

758. *The ortho : para-Ratio in Aromatic Substitution. Part IV.*¹
The Nitration of Biphenyl.

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The *ortho* : *para*-ratios of nitro-derivatives obtained by nitrating biphenyl under five sets of conditions are reported. In homogeneous solution, the ratio is approximately constant (about 2 : 1) irrespective of the conditions, but in a heterogeneous system the *para*-isomer predominates. An explanation is suggested for the change in orientation. Partial rate factors for the nitration of biphenyl in acetic anhydride have also been measured.

THE nitration of biphenyl has been studied quantitatively by three groups of investigators. Nitric acid in acetic anhydride was reported by Simamura and Mizuno² to give the 2- and 4-nitro-derivatives in a ratio of 68 : 32, while Dewar and his co-workers reported a ratio of 77 : 23 under similar conditions.³ After nitration by mixed acid in a heterogeneous system, Jenkins, McCullough, and Booth isolated the two derivatives in 34 and 57% yield, respectively.⁴ This change in the relative reactivities of the 2- and the 4-position of biphenyl with change in nitrating conditions is similar to the behaviour of anisole,^{5,6} acetanilide,⁷ and methyl phenethyl ether,⁸ each of which gives a very much higher proportion of the *ortho*-derivative when nitration is carried out in acetic anhydride solution than under other conditions. A mechanism for the enhanced reactivity of the *ortho*-position relative to the *para*-position in methyl phenethyl ether in its reaction in acetic anhydride solution has recently been suggested,⁸ and it was therefore of interest to determine whether the comparable behaviour of biphenyl has a similar basis.

Isomer distributions in the nitration of biphenyl under the conditions stated in Table I were determined by gas chromatography. The high-boiling 2- and 4-nitrobiphenyls were completely resolved on a column packed with glass micro-beads coated with 1% by

¹ Part III, Norman and Radda, *J.*, 1961, 3610.

² Simamura and Mizuno, *Bull. Chem. Soc. Japan*, 1957, **30**, 196.

³ Dewar, Mole, Urch, and Warford, *J.*, 1956, 3572.

⁴ Jenkins, McCullough, and Booth, *Ind. Eng. Chem.*, 1930, **22**, 31.

⁵ Griffiths, Walkey, and Watson, *J.*, 1934, 631.

⁶ Halvarson and Melander, *Arkiv Kemi*, 1957, **11**, 77.

⁷ Arnall and Lewis, *J. Soc. Chem. Ind.*, 1929, **48**, 159r.

⁸ Norman and Radda, *Proc. Chem. Soc.*, 1960, 423.

weight of a silicone-gum rubber. The proportion of the 3-nitro-derivative formed was not determined accurately, but it was shown that under each set of conditions it was formed in less than 2% yield.

TABLE I. *Isomer distributions in the nitration of biphenyl.*

Nitrating conditions	Temperature	Isomer distribution (%)	
		2-nitro-	4-nitro-
HNO ₃ in acetic anhydride	0°	69.2	30.8
HNO ₃ in acetic acid	0	64.4	35.6
HNO ₃ -H ₂ SO ₄ (1 : 5) in nitrobenzene	0	65.0	35.0
HNO ₃ -H ₂ SO ₄ -biphenyl (heterogeneous)	0	42.3	57.7
	35	43.1	56.9

Our value for nitration in acetic anhydride is close to that obtained by Simamura and Mizuno,² and differs from the value obtained by Dewar *et al.*³ In heterogeneous conditions we found a rather larger proportion of the 2-nitro-derivative than had been found previously by product analysis,⁴ and this proportion did not alter when reaction was at the higher temperature (30–40°) used by the previous workers.

These results show that biphenyl does not behave analogously to anisole, acetanilide, and methyl phenethyl ether in nitration. These three compounds change from *ortho*-orientation in acetic anhydride to predominant *para*-orientation under other nitrating conditions, whereas the corresponding change is small for biphenyl and may simply be due to a solvent effect. That the selectivity of a reagent can vary over a wide range with change of solvent has recently been demonstrated for the chlorination of toluene.⁹

Two problems are raised by these results: to account for the high *ortho* : *para*-ratio compared with those obtained from other monosubstituted benzenes in which the substituent is, like phenyl, of $-I$, $+E$ type;¹ and to account for the different orientation in heterogeneous conditions.

