under pressure led to the formation of a complex mixture of high melting solids. The fact that the types of *o*-substituted diazonium salts mentioned are relatively stable has been observed previously in the cases of some of the corresponding diazonium chlorides[7] and may possibly result from a type of electronic interaction involving an unshared electron pair of the ortho-substituted atom or group and the outer nitrogen atom in the diazonium group.

The following compounds were obtained from the corresponding amines only in very poor yields: 1-fluoro-2,4-dinitrobenzene, *p*-fluorophenol, *p*-fluoroanisole, α-fluoronaphthalene, β-fluoronaphthalene, *p*-fluoroaniline (from *p*-aminoacetanilide) and 2-fluoro-3-methylpyridine.[8]

Treatment of sulfanilamide in the usual manner gave a small amount of *p*-fluorobenzenesulfonyl fluoride, which was obtained in 38% yield when a two-molar ratio of sodium nitrite was used. The general applicability of this hitherto unreported reaction was shown by its extension to the synthesis of *p*-toluenesulfonyl fluoride from *p*-toluenesulfonamide in 70% yield.

Experimental

General Procedure.—Approximately 20 moles of anhydrous hydrogen fluoride was added slowly to 1 mole of the purified amine contained in a 1-liter, 2-necked monel metal flask[9] cooled in ice. The solution was stirred at 0° by means of a stainless steel paddle stirrer while 82.8 g. (1.2 moles) of dried, reagent grade sodium nitrite was added in small portions over a period of one hour. The flask was then connected to an ice-cooled copper reflux coil and the reaction mixture was warmed slowly by means of an electrically heated water-bath until moderately rapid evolution of nitrogen ceased. In most cases, the reaction mixtures were then cooled, diluted with ice, and steam distilled. In the synthesis of 2-fluoro-3-methylpyridine and *p*-fluoroaniline, excess hydrogen fluoride was evaporated, the residue neutralized with aqueous potassium hydroxide, and the products steam distilled. In the cases of the fluorobenzoic acids and of *o*-fluorodiphenyl, the reaction mixtures were cooled, diluted with ice, and the precipitated products removed by filtration.

Acknowledgment.—The authors are indebted to the Office of Naval Research for a grant which made this and continuing investigations possible.

---

[7] See, for example, Euler, *Ann.*, **325**, 292 (1902); Cain and Nicoll, *J. Chem. Soc.*, **81**, 1412 (1902); Gubelmann, Weiland and Stallmann, U. S. Patent 1,623,949, April 5, 1927; Snow, *Ind. Eng. Chem.*, **24**, 1420 (1932); Yamamoto, *J. Soc. Chem. Ind., Japan*, **35**, Suppl. binding 298 (1932); *ibid.*, **35**, Suppl. binding, No. 12, 564 (1932); *ibid.*, **36**, Suppl. binding 59 (1933).

[8] B. p. 144–146° at 737 mm. *Anal.* Calcd. for C_6H_6NF: C, 64.9; H, 5.4; N, 12.6. Found: C, 64.8; H, 5.6; N, 12.5.

[9] Monel metal proved superior to copper or stainless steel.

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF KANSAS
LAWRENCE, KANSAS

RECEIVED JUNE 13, 1950

Vapor Phase Alkylation of Phenols and Thiophenols[1]

BY CORWIN HANSCH AND DALE N. ROBERTSON

For the synthesis of thianaphthenes and benzofurans[2] by dehydrocyclization it was necessary to synthesize a number of *o*-alkylphenols and thiophenols. Among the methods investigated for the preparation of these compounds was the vapor phase alkylation mentioned by Aleksandrova.[3] Aleksandrova processed phenol and ethanol in a 1/7 ratio over a thoria on alumina catalyst at 440–460° at a very slow space velocity. He obtained an alkylated product consisting of about half mono and half higher alkylated phenols.

A study of this reaction for the preparation of *o*-ethylphenol reveals that the optimum temperature is 350° with a space velocity of 600–900 (Table Ib) with a mol ratio of 1 to 1 of 95% ethanol and phenol.

