

Homolytic Aromatic Substitution. Part V. Partial Rate Factors for the Phenylation of Diphenyl.*

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The rate of phenylation of diphenyl relative to that of nitrobenzene by phenyl radicals (generated from benzoyl peroxide) has been measured, and the rate of attack relative to benzene calculated. The percentages of the 2-, 3-, and 4-isomerides formed in the phenylation of diphenyl have been measured by ultra-violet spectrophotometry, thus enabling the calculation of partial rate factors to be made. The values obtained are discussed with reference to the predictions of molecular orbital theory.

THE determination of partial rate factors for the homolytic phenylation of nitrobenzene and the four halogenobenzenes was reported in Parts I—IV (I, Hey, Nechvatal, and Robinson, *J.*, 1951, 2892; II, Augood, Hey, and Williams, *J.*, 1952, 2094; III, *J.*, 1953, 44; Part IV*). In a discussion of these and other results by Hey and Williams (*Discuss. Faraday Soc.*, 1953, 14, 216) it was pointed out that the theoretical prediction of partial rate factors for homolytic substitution in benzene derivatives containing a hetero-substituent is dependent upon the somewhat arbitrary choice of values for the parameters α_X and β_{C-X} for the hetero-atom X and the C—X bond. These difficulties, however, do not occur in hydrocarbons, in which cases more reliable predictions should be possible. The phenylation of the alkylbenzenes is complicated by the possibility of attack in the side-chain (Augood, Hey, Nechvatal, Robinson, and Williams, *Research*, 1951, 4, 386), which renders these compounds unsuitable for an investigation of this type, since an estimate of the extent of side-chain attack must first be made. The phenylation of a series of alkylbenzenes will be the subject of later papers in this series. Polynuclear hydrocarbons, on the other hand, present practical difficulties on account of their low volatility, which renders impossible in most cases the separation of the various fractions of the mixture produced. In diphenyl, however, such a separation has been found to be possible.

The arylation of diphenyl by means of the Gomberg reaction has been studied qualitatively by Grieve and Hey (*J.*, 1938, 108), who allowed diphenyl in chloroform solution to react with diazotised aniline and *p*-nitroaniline, and in both cases isolated the 4-substituted isomeride from the product mixture. Once again (cf. Parts II and III, *loc. cit.*) the proportions of isomerides found in the present investigation do not bear out the results of the previous preparative experiments, owing to the fact that the very much lower solubility of the 4-isomeride had rendered extremely difficult the isolation of the 2- and 3-isomerides in Grieve and Hey's work.

EXPERIMENTAL METHODS AND RESULTS

Determination of $\frac{Ph-NO_2}{PhPh}K$.—Benzoyl peroxide (6 g.) was allowed to decompose in an equimolar mixture of nitrobenzene and diphenyl (200 g.) in a thermostat at 80° for 72 hr. The mixed product was isolated and the nitro-compound was determined therein by titration with titanous chloride. The standard procedure described in Part II (*loc. cit.*) was employed, except that in the chromatography step the column was eluted with a larger predetermined amount of benzene (300 ml.) in order to ensure the complete removal of the rather insoluble diphenylbenzenes. In the final distillation, fore-runs, *i.e.*, mixed fractions containing the last traces of diphenyl and the first traces of nitrodiphenyls, were collected separately from the nitrodiphenyl-diphenylbenzene product fractions, so that the latter should not be contaminated with the last traces of diphenyl. The fore-runs were analysed for nitrodiphenyls by titanous chloride titration, and a correction in terms of nitrodiphenyls applied to the composition of the nitrodiphenyl-diphenylbenzene fraction. A fraction taken immediately before the fore-run proved to consist entirely of diphenyl, showing that neither the fore-run nor the product fraction was contaminated with residual nitrobenzene. It may safely be assumed that the fore-runs contained no diphenylbenzenes, since these were found not to be distilled until a temperature 60° above that at which

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where x , y , and z are the fractions of the *o*-, *m*-, and *p*-isomerides, respectively, in the mixture, and ϵ_o , ϵ_m , and ϵ_p are their respective extinction coefficients at the wave-length considered.

