432. *Amphoteric Aromatic Substitution. Part II. Reactions of Benzoyl Peroxide and Phenylazotriphenylmethane.*

By Donald H. Hey.

In Part I (this vol., p. 1797) it was shown that whenever either sodium benzenediazoate or nitrosoacetanilide is allowed to react with a neutral aromatic compound C_6H_5·R, a biaryl compound is formed in which the phenyl group is attached to the ortho- and/or para-position with respect to R, whether R is a *so-called* ortho-para-directive group or a *so-called* meta-directive group. It was further suggested that these reactions could be most readily explained by postulating a mechanism involving, primarily, the formation and transient existence of free phenyl radicals, and experimental evidence was adduced in support of this view. In order to obtain further corroboration attention is now directed to the reactions of benzoyl peroxide and of phenylazotriphenylmethane, which might serve as possible sources of free phenyl radicals under conditions somewhat similar to those used in the cases of sodium benzenediazoate and nitrosoacetanilide.

Gelissen and Hermans (*Ber.*, 1925, **58**, 285, 476, 479, 764, 765, 770, 984, 2396; 1926, **59**, 63, 662) have found that in boiling benzene solution benzoyl peroxide gave mainly diphenyl, benzoic acid and carbon dioxide, according to the equation $\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}O{\cdot}COPh} + C_6H_6 \longrightarrow \mathrm{Ph{\cdot}Ph} + \mathrm{Ph{\cdot}CO{\cdot}OH} + CO_2$, and that in addition smaller quantities of phenyl benzoate, terphenyl, and quaterphenyl were obtained. The participation of benzene in the reaction was proved by the fact that *p*-chlorobenzoyl peroxide and benzene gave 4-chlorodiphenyl, and not 4 : 4′-dichlorodiphenyl, and similarly *m*-nitrobenzoyl peroxide and benzene gave 3-nitrodiphenyl, and not 3 : 3′-dinitrodiphenyl (cf. Lippmann, *Monatsh.*, 1886, **7**, 523). With toluene at 100° benzoyl peroxide gave 2- and 4-methyldiphenyl, while with diphenyl at 110° terphenyl was obtained. Reactions have now been carried out, in turn, with chlorobenzene, nitrobenzene, and ethyl benzoate. With chlorobenzene, 4-chlorodiphenyl was identified in the product, while with nitrobenzene both 2- and 4-nitrodiphenyl were formed. The reactions of benzoyl peroxide with neutral aromatic compounds thus resemble those of sodium benzenediazoate and of nitrosoacetanilide in giving rise to nuclear substitution at the ortho- and/or para-position with respect to the nitro-group as well as to the methyl and chloro-groups. This similarity extends further the analogies between certain reactions of organic peroxides and the reactions of aromatic diazonium compounds, previously noted by Gelissen and Hermans (*Ber.*, 1925, **58**, 984). In addition, Overhoff and Tilman (*Rec. trav. chim.*, 1929, **48**, 993) have isolated both 2- and 4-phenylpyridine from the action of benzoyl peroxide on pyridine, thus confirming the ability of the substituting agent to function as an anionoid reagent, as now revealed in its reaction with nitrobenzene.

With ethyl benzoate, benzoyl peroxide gave ethyl diphenyl-4-carboxylate together with some ethyl diphenyl-3-carboxylate. The formation of the latter is not entirely unexpected, since the differences in reactivity at the ortho- and meta-positions in ethyl benzoate have not the clear demarcation found, for example, in nitrobenzene. The isolation of ethyl diphenyl-3-carboxylate, in addition to the 4-carboxylic ester, made it desirable to examine further the esters obtained from the action of sodium benzenediazoate on ethyl benzoate (Part I, p. 1803), and it is found that the product consists mainly of ethyl diphenyl-4-carboxylate together with smaller quantities of both the corresponding 2- and 3-carboxylic esters. In the action of sodium benzenediazoate on methyl benzoate, Gomberg and Bachmann (*J. Amer. Chem. Soc.*, 1924, **46**, 2343) report the formation of methyl diphenyl-4-carboxylate only.

