68. *A Quantitative Study of the Arylation of Naphthalene by Means of Diazonium Salts and Zinc.*

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Free radicals generated by the decomposition, with zinc powder, of acetone suspensions of four aryldiazonium salts have been used to effecthomolytic monosubstitution of naphthalene in both the α- and the β-position. The resulting mixtures of α- and β-arylnaphthalenes have been separated and analysed spectroscopically, comparison being made with synthesised pure reference compounds. The variation in the α : β ratios for the arylations is tabulated and discussed.

NORMAN and WATERS[1] have demonstrated the wide scope, for homolytic arylation of organic solids, inherent in Waters's reaction[2] whereby aryldiazonium salts, in acetone or ethyl acetate suspension, give free aryl radicals on treatment with zinc and similar metals:

$$2Ar{\cdot}N_2^+ + Zn \longrightarrow 2Ar{\cdot} + 2N_2 + Zn^{2+}$$

This reaction, which was shown to yield both α- and β-phenylnaphthalene from naphthalene, has now been used for the substitution into naphthalene at 20—50° by phenyl, *p*-nitrophenyl, *p*-methoxyphenyl, and *p*-acetamidophenyl free radicals. In each instance the mixed isomeric α- and β-arylnaphthalene have been separated chromatographically from other products and then analysed spectroscopically, authentic reference compounds having been synthesised by unequivocal methods for comparison.

Naphthalene was in every instance used in considerable excess as a concentrated solution in acetone, so as to avoid disubstitution and possible differential loss thereby of either the α- or the β-monosubstituted product. Recoveries and product yields are listed

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[1] Norman and Waters, *J.*, 1958, 167.
[2] Waters, *J.*, 1939, 864.

in Table 1. The percentage purity of the mixtures of arylnaphthalenes was estimated by comparing the total weight of any mixture isolated with that calculated from the infrared spectrum of a weighed sample.

TABLE 1. *Quantitative arylation of naphthalene by* p-$R{\cdot}C_6H_4$ *radicals.*

Group R and Source	$C_{10}H_8$ used (mole)	Radical source (mole)	$C_{10}H_8$ recovered (mole)	$R{\cdot}C_6H_4{\cdot}C_{10}H_7$ obtained (mole)	(% purity)
NO_2	0·16	0·08	0·141	0·012	99·6
$Ar{\cdot}N_2{\cdot}BF_4$	0·16	0·08	0·117	0·016	99·3
H	0·16	0·04	0·144	0·004	96·7
$(Ar{\cdot}N_2)_2ZnCl_4$	0·16 *	0·04	0·133	0·007	93·0
NH·COMe	0·16	0·08	0·129	0·003	98·6
$Ar{\cdot}N_2{\cdot}BF_4$	0·20	0·08	0·164	0·009	100·0
OMe	0·16	0·06	0·141	0·007	100·0
$(Ar{\cdot}N_2)_2ZnCl_4$	0·16	0·06	0·125	0·008	80·0

* Benzene used as co-solvent.

A high percentage of the generated $R{\cdot}C_6H_4{\cdot}$ radicals inevitably attack the acetone, forming benzene derivatives $R{\cdot}C_6H_5$, with consequent low yields of arylated naphthalenes. In one instance benzene was used as co-solvent for the phenylation of naphthalene, but the formation of diphenyl then complicated the separation and a trace of bis-4-diphenylyl (quaterphenyl) was also formed.

TABLE 2. *Isomer percentages obtained in the arylation of naphthalene by* *p*-$R{\cdot}C_6H_4{\cdot}$ *radicals.*

R	α (%)	β (%)	R	α (%)	β (%)
NO_2	83·3, 83·1	16·7, 16·9	NH·COMe	77·0, 76·5	23·0, 23·5
H	80·7, 80·0	19·3, 20·0 *	OMe	74·1, 73·5	25·9, 26·5

* Benzene used as co-solvent.

