896. *The Quantitative Study of the Arylation of Naphthalene by Means of Diazonium Salts and Zinc. Part II.*[1]

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Further homolytic arylations of naphthalene have been carried out with radicals $R{\cdot}C_6H_4{\cdot}$ of both *ortho*- and *para*-substituted type, and isomer ratios for the resulting mixtures of 1- and 2-arylnaphthalenes have been determined with an average accuracy of ~1%. Steric effects due to *ortho*-substitution of the attacking radical are discernible but are of the same order of magnitude as effects ascribable to the polar nature of the radicals concerned. Several new monosubstituted 1- or 2-arylnaphthalenes have been prepared in the course of this work.

In 1959 Marshall and Waters (their paper[1] will be referred to as Part I) reported a quantitative study of the homolytic arylation of naphthalene in which they generated aryl radicals by Waters's reaction[2] between aryldiazonium salts and zinc in suspension in acetone. In that work the percentages of 1- and 2-arylnaphthalenes resulting from reactions involving phenyl, *p*-nitrophenyl, *p*-methoxyphenyl, and *p*-acetamidophenyl radicals were determined spectroscopically, after the required isomeric products had been separated from other materials by chromatography through activated alumina. The

[1] Part I, see Marshall and Waters, *J.*, 1959, 381.

[2] Waters, *J.*, 1939, 864.

analytical procedure usually involved the comparison of the infrared absorption, in the 11—15 μ region, of the isomer mixture in carbon disulphide solution with those of a series of mixtures of the two pure isomers each of which had been prepared, to adequate analytically purity, by an unequivocal route.

TABLE 1.

Mean values for the percentage composition of the isomer mixture resulting from the substitution of naphthalene by radicals, $R\cdot C_6H_4\cdot$.

R	1-Isomer (%)	2-Isomer (%)	Range of error (%)	R	1-Isomer (%)	2-Isomer (%)	Range of error (%)
H *	80·3	19·7	0·7	*o*-Me	72·0	28·0	1·7
o-NO_2	78·2	21·8	0·1	*p*-Me	82·3	17·7	1·1
m-NO_2	80·3	19·7	1·0	*o*-OMe	74·9	25·1	0·3
p-NO_2 *	83·2	16·8	0·1	*p*-OMe *	73·8	26·2	0·6
p-CN	81·6	18·4	0·5	*o*-OPh	(76·3)	—	(? 5)
o-Cl	70·7	29·3	1·2	*p*-NH·COMe *	76·8	25·2	0·5
p-Cl	84·0	16·0	1·9				

* Results reported in Part I.

We have now investigated similarly the substitution of naphthalene in boiling acetone by *o*- and *m*-nitrophenyl, *o*- and *p*-tolyl, *o*- and *p*-chlorophenyl, *o*-methoxyphenyl, and *p*-cyanophenyl radicals. With these radicals we estimate that the isomer percentage can be determined in replicate experiments with an accuracy of 1—2%. A less accurate estimate (± *ca.* 5%) has been made for substitution by the *o*-phenoxyphenyl radical. Our results, together with those of Part I, are collected in Table 1. Several new compounds prepared in this work are described in the Experimental section.

It can be seen that the extreme variation of the percentage of 1-arylnaphthalene formed by the attack of any radical $\cdot C_6H_4R$ is limited (70·7—84%) though it is far greater than our estimate of experimental errors. With the *para*-substituted radicals the effect of the substituent follows the order $Cl > NO_2 > Me > CN > H > NHAc > OMe$, which is neither the sequence of the dipole moments of the compounds $R\cdot C_6H_4X$ nor the sequence of the σ, $\sigma+$, σ_n, or σ_G values for the substituents R as given in recent Reviews.[3] Both the small effect of the cyano-group and the sign of the effect of the methyl group are anomalous to an extent that could be explained only by the supposition that in these cases our experiments have been subject to a systematic but yet repeatable error, leading to the differential loss of one isomer in an early stage of the separation.

It is interesting that the only *meta*-substituted phenyl radical gives an isomer ratio equal to that of the unsubstituted phenyl radical. This accords with the general finding that even in heterolytic substitution directive influences exerted from *meta*-positions are small.

