256. *Studies in the Terphenyl Series. Part I.* p-*Terphenyl, Nitro-, Amino-, and Halogeno-*p-*terphenyls.*

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Methods for the preparation of *p*-terphenyl (1 : 4-diphenylbenzene) are reviewed. The hydrocarbon is prepared in quantity by two new methods, *viz.*, the action of either 4-*nitrosoacetamidodiphenyl* or *dinitrosodiacetyl*-1 : 4-*phenylenediamine* on benzene. Similar reactions are also carried out using *dinitrosodiformyl*- and *dinitrosodi*-n-*propionyl*-1 : 4-*phenylenediamine*. Nitration of the hydrocarbon gives 4 : 4''-*dinitro*-p-*terphenyl* and 4 : 2' : 4''-*trinitro*-p-*terphenyl*. 4-Nitro-*p*-terphenyl and 2-*nitro*-p-*terphenyl* are prepared by the interaction of 4-nitrosoacetamidodiphenyl with nitrobenzene. 2-Nitro-*p*-terphenyl, also obtained from the reaction between 2-*nitro*-4'-*nitrosoacetamidodiphenyl* and benzene, is oxidised to 2-nitrodiphenyl-4'-carboxylic acid and reduced to 2-*amino*-p-*terphenyl*. Similarly, 4-nitro-*p*-terphenyl, also obtained from the reaction between 4-*nitro*-4'-*nitrosoacetamidodiphenyl* and benzene, is reduced to 4-amino-*p*-terphenyl. 4 : 4''-Dinitro-*p*-terphenyl, also obtained from the reaction between dinitrosodiacetyl-1 : 4-phenylenediamine and nitrobenzene, gives *p*-nitrobenzoic acid on oxidation. 4 : 3'-*Dinitro*-p-*terphenyl* is formed by the interaction of the nitroso-derivative of 3 : 4'-dinitro-4-acetamidodiphenyl and benzene. The further nitration of 4-nitro-, 4 : 4''-dinitro-, and 4 : 3'-dinitro-*p*-terphenyl is also described. 2-*Chloro*-, 3-*chloro*-, and 4-chloro-p-*terphenyl* are formed in the reaction between 4-nitrosoacetamidodiphenyl and chlorobenzene, and 2-*bromo*-, 3-*bromo*-, and 4-bromo-p-*terphenyl* are prepared in similar manner from bromobenzene. 2-Chloro-*p*-terphenyl is also obtained from 2-amino-*p*-terphenyl. Oxidation of 2-bromo-*p*-terphenyl gives 2-bromodiphenyl-4′-carboxylic acid, the constitution of which is proved in an unambiguous manner. 4-Bromo-*p*-terphenyl is also obtained from the reaction between 4-*bromo*-4′-*nitrosoacetamidodiphenyl* and benzene, as well as by direct bromination of *p*-terphenyl, a reaction which also yields 4 : 4″-dibromo-*p*-terphenyl. 4-Iodo-*p*-terphenyl is prepared in similar manner from 4-*iodo*-4′-*nitrosoacetamidodiphenyl* and benzene. 4-*Bromofluorenone* is obtained from 2′-bromodiphenyl-2-carboxylic acid on ring closure. The action of dinitrosodiacetyl-1 : 4-phenylenediamine on *p*-dichlorobenzene gives 2 : 5 : 2″ : 5″-*tetrachloro*-p-*terphenyl*.

