The Competitive Nitration of Biphenyl and Benzene by Nitric Acid in Acetide Anhydride

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Biphenyl is known to undergo electrophilic substitutions at positions 2 and 4[1], and the chlorination in acetic acid[2] and the Friedel-Crafts acetylation[3] have been shown to take place more rapidly than benzene. In accord with these observations, a theoretical consideration by means of the molecular orbital method[4] predicts more facile substitutions at positions 2 and 4 of biphenyl than at one nuclear position of benzene. The relative rate of nitration of biphenyl appeared, however, to have not yet been studied experimentally, and we have been carrying out experiments on this subject and also on the nitration of substituted biphenyls to elucidate the nature of the polar effect of substituents in the biphenyl system in general. In view of the recent announcement in the Current Chemical Papers, 1956, No. 9, that Dewar and his collaborators have published several papers concerning the nitration of aromatic hydrocarbons including biphenyl, which are not yet available to us, we wish to publish here part of the results of our study on the nitration of biphenyls.

The experimental conditions and the results are listed in Tables I and II.

TABLE I
COMPETITIVE NITRATION OF BIPHENYL AND BENZENE

Expt. No.	1	2	3
Benzene (millimol.)	125	125	177
Biphenyl (millimol.)	12.5	12.5	12.5
Acetic Anhydride (millimol.)	200	200	200
Nitric Acid (millimol.)	10	7.5	9
Reaction Time (hrs.)	3	3.5	3.5
Nitrobenzene formed (millimol.)	2.37	1.62	2.14
Nitrobiphenyls formed (millimol.)	6.99	5.11	4.76
Relative Rate	42	40	39

TABLE II
THE ISOMERIC RATIO OF NITROBIPHENYLS FORMED AND THE PARTIAL RATE FACTORS FOR THE NITRATION OF BIPHENYL

Nuclear Position	2-	3-	4-
Isomer Formed (%)	68	<1	32
Partial Rate Factor	41	<0.6	38

A mixture of biphenyl and benzene was nitrated with nitric acid in acetic anhydride at 0°C. The reaction mixture was added to 400 cc. of ice water, left to stand over-night, neutralized with

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1) For a review of the literature see Y. Mizuno, *J. Soc. Org. Synthet. Chem., Japan*, **14**, 479 (1956).

2) P. W. Robertson, cited by P. B. D. de la Mare, *J. Chem. Soc.*, **1954**, 4450.

3) Y. Ogata and R. Oda, *Bull. Inst. Phys. Chem. Research* (Tokyo), **21**, 728 (1942).

4) F. Seel, *Z. Naturforsch.*, **3a**, 35 (1948) ; R. D. Brown, *J. Am. Chem. Soc.*, **75**, 4077 (1953).

sodium hydrogen carbonate and extracted thoroughly with ether. The ethereal solution was washed with water and dried over anhydrous calcium chloride, and the ether and part of benzene were removed through a Vigreux column. The residue was analyzed for the nitro group by titrating an aliquot with 0.1 N titanium trichloride to determine the total amount of the nitration products. The remainder of the residue was distilled at 20 mmHg, with occasional addition of a little aniline as a carrier for nitrobenzene, until removal of nitrobenzene was complete. Analysis for the nitro group of an aliquot portion of the residue from this distillation gave the amount of isomeric nitrobiphenyls formed and hence that of the nitrobenzene by difference. These analytical results gave the relative rate of nitration of biphenyl with respect to benzene (Table I) according to the method of Ingold and Shaw[5]. The remaining mixture of nitrobiphenyls and unreacted biphenyl was dissolved in petroleum ether and chromatographed through a column of alumina, yielding a mixture of isomeric nitrobiphenyls, the composition of which was estimated spectrophotometrically (Table II), absorptions at 245, 250, 262.5, 300 and 310 mμ being used. In a separate experiment, nitration of biphenyl without benzene under otherwise the same experimental conditions as above gave a mixture of nitrobiphenyls of the same isomeric composition. The ratio of the isomers formed and the relative rate (the mean value of 40) gave the partial rate factors for the nitration of biphenyl, the rate constants of separate nuclear positions of biphenyl relative to one nuclear position of benzene as unity.

The present results show that positions 2 and 4 of biphenyl are very much activated towards nitration by the electromeric effect of the phenyl group, whereas position 3 is deactivated, probably owing to the electron attracting inductive effect of the phenyl group. The possibility can not be excluded that the deactivation is attributable to a destabilizing conjugation, in the transition state, of the substituent phenyl group with the nucleus undergoing substitution at position 3.

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[5] C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, **1927**, 2918.