Methoxy-1,3-butadiene: b. p. 75° at 745 mm.; $n^{20}D$ 1.4442; d^{20} 0.8281. 3,3-Dimethoxy-1-butene: b. p. 98–100° at 745 mm.; $n^{20}D$ 1.4038; d^{20} 0.8756.

In another experiment 65 g. of 3,3-dimethoxy-1-butene was decomposed in a similar manner. There was obtained 40 g. of 2-methoxy-1,3-butadiene (85% yield).

Similar decomposition of 148 g. of 1,3-dimethoxy-2-butene gave 25 g. of 3,3-dimethoxy-1-butene (17% yield) and 42 g. of 2-methoxy-1,3-butadiene (39% yield).

Hydrolysis of 1,3-Dimethoxy-2-butene.—Thirty grams (0.25 mole) of 1,3-dimethoxy-2-butene was added to 20 ml. of water containing 1 drop of hydrochloric acid. After standing for fifteen minutes the product was dried over anhydrous potassium carbonate and distilled. There was obtained 17 g. (65% yield) of 1-methoxy-3-butanone, previously described:[2] b. p. 139° at 745 mm.; $n^{26}D$ 1.4019; d^{26} 0.9125.

Addition of Methanol to 1,3-Dimethoxy-2-butene.—To a mixture of 20 g. of 1,3-dimethoxy-2-butene and 10 g. of anhydrous methanol was added a few crystals of *p*-toluenesulfonic acid. The reaction was quite vigorous and it was necessary to cool in a water-bath. After the reaction was complete (few minutes) the acid was neutralized with a small amount of sodium methylate solution. Distillation gave 25 g. (96% yield) of 1,3,3-trimethoxybutane, b. p. 63–65° at 25 mm.; $n^{20}D$ 1.4110; d^{20} 0.9395.

Addition of methanol to 3,3-dimethoxy-1-butene and to 2-methoxy-1,3-butadiene was accomplished in a similar manner.

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Summary

The thermal catalytic desaturation of 1,3,3-trimethoxybutane has been investigated and the products described. Three reversible and three non-reversible reactions leading to 1,3,3-trimethoxybutane are given.

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

Phosphoric Acid as Catalyst in the Ethylation of Phenol

BY V. N. IPATIEFF, HERMAN PINES AND LOUIS SCHMERLING

That sulfuric acid is a catalyst for the reaction of phenol with olefins has long been known.[1] An exhaustive study of its use in the alkylation of phenol has been made in recent years by Niederl and co-workers.[2] However, sulfuric acid does not catalyze the reaction between phenol and ethylene.

Ipatieff and Pines[3] have shown that phosphoric acid is a catalyst for the alkylation of phenol with olefins including ethylene. In the present investigation the reaction with the latter was studied in greater detail. It was found that the product consists of ethylphenols, phenetole and ethylphenetoles, and that the yield of the former may be increased at the expense of the latter by carrying out the reaction in the presence of cyclohexane as solvent.

This is somewhat analogous to Claisen's method[4] of inducing C-allylation of phenol by the reaction of sodium phenoxide with allyl bromide in the presence of a non-dissociating solvent.

In order to determine whether the nuclear alkylation had necessarily taken place by way of the intermediate formation of the ether, phenetole was alkylated with propene. The product consisted entirely of propylated phenetole. Dealkylation of this product with hydriodic acid yielded only ethyl iodide and *o*- and *p*-isopropylphenols, as well as more highly propylated phenols. This agrees with the results of Sowa, Hinton and Nieuwland,[5] who showed that propene could be condensed readily with anisole in the presence of boron fluoride, with the isolation of 2-isopropylphenyl methyl ether and higher condensation products. It may be concluded, then, that contrary to the opinion of Niederl and Natelson[2] and the more positive subsequent statement of Natelson,[6] ether formation is not *necessarily* an intermediate step in nuclear alkylation with olefins and that direct C-alkylation can occur in the presence of phosphoric acid.

It was further shown that phenetole does not rearrange under the conditions of the alkylations.

Experimental

Reaction of Ethylene with Phenol.—The alkylations were carried out in a rotating Ipatieff type autoclave of 850-cc. capacity. Phenol and phosphoric acid were weighed into a glass liner equipped with a capillary seal which was then placed in the bomb. The latter was charged with ethylene to an intial pressure of 50 atmos-

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[1] Koenigs, *et. al.*, *Ber.*, **23**, 3144 (1890); **24**, 179, 3889 (1891).

[2] Niederl and Natelson, THIS JOURNAL, **53**, 272, 1928 (1931); and subsequent papers.

[3] Ipatieff, "Catalytic Reaction at High Pressure and Temperature," The Macmillan Co., New York, N. Y., 1936, p. 668.

[4] Claisen, *Ber.*, **58**, 279 (1925); *Ann.*, **442**, 210 (1925).

[5] Sowa, Hinton and Nieuwland, THIS JOURNAL, **55**, 3402 (1933).

[6] Natelson, *ibid.*, **56**, 1583 (1934).