No systematic investigation of the chemistry of *p*-terphenyl* (1 : 4-diphenylbenzene) has hitherto been attempted. The pyrogenic synthesis of the hydrocarbon has been recorded by several authors who obtained it in very small yield, together with diphenyl and *m*-terphenyl (1 : 3-diphenylbenzene), either by passing benzene vapour through a red-hot tube (Schultz, *Annalen*, 1874, **174**, 230; Schmidt and Schultz, *ibid.*, 1880, **203**, 119; Carnelley, J., 1880, **37**, 712), or by heating benzene under pressure to temperatures varying from 525° to 900° (Herndon and Reid, *J. Amer. Chem. Soc.*, 1928, **50**, 3069; Kosaka, *J. Fuel Soc. Japan*, 1928, **7**, 121; see also D.-R.P. 555079 and A.P. 197988). It is also formed together with diphenyl when benzene is heated with potassium under pressure to 230—250° (Abeljanz, *Ber.*, 1876, **9**, 12; Schlenk and Meyer, *Ber.*, 1913, **46**, 4060). Again, *p*-terphenyl is produced, together with chlorobenzene and *m*-terphenyl, when solid benzenediazonium chloride reacts with molten diphenyl in the presence of aluminium chloride (Möhlau and Berger, *Ber.*, 1893, **26**, 1998). Fichter and Grether (*Ber.*, 1903, **36**, 1410) obtained the hydrocarbon by distillation of 2-hydroxy-1 : 4-diphenylbenzene with zinc dust in hydrogen. The action of dibenzoyl peroxide on boiling toluene (Dietrich, *Helv. Chim. Acta*, 1925, **8**, 151), on boiling benzene (Gelissen and Hermanns, *Ber.*, 1925, **58**, 286), and on molten diphenyl (*idem*, *ibid.*, p. 293) yields, among other products, appreciable amounts of *p*-terphenyl. A more convenient synthesis of *p*-terphenyl is described by von Braun (*Ber.*, 1927, **60**, 1180), who obtained the hydrocarbon by the dehydrogenation of 1 : 4-di*cyclo*hexylbenzene with bromine (cf. also von Braun, Irmisch, and Nelles, *Ber.*, 1933, **66**, 1476). *p*-Terphenyl has also been synthesised by means of the Diels–Alder condensation of 1 : 4-diphenylbutadiene with maleic anhydride (Kuhn and Wagner-Jauregg, *Ber.*, 1930, **63**, 2662), and with acetylenedicarboxylic esters (Lohaus, *Annalen*, 1935, **516**, 295). Mayer and Schiffner (*Ber.*, 1932, **65**, 1337) have prepared *p*-terphenyl by the interaction of *cyclo*hexane-1 : 4-dione with phenylmagnesium bromide. The hydrocarbon was also obtained by Grieve and Hey (this vol., p. 112) by the action of an aqueous solution of diazotised aniline on a solution of diphenyl in either chloroform or carbon tetrachloride in the presence of aqueous alkali, but the yield was poor. Other diverse reactions from which *p*-terphenyl has been isolated in small amounts are recorded by Barth and Schreder (*Ber.*, 1878, **11**, 1339), Pummerer, Binapfl, Bittner, and Schuegraf (*Ber.*, 1922, **55**, 3104), Kögl and Postowsky (*Annalen*, 1925, **445**, 159), Kuhn and Winterstein (*Ber.*, 1927, **60**, 432), Gilman and McCracken (*J. Amer. Chem. Soc.*, 1929, **51**, 821), Schorygin and Issaguljanz (*Chem. Zentr.*, 1936, ii, 2345), and Busch and Weber (*J. pr. Chem.*, 1936, **146**, 1).

In the present communication several methods of preparation of *p*-terphenyl have been investigated. The dehydrogenation of 1 : 4-di*cyclo*hexylbenzene (von Braun, *loc. cit.*) gave *p*-terphenyl in 20% yield, but the poor yield of 1 : 4-di*cyclo*hexylbenzene from either benzene or *cyclo*hexylbenzene and *cyclo*hexyl bromide by the Friedel–Crafts reaction rendered this method unsuitable. Selenium dehydrogenation of 4-*cyclo*hexyldiphenyl

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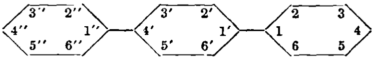
* There appears to be no recognised system for the numbering of the carbon atoms in *p*-terphenyl; early workers refer mono-substituted derivatives to 1 : 4-diphenylbenzene (cf. Olgiati, *Ber.*, 1894, **27**, 3393; Castellaneta, *ibid.*, 1897, **30**, 2800; *et alia*). However, von Braun, Irmisch, and Nelles (*Ber.*, 1933, **66**, 1472, footnote) adopt the following nomenclature:



and it is proposed to use this method of numbering in this series of papers (cf. also Busch and Weber, *J. pr. Chem.*, 1936, **146**, 29, footnote).

gave similar results, but here again low yields were encountered in the preparation of the starting material; this finding has since been independently confirmed by Basford (J., 1936, 1593).