The isomer percentages given in Table 2 for the phenylation of naphthalene in acetone accord with those determined by Huisgen and Grashey [3] in a series of solvents at about the same temperature, using *N*-nitrosoacetanilide, and with the results of Davies, Hey, and Williams [4] using benzoyl peroxide at 85°. The *para*-substituents alter the α : β ratios slightly, though to an extent far beyond the possible analytical error.

Theoretical calculations show that naphthalene has a higher electron-availability at α- than at β-positions. In accordance with this, heterolytic electrophilic substitution of naphthalene below 100° always gives much more α- than β-isomer. As Table 2 shows, the homolytic substitution into naphthalene by the *p*-nitrophenyl group results in an increased percentage of α-compound, as would be expected for a slightly electrophilic substituting agent. The other two substituents have opposite electrical character and both definitely depress the α : β ratio. This sequence is in the order of Hammett's σ constants for the relative rates of reactions involving aromatic side-chains, but the magnitudes of the relative effects of NO_2, H, NH·COMe, and OMe groups accord better with the σ^+ constants of Brown and Okamoto [5] for reactions in which carbon atoms of aromatic nuclei are directly involved. However, too few figures concerning naphthalene are yet available for discussion of the type of σ factors that should be apposite for the small dipole effects influencing this particular example of homolytic aromatic substitution.

EXPERIMENTAL

Phenylation of Naphthalene in Acetone.—Benzenediazonium zincichloride, prepared by addition of concentrated aqueous zinc chloride (0·2 mole) to aniline (0·3 mole) diazotised in concentrated hydrochloric acid, was collected, washed with alcohol and ether, and stored under dry

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[3] Huisgen and Grashey, *Annalen*, 1957, **607**, 46.
[4] Davies, Hey, and Williams, *J.*, 1958, 1878.
[5] Brown and Okamoto, *J. Amer. Chem. Soc.*, 1957, **79**, 1913.

ether at −10°. This solid (16 g.), vigorously stirred in a cold solution of naphthalene (20 g.) in dry acetone (50 ml.), was treated portionwise with zinc powder (6 g.) so that smooth reaction occurred. When no diazonium salt remained (test with H-acid) the solvent was removed on the water-bath and the residue was thoroughly extracted with hot benzene. The filtered extract was evaporated to dryness and the product, in light petroleum (b. p. 40—60°)–benzene (3 : 1), was passed through an alumina column. Most of the naphthalene (18·5 g.; m. p. 80°) was removed from the resulting mixture by crystallisation from methanol, and the remainder, together with the mother-liquors from the crystallisation, was fractionally distilled through a short column, giving the mixed phenylnaphthalenes (0·82 g.) as an oil, b. p. 120—220°/0·5 mm. This was dissolved in " AnalaR " carbon disulphide and its infrared spectrum was measured over the 11—15 μ band, both at the concentration given and after further dilution (1 : 4) with carbon disulphide, in a Perkin-Elmer recording spectrophotometer, Model 21. Infrared spectra were also recorded for solutions of both α- and β-phenylnaphthalene in carbon disulphide at concentrations of 89 mg./25 ml. From these the approximate composition of the mixture was calculated, by using the absorption maxima at 12·5 μ for the α-isomer and 12·25 μ for the β-isomer with correction for the background absorption of the solvent. Thereupon, a series of synthetic mixtures of pure α- and β-phenylnaphthalene was prepared covering, in stages, the range from 80·2 to 81·2% in α-isomer content and thereby a spectrum of a synthetic mixture matching that of the reaction product was found. The deduced composition of the latter was 80·7 ± 0·2% of α-isomer.