TABLE I

	Reactants								Products						
	"Phenol"		H_3PO_4	Olefin		Reaction		Alkali soluble[a]			Alkali insoluble[a]			Lower layer H_3PO_4, Wt., g.
Expt.	Kind	Wt., g.	Wt., g.	Kind	Wt., g.	Temp. °C.	Time hrs.	C_6H_5OH	Et-C_6H_4OH	Et_2-C_6H_3OH, etc.	C_6H_5-OEt	Et C_6H_4OEt	Et_2-C_6H_3Et, etc.	
1	Phenol	94	30	C_2H_4	27[c]	225	12	21.6	12.5	5.0	9.2	16.7	35.0	31
2	Phenol	94	30	C_2H_4	47[c]	225	22	12.9	20.2	16.5	7.9	11.6	30.9	32
3	Phenol	94[b]	30	C_2H_4	31[c]	225	16	14.6	43.1	19.6	7.3	9.7	5.7	32
4	Phenetole	183	60	C_3H_6	90[d]	145	7	0	0	0	63.5[e]	16.2[f]	20.3[g]	61
5	Phenetole	151	59		0	145	12	4.3	0	0	95.7	0	0	59

[a] Per cent. by weight of upper (organic) layer. [b] Dissolved in 63 g. of cyclohexane. Data given on a solvent-free basis. [c] Estimated by the increase in weight of reaction mixture. [d] Propylene recovered after reaction, 29 g. [e] Unreacted phenetole: *Anal.* Calcd. for $C_6H_5OC_2H_5$: C, 78.69; H, 8.20. Found: C, 78.52; H, 8.54. [f] Monoisopropylphenetoles: *Anal.* of fraction boiling at 212–214°: calcd. for $C_6H_4(C_3H_7)OC_2H_5$: C, 80.49; H, 9.72; mol. wt., 154. Found: C, 80.58; H, 10.21; mol. wt., 152. [g] Diisopropylphenetoles and higher propylated phenetoles.

pheres at 25°. The maximum pressure developed at 225° never exceeded 95 atmospheres. At the end of the run the unreacted ethylene was released and the reaction product consisted of the two layers; the lower phosphoric acid layer was separated from the organic layer. The latter was separated into alkali-soluble and alkali-insoluble portions and each was fractionated. The data are summarized in the table. The phenols were characterized by means of the aryloxyacetic acid derivatives; the ethers, by dealkylation with hydriodic acid followed by the identification of the phenol and the ethyl iodide by means of solid derivatives.

The aryloxyacetic acids were prepared according to the method of Koelsch,[7] with the exception that sodium bicarbonate was used instead of sodium carbonate in the extraction of the derivative. The *o*-ethylphenoxyacetic acid was recrystallized from water; m. p. 136–137°. Calcd. for $C_{10}H_{12}O_3$: C, 66.67; H, 6.67. Found: C, 67.08, 66.64; H, 6.86, 6.94.

The *p*-ethylphenoxyacetic acid, also recrystallized from water melted at 96°.[8] Calcd. for $C_{10}H_{12}O_3$: C, 66.67; H, 6.67. Found: C, 66.30; H, 6.68.

The structure of the *o*- and of the *p*-ethylphenoxyacetic acids was proved by preparing the compounds from authentic specimens of *o*- and *p*-ethylphenol obtained via the diazotization of *o*- and *p*-aminoethylbenzene. The derivatives so prepared were identical with the respective compounds obtained from the alkylation products.

The dealkylation of the ethers was carried out by refluxing 2 g. of the ether with 15 cc. of constant boiling hydriodic acid for four hours. Sufficient glacial acetic acid to give a single clear solution was used as solvent. The product was diluted with twice its volume of water, ether extracted and the extract washed with water and then with dilute alkali. Acidification of the alkaline solution yielded the phenol, which was characterized by means of the aryloxyacetic acid derivative. The ether was distilled from the solution containing the unreacted phenetole and ethyl iodide and the residue treated with silver 3,5-dinitrobenzoate in alcohol.[9] The ethyl 3,5-dinitrobenzoate crystallized as needles from dilute alcohol; m. p. 92°.

Reaction of Propene with Phenetole.—Data for the reaction of propene with phenetole at 145° in the presence of phosphoric acid are given in the table. The apparatus and procedure was the same as that in the ethylation of phenol. The maximum pressure developed was 35 atmospheres. No alkali-soluble material was found. The product was carefully fractionated and refractionated through a high temperature Podbielniak column and various fractions identified by the method outlined above. The *o*- and *p*-isopropylphenoxyacetic acids melted at 130–131°[10] and 85–86°,[11] respectively. The product obtained by the reaction of the alkyl iodide with silver 3,5-dinitrobenzoate melted at 92° in all cases. Apparently no isopropyl 3,5-dinitrobenzoate (m. p. 122°) was present. It may be concluded that only propylated phenetoles were formed in the alkylation reaction.

Reaction of Phenetole with Phosphoric Acid.—The data for the reaction are given in the table. The autoclave was the same as that used in previous experiments. Ninety-six per cent. of the phenetole was recovered unchanged; a 4% yield of phenol was obtained, b. p. 177–179°, m. p. 38–40°.

Summary

Ethylene reacts readily with phenol in the presence of phosphoric acid at 200°, yielding *o*- and *p*-ethylphenol, diethylphenol, and higher ethylated phenols, as well as phenetole, *o*- and *p*-ethylphenetole. and higher ethylated phenetoles.

The use of cyclohexane as solvent for the reaction results in a higher yield of alkali-soluble product at the expense of the alkali-insoluble material.

Propene reacts with phenetole in the presence of phosphoric acid, yielding nuclear alkylated products. The results indicate that the formation of an ether is not a necessary intermediate step in the C-alkylation of phenols.

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(7) Koelsch, THIS JOURNAL, **53**, 304 (1931).

(8) Niederl, Niederl, Shapiro and McGreal, *ibid.*, **59**, 1114 (1937), report 90°.

(9) Mulliken, "A Method for the Identification of Pure Organic Compounds," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1922, p. 11.

(10) Fileti, *Gazz. chim. ital.*, **16**, 117 (1886); Beilstein, 4th ed., Vol. VI, p. 504.

(11) Spica, *Gazz. chim. ital.*, **10**, 248 (1880), reported 81° as the melting point. *Cf.* Beilstein, 4th ed., Vol. VI, p. 506.