

*Anal.* Calcd. for  $C_6H_5O_2$ : C, 65.45; H, 5.45. Found: C, 65.31; H, 5.46.

The mother liquor, after being made alkaline with sodium carbonate, was shaken six times with ether. On evaporating the solvent, 0.02 g. of almost colorless leaflets was obtained which after treatment with alcohol melted at 187–188°, and gave, in contact with calcium hypochlorite, color reactions specific to *p*-aminophenol.

*Anal.* Calcd. for  $C_6H_7ON$ : N, 12.84. Found: N, 12.94.

TABLE I  
REDUCTION OF NITROPHENOL

Reactant	G.	Products	Yield, g.	M. p., and mixed m. p., °C.
<i>p</i> -Nitrophenol	2.8	Hydroquinone	0.45	169–170
		<i>p</i> -Aminophenol	.90	187
<i>o</i> -Nitrophenol	2.8	<i>o</i> -Aminophenol	1.65	179

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### Summary

By reduction of nitrosophenols by iron and hydrochloric acid, the following compounds have been prepared: 5-acetyl-7,8-dihydroxyquinoline, 5,8-dihydroxyquinoline and hydroquinone.

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## PHENOLIC DECOMPOSITION OF CERTAIN MIXED ETHERS. II. THE EFFECT OF SUBSTITUTION. THE RATE CONSTANT

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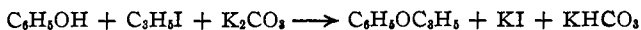
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In the first paper<sup>1</sup> of this series it was pointed out that the phenolic decomposition of mixed ethers is influenced by a number of factors. In the present investigation, the influence of substitution in the phenyl residue upon the decomposition of certain mixed ethers by hydrogen bromide in glacial acetic acid at the temperature of the steam-bath has been determined.

### Experimental

**Preparation of Materials.**—When it was possible, the procedure adopted by Claisen<sup>2</sup> in preparing phenyl allyl ethers was followed to synthesize the mixed ethers used in this investigation. The scheme of procedure is



<sup>1</sup> Birosel, *THIS JOURNAL*, **52**, 1944 (1930).

<sup>2</sup> Claisen, *Ber.*, **45**, 3157 (1912); *Ann.*, **401**, 21 (1913); *ibid.*, **418**, 69 (1919).

Claisen recommended a non-dissociating solvent for this reaction; otherwise, one obtains the isomeric phenol instead of the ether. Acetone was used in all the preparations. The above equation calls for a monomolecular proportion of the active components but in practice alkyl halide and anhydrous potassium carbonate are taken in excess of the theoretical amount. The mixture is digested on the water-bath at the boiling temperature of acetone in a reflux condenser during a period of from six to eight hours. At the end of the digestion, water is added to the mixture to dissolve the solid carbonate and the product separates as liquid which is

TABLE I  
PREPARATIONAL DATA OF THE PHENETOLES

Phenol	Reagent	g.	EtI, g.	K <sub>2</sub> CO <sub>3</sub> , g.	Acetone, cc.	Crystals		M. p., °C.	Yield		Ref.
						From	Form		g.	%	
<i>o</i> -Nitro-		8.5	14	13	40	EtOH	Prisms	57.8	3	29	1
<i>p</i> -Chloro-		29	38	50	50	Liquid,	b. p.	210-212	23	74	2
<i>p</i> -Bromo-		10	15	10	25	Liquid,	b. p.	228	..	100	3
<i>p</i> -Cresol		12	12	20	40	Liquid,	b. p.	186-188	12	79	4
2,4-Dibromo <sup>a</sup>		7	9	8	40	Liquid,	b. p.	266-268	..	99	5
						EtOH	Rhombs	53-54	..	...	
2,4-Dichloro-		10	20	12	40	Liquid,	b. p.	235-236	10.6	90	6
2,4,6-Tribromo-		6	6	4	40	EtOH	Needles	71-72	..	100	7
Silver picrate		..	..	..	..	EtOH	Needles	78.5	..	...	8

<sup>a</sup> From phenolic decomposition of 2,4-dibromoanisole (m. p. 63°).

(1) Fritzsche, *Ann.*, 110, 166 (1859), prepared *p*-nitrophenyl ethyl ether from the silver salt of *p*-nitrophenol and ethyl iodide; prismatic crystals from ether, m. p. 57-58°.

(2) Beilstein and Kurbatow, *ibid.*, 176, 30 (1875), prepared *p*-chlorophenyl ethyl ether by digesting equivalent amounts of *p*-chlorophenol, ethyl iodide and potassium hydroxide; b. p. 210-212°.

(3) Lippmann, *Jahrsb. Chem.*, 548 (1870), made *p*-bromophenyl ethyl ether from ethyl bromide and potassium *p*-bromophenolate; oil, b. p. 233°. Autenrieth and Mühlhinghaus, *Ber.*, 39, 4098 (1906), from phenetole and phosphorus pentabromide; liquid, b. p. 225-226°.