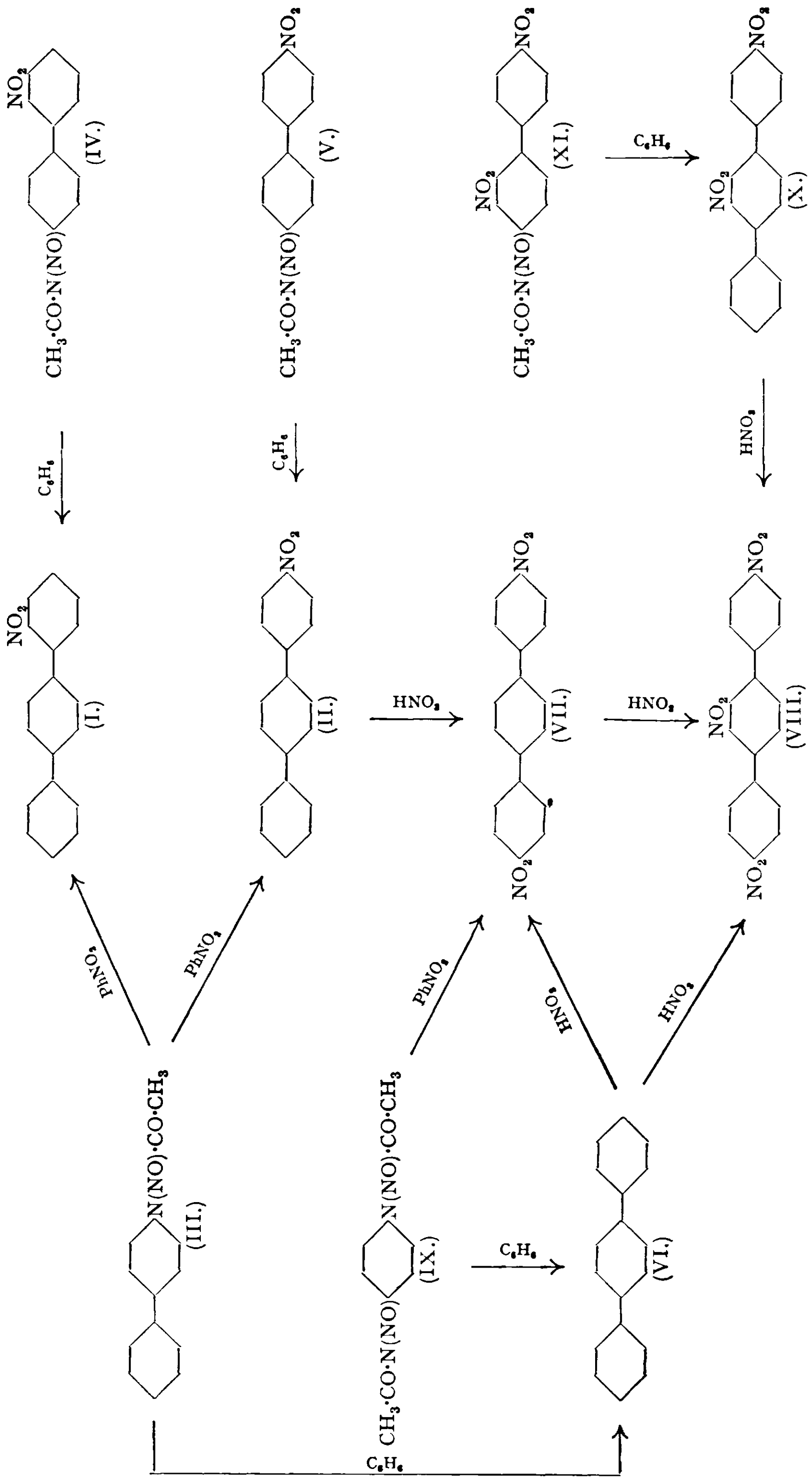
Recourse was then made to the reaction, originally due to Bamberger (*Ber.*, 1897, **30**, 366; see also Grieve and Hey, J., 1934, 1797), whereby a union of two aryl nuclei is effected by means of the reaction between a *N*-nitrosoacetylarylamine and an aromatic hydrocarbon, thus:

$$\mathrm{Ar{\cdot}N(NO){\cdot}CO{\cdot}CH_3 + Ar'H \longrightarrow Ar{\cdot}Ar' + N_2 + CH_3{\cdot}CO_2H}$$