One would expect that with *ortho*-substituted aryl radicals steric hindrance to attack in the 1-position in naphthalene from the adjacent *peri*-hydrogen should decrease the resultant percentage of 1-arylation. This has been observed, for the 1-isomer percentage which increases in the sequence Cl < Me < OMe (< OPh) < NO_2 for *ortho*-substituents

TABLE 2.

Substituent	Cl	Me	NO_2	OMe
% *p*- minus % *o*- for substitution in 1-position	13·3	10·3	5·0	−1·1

is in each case less than is found for phenylation. However, the isomer percentage itself should indicate the combined effect of steric and polar influences and a better impression of the relative magnitudes of the steric influences can be gained from Table 2 which lists the change in product composition resulting from the movement of a substituent from a

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[3] G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, London, 1960; McDaniel and Brown, *J. Org. Chem.*, 1958, **23**, 420; Brown and Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979; Knowles, Norman, and Radda, *J.*, 1960, 4885; van Bekkum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

para- to an *ortho*-position. This Table shows that the maximum steric effect is exhibited by the spherical substituents chlorine and methyl; the flatter nitro- and methoxy-groups that could orient themselves so as to have much less impeding action appear to do so. The effect of the methoxy-group, however, seems to be anomalous and it must be remembered that polar and mesomeric effects exerted from *ortho*-positions need not correspond to those exerted from *para*-positions.

The main conclusion to be drawn from this study of the homolytic arylation of naphthalene is that polar and steric effects of substituent groups are of comparable magnitude and that both are small.

EXPERIMENTAL

o-*Nitrophenylation of Naphthalene in Acetone,*—*o*-Nitrobenzenediazonium tetrachlorozincate (125 g.) was prepared by diazotising *o*-nitroaniline (69 g.) in 17% aqueous hydrochloric acid (350 ml.) with sodium nitrite (35 g. in 75 ml. of water) and adding the resulting filtered solution with stirring to a cold concentrated aqueous solution of zinc chloride (40 g.). The solid was collected, washed with water, alcohol, and ether, and stored under dry ether at −10°. The arylation of naphthalene (20 g.) in dry acetone (50 ml.) was carried out by stirring in the above diazonium salt (18 g.) and then adding zinc powder (6 g.) in small portions during 1 hr. On the following day the solvent was removed and the residue extracted with benzene (3 × 100 ml.) to separate completely the nitrophenylnaphthalenes from tar. The filtered solution was evaporated and the solid residue chromatographed through alumina (type H) with light petroleum–benzene (9 : 1) to yield a mixture of 1- and 2-*o*-nitrophenylnaphthalene (3·5 g.). This was analysed spectrographically in carbon disulphide solution as described in Part I [1] by using the absorption band of the 1-isomer at 12·55 and of the 2-isomer at 12·25 μ. Mixtures from complete duplicate experiments contained 78·1 and 78·2% of the 1-isomer.

A similar procedure was used successfully for the arylations listed below, where the wavelengths quoted are those used for determination of the 1- and 2-isomer, respectively.

m-Nitrophenyl: 1-isomer, 79·7, 80·4, 80·7%; 12·875 μ, 13·375 μ.
p-Cyanophenyl: 1-isomer, 81·4, 81·6, 81·9%; 12·85 μ, 12·25 μ.
o-Methoxyphenyl: 1-isomer, 75·0, 74·7, 75·0%; 12·525 μ, 12·25 μ.
o-Methylphenyl: 1-isomer, 71·1, 72·8%; 12·50 μ, 12·25 μ.
p-Methylphenyl: 1-isomer, 81·6, 82·7, 82·5%; 12·875 μ, 12·375 μ.
o-Chlorophenyl: 1-isomer, 70·0, 71·0, 71·2%; 12·525 μ, 12·25 μ.
p-Chlorophenyl: 1-isomer, 82·8, 84·7, 84·6%; 12·9 μ, 12·325 μ.
o-Phenoxyphenyl: 1-isomer, 76·5—81%; 12·5 μ, 12·25 μ.

The last reaction gave trouble since the last trace of diphenyl ether was separated from the isomer mixture only by prolonged steam-distillation. The lower percentage of 1-isomer was found by analysis of a mixture which still contained a trace of diphenyl ether, whilst the higher figure was obtained after prolonged steam-distillation. It is possible that some differential loss of one of the substituted arylnaphthalenes might have resulted from this drastic treatment.