With regard to the mechanism of the reactions of benzoyl peroxide in aromatic solvents, it is held by Wieland and Razubaiev (*Annalen*, 1930, **480**, 157) that the primary process is a reaction between the solvent and the peroxide rather than a decomposition of the peroxide to give free radicals (cf. Gelissen and Hermans, *Ber.*, 1926, **59**, 662, etc.). The close correspondence now revealed between its reactions with neutral aromatic solvents and those of sodium benzenediazoate and nitrosoacetanilide, as well as with those of phenylazotriphenylmethane, makes it seem probable that the primary process, in part at least, involves the formation of free radicals.

The reactions of phenylazotriphenylmethane and similar compounds have been studied by Gomberg and his co-workers (*Ber.*, 1897, **30**, 2043; 1903, **36**, 1088; *J. Amer. Chem. Soc.*, 1898, **20**, 773) and more recently by Wieland, Popper, and Seefried (*Ber.*, 1922, **55**, 1816). The latter workers have shown that solutions of phenylazotriphenylmethane in specially purified light petroleum, xylene or ethyl benzoate evolve nitrogen at about 80° with liberation of free triphenylmethyl and phenyl radicals, thus: $Ph_3C{\cdot}N{:}NPh \longrightarrow Ph_3C + N_2 + Ph$. The free triphenylmethyl was identified spectrographically and isolated as its peroxide, but the fate of the phenyl radical was somewhat obscure. No polymerisation to diphenyl could be detected, but the phenyl radical was partly converted into benzene, which was isolated from the product, the exact source which supplied the hydrogen atom being unknown. The product also contained triphenylmethane and some tetraphenylmethane, the formation of the latter accounting for the destination of part of the free phenyl. According to the hypothesis preferred in Part I (*loc. cit.*), if the decomposition of phenylazotriphenylmethane is carried out in an aromatic solvent, reaction should take place between the phenyl radical and the solvent to give a biaryl compound. The decomposition of phenylazotriphenylmethane has now been studied from this standpoint in benzene, chlorobenzene, and nitrobenzene solutions. In benzene solution diphenyl was detected in the product, while in chlorobenzene solution some 4-chlorodiphenyl was formed, and hence the ability of the free phenyl radical to react with a neutral aromatic compound is now confirmed. In the case of the decomposition of phenylazotriphenylmethane in nitrobenzene solution, apart from some triphenylmethane, no definite compounds could be isolated. The diphenyl compounds obtained from the decomposition of phenylazotriphenylmethane in an aromatic solvent form only a very small fraction of the total product, since the phenyl radical itself constitutes only some 22% by weight of the phenylazotriphenylmethane molecule and part of this amount combines with triphenylmethyl to give tetraphenylmethane. The detection of diphenyl and 4-chlorodiphenyl in the above reactions was rendered possible by nitration and bromination respectively.

EXPERIMENTAL.

Reactions with Benzoyl Peroxide.—(a) *With chlorobenzene.* A solution of benzoyl peroxide (30 g.) in chlorobenzene (200 c.c.) was heated on the steam-bath for 2 hours, carbon dioxide being evolved, and then boiled under reflux for 1 hour. After the removal of about 100 c.c. of the excess of chlorobenzene by distillation, the product was diluted with ether, shaken with aqueous sodium hydroxide (a small quantity of insoluble material then separated), washed with water, and dried. Acidification of the alkaline washings gave benzoic acid (13 g.). Evaporation of the ether and excess of chlorobenzene left a dark oil, which on distillation yielded a yellow oil (8 g.), b. p. 270—280°, and a small quantity of a higher-boiling resinous residue. A portion of the oil (2 g.) was boiled for 2 hours under reflux in 90% acetic acid with the gradual addition of chromic anhydride (10 g.); the product was poured into water, from which ether extracted *p*-chlorobenzoic acid (m. p. and mixed m. p. 235—236°). A second portion of the oil (2 g.) was heated on the steam-bath for 5 hours with bromine (1 c.c.) in glacial acetic acid (10 c.c.). On cooling, white prisms of 4-chloro-4′-bromodiphenyl separated, m. p. and mixed m. p. 153—154° after recrystallisation from absolute alcohol (cf. Shaw and Turner, J., 1932, 297).