This reaction necessitates a large excess of a liquid aromatic hydrocarbon, and the use of molten diphenyl is impracticable because of the ready decomposition of nitrosoacetanilide at that temperature. Attempts to condense nitrosoacetanilide with diphenyl in benzene or dioxan solution were not encouraging, very small yields of *p*-terphenyl being obtained. The presence of a solvent and the high reactivity of the nitroso-compound led to a variety of secondary reactions with the solvent and consequent loss of yield. The condensation of 4-*nitrosoacetamidodiphenyl* (III) with benzene, however, gave *p*-terphenyl in 50% yield. In addition, it was found possible to prepare *dinitrosodiacetyl*-1 : 4-*phenylenediamine* (IX), and in reaction with benzene this gave *p*-terphenyl in 55—60% yield. The high yield and the easy access to diacetyl-1 : 4-phenylenediamine led to the adoption of this method for the preparation of the hydrocarbon in quantity. As far as the authors are aware, this constitutes the first known example of a dinitroso-compound of this type. Unlike nitrosoacetanilide and other known nitrosoacylarylamines, dinitrosodiacetyl-1 : 4-phenylenediamine is a comparatively stable compound and may be kept for several weeks without any perceptible decomposition. It dissolves slowly in aqueous alkali to give an alkaline solution of benzene-1 : 4-*iso*tetrazotate, which on careful acidification gives a solution of tetrazotised *p*-phenylenediamine, which readily couples with alkaline β-naphthol. In similar manner *dinitrosodiformyl*- and *dinitrosodi*-n-*propionyl*-1 : 4-*phenylenediamine* were obtained, both of which yielded *p*-terphenyl on reaction with benzene. The yields, however, particularly in the case of the diformyl derivative, were somewhat inferior to those obtained with dinitrosodiacetyl-1 : 4-phenylenediamine.

Nitro- and Amino-derivatives.—The direct nitration of *p*-terphenyl with fuming nitric acid in glacial acetic acid solution gives a dinitro- and trinitro-derivative (Schmidt and Schultz, *Annalen*, 1880, **203**, 125); these authors also describe a base obtained by reduction of the above trinitro-compound. 4-Nitro-*p*-terphenyl and 2′-nitro-*p*-terphenyl are described by Basford (J., 1937, 1440), who obtained them by the dehydrogenation of 4′-nitro-4-*cyclo*hexyldiphenyl and 2-nitro-4-*cyclo*hexyldiphenyl respectively with bromine. 4-Nitro-*p*-terphenyl has also been obtained by Grieve and Hey (this vol., p. 112) by the action of diazotised *p*-nitroaniline on a solution of diphenyl in chloroform in the presence of aqueous alkali. 2′-Amino-*p*-terphenyl is reported by Basford (J., 1937, 1441), who obtained it by reduction of 2′-nitro-*p*-terphenyl. 4-Amino-*p*-terphenyl is produced by the interaction of azobenzene hydrochloride, diphenyl, and aluminium chloride (Pummerer, Binapfl, Bittner, and Schuegraf, *loc. cit.*; Pummerer and Bittner, *Ber.*, 1924, **57**, 85).

The present authors have been unable to obtain a mononitro-derivative of *p*-terphenyl by direct nitration, even under conditions where such might be expected, as exemplified by the mononitration of diphenyl. Attempts to obtain a mononitro-derivative by "milling" with nitric acid of concentrations of 25%, 50%, and 75% were unsuccessful, the *p*-terphenyl being recovered unchanged; increase in the concentration to 90% gave a trinitro-derivative (see below). This behaviour contrasts with that of *m*-terphenyl towards nitration, where a mononitro-derivative is obtained with fuming nitric acid in acetic anhydride at 0° (Wardner and Lowy, *J. Amer. Chem. Soc.*, 1932, **54**, 2510). Both 2-*nitro*-p-*terphenyl* (I) and 4-nitro-*p*-terphenyl (II) have now been prepared by the action of 4-nitrosoacetamidodiphenyl (III) on nitrobenzene. The constitution of (I) has been established (*a*) by its oxidation to 2-nitrodiphenyl-4′-carboxylic acid and (*b*) by direct synthesis from 2-*nitro*-4′-*nitrosoacetamidodiphenyl* (IV) (from 2-*nitro*-4′-*acetamidodiphenyl*) and benzene. 2-*Amino*-p-*terphenyl* was obtained on reduction. The structure of (II)