(4) Pinette, *Ann.*, 243, 41 (1888), obtained *p*-cresyl ethyl ether by digesting *p*-cresol with alcoholic potash and ethyl iodide; oil, b. p. 189.9°. Englehardt and Latschinow, *Z. Chem.*, 619 (1869), reported b. p. 186-188°.

(5) Autenreith and Mühlhinghaus, *Ber.*, 39, 4098 (1906), prepared 2,4-dibromophenyl ethyl ether from phenetole and phosphorus pentabromide; large rhombs, m. p. 50°. Pope, *J. Chem. Soc.*, 101, 1823 (1912), from 2,4-dibromophenol, alcoholic potash and ethyl iodide; rhombic plates, m. p. 53.3°. Lippmann, *Jahrsb. Chem.*, 739 (1870), from phenetole and two moles of bromine.

(6) Fischer, *Ann. Suppl.*, 7, 183 (1870); oil, b. p. 236-237°.

(7) Raiford and Birosel, *This Journal*, 51, 1776 (1929), from phenetole and three moles of bromine in chloroform; needles from alcohol, m. p. 69°. Purgotti, *Gazz. chim. ital.*, 16, 528 (1886), from silver 2,4,6-tribromophenolate and ethyl iodide; m. p. 69°. Varda, *ibid.*, 23, 494 (1893), from the potassium salt; m. p. 72-73°.

(8) Willgerodt, *Ber.*, 12, 1277 (1879), prepared 2,4,6-trinitrophenyl ethyl ether from alcoholic potash and picryl chloride; needles, m. p. 78°. Müller and Stenhouse, *Ann.*, 141, 80 (1867), from silver picrate and ethyl iodide; needles, m. p. 78.5°.

extracted with ether. The ether solution is separated, washed with dilute sodium hydroxide, and then with distilled water. The ether solution is dried with anhydrous sodium carbonate and filtered. The solvent is evaporated and if the residue is a liquid it is distilled and the portion which boils over at the temperature recorded in the literature for the particular compound is reserved for use. When the residue is a solid, it is crystallized from the appropriate solvent and the melting point and crystalline form are noted.

**2,4,6-Trinitrophenetole.**—Attempts to prepare this compound by Claisen's and Willgerodt's methods, respectively, were unsuccessful. The ether was successfully synthesized by following the method adopted by Raiford and Birosel (Ref. 7, Table I) in preparing 2,4,6-trinitrophenyl allyl ether. Silver picrate prepared from the ammonium salt was digested with ethyl iodide using acetate as reaction medium. During the course of digestion yellow silver iodide salt was precipitated. When digestion was complete, the salt was filtered and washed with acetone. The solvent was evaporated and the solid residue was dissolved in ether. The ether solution was washed with dilute sodium hydroxide, then with distilled water. The solvent was evaporated and the residue was crystallized from ethyl alcohol.

**Procedure of Decomposition.**—The extent of the phenolic decomposition of the mixed ethers recorded above and velocity constants were determined at the temperature of the steam-bath by a reflux condenser. The procedure is the same as that followed in a previous work.<sup>1</sup> The acid

TABLE II  
EXTENT OF DECOMPOSITION OF CERTAIN MIXED ETHERS

Expt.	Compound, ethyl ether	Time, min.	Ether used, g.	Acid soln., cc.	Phenol obtained, g.	Decomposition, %
1	<i>p</i> -Nitrophenyl	120	0.5000	30	0.0660	13.20
2	<i>p</i> -Chlorophenyl	120	1.0410	30	.7488	85.28
3	<i>p</i> -Bromophenyl	120	1.0540	30	.7792	85.95
4	<i>p</i> -Methylphenyl	120	1.4010	30	.5000	44.95
5	2,4-Dibromophenyl	120	0.5000	30	.2726	60.59
6	2,4-Dichlorophenyl	120	1.0180	30	.4644	40.35
7	2,4,6-Tribromophenyl	120	0.5000	30	.1000	21.78
8	2,4,6-Trinitrophenyl	120	.5000	30	Complete decomposition	

TABLE III  
RATE OF DECOMPOSITION OF 2,4,6-TRIBROMOPHENYL ETHYL ETHER IN GLACIAL ACETIC ACID MEDIUM

Expt.	Time, min.	Ether used, g.	Acid soln., cc.	Tribromophenol <sup>a</sup> obtained, g.	Calcd. amount of dec. ether, g.	Decomposition, %	$K \times 10^{-3}$
1	30	0.5000	30	0.0340	0.0369	7.40	2.56
2	60	.5000	30	.0620	.0672	13.50	2.42
3	90	.5000	30	.0840	.0911	18.29	2.24
4	120	.5000	30	.1000	.1085	21.78	2.25
5	150	.5000	30	.1130	.1225	24.60	2.02

<sup>a</sup> Crystallization from alcohol gave fine needle crystals melting at 92°. No depression in melting point was noted when it was mixed with the original tribromophenol.