(b) *With nitrobenzene.* A solution of benzoyl peroxide (37 g.) in nitrobenzene (200 c.c.) was heated on the steam-bath for 2 hours and then in an oil-bath at 130° for 1 hour. Carbon dioxide was evolved. About 100 c.c. of the excess of nitrobenzene were removed by distillation and the residue was diluted with benzene, shaken with aqueous sodium hydroxide, and filtered from insoluble tarry matter. The benzene and excess of nitrobenzene were removed at atmospheric pressure and further distillation was continued under reduced pressure, two fractions being collected, (i) 9 g., b. p. 160—200°/9 mm., and (ii) 3 g., b. p. 200—210°/9 mm. Fraction (i), which partly solidified, after trituration with light petroleum and filtration, gave 4-nitrodiphenyl (3·5 g., m. p. and mixed m. p. 112—113°). Evaporation of the solvent from the filtrate left a yellow oil, a portion of which (2 g.) was reduced with hot alcoholic hydrochloric acid and stannous chloride (12 g.). The product, made strongly alkaline, was extracted with ether, evaporation of which left a brown oily base. Treatment with acetic anhydride, followed by trituration with light petroleum, gave an acetyl derivative, which after several crystallisations from aqueous alcohol melted at 117—119°, both alone and on admixture with 2-acetamidodiphenyl (Found: N, 6·6. Calc. for $C_{14}H_{13}ON$: N, 6·6%). Fraction (ii) solidified completely and on crystallisation from alcohol gave 4-nitrodiphenyl, m. p. and mixed m. p. 112—113°.

(c) *With ethyl benzoate.* A solution of benzoyl peroxide (30 g.) in ethyl benzoate (200 c.c.) was heated on the steam-bath for 2 hours and then at 120° for 1 hour. Carbon dioxide was evolved freely. The cold solution was diluted with benzene, shaken with aqueous sodium carbonate, and washed with water. Benzene and the excess of ethyl benzoate were removed; the dark viscous residue, distilled under reduced pressure, gave a yellow oil (b. p. 190—230°/12—15 mm., 10 g.), leaving a black resinous residue. A portion of the oil was boiled for 2 hours with 30% aqueous sodium hydroxide, a solid slowly separating in crystalline flakes. The product was diluted and filtered. The insoluble residue, boiled with concentrated hydrochloric acid and filtered, gave diphenyl-4-carboxylic acid (m. p. and mixed m. p. 220—222°). Acidification of the alkaline filtrate precipitated a gummy solid, which after several crystallisations from light petroleum melted at 155—157°, both alone and on admixture with diphenyl-3-carboxylic acid (Found: C, 79·2; H, 5·3. Calc. for $C_{13}H_{10}O_2$: C, 78·8; H, 5·05%). A second portion of the oil was hydrolysed by boiling for 6 hours with concentrated hydrochloric acid. The mixture was then made alkaline and extracted with ether, and the aqueous solution acidified. The white precipitate which separated was digested with hot light petroleum and filtered. The residue consisted of diphenyl-4-carboxylic acid, and diphenyl-3-carboxylic acid separated from the filtrate. In both hydrolyses the amount of the 4-carboxylic acid obtained was considerably greater than that of the 3-carboxylic acid.

Further Examination of the Product of the Action of Sodium Benzenediazoate on Ethyl Benzoate.—The two fractions obtained from this reaction (this vol., p. 1803), *viz.*, (i) b. p. 314—316° and (ii) b. p. 325—330°, were separately hydrolysed by boiling for 5 hours with 30% aqueous sodium hydroxide. During both hydrolyses some of the sodium salts of the diphenylcarboxylic acids separated from solution. The product from fraction (i) was filtered and acidification of the filtrate gave mainly diphenyl-2-carboxylic acid, m. p. 109—110° after crystallisation from light petroleum, together with a smaller quantity of diphenyl-3-carboxylic acid (m. p. and mixed m. p. 162—164°). The sodium salt which separated during the hydrolysis of fraction (ii) was warmed with concentrated hydrochloric acid and filtered. The residue, crystallised from alcohol–light petroleum, consisted of diphenyl-4-carboxylic acid (m. p. and mixed m. p. 221—222°).