(I.)
(II.)
(III.)
(IV.)
(V.)
(VI.)
(VII.)
(VIII.)
(IX.)
(X.)
(XI.)
CH₃·CO·N(NO)
N(NO)·CO·CH₃
NO₂
C₆H₆
HNO₃
PhNO₂

was determined by direct synthesis from 4-*nitro*-4′-*nitrosoacetamidodiphenyl* (V) (from 4-nitro-4′-acetamidodiphenyl) and benzene. Moreover, the compound was identical with that previously obtained by Grieve and Hey (this vol., p. 112) and was reduced to the known 4-amino-*p*-terphenyl. Nitration of *p*-terphenyl (VI) with fuming nitric acid in glacial acetic acid gave both 4 : 4″-*dinitro*-p-*terphenyl* (VII) and 4 : 2′ : 4″-*trinitro*-p-*terphenyl* (VIII), which correspond with the nitro-derivatives previously described, but not characterised, by Schmidt and Schultz (*loc. cit.*). Various other nitrating mixtures were also used, but in most cases where the dinitro-derivative was formed some of the trinitro-compound was produced concurrently. The structure of 4 : 4″-dinitro-*p*-terphenyl was established by oxidation, considerably more than one molecular proportion of *p*-nitrobenzoic acid resulting. The same dinitro-derivative was also obtained by the action of dinitrosodiacetyl-1 : 4-phenylenediamine (IX) on nitrobenzene, as well as by the further nitration of 4-nitro-*p*-terphenyl (II). 4 : 2′ : 4″-Trinitro-*p*-terphenyl (VIII) was formed either as above, or by the nitration of *p*-terphenyl with fuming nitric acid alone, or with a mixture of concentrated nitric acid and sulphuric acid (*d* 1·80) at about 50°. It was also produced by the further nitration of 4 : 4″-dinitro-*p*-terphenyl (VII). Its structure was determined (*a*) by its marked resistance to oxidation (cf. Schmidt and Schultz, *loc. cit.*), which would indicate that one nitro-group is in each of the three aromatic nuclei, (*b*) by its formation by the further nitration of 4 : 3′-*dinitro*-p-*terphenyl* (X), which was prepared from the reaction between 3 : 4′-dinitro-4-nitrosoacetamidodiphenyl (XI) and benzene, and (*c*) by its formation by the further nitration of 4 : 4″-dinitro-*p*-terphenyl (VII).

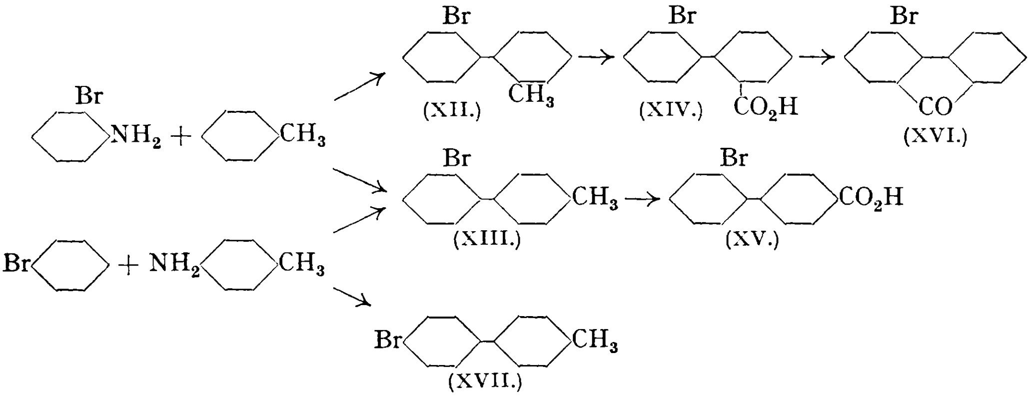
Attempts were made to prepare 2′-nitro-*p*-terphenyl (cf. Basford, J., 1937, 1442) (*a*) from 3-nitro-4-acetamidodiphenyl by nitrosation and reaction with benzene, but this failed owing to inability to obtain the required nitroso-compound, and (*b*) from the nitroso-derivative of 2-nitrodiacetyl-1 : 4-phenylenediamine and benzene, but this also failed, the only product being 3-nitro-4-acetamidodiphenyl. This result forms an interesting contrast to the behaviour of unsubstituted diacetyl-1 : 4-phenylenediamine under similar conditions (see above) when both acetamido-groups are nitrosated and subsequently eliminated. In an attempt to prepare 2′ : 3′-dinitro-*p*-terphenyl it was found that the 2 : 3-dinitrodiacetyl-1 : 4-phenylenediamine of Nietzki and Hagenbach (*Ber.*, 1887, **20**, 328; see also Kym, *Ber.*, 1911, **44**, 2924) failed to form any nitroso-derivative.

