[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OKLAHOMA]

The Effect of Substituent Groups upon the Course of the Condensation Reaction between Benzenediazonium Salts and Phenols[1]

BY J. C. COLBERT AND ROBERT M. LACY[2]

In 1890 Hirsch[3] reported that diazo compounds can be extracted from aqueous solution by phenols and upon heating react to form hydroxybiphenyls. The reaction medium was kept acid so that no azo-type coupling occurred. Norris, Macintire and Corse[4] later studied this reaction, reporting similar results together with the formation of a black, brittle material probably formed by the introduction of several phenyl groups into the diazo nucleus. Scattered examples[5,6,7] of this reaction are to be found in the literature, but no systematic study of the effects of substituent groups has been made.

The results obtained in two series of reactions are reported in the present paper. The effect of substituents in the para position in the diazonium salt upon reaction with phenol and the effect of substituents in the ortho position in the phenol upon reaction with benzene diazonium chloride has been studied. Low yields and difficulty of extraction from the tars formed lead to curtailment of the original plan which would have tested substituents in each of the three positions first in the salt and second in the phenol. Following initial experience with the para-substituted diazonium salts the ortho-substituted phenols were investigated in the belief that fewer isomers would be formed and isolation of the products simplified.

In the procedure adopted the amine was diazotized in a strongly acid solution (6 moles hydrochloric acid: 1 mole amine)[8] in order to minimize the formation of azo compounds. The clear solution of the diazonium salt at 0° was added with stirring to a flask containing the phenol (1 mole amine: 3 moles phenol)[9] which was heated in a boiling water-bath. After two hours of further heating the mixture was cooled, and the dark reaction products separated from the aqueous layer. This oil was separated into its components by either distillation with superheated steam or by vacuum distillation. A large quantity of black, tarry material remained which could not be purified.

A "control" reaction between phenol and benzenediazonium chloride under the conditions described above gave a 5.9% yield of 4-hydroxybiphenyl and a 1.8% yield of the 2-hydroxy isomer. The results of this work are summarized in Table I.

TABLE I

Reactants		% Yields			
p-(X-$C_6H_4N_2$)Cl	Phenol	4-OH isomer	2-OH isomer	Total yield	Azo compd.
X = H	Phenol	5.9	1.8	7.7	...
CH_3	Phenol	4.5	...	4.5	...
Cl	Phenol	0.3	1.5	1.8	Trace
Br	Phenol	0.14	1.3	1.4	Trace
NO_2	Phenol	..	...	...	52.2
($C_6H_5N_2$)Cl	*o*-X-C_6H_4OH	3-X-4-Hydroxy biphenyl	3-X-2-Hydroxy biphenyl		
($C_6H_5N_2$)Cl	X = CH_3	4.1	5.6[a]	9.7	...
($C_6H_5N_2$)Cl	Cl	..	27.8	27.8[b]	...
($C_6H_5N_2$)Cl	Br	..	15.3	15.3	...
($C_6H_5N_2$)Cl	NO_2	..	...	...[c]	...
	p-X-C_6H_4OH	5-X-2-Hydroxy biphenyl			
($C_6H_5N_2$)Cl	X = CH_3	2.6[d]			

[a] Isolated as (2-methyl-6-phenyl)-phenyl benzenesulfonate; m. p. 37–38°. [b] *p*-Toluenesulfonate derivative was also prepared; m. p. 117–118°. [c] No reaction. Almost quantitative recovery of *o*-nitrophenol. [d] Isolated as (4-methyl-6-phenyl)-phenyl benzenesulfonate; m. p. 65–66°.

Experimental

The two procedures which follow are representative of the reactions studied and serve to illustrate the method.

Reaction between *p*-Toluenediazonium Chloride and Phenol.—Thirty-two and one-tenth grams (0.3 mole) of *p*-toluidine was diazotized in 65.8 g. (6 × 0.3 mole) of hydrochloric acid and reacted with 84.6 g. (3 × 0.3 mole) of phenol. The reaction mixture was distilled at atmospheric pressure yielding 70 g. of phenol. No *p*-cresol was isolated from the reaction mixture. The residue was then distilled under reduced pressure and the fraction boiling at 150–165° under a pressure of 2 mm. was collected. This fraction was a reddish-yellow oil which solidified in the receiver. This solid was dissolved in a dilute sodium hydroxide solution, acidified, and a black pasty mass obtained. This mass was removed from the acid by a benzene extraction, the solvent evaporated, and the solid crystallized from dilute acetic acid. A yield of 2.5 g. (4.5%) of 4'-methyl-4-hydroxybiphenyl melting at 153–154° was obtained. The small amount of black material was not identified. A black brittle mass remained in the flask after distillation. Hirsch[10] reports 155° for this compound.

Anal. Calcd. for $C_{13}H_{12}O$: C, 84.7, H, 6.56. Found: C, 84.6, H, 6.54.

---

[1] Abstracted from a thesis presented by Robert M. Lacy to the Graduate Faculty of the University of Oklahoma in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Present address: General Electric Company, Bridgeport, Conn.

[3] Hirsch, *Ber.*, **23**, 3705 (1890); **25**, 1196 (1892).

[4] Norris, Macintire and Corse, *Am. Chem. J.*, **29**, 120 (1903).

[5] Kliegl and Huber, *Ber.*, **53**, 1646 (1920).

[6] Chatterjee, *J. Indian Chem. Soc.*, **12**, 410 (1935).

[7] Anchell and Blatt, THIS JOURNAL, **63**, 1950 (1941).