Similarly, at another wave-length λ' ,

$$\epsilon'_{\text{mixt.}} = \epsilon'_o x + \epsilon'_m y + \epsilon'_p z \quad \dots \quad (2)$$

Also

$$x + y + z = 1 \quad \dots \quad (3)$$

Thus, the composition of the mixture may be calculated by solution of the equations (1), (2), and (3), the values of the various extinction coefficients being obtained from the spectra of the mixture and the three pure isomerides. It was found that, whereas all three isomerides absorbed strongly in the region of maximum absorption of *o*-diphenylbenzene, the absorptions due to the other isomerides were relatively small in the regions of maximum absorption of *m*- and *p*-diphenylbenzene. Accordingly, the twelve pairs of wave-lengths λ and λ' at which measurements were made were chosen so that they lay near the absorption peaks of the *meta*- and the *para*-isomeride.

The accuracy of the determination was checked by using equation (1) in conjunction with the determined values of x , y , and z , to calculate $\epsilon_{\text{mixt.}}$ at a large number of wave-lengths for a mixture of a composition represented by x , y , and z . Comparison of this calculated value with the extinction coefficient as actually determined gave a measure of the accuracy of the analysis at that wave-length. This procedure was carried out at 34 different wave-lengths taken over the whole range, and the percentage error calculated at each wave-length. At the peaks the error was zero, but the determination was less accurate at points of low optical density. From this set of 34 points the arithmetical mean error and the standard deviation from the mean error were calculated. The standard deviation from the mean error (+0.5) for the determination of the composition of mixture 6 was found to be $\pm 2.5\%$. The determination of the composition of mixture 5 was equally satisfactory.

Reagents.—Diphenyl (B.D.H.) was dissolved in ethanol, treated with activated charcoal, and recrystallised to constant m. p. (70°) from the same solvent. *o*-Diphenylbenzene was prepared by decomposition of 2-nitrosoacetamidodiphenyl in benzene. 2-Acetamidodiphenyl (8.8 g.), m. p. 120° (from benzene–light petroleum), prepared from 2-aminodiphenyl (B.D.H.), was stirred at 0° with acetic acid (25 ml.), acetic anhydride (25 ml.), fused potassium acetate (5 g.), and phosphoric oxide (0.5 g.), while nitrosyl chloride (3 g.) in acetic anhydride (14 g.) was slowly added. Stirring was continued for 90 min. at 0°. The pale yellow mixture was poured very slowly into cold water (500 ml.) containing sufficient sodium hydrogen carbonate to neutralise the acetic acid. The yellow solid which was precipitated was collected on a cooled filter and washed with cold water (100 ml.). The product rapidly darkened, even in a desiccator at 0°. The entire yield (about 8 g.) was therefore dissolved in benzene (200 ml.), stirred over anhydrous sodium sulphate at room temperature until no more nitrogen was evolved (2 days), and then warmed to 45° for 2 hr. The dark red solution was filtered, the solvent removed under reduced pressure, and the black residue distilled *in vacuo*, yielding an orange solid (4 g.), b. p. 120–130°/0.1 mm., m. p. 94–110°. Recrystallisation from benzene–light petroleum gave 2-acetamidodiphenyl, m. p. and mixed m. p. 119°. The mother-liquors from the recrystallisation were diluted with benzene and extracted repeatedly with concentrated sulphuric acid until both layers were colourless. The benzene solution was washed with alkali and then water (twice) and was evaporated to give *o*-diphenylbenzene (1.0 g.), which was recrystallised to constant m. p. (57°) from methanol.

m- and *p*-Diphenylbenzene (B.D.H.) were decolorised by means of activated charcoal, and recrystallised to constant m. p. from benzene–light petroleum (*m*-diphenylbenzene, colourless prisms, m. p. 85–86°; *p*-diphenylbenzene, colourless plates, m. p. 210°). Benzoyl peroxide (May and Baker) and nitrobenzene (B.D.H. "AnalaR") were purified according to the procedures described in Part II (*loc. cit.*).