Phenylation of Naphthalene in Benzene.—A similar reaction was performed using benzene (50 ml.) plus acetone (5 ml.) as solvent. After removal of naphthalene (17 g.) the mixed phenylnaphthalenes were found to contain 80·0 ± 0·2% of α-isomer. Further elution of the alumina column with benzene gave 4 mg. of a solid, m. p. 312—313°, having log ε 4·61 at $\lambda_{\text{max.}}$ 2980 Å; this probably being bis-4-diphenylyl, m. p. 312°, log ε 4·59 at $\lambda_{\text{max.}}$ 2980 Å.[6]

p-*Nitrophenylation of Naphthalene in Acetone.*—*p*-Nitrobenzenediazonium fluoroborate (100 g.) was obtained by adding cold saturated aqueous sodium fluoroborate (50 g.) to the product of diazotisation of *p*-nitroaniline (69 g.) in aqueous hydrochloric acid (300 ml. of 1 : 1) with sodium nitrite (35 g. in 80 ml. of water). The yellow solid, after being washed with cold water and then alcohol, was stored under dry ether at −10°. Arylation of naphthalene (20 g.) in dry acetone (50 ml.) was carried out with this diazonium salt (19 g.) and zinc (6 g.) as described above. The benzene-soluble products were chromatographed through alumina (type H) with light petroleum–benzene (9 : 1) which removed naphthalene (18 g.), and then with a 1 : 1 mixture of the same solvents which separated the *p*-nitrophenylnaphthalenes (2·988 g.) from residual tar. This mixture, in carbon disulphide (250 ml.), was analysed spectroscopically, as above, by means of the absorption band of the pure α-isomer at 12·9 μ and of the mixed isomers at 12·3 μ, which is an absorption maximum for the β-compound, the final comparison again being made with synthetic mixtures, giving α-isomer contents of 83·3 ± 0·2% and 83·1 ± 0·2% in a complete duplicate experiment.

p-*Acetamidophenylation of Naphthalene.*—This was conducted with *p*-acetamidobenzenediazonium fluoroborate, as in the previous example. The isomeric α- and β-*p*-acetamidophenylnaphthalene (0·471 g.) were too insoluble in carbon disulphide for accurate measurement of their infrared spectra, whilst solutions in nitromethane or dimethylformamide had too much background absorption in the 11—15 μ wave-band. Use was therefore made of the ultraviolet spectrum of the mixture in ethanol (100 ml.), a record covering the band 3500—2100 Å being taken on a Carey recording spectrophotometer, model 14M-50. Records were also taken of the spectra of the two pure isomers. From the following data (where gram extinction coefficients are given, *i.e.*, ε in ml. g.$^{-1}$ cm.$^{-1}$), the composition of the mixture of isomers was computed by the method of Dewar and Urch,[7] giving replicate values for the α-isomer of 77·0 ± 0·5% and 76·5 ± 0·5%.

Compound	$\lambda_{\text{max.}}$ (Å)	ε	Compound	$\lambda_{\text{max.}}$ (Å)	ε
α-*p*-Acetamidophenylnaphthalene (1·203 mg. in 100 ml. of alcohol)	2915 2540 2235	57,930 56,180 240,600	β-*p*-Acetamidophenylnaphthalene (1·531 mg. in 500 ml. of alcohol)	2965 2715 2235	116,300 208,200 186,200

p-*Methoxyphenylation of Naphthalene.*—This was conducted as for phenylation, using the diazonium zincichloride prepared from *p*-anisidine. Chromatographic separation of

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[6] Gillam and Hey, *J.*, 1939, 1170.

[7] Dewar and Urch, *J.*, 1957, 345.

naphthalene (18 g.) and isomeric *p*-methoxyphenylnaphthalenes (1·605 g.) was followed by spectrographic analysis, in the infrared region, in a carbon disulphide solution, with, for comparison, the absorption maximum of the α-isomer at 12·9 μ and of the β-isomer at 13·44 μ, final comparison again being made with synthetic mixtures.