Halogeno-derivatives.—Several halogen derivatives of *p*-terphenyl have been described. 4-Chloro-*p*-terphenyl is obtained, together with 4 : 4′-dichlorodiphenyl, by the interaction of diphenyl-4 : 4′-bisdiazonium chloride and benzene in the presence of aluminium chloride (Castellaneta, *Ber.*, 1897, **30**, 2800). A fully chlorinated derivative, $C_{18}Cl_{14}$ (tetradecachloro-*p*-terphenyl), is described by Merz and Weith (*Ber.*, 1883, **16**, 2884), who obtained it by the action of antimony pentachloride on *p*-terphenyl at 360°. Direct action of bromine in the cold on *p*-terphenyl yields 4-bromo-*p*-terphenyl and 4 : 4″-dibromo-*p*-terphenyl (Olgiati, *Ber.*, 1894, **27**, 3393). The dibromo-derivative is also formed by the action of bromine on the monobromo-derivative, while the action of excess bromine on *p*-terphenyl or on its monobromo- or dibromo-derivative gives a tetrabromo-compound, 4 : 4″ : *x* : *x*-tetrabromo-*p*-terphenyl. The constitutions of these bromo-compounds were determined by their oxidation to *p*-bromobenzoic acid (Olgiati, *loc. cit.*). Bromination of *p*-terphenyl in trichlorobenzene solution at 100° in the presence of a trace of iodine gives 4 : 4″-dibromo-*p*-terphenyl and a small amount of 4-bromo-*p*-terphenyl (von Braun, Irmisch, and Nelles, *loc. cit.*, p. 1481). The latter has also been synthesised by the dehydrogenation of the product of reaction between 4-*cyclo*hexyl*cyclo*hexanone and *p*-bromophenylmagnesium bromide (von Braun, Irmisch, and Nelles, *loc. cit.*). 4-Iodo-*p*-terphenyl has been prepared from 4-amino-*p*-terphenyl by means of the Sandmeyer reaction (Pummerer and Bittner, *loc. cit.*).

In this investigation monohalogen derivatives of *p*-terphenyl have been prepared by the reaction between the nitroso-derivative of 4-acetamidodiphenyl and a halogenobenzene. A mixture of three monochloro-derivatives of *p*-terphenyl was obtained by the action of 4-nitrosoacetamidodiphenyl on chlorobenzene. After separation by fractional crystallisation, they had m. p.'s of 220—221°, 136—137°, and 110—111° severally. The first compound corresponds with the 4-chloro-*p*-terphenyl described by Castellaneta (*loc. cit.*), and the third is shown to be 2-*chloro*-p-*terphenyl* by its identity with the compound synthesised from 2-amino-*p*-terphenyl by means of the Sandmeyer reaction. It follows that the remaining compound, m. p. 136—137°, must be 3-*chloro*-p-*terphenyl*. From the reaction between dinitrosodiacetyl-1 : 4-phenylenediamine and liquid *p*-dichlorobenzene at about 50°, 2 : 5 : 2'' : 5''-*tetrachloro*-p-*terphenyl* was obtained. The para-derivative was chosen since this alone of the isomeric dichlorobenzenes could give one product.