DISCUSSION

The relative rate of substitution in diphenyl, $\frac{\text{PhPh}}{\text{PhH}}K$, may be calculated from $\frac{\text{PhPh}}{\text{Ph-NO}_2}K$ and $\frac{\text{Ph-NO}_2}{\text{PhH}}K$, the determination of which was reported in Part II (*loc. cit.*). In this way, $\frac{\text{PhPh}}{\text{PhH}}K$ is found to be equal to 4.0, that is, diphenyl is phenylated at almost exactly the same rate as nitrobenzene. By using this value, and the mean values obtained in spectrophoto-

metric analysis for the ratio of isomerides (Table 3), the following values are obtained for the partial rate factors :

$$F_o = 2.9; F_m = 1.4; F_p = 3.4;$$

since

$$\frac{\text{PhPh}}{\text{PhH}}K = \frac{1}{6}\{4\frac{\text{PhPh}}{\text{PhH}}F_o + 4\frac{\text{PhPh}}{\text{PhH}}F_m + 2\frac{\text{PhPh}}{\text{PhH}}F_p\}$$

and this takes into consideration the fact that there are 4 *ortho*-, 4 *meta*-, and 2 *para*-positions in the diphenyl molecule.

It may be noted that diphenyl conforms to the general pattern of homolytic substitution established in the preceding Parts, in that it is moderately activated towards substitution and that substitution takes place largely in the *ortho*-positions. It is also noteworthy that the sum of the partial rate factors (11.6) for the four *ortho*-positions in diphenyl, which is proportional to the amount of the 2-isomeride produced, is close to the corresponding figure (14.0) for the two *ortho*-positions in nitrobenzene. A similar relationship exists for the *meta*- and the *para*-positions in the two molecules. It appears, therefore, that a phenyl and a nitro-group influence the properties of an aromatic nucleus in homolytic substitution reactions in a similar manner. That this should be so for two groups of such dissimilar polar character, is a striking indication of the insensitivity of homolytic reactions to polar influences.

Calculations have been performed for diphenyl of atom localisation energies for homolytic substitution (Seel, *Z. Elektrochem.*, 1948, **52**, 191; *Z. Naturforsch.*, 1948, **3a**, 35), and free valence numbers (Burkitt, Coulson, and Longuet-Higgins, *Trans. Faraday Soc.*, 1951, **47**, 553). Both sets of calculations predict qualitatively that the 2- and the 4-positions should be activated towards homolytic attack, the activation being greater in the 2-position, and that the 3-position should be slightly deactivated. This qualitative result is in agreement with the experimental data, except in the case of the 3-position, which has been found to be slightly activated.

The predictions are, however, not borne out in a quantitative sense. The degree of activation predicted by the atom localisation energies is very much too large, and in the case of the free valences the expected relation

$$\log F_r \propto (f_r - f_b),$$

where F_r is the partial rate factor of the r th position of the molecule, f_r is the free valence of that position, and f_b is the free valence of any position in benzene, is not obeyed. Thus, although these calculations are capable of making fairly reliable qualitative predictions of the rate and position of homolytic attack in simple aromatic systems, yet they are at present too crude to be of any quantitative value for this purpose. This crudity may possibly be attributed, in the present instance, to a neglect of overlap integrals in making the calculations. The much greater success of Wheland's calculations (*J. Amer. Chem. Soc.*, 1942, **64**, 900) for nitrobenzene and chlorobenzene (cf. Parts II and III, *loc. cit.*) may be due to the fact that in these calculations overlap integrals were not neglected.

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