Syntheses of Reference Compounds.—*α-Phenylnaphthalene.* The Grignard reagent from α-bromonaphthalene was condensed with *cyclo*hexanone and the product was dehydrated and then dehydrogenated with palladium–charcoal at 340—360° to α-phenylnaphthalene, b. p. 142—147°/0·5 mm., n_D^{20} 1·6644 (lit.,[8] n_D^{20} 1·6646).

β-*Phenylnaphthalene.* Phenylacetaldehyde was self-condensed to give β-phenylnaphthalene by refluxing it with hydrobromic acid,[9] and the product, m. p. 101—102° (lit., 101°), was crystallised from acetic acid and then from 1 : 1 ethanol–methanol.

α- *and* β-p-*Nitrophenylnaphthalene.* The preparation of the mixed isomers, described above, was repeated several times and a quantity of the mixture was carefully chromatographed through alumina. On elution with light petroleum–benzene (3 : 1) the α-isomer separated first. From alcohol it gave pale yellow needles, m. p. 132—133° (Kühling,[10] by reaction between naphthalene and *p*-nitrobenzene diazohydroxide, obtained orange needles, m. p. 129°) (Found: C, 76·8; H, 4·5; N, 5·7. Calc. for $C_{16}H_{11}O_2N$: C, 77·1; H, 4·7; N, 5·6%). β-*p*-Nitrophenylnaphthalene was thereafter separated with 1 : 1 light petroleum–benzene; it crystallised from alcohol in yellow needles, m. p. 174°. The same compound was obtained on decomposition of neutral diazotised β-naphthylamine solution, together with nitrobenzene, as described by Hey and Lawton.[11] This procedure yielded, in quantity, β-*p*-nitrophenylnaphthalene as a red powder, m. p. 174° (as described), but this, evidently containing some impurity, after sublimation at 140—200°/0·01 mm. gave a yellow solid which, from alcohol, gave yellow needles, m. p. 174° (Found: C, 77·3; H, 4·5; N, 5·6%).

α-p-*Acetamidophenylnaphthalene.* α-*p*-Nitrophenylnaphthalene (0·5 g.) was reduced to α-*p*-aminophenylnaphthalene (0·4 g.) by stannous chloride in alcoholic hydrochloric acid, and then acetylated. The *acetamido-compound* crystallised from light petroleum (b. p. 60—80°)–benzene (1 : 1) in needles, m. p. 198—199° (Found: C, 82·8; H, 5·8; N, 5·6. $C_{18}H_{15}ON$ requires C, 82·7; H, 5·8; N, 5·4%). β-*p*-Acetamidophenylnaphthalene, prepared similarly, crystallised from alcohol in plates, m. p. 206—207° (lit.,[11] m. p. 206°).

α-*p*-Methoxyphenylnaphthalene was prepared by treating *p*-methoxyphenylmagnesium bromide with 1-tetralone and then dehydrating and dehydrogenating the product.[12] It crystallised from 70% ethanol in needles, m. p. 116° (lit., 116·5°) (Found: C, 86·7; H, 6·1. Calc. for $C_{17}H_{14}O$: C, 87·1; H, 6·0%).

β-p-*Methoxyphenylnaphthalene* was separated from the mixture of isomers obtained by the diazo-reaction described above, being eluted from alumina less easily than the α-isomer. The pure β-compound crystallised in plates, m. p. 136—137° (Found: C, 86·6; H, 5·9%). Its infrared absorption spectrum had peaks at 8·0 μ (ether) and at 11·95, 12·05, 12·30, 12·70, and 13·5 μ (1 : 2-, 1 : 4-, and 1 : 2 : 4-substituted benzene).

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[9] Orchin and Reggel, *J. Amer. Chem. Soc.*, 1947, **69**, 505.
[8] Bailey and Case, *Tetrahedron*, 1958, **3**, 129.
[10] Kühling, *Ber.*, 1896, **29**, 165.
[11] Hey and Lawton, *J.*, 1940, 374.
[12] Howell and Robertson, *J.*, 1936, 587.