Syntheses of Reference Compounds.—1-o-*Nitrophenylnaphthalene.* The mixture of 1- and 2-isomers, prepared as described above, was separated chromatographically on alumina by elution with light petroleum–benzene (3 : 1). The main component (2 g.) was crystallised repeatedly from ethanol, to give 1-o-*nitrophenylnaphthalene* as pale yellow needles, m. p. 91—92° (Found: C, 77·3; H, 4·3; N, 5·45. $C_{16}H_{11}NO_2$ requires C, 77·1; H, 4·45; N, 5·6%), $\nu_{max.}$ 12·55, 12·9, and 13·5 μ (1,2- and 1,2,3-substituted benzene). 2-*o*-Nitrophenylnaphthalene was prepared from diazotised β-naphthylamine and nitrobenzene by Hey and Lawton's method [4] and repeatedly crystallised from ethanol to give yellow needles, m. p. 102° (Found: C, 76·8; H, 4·5; N, 5·7%).

1- and 2-*m*-Nitrophenylnaphthalene were separated chromatographically from the mixture obtained from the arylation of naphthalene with *m*-nitrobenzenediazonium tetrachlorozincate; the 1-isomer was eluted from alumina with a 5 : 1 and the 2-isomer with a 1 : 1 light petroleum–benzene mixture. Each was crystallised repeatedly from ethanol. The 1-*isomer*, m. p. 67·5—68·5°, had $\nu_{max.}$ 12·5, 12·9, 13·5, and 14·5 μ (Found: C, 77·2; H, 4·5; N, 5·75. $C_{16}H_{11}NO_2$ requires C, 77·1; H, 4·45; N, 5·6%); the 2-*isomer*, m. p. 131—132°, had $\nu_{max.}$ 12·25, 12·45, 13·35, and 14·6 μ (1,2-, 1,3-, and 1,2,4-substituted benzene) (Found: C, 77·2; H, 4·4; N, 5·6%).

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[4] Hey and Lawton, *J.*, 1940, 374.

1- *and* 2-p-*Cyanophenylnaphthalene*. These were also separated from the corresponding arylation mixture; the 1-isomer was eluted from alumina with 3 : 1 light petroleum–benzene, and the 2-isomer with pure benzene. The 1-*isomer*, crystallised from light petroleum (b. p. 60—80°), had m. p. 86—87°, $\nu_{max.}$ 11·8, 12·5, and 12·75 μ (Found: C, 89·3; H, 4·7; N, 5·9. $C_{17}H_{11}N$ requires C, 89·1; H, 4·8; N, 6·1%). The 2-*isomer* crystallised from ethanol in needles, m. p. 158·5—159·5°, $\nu_{max.}$ 11·95, 12·25, and 13·35 μ (Found: C, 89·05; H, 4·9; N, 5·9%).

1-*o*-Methoxyphenylnaphthalene was separated from the corresponding arylation mixture and crystallised repeatedly from ethanol. It had m. p. 92·5—93·5° (Found: C, 86·9; H, 6·0. Calc. for $C_{17}H_{14}O$: C, 87·2; H, 6·0%); Orchin[5] gives m. p. 91·2—92·6°.

2-o-*Methoxyphenylnaphthalene*. This was prepared by treating β-tetralone (5 g.)[6] with the Grignard reagent from *o*-bromoanisole (10 g.). The crude product was steam-distilled to remove starting materials, and the involatile residue was collected and refluxed for 30 min. with acetic anhydride (5 ml.). The anhydride was distilled off and the residue was heated for 30 min. at 250° with sulphur (2 g.). The melt was extracted with benzene and the extract purified by chromatography on alumina. The product (2·7 g.), after three low-temperature crystallisations from ethanol, gave crystals having m. p. 43—44·5° (Found: C, 87·0; H, 5·9%), $\nu_{max.}$ 11·2, 12·25, and 13·35 μ.

1-*o*-Tolylnaphthalene was prepared similarly from 2-methylcyclohexanone and α-naphthylmagnesium bromide. It was obtained as needles, m. p. 67·5—68·5, as previously described[7] (Found: C, 93·4; H, 6·5. Calc. for $C_{17}H_{14}$: C, 93·5; H, 6·5%). A similar sequence of reactions, starting from β-bromonaphthalene, was used to prepare 2-*o*-tolylnaphthalene which crystallised from ethanol in plates, m. p. 185—186°, $\nu_{max.}$ 12·25, 12·85, and 13·8 μ (Found: C, 93·8; H, 6·3%).