It was suggested by de la Mare and Hassan¹⁰ that the high reactivity of the *ortho*-position relative to that of the *para*-position in the nitration of biphenyl in acetic anhydride depends on the fact that in the transition state for *ortho*-substitution the tetrahedral disposition of bonds at the *ortho*-carbon atom allows the two benzene rings to be coplanar. This permits the maximum delocalisation of the positive charge on the aromatic system in this state.¹⁰ In pointing out that there may be a similar explanation for the greater reactivity of 2- than of 4-trimethylsilylbiphenyl in protodesilylation, Deans, Eaborn, and Webster note that it is difficult to generalise this explanation since, in nitration by mixed acid, biphenyl is more reactive in the *para*- than in the *ortho*-position.¹¹ While our results confirm this fact, they also demonstrate that under all conditions of homogeneous nitration, the *ortho*-position is the more reactive. The criticism of de la Mare and Hassan's theory is not therefore necessarily valid. Furthermore, in terms of their theory, the change in orientation under heterogeneous conditions may be rationalised: in the solid biphenyl is a planar molecule, so that there is no longer a stereochemical facilitation of *ortho*-substitution.

The partial rate factors for nitration, in acetic anhydride, at the 2- and the 4-position in biphenyl were found by Simamura and Mizuno to be 41.5 and 38,² while from the experiments of Dewar and his collaborators,¹² the calculated values are 18.5 and 11, respectively.¹³ Because of this discrepancy, we re-determined the partial rate factors. The reactivity of biphenyl relative to that of *t*-butylbenzene was measured by competitive nitration of the two compounds, and from this value, together with the value for the reactivity of *t*-butylbenzene relative to benzene previously determined¹⁴ and the isomer distribution for the

⁹ Stock and Himoe, *Tetrahedron Letters*, 1960, No. 13, 9.

¹⁰ de la Mare and Hassan, *J.*, 1957, 3004.

¹¹ Deans, Eaborn, and Webster, *J.*, 1959, 3031.

¹² Dewar, Mole, and Warford, *J.*, 1956, 3576.

¹³ de la Mare and Ridd, "Aromatic Substitution," Butterworths Scientific Publications, 1959, p. 157.

¹⁴ Knowles, Norman, and Radda, *J.*, 1960, 4885.

nitration of biphenyl reported in Table 1, the following partial rate factors were obtained: 2-position, 36.4; 4-position, 32.6. Like the isomer ratios, these results resemble closely those reported by Simamura and Mizuno.²

EXPERIMENTAL

Materials.—Biphenyl, *t*-butylbenzene, and nitrobenzene were commercial materials. Fuming nitric acid (B.D.H. "AnalaR," *d* 1.5) was employed for all nitrations. 2-Nitrobiphenyl, *m. p.* 36°, and 4-nitrobiphenyl, *m. p.* 113°, were supplied by Mr. P. S. Johnson. 3-Nitrobiphenyl was prepared by a modified Gomberg reaction between *m*-nitroaniline and benzene¹⁵ and had *m. p.* 61° (from light petroleum, *b. p.* 60–80°). The silicone-gum rubber and glass beads used for the chromatographic column were kindly supplied by Dr. F. L. Bach of the American Cyanamid Company.

Isomer Distributions.—(a) *Homogeneous nitrations.* Nitrations were carried out at 0° with careful temperature control. The nitrating mixture (see Table 2) was added slowly to a solution of biphenyl (0.04 mole) in the appropriate solvent. Reactions were stopped by the addition of water, and the mixture was extracted three times with benzene. After removal of the benzene, the residue was dissolved in acetone and this solution was analysed by gas chromatography.

