Influence of Substituent Groups on Nuclear Reactivity in Formations of Substituted Biphenyls through Reactions of Aromatic Diazo and Cognate Compounds with Aromatic Liquids. II. The Bromine Atom

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In a previous paper(1) the results of an investigation on the directive influence of the nitro group on the formation of isomeric nitrobiphenyls by the decomposition of N-nitrosoacetanilide or benzenediazo hydroxide in nitrobenzene have been reported. The nitro group has been found to activate all the nuclear positions of nitrobenzene towards substitution by the phenyl radical as compared with the reactivity of the nucleus of benzene itself. The present report is concerned with the results of a similar investigation on the influence of the bromine substituent on the formation of isomeric bromobiphenyls from bromobenzene by the decomposition of N-nitrosoacetanilide or of benzenediazo hydroxide produced by the reaction between benzenediazonium chloride and alkali:

$$C_6H_5Br + C_6H_5N(NO)COCH_3 \rightarrow C_6H_5C_6H_4Br + N_2 + CH_3COOH,$$

$$C_6H_5Br + C_6H_5N_2Cl + NaOH \rightarrow C_6H_5C_6H_4Br + N_2 + NaCl + H_2O.$$

At first we have tried to determine the ratio of *o*-, *m*- and *p*-bromobiphenyls in the product by oxidizing the isomeric mixture formed with chromic trioxide in acetic acid to a mixture of the corresponding bromobenzoic acids and then fractionating the latter. It was shown by preliminary experiments that this method could not give reliable results, because the isomeric bromobiphenyls undergo oxidation with different yields of the corresponding bromobenzoic acids, and, moreover, the yields were hardly reproducible enough to permit the accurate determination. However, it could be demonstrated in this way that all the possible isomerides of bromobiphenyls are produced in these reactions. Thus, the approximate percentages of the *o*-, *m*- and *p*-bromobiphenyls formed in the decomposition of benzenediazo hydroxide in bromobenzene were estimated to be 30.1, 25.5 and 44.4%, respectively, and the corresponding percentages in the decomposition of nitrosoacetanilide in bromobenzene were

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(1) O. Simamura, T. Inukai and M. Kanazashi, This Bulletin, **23**, 205 (1950).

22.3, 26.5 and 51.1%, respectively. As the formation of only *o*- and *p*-bromobiphenyls in a similar reaction(2) is recorded in the literature, it is to be noted that the meta isomeride was formed in a considerable amount as in the reaction in nitrobenzene which gave as much as 23% of *m*-nitrobiphenyl along with *o*- and *p*-isomerides.(1) Competitive reactions carried out in a mixture of bromobenzene and benzene showed that bromobenzene reacted with phenyl radicals 1.4 to 2.6 times as fast as benzene.(3)

Snbsequently, infra-red spectrophotometric analysis of the reaction products carried out by Mr. K. Kuratani in the Institute of Science and Technology of this university revealed that the results shown above were too high in the percentage of the para isomeride. In this analysis, absorptions were measured at 9.70, 12.06 and 12.70 microns, each an absorption band characteristic of *o*-, *p*- and *m*-bromobiphenyls, respectively. Table 1 illustrates the accuracy of this analytical method. The results of reinvestigation performed by means of the spectrophotometric determination are summarized in Table 2.

Table 1

Percentages of isomerides in known mixtures

	Taken	Found	Taken	Found
Ortho	60	60	52	50
Meta	11	9	35	34
Para	29	29	13	16

Table 2

Expt. No.*	Reactants		Bromobiphenyls			
				Isomeric ratio		
		C_6H_5Br	Yield, millimoles	*o*	*m*	*p*
1	$C_6H_5N_2OH$(from 6.5 g. aniline)	200 cc.	19.8	59	26	14
2	$C_6H_5N_2OH$(from 24 g. aniline)	335 cc.	52.4	53	26	21
3	$C_6H_5N_2OH$(from 6.5 g. aniline)	217 cc. $+C_6H_6$ 373 cc.	9.18 +Biphenyl 5.96			
4	$C_6H_5N(NO)$-$COCH_3$ 5.0 g	287 cc.	28.8*	60	22	18
5	$C_6H_5N(NO)$-$COCH_3$ 39.5g.	183 cc. $+C_6H_6$ 155 cc.	22.5 +Biphenyl 8.77			

* See Experimental Part.

The percentage of the ortho isomeride formed was remarkably high, and this is in line with the preponderant formation of *o*-nitrobiphenyl in the reactions of N-nitrosoacetanilide, benzenediazo hydroxide and dibenzoyl peroxide with nitrobenzene, and of *o*-methoxybiphenyl in the decomposition of dibenzoyl peroxide in anisole as shown in Table 3.