[8] In the case of *p*-chloro-benzenediazonium chloride, if the acid-amine ratio was 3 to 1, a relatively high yield of the azo compound was formed. If, however, the ratio was increased to 6 to 1, only a trace of the azo compound was isolated. This ratio was therefore adopted in the work.

[9] The yield of 4'-methyl-4-hydroxybiphenyl from the reaction of 3 moles of phenol with 1 mole of *p*-toluenediazonium chloride (acid-amine ratio 6:1) amounted to 4.5% whereas a reaction between 3 moles of the diazonium salt with 1 mole of phenol (acid-amine ratio 6:1) amounted to 2.6%. The ratio of 1 mole of amine to 3 moles of phenol was adopted for all reactions.

[10] Hirsch, *Ber.*, **23**, 3705 (1890).

TABLE II

DATA FOR PREPARATIONS NOT REPORTED IN DETAIL

Reactants	Products	M. p. or B. p. found	previously known	Analytical data, % Calcd.	Found
p-Chloroaniline, phenol[a]	4′-Chloro-4-hydroxybiphenyl	145	Same[d]	Cl, 17.35	Cl, 17.5
	4′-Chloro-2-hydroxybiphenyl	53	52[e]	Cl, 17.35	Cl, 17.28
	p-Chlorobenzene-p-azo-phenol	153	Same[f]	...	...
p-Bromoaniline, phenol[a]	4′-Bromo-4-hydroxybiphenyl	156	Same[d]	Br, 32.12	Br, 32.5
	4′-Bromo-2-hydroxybiphenyl	60–61	New cpd.	Br, 32.12	Br, 32.18
p-Nitroaniline, phenol[b]	4′-Nitro-2-hydroxybiphenyl	122	124[g]	N, 6.51	N, 6.55
	p-Nitrobenzene-p-azo-phenol	210	Same[h]	...	...
	(6-p-Nitrophenyl)-phenyl p-toluene sulfonate	128	New cpd.	...	...
Aniline, p-cresol[c]	(4-Methyl-6-phenyl) phenyl benzene sulfonate	65–66	New cpd.	S, 9.87	S, 9.70
Aniline, o-cresol[c]	3-Methyl-4-hydroxybiphenyl	115	114[i]	C, 84.7; H, 6.56	C, 84.5; H, 6.4
	(2-Methyl-6-phenyl)-phenyl benzene sulfonate	37–38	New cpd.	S, 9.87	S, 9.8
Aniline, o-chlorophenol[c]	3-Chloro-2-hydroxybiphenyl	136–137 (2 mm.)	166–171 (10 mm.)[j]	Cl, 17.35	Cl, 17.16
	(2-Chloro-6-phenyl)-phenyl p-toluene sulfonate	117–118	New cpd.	...	...

[a] Isolation and separation of products was by superheated steam, extraction with benzene, formation of calcium salts, and extraction with 35–40° petroleum ether following acidification of salt solution. [b] Superheated steam was used followed by benzene extraction of the distillate. [c] The oil formed was extracted with benzene and vacuum distilled. [d] Angeletti and Gatti, *Gazz. chim. ital.*, **58**, 630 (1929). [e] Harris, *C. A.*, **31**, 5381 (1937). [f] Fox and Hewitt, *J. Chem. Soc.*, **93**, 340 (1908). [g] Harris and Christiansen, *C. A.*, **29**, 4382 (1935). [h] Hewitt, Moore and Pitt, *Ber.*, **31**, 2122 (1898). [i] Reference 6. [j] Rittler and Heller, *C. A.*, **29**, 6247 (1935).

Reaction between Benzenediazonium Chloride and o-Bromophenol. Nine and three-tenths grams (0.1 mole) of aniline were diazotized in 21.9 g. (6 × 0.1 mole) of hydrochloric acid and reacted with 51.9 g. (3 × 0.1 mole) of o-bromophenol. The oil obtained was distilled under atmospheric pressure and from the first fraction (175–195°) were recovered 2 g. of phenol and 43 g. of o-bromophenol.

Under a pressure of 2 mm., Fraction 2 boiling at 80–85° was collected. This fraction weighed 6.6 g. and gave a positive test for bromine after fusion with sodium. This fraction is probably a mixture of o-bromophenol and a bromo-hydroxybiphenyl. The separation and identification of the components of this fraction was not carried out.

A third fraction boiling at 170–180° under a pressure of 12 mm. was collected. This fraction weighed 3.8 g. Rittler and Grundel[11] prepared 3-bromo-2-hydroxybiphenyl and reported a boiling range of 173–178° under a pressure of 12 mm. Fraction 3, therefore, is probably this compound. A sample of this fraction gave a positive bromine test when fused with sodium.

Anal. Calcd. for $C_{12}H_9BrO$: Br, 32.12. Found: Br, 32.17.

Assuming Fraction 3 to be 3-bromo-2-hydroxybiphenyl, the 3.8 g. represent a 15.3% yield.

Attempts to prepare the methoxy and benzoate derivatives of this biphenyl yielded uncrystallizable oils.

Summary

1. Para substituents in the diazonium salt decrease the formation of hydroxybiphenyls when such salts are condensed with phenol.

2. Chlorine or bromine para to the diazo group diminish the yield of hydroxybiphenyls more than methyl while the nitro group stabilizes the diazo form enabling the compound to couple even in a strongly acid solution.

3. Ortho substituents in the phenol increase the formation of hydroxybiphenyls when such phenols are condensed with benzenediazonium chloride. The effectiveness of the substituent increases from methyl to bromine to chlorine. The presence of the nitro group completely inhibits the formation of hydroxybiphenyls.

NORMAN, OKLAHOMA RECEIVED MAY 26, 1945

---

(11) Rittler and Grundel, *C. A.*, **30**, 112 (1936).