1-*p*-Tolylnaphthalene could not be obtained pure by reaction of α-tetralone with *p*-tolylmagnesium iodide and so a mixed Ullmann reaction was used. 1-Iodonaphthalene (25·4 g.) and *p*-iodotoluene (21·8 g.) were heated together at 210° and copper bronze powder (18 g.) was added in portions during 1 hr. After cooling, the melt was extracted with ether, the ether removed, and the residue distilled, to give products (5 g.), b. p. 100—140°/15 mm. (after crystallisation from light petroleum this proved to be mainly 4,4′-dimethylbiphenyl, m. p. 125°) and (9 g.) an oil, b. p. 200—240°/15 mm., [separated chromatographically with light petroleum (b. p. 40—60°) on alumina into an oil (5 g.) and a solid (3·5 g.) which proved to be 1,1′-binaphthyl, m. p. 160°]. Repeated crystallisation of the oil from light petroleum gave solid 1-p-*tolylnaphthalene*, m. p. 53·5—54·5°, $\nu_{max.}$ 12·17, 12·55, and 13·87 μ (Found: C, 93·65; H, 6·55. $C_{17}H_{14}$ requires C, 93·5; H, 6·5%). 2-p-*Tolylnaphthalene* was prepared as above by a Grignard reaction between β-tetralone and *p*-tolylmagnesium iodide, final dehydrogenation being by 5% palladium–charcoal at 325°. The pure compound crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 97—98°, $\nu_{max.}$ 11·2, 12·35, and 13·45 μ (Found: C, 93·6; H, 6·5%).

1-o-*Phenoxyphenylnaphthalene*, prepared as above by a Grignard reaction involving α-tetralone and *o*-iododiphenyl ether (m. p. 52—54°) and crystallised from ethanol, had m. p. 89—90°, $\nu_{max.}$ 12·5, 12·87, 13·3, and 14·55 μ (Found: C, 89·0; H, 5·6. $C_{22}H_{16}O$ requires C, 89·2; H, 5·4%). 2-o-*Phenoxyphenylnaphthalene*, prepared from β-tetralone by a similar route, had m. p. 91—92·5°, $\nu_{max.}$ 12·25, 13·25, and 14·5 μ (Found: C, 89·0; H, 5·4%).

1-o-*Chlorophenylnaphthalene*, m. p. 60—61°, $\nu_{max.}$ 12·52, 12·9, 13·25, 13·6, and 13·9 μ (Found: C, 80·3; H, 4·75; Cl, 15·05. $C_{16}H_{11}Cl$ requires C, 80·5; H, 4·7; Cl, 14·9%), 2-o-, m. p. 63·5—64°, $\nu_{max.}$ 11·2, 12·25, 13·25, and 13·8 μ (Found: C, 80·25; H, 4·5; Cl, 15·2%), 1-p-, b. p. 152—157°/0·5 mm., $\nu_{max.}$ 11·85, 12·2, 12·5, 12·87, and 13·65 μ (Found: C, 80·7; H, 4·7; Cl, 14·9%), and 2-p-*chlorophenylnaphthalene*, m. p. 136·5—138°, $\nu_{max.}$ 11·2, 12·05, 12·3, and 13·4 μ (Found: C, 80·3; H, 4·8; Cl, 14·85%), were prepared by Grignard reactions from the appropriate tetralones and chloroiodobenzenes. A by-product in the synthesis of 1-*p*-chlorophenylnaphthalene was a solid, m. p. 155—157°, which is thought to be 1′-p-*chlorophenyl*-1,2′-*binaphthyl*[7] (Found: C, 85·3; H, 4·6; Cl, 10·1. $C_{26}H_{17}Cl$ requires C, 85·5; H, 4·7; Cl, 9·75%).

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[5] Orchin, *J. Amer. Chem. Soc.*, 1948, **70**, 495.
[6] Cornforth, Cornforth, and Robinson, *J.*, 1942, 689.
[7] Cf. Cook and Lawrence, *J.*, 1936, 1431.