TABLE IV  
RATE OF DECOMPOSITION OF CERTAIN MIXED ETHERS IN GLACIAL ACETIC ACID AS REACTION MEDIUM

Expt.	Compound, ethyl ether	Time, min.	Ether used, g.	Acid soln., cc.	Phenol obtained, g.	Calcd. amount of dec. ether, g.	Velocity constant $K \times 10^{-3}$
2	<i>p</i> -Nitrophenyl	60	0.5000	30	0.0316	0.0380	1.28
		120	.5000	30	.0549	.0660	1.18
3	<i>p</i> -Bromophenyl	30	1.2185	30	.3935	.4573	15.68
		60	1.3350	30	.6920	.8042	15.48
		120	1.0540	30	.7792	.8955	15.79
3	<i>p</i> -Chlorophenyl	30	1.0035	30	.3140	.3727	15.14
		60	1.0410	30	.5380	.6385	15.77
		120	1.0410	30	.7488	.8770	15.38
2	<i>p</i> -Methylphenyl	30	0.9190	30	.1000	.1259	4.91
		60	1.3240	30	.2650	.3337	4.84
		120	1.4010	30	.5000	.6297	4.97
3	2,4-Dibromophenyl <sup>a</sup>	30	0.5000	30	.0925	.1028	7.67
		90	.5000	30	.2200	.2556	7.95
		120	.5000	30	.2726	.3030	7.84

<sup>a</sup> A nitro derivative, 2,4-dibromo-6-nitrophenol was prepared according to the directions of Kohn and Dömötör, *Monatsh.*, **48**, 211 (1927), from the dibromophenol obtained from the phenolic decomposition of 2,4-dibromophenyl ethyl ether; crystallization from alcohol gave small yellow plate crystals melting at 118°.

solution used in this present investigation was made in the same proportion as the material used in former work; one volume of constant boiling hydrobromic acid was added to two volumes of glacial acetic acid. The results obtained from experiments are given in the tables.

### Discussion

In Table II are given the detailed results of experiments on the extent of decomposition of eight derivatives of phenyl ethyl ether by constant boiling hydrobromic acid in glacial acetic acid as reaction medium. The influence of substitution was determined with particular regard to four different radicals: nitro, chloro, bromo and methyl replacing the hydrogen atom attached to the *p*-carbon atom of the benzene nucleus. Comparing the figures obtained from experiments for the extent of decomposition of the mono substituted derivatives of phenetole, the influence of substitution is very apparent. When the substituting group is multiplied in the phenyl residue, the extent of the phenolic decomposition of certain mixed ethers decreases in magnitude. When *p*-bromophenyl ethyl ether was subjected to the action of constant boiling hydrobromic acid in glacial acetic acid as reaction medium at the temperature of the steam-bath for two hours, the decomposition was 85.95% complete; for 2,4-dibromophenyl ethyl ether the extent of decomposition is 60.59%; and for 2,4,6-tribromophenyl ethyl ether the magnitude of decomposition has decreased to 21.78%

which is about one-fourth the magnitude of the value obtained for the monobromo derivative. *p*-Chlorophenyl ethyl ether was decomposed to the extent of 85.28%, while the dichloro derivative for the same interval of time was only decomposed 40.35%, which is less than one-half of the value obtained for the monochloro derivative. The result for 2,4,6-trinitrophenyl ethyl ether shows that the compound is not stable toward hydrogen bromide.

In Table III are shown the results of the experiments on the velocity constant of the phenolic decomposition of 2,4,6-tribromophenyl ethyl ether at the temperature of the steam-bath. The rate constants  $K$  are those calculated from the integrated form of the differential equation for the first order reactions, using logarithms to the base  $e$ . It will be noted that the constancy of  $k$  is quite satisfactory. The calculated amount of decomposed ether was obtained by multiplying the amount of tribromophenol directly determined from experiment by the factor 1.0847.

In Table IV are recorded the rate constants of the phenolic decomposition of *p*-nitro-, *p*-bromo-, *p*-chloro-, *p*-methyl and 2,4-dibromophenyl ethyl ethers. The figures obtained for each compound from two or three experiments are in close agreement. The monohalogen derivatives give much higher rate constants than either the mononitro or monomethylphenyl ethyl ether. The magnitude of the rate constant is decreased when the same halogen substituent is multiplied in the phenyl residue. Comparing the velocity constants obtained for monobromo, dibromo and tribromo phenetoles, it appears that the rate constant is also dependent upon the number of substituents actually present in the benzene nucleus.

### Summary

1. The kinetics of the phenolic decomposition of mixed ethers have been studied further in the case of 2,4,6-tribromophenyl ethyl ether and to a less extent with the case of *p*-nitro-, *p*-bromo-, *p*-chloro-, *p*-methyl- and 2,4-dibromophenyl ethyl ethers. Experiments were made in glacial acetic acid as reaction medium.

2. The rate constants of 2,4,6-tribromophenyl ethyl ether and of the other compounds were calculated from the experimental results and their constancy is quite satisfactory. The phenolic decomposition of mixed ethers appears to be a first order reaction.

3. The rate constant is influenced by the number of substituents actually present in the phenyl residue.

4. The phenolic decomposition of mixed ethers is influenced by the substituting group present in the benzene nucleus.

The influence of position of substitution on the phenolic decomposition of mixed ethers is being studied.