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(1) (a) Ipatieff and Komarewsky, THIS JOURNAL, **56**, 1926 (1934); (b) Grosse and Ipatieff, *ibid.*, **57**, 2415 (1935).

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

(3) W. Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **5**, 172 (1933).

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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Influence of Sulfuric Acid Concentration upon Reaction between Olefins and Benzene

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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).