Table 3

Reactants		Isomeric ratio of biphenyls formed			Reference
		o	*m*	*p*	
$C_6H_5N_2OH$	$C_6H_5NO_2$	46	19	35	(1)
		55	4	41	(4)
$C_6H_5N(NO)Ac$	$C_6H_5NO_2$	58	23	19	(1)
		60	9	31	(4)
$(C_6H_5CO_2)_2$	$C_6H_5NO_2$	72	2	26	(4)
$(C_6H_5CO_2)_2$	$C_6H_5OCH_3$	67	18	15	(5)

In experiment 3, biphenyl and bromobiphenyls were formed in a molar ratio of 1:1.54, and as benzene was used in an amount about twice that of bromobenzene, the ratio of the reactivities of benzene and bromobenzene is 1:3.2. Since it may reasonably be assumed that the isomeric ratio found in experiment 1 obtains in the competitive reaction, the relative reactivities(6) of the *o*-, *m*- and *p*-nuclear positions of bromobenzene are calculated to be 5.7, 2.5 and 2.7, respectively, the reactivity of one position of the unsubstituted benzene nucleus being taken as unity. Similarly, from the data of experiments 4 and 5 the reactivities for the isomeric positions are found to be 4.6, 1.7 and 2.8, respectively.

The common tendency observed in the isomeric ratios of substituted biphenyls formed in the various reactions which include the decomposition of dibenzoyl peroxide and the activating influence of substituent groups, such as the bromine atom (Expts. 3 and 5) and the nitro group,(1) on the reactivity of the benzene nucleus to which these groups are attached towards attack by the phenyl group afford strong supports for a hypothesis that these reactions take place through a mechanism involving free phenyl radicals.(7)

Experimental

Materials.—N-Nitrosoacetanilide was prepared by the method of O. Fischer(8) as in the previous investigation. Benzene, bromobenzene and aniline were purified by repeated distillation.

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(2) M. Gomberg and W. E. Bachmann, *J. Am. Chem. Soc.*, **46**, 2339 (1924).

(3) The above results were reported at the third annual meeting of the Chemical Society of Japan, Kyoto, April 1950.

(4) DeLos F. DeTar and H. J. Scheifele, *J. Am. Chem. Soc.*, **73**, 1442 (1951).

(5) T. Suehiro, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **72**, 301 (1951).

(6) See reference 1.

(7) See, *e. g.*, W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, London, 1948.

(8) O. Fischer, *Ber.*, **9**, 463 (1876).

Reactions with Benzenediazo Hydroxide.—Experiment 1. Aniline (6.5 g.) dissovled in 6 cc. of water and 14 cc. of concentrated hydrochloric acid was diazotized by adding a solution of 5.1 g. of sodium nitrite in 10 cc. of water. The resulting solution was added to 200 cc. of bromobenzene, and to this mixture a solution of 6.7 g. of sodium hydroxide in 20 cc. of water was added dropwise with vigorous stirring at 5-8° in the course of thirty minutes. The stirring was continued for a further four hours. The reaction mixture was separated from the aqueous layer and distilled through a Vigreux column 30 cm. in length to remove bromobenzene. The residue was subjected to vacuum distillation and the distillate treated with a little zinc and hydrochloric acid. The colourless liquid thus obtained was distilled under diminished pressure to yield 4.61 g. of a mixture of bromobiphenyls boiling at 130 to 143° at 8.5 mm. Hg (Found: Br, 34.03%. Calcd. for $C_{12}H_9Br$: Br, 34.28%). Experiment 2 was carried out similarly.

Experiment 3. For a competitive reaction a mixture of 217 cc. (2.02 moles) of bromobenzene and 373 cc. (4.21 moles) of benzene was used instead of 200 cc. of bromobenzene, the amounts of the other reagents being equal to those in the run described above. After the usual treatment benzene and bromobenzene were removed through a fractionating column. The distillate was again fractionated and the residue in the distilling flask was combined with the residue from the initial distillation. The mixture was fractionated under diminished pressure, giving a very small amount of bromobenzene, and then a fraction, from which biphenyl deposited, and another containing bromobiphenyls. The crystallized biphenyl was separated and weighed. The mother liquor was combined with the crude bromobiphenyls, and the mixture was freed from traces of bromobenzene by fractional distillation under diminished pressure and analyzed for bromine in order to estimate the content of bromobiphenyls. Thus, it was found that 2.14 g. of bromobiphenyls and 0.9 g. of biphenyl were produced in this reaction, the yields being 13.2 and 8.5%, respectively, based on the aniline used.

Reactions with N-Nitrosoacetanilide.—Experiment 4. N-Nitrosoacetanilide (5 g.) was added to bromobenzene (286 cc.). The dissolution took place at 16.5 without evolution of heat and the decomposition proceeded gradually. Two such reaction mixtures were combined after three days and worked up as described above. The final product, b. p. 136-145° at 9.5 mm. Hg, weighed 6.72 g. (Found: Br, 34.49%. Calcd. for $C_{12}H_9Br$: Br, 34.28%).

Experiment 5. For a competitive run, 39.5 g. (0.24 mole) of N-nitrosoacetanilide was allowed to decompose in a mixture of 155 cc. of benzene and 183 cc. of bromobenzene (both 1.74 moles), and 5.25 g. of bromobiphenyls and 1.25 g. of biphenyl were obtained.

Summary

The reaction of N-nitrosoacetanilide or benzenediazo hydroxide with bromobenzene gives all three isomerides of bromobiphenyls, the yields decreasing in the order ortho > meta > para. All the nuclear positions of bromobenzene are more reactive than benzene towards attack by the phenyl radicals.

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