TABLE 2. *Experimental conditions for homogeneous nitrations.*

Solvent for biphenyl	Nitrating mixture	Reaction time (hr.)
Acetic anhydride (200 ml.)	HNO ₃ (0.04 mole) in Ac ₂ O (0.1 mole)	20
Acetic acid (200 ml.)	HNO ₃ (0.04 mole) in HOAc (0.2 mole)	50
Nitrobenzene (10 ml.)	HNO ₃ (0.04 mole)—H ₂ SO ₄ (<i>d</i> 1.82) (0.2 mole)	0.5

(b) *Heterogeneous nitrations.* Nitrations were carried out at 0° and 35° by the method of Jenkins, McCullough, and Booth,⁴ using one-hundredth quantities. The nitrating mixture was added during 10 min., and the reaction was stopped after 1 hr. by addition of water. Extraction and analysis procedures were the same as those for homogeneous nitration.

Gas-chromatographic Analysis.—The column (200 cm × 4.5 mm.) was packed with silicone-gum rubber (SE-30 General Electric Company) (1% w/w) coated on glass micro-beads (70–80 mesh; Prismo Safety Corporation), and was operated with an inlet heater temperature of 270°. Nitrogen (30 ml./min.) was used as carrier gas. A hydrogen-inject flame ionisation detector coupled to a Sunvic recorder gave a linear response. At a column temperature of 135° the retention times of 2- and 4-nitrobiphenyl were 17.5 and 25 min., respectively. The injection of known mixtures of these compounds showed that the ratio of peak areas (measured by constructing triangles made up of tangents to the Gaussian curves and the intercepts on the base line) was proportional within 2% to the ratio of the quantities of the two materials. Analysis of known mixtures of isomers submitted to the extraction procedure showed that this was quantitative. Each result recorded in Table 1 is the mean of at least four analyses. The mean deviation was ±0.5%.

3-Nitrobiphenyl was not resolved from the 4-nitro-isomer under these conditions, but its presence as a nitration product in at most 2% yield was proved as follows: after injection of a sample of reaction product into the column, material eluted during the period of emergence of the 3- and 4-nitro-isomers was collected by condensation on a microscope slide. Its *m. p.*, measured on a micro-Kofler block, corresponded to that of pure 4-nitrobiphenyl. When a known mixture containing 2% of 3-nitrobiphenyl was similarly treated, a marked depression of *m. p.* was observed.

Overall Reactivity.—A mixture of *t*-butylbenzene (0.0075 mol.), biphenyl (0.04 mol.), and the internal standard, nitrobenzene (2.5 ml.), was dissolved in acetic anhydride (200 ml.) and divided into two parts. To one portion was added a mixture of nitric acid (0.025 mole) in acetic anhydride (2 ml.). Reaction took 24 hr. and was stopped by the addition of water. Both portions were extracted with ether, and the extracts, after concentration and drying (Na₂SO₄), were analysed by gas chromatography. The column (400 cm. × 4.5 mm.) was

¹⁵ Elks, Haworth, and Hey, *J.*, 1940, 1284.

¹⁶ Hishta, Messerly, Reshke, Fredericks, and Cooke, *Analyt. Chem.*, 1960, **32**, 880.

packed with "Apiezon L" grease (30% w/w) coated on "Embacel" and was operated at 186° with hydrogen (60 ml./min.) as carrier gas. Retention times were: t-butylbenzene, 6 min.; nitrobenzene, 9 min.; biphenyl, 47 min. The nitrated and unchanged extracts from several mixtures were injected consecutively into the column, and by comparison of the heights of the peaks of t-butylbenzene and biphenyl relative to the standard, the amounts of each used up in the nitrations were calculated. The average value obtained for the reactivity of biphenyl relative to t-butylbenzene¹⁴ was 2.33 ± 0.04 . Since the reactivity of t-butylbenzene relative to benzene under these conditions is 15.1,¹⁴ the reactivity of biphenyl relative to benzene is 35.1 ± 0.06 .

That changes in amounts of the two reactants relative to the standard were proportional to changes in peak heights produced by these reactants relative to that produced by the standard, was proved by the injection of synthetic mixtures of varying proportions. It was also shown that, under the conditions of the nitrations, the internal standard did not react. This was done by adding equal amounts of an external standard to equal amounts of the internal standard before and after attempts to nitrate it, and comparing peak heights produced by the mixture at each stage.

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