Reactions with Phenylazotriphenylmethane.—(a) *With benzene.* Phenylazotriphenylmethane (5 g.) (Wieland, Popper, and Seefried, *loc. cit.*) and benzene (40 c.c.) were gradually heated to 80°. The yellow solid dissolved, giving a yellow solution, which at about 70° became red and evolved nitrogen. The red solution was boiled under reflux for 2 hours. After 12 hours at room temperature the red colour had faded to a light straw colour, which did not change when the solution was reheated. After the removal of the excess of benzene, two main fractions were collected, (i) 0·7 g., b. p. 240—300°, and (ii) 1·0 g., b. p. 340—370°, both of which solidified. Fraction (i) was dissolved in 95% alcohol, from which triphenylmethane separated (m. p. 88—90°); the mother-liquor deposited a mixture of triphenylmethane and diphenyl (m. p. 45—50°). The residual mother-liquor was now evaporated to dryness and the solid residue, which smelled strongly of diphenyl, was heated on the steam-bath with a mixture of concentrated nitric and glacial acetic acids. The crystalline yellow solid which separated on cooling, after recrystallisation from light petroleum (b. p. 60—80°), gave 4-nitrodiphenyl in yellow needles

(m. p. and mixed m. p. 111—112°). Fraction (ii) was boiled with absolute alcohol and filtered. The insoluble residue was crystallised from boiling toluene, from which tetraphenylmethane separated in fine needles, m. p. 273—275°. The alcoholic filtrate deposited triphenylmethane (m. p. and mixed m. p. 90—92°).

(b) *With chlorobenzene.* A solution of phenylazotriphenylmethane (10 g.) in chlorobenzene (100 c.c.) was heated on the steam-bath. Nitrogen was evolved and the colour of the solution changed from orange-yellow to deep red. After the removal of the excess of chlorobenzene by distillation, a crystalline solid separated from the residual solution. This was filtered off and washed with light petroleum. Recrystallisation from boiling toluene gave tetraphenylmethane (m. p. 273—275°). Distillation of the main product yielded two fractions, (i) 3 g., b. p. 250—300°, and (ii) 5 g., b. p. 300—370°, and a dark higher-boiling residue. Fraction (i) partly solidified, giving, after filtration and crystallisation from alcohol, triphenylmethane (m. p. and mixed m. p. 91—92°). The yellow oily filtrate was heated on the steam-bath with an excess of a 10% glacial acetic acid solution of bromine. Hydrogen bromide was evolved. When cold, the solution gradually deposited a crystalline solid (m. p. 137—147°), which after recrystallisation from alcohol melted at 157—158°. On admixture with 4-chloro-4′-bromodiphenyl the m. p. was depressed to 130—140°, but no depression was observed on admixture with triphenylcarbinol (Found : C, 86·7; H, 6·2. Calc. for $C_{19}H_{16}O$: C, 87·7; H, 6·15%). On further standing at 0° the acetic acid solution deposited a second crop of crystals, m. p. 153—154°, which now gave no depression in m. p. on admixture with 4-chloro-4′-bromodiphenyl (Found : C, 53·9; H, 3·1. Calc. for $C_{12}H_8ClBr$: C, 53·8; H, 3·0%). When the two solids thus obtained from the acetic acid solution were mixed, a depression in m. p. of about 20° resulted. Fraction (ii), which solidified completely, was boiled with alcohol and filtered. The residue consisted of tetraphenylmethane, and the filtrate deposited triphenylmethane. The total weight of each of the two hydrocarbons was 2·5 g.

(c) *With nitrobenzene.* A solution of phenylazotriphenylmethane (17 g.) in nitrobenzene (70 c.c.) was heated on the steam-bath. A steady evolution of nitrogen began at about 70° and the clear solution became darker in colour. After the removal of the excess of nitrobenzene, distillation was continued up to 265° and some triphenylmethane, together with a small quantity of a phenolic product, was collected. Subsequent distillation, carried out below 1 mm. pressure, yielded only a small quantity of a colourless solid of unknown constitution (m. p. 240—241° after crystallisation from benzene; Found : C, 86·5; H, 5·2%). The greater portion of the product consisted of a black tarry non-volatile mass.

THE UNIVERSITY, MANCHESTER.

[*Received, September 3rd,* 1934.]