Under these conditions about 53% of the phenol is converted to alkylphenols and 18% is converted to *o*-ethylphenol. Using a mol ratio of 2 alcohol to 1 phenol gave 80% conversion to alkylphenols with about the same per cent. *o*-ethylphenol. At a temperature of 450°, 70% alkylation was obtained of which only 4% was *o*-ethylphenol. In each case only the *o*-ethylphenol was isolated by fractionation through a 20 plate spinning band column, b. p. 201–203° (730 mm.).

Absolute ethanol gave the same conversion as 95% ethanol. Also it was discovered that pure alumina[4] was just as effective as the thoria on alumina reported by Aleksandrova. Neither catalyst caused noticeable charring and both seemed resistant to poisoning. The catalyst activity did not decrease during the longest runs made in this research, 10 hr.

Two other phenols were also alkylated with ethanol with the results indicated in Table I.

TABLE I[a]

	Moles phenol	Moles ethanol	Temp., °C.	S. V.[b]	% Conversion to[c] alkylphenols	% Conversion to *o*-alkylphenol
p-Methylphenol	0.5	0.5	350	1245	75	15.0[d]
p-Chlorophenol	.5	.5	350	647	48	7.5[e]
p-Chlorophenol	.5	1.0	350	365	72	15.0

[a] The results reported here are with thorium on alumina catalysts, although later work indicated alumina alone to be just as effective. [b] Calculated as ml. of phenol vapor s. t. p./ml. cat./hr. [c] The results are calculated as monoethylphenol and hence are high since some higher alkylphenols were also formed. [d] The 2-ethyl-4-methylphenol had a b. p. 216–219° (730 mm.). Hill and Graf, THIS JOURNAL, **37**, 1843 (1915) report 216–218°. Further identification was obtained by preparation of the phenoxyacetic acid m. p. 130–131°. Niederl and co-workers report 133° (THIS JOURNAL, **59**, 1114 (1939)). [e] The 2-ethyl-4-chlorophenol boiled at 238–241° (730 mm.). Other investigators (Auwers and Wittig, *Ber.*, **57**, 1270 (1924)) have reported the boiling point at reduced pressure. The phenol was identified by its phenoxyacetic (Newman, Fones and Renoll report m. p. 109–112°, THIS JOURNAL, **69**, 720 (1947)) acid m. p. 111–112°.

---

[1] This work was supported in part by a grant from the Research Corporation and in part under ONR contract NR-055-149.

[2] Hansch, Saltonstall and Settle, THIS JOURNAL, **71**, 943 (1949).

[3] Z. P. Aleksandrova, *J. Gen. Chem.* (U. S. S. R.), **12**, 522 (1942); *C. A.*, **37**, 2723 (1943).

[4] The alumina used in this work was ALRCO type H-40, Grade R 2200, 8–14 mesh. In all of the runs reported in this paper 10 cc. of catalyst was used.

It was hoped that this method of alkylation could be applied to the thiophenols, but S-alkylation occurred instead of C-alkylation to give good yields of the ethylsulfides. Table II summarizes the results obtained with thiophenols.

TABLE II[a]

ALKYLATION OF THIOPHENOLS WITH ETHANOL

	Moles thiophenol	Moles ethanol	Temp., °C.	S. V.[b]	% Conversion to ethylarylsulfide[c]
Thiophenol	0.5	0.5	450	708	13.3[d]
Thiophenol	1.0	1.0	350	639	62.0
p-Methylthiophenol	0.24	0.24	350	633	55.0[d]
p-Methylthiophenol	0.75	1.12	350	515	74.0

[a, b] See Table I. [c] In every case most of the unreacted thiophenol was recovered producing yields of nearly 90%. Still better conversions could be obtained by using larger ratios of alcohol to thiophenol since there was almost no tendency to form higher alkylated products. (Traces of C-alkylated thiophenols were obtained.) [d] The ethylarylsulfides were identified by means of their boiling points as follows: ethylphenyl sulfide (Stadler, *Ber.*, **17**, 2077 (1884)), b. p. 202.5° (730 mm.) and *p*-methylphenyl sulfide (Otto, *Ber.*, **13**, 1277 (1880)), 222–223°. The structure of the two sulfides was also confirmed by comparison with a sample of each made from the thiophenol and from diethyl sulfate. Ethylphenylsulfide both catalytic and from diethyl sulfate had the same refractive index $n^{25}\text{D}$ 1.5640, as did *p*-methylphenyl sulfide $n^{25}\text{D}$ 1.5544.

As with the phenols the straight alumina catalyst was found to be just as effective as thoria on alumina. The catalyst activity did not appear to decrease appreciably during runs of a few hours duration. No darkening of the catalyst occurred. Actually it appeared to be somewhat bleached by use. The condensation products were almost water white. Higher temperatures did not result in appreciable amounts of C-alkylation.

DEPARTMENT OF CHEMISTRY
POMONA COLLEGE
CLAREMONT, CALIFORNIA

RECEIVED JANUARY 31, 1950

Benzylidene Derivatives of L-Arabinose Diethyl Acetal and Dimethyl Acetal[1]

BY CHARLES F. HUEBNER,[2] RUSSELL A. PANKRATZ AND KARL PAUL LINK

L-Arabinose diethyl mercaptal condenses rapidly with benzaldehyde in the presence of hydrogen chloride to yield a dibenzylidene compound (I) which must be removed immediately after the completion of the reaction because it is further transformed in this environment to sirupy decomposition products. The following evidence shows I to be 2,3;4,5-dibenzylidene-L-arabinose diethyl mercaptal. By mild acetic acid hydrolysis it was possible to obtain a monobenzylidene derivative (II) which consumes one molar equivalent of lead tetraacetate to produce formaldehyde. This behavior eliminates five of the possible six isomeric monobenzylidene mercaptals and shows II to be 2,3-benzylidene-L-arabinose diethyl mercaptal. Barring rearrangement during the hydrolysis of I to II the latter must have the proposed structure.

The divalent sulfur atoms in II complicate the oxidation since they appear also to consume tetraacetate. The oxidation of divalent sulfur by periodate has been indicated.[3] Controls run on I and on D-galactose diethyl mercaptal tetraacetate showed that one molar equivalent of oxidant was consumed within five to fifteen minutes and a second within two hours. This is presumably due to an almost immediate oxidation of the first sulfur followed by a much slower oxidation of the second. II, in contrast to these two compounds (Fig. 1), used up two molar equivalents within five minutes and four within two hours. The rapid consumption (within five minutes) of the extra molar equivalent of tetraacetate by II above the one molar equivalent used in the control oxidations of I and D-galactose diethyl mercaptal tetraacetate is accounted for by the presence of a glycol grouping in II. To detect the presence of formaldehyde among the primary oxidation products of II, the oxidation was carried out with only two molar equivalents of tetraacetate, thus preventing the formation of formaldehyde by a more extensive degradation involving hydrolysis and further oxidation by excess tetraacetate.

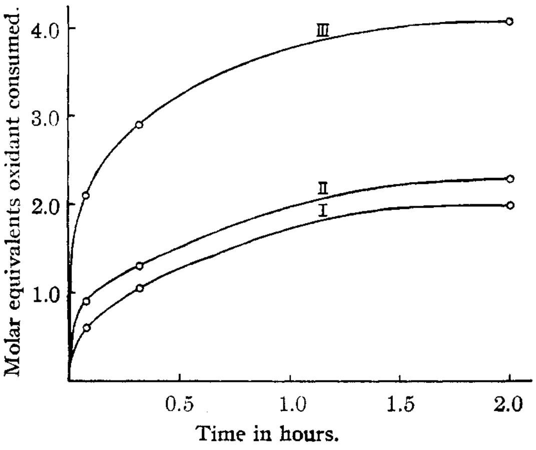

Fig. 1.—Oxidation of D-galactose diethylmercaptal tetraacetate (I), 2,3–4,5-dibenzylidine-L-arabinose mercaptal (II) and 2,3-benzylidene-L-arabinose diethylmercaptal (III) with lead tetraacetate (5.85 molar equivalents).

I was demercaptalated in methyl alcohol according to the general procedure of Green and Pacsu[4] yielding the dibenzylidene dimethyl acetal (III). III was subjected to hydrogenolysis over platinum and L-arabinose dimethyl acetal (IV)

---

[1] Published with the approval of the Director of the Wisconsin Agricultural Experiment Station.

[2] Ciba Pharmaceutical Products, Inc., 556 Morris Avenue, Summit, N. J.

[3] Nicolet and Shinn, THIS JOURNAL, **61**, 1615 (1939).

[4] Green and Pacsu, *ibid.*, **59**, 1205 (1937).