Three monobromo-*p*-terphenyls were obtained from the reaction between 4-nitrosoacetamidodiphenyl and bromobenzene and had m. p.'s 231—232°, 86—88°, and 147—148° severally. The first corresponds with the 4-bromo-*p*-terphenyl described by Olgiati (*loc. cit.*) and by von Braun, Irmisch, and Nelles (*loc. cit.*), and its identity is further confirmed by its synthesis from 4-*bromo*-4'-*nitrosoacetamidodiphenyl* and benzene. The second compound is shown to be 2-*bromo*-p-*terphenyl*, for, on oxidation, it gives 2-bromodiphenyl-4'-carboxylic acid. By elimination the compound, m. p. 147—148°, must be 3-*bromo*-p-*terphenyl*. Direct bromination of *p*-terphenyl in acetic acid solution containing a trace of iodine yielded 4-bromo-*p*-terphenyl and 4 : 4''-dibromo-*p*-terphenyl. 4-Iodo-*p*-terphenyl has been obtained from the reaction between 4-*iodo*-4'-*nitrosoacetamidodiphenyl* and benzene and is obviously identical with that previously prepared by Pummerer and Bittner (*loc. cit.*).

Although 2-bromodiphenyl-4'-carboxylic acid is described by Gomberg and Pernert (*J. Amer. Chem. Soc.*, 1926, **48**, 1379), its constitution was not proved by these authors. Since the constitutions of the bromo-*p*-terphenyls depend, in part, on the correct identity of this compound, its constitution was unambiguously determined in the following way: *o*-Bromoaniline was diazotised and treated with toluene in the presence of aqueous alkali (cf. Gomberg and Pernert, *loc. cit.*); the resultant mixture of bromomethyldiphenyls (XII, XIII) was oxidised to the corresponding carboxylic acids (XIV, XV). By treatment of the mixture of acids with sulphuric acid, the 2-bromodiphenyl-2'-carboxylic acid (XIV) was converted into 4-*bromofluorenone* (XVI), and in the remaining unchanged acid (XV), m. p. 240—242°, the bromine atom must occupy the 2-position. In a similar manner the reaction between diazotised *p*-toluidine and bromobenzene yielded a mixture of bromomethyldiphenyls (XIII, XVII), from which 4-bromo-4'-methyldiphenyl (XVII) was separated by distillation and crystallisation. The remaining bromomethyldiphenyl (XIII) was oxidised to the corresponding carboxylic acid, which must have the carboxyl group in the 4'-position. This acid proved to be identical with (XV), obtained as above from *o*-bromoaniline and toluene, and hence it must be 2-bromodiphenyl-4'-carboxylic acid.



The production of all three monohalogen derivatives of *p*-terphenyl from the interaction of 4-nitrosoacetamidodiphenyl with a halogenobenzene, which in effect entails the entry of a diphenylyl group into the molecule of a halogenobenzene at the *o*-, *m*-, and *p*-positions, is unusual in that in accordance with known results in similar reactions, only the 2- and 4-halogeno-*p*-terphenyls might be anticipated. It may be pointed out, however, that Hey (J., 1934, 1967) obtained all three diphenylcarboxylic esters from the cognate reaction between sodium benzenediazotate and ethyl benzoate. Attention may be drawn to the fact that, in the reaction of 4-nitrosoacetamidodiphenyl with nitrobenzene, only 2- and 4-nitro-*p*-terphenyl were isolated. The relative yields of the isomeric chloro- and bromo-*p*-terphenyls show that the quantity of both the 2- and the 4-isomerides is considerably greater than that of the 3-derivative. The concomitant formation of all three isomerides in the reaction between a nitrosoacetylarylamine and a monosubstituted derivative of benzene is in agreement with the representation of the reaction as a typical non-polar process, probably involving the participation of free radicals, as opposed to the normal polar mechanism of aromatic substitution by kationoid or anionoid reagents.

EXPERIMENTAL.

A. Preparation of p-*Terphenyl.*

1 : 4-*Di*cyclo*hexylbenzene*.—This hydrocarbon was prepared (*a*) from benzene and *cyclo*hexyl bromide as described by von Braun (*Ber.*, 1927, **60**, 1180), and (*b*) from *cyclo*hexylbenzene (obtained as a by-product in the above method) and *cyclo*hexyl bromide. *cyclo*Hexyl bromide (40 g.) was added dropwise to a stirred solution of *cyclo*hexylbenzene (30 g.) in tetrachloroethane (50 c.c.) containing aluminium chloride (1·5 g.) at room temperature. Instantaneous reaction occurred, and when three-quarters of the halide had been introduced a further quantity of aluminium chloride (1 g.) was added and the addition of the halide continued. After the reaction had moderated, the temperature was raised to 60° for ½ hour. The product, worked up in the usual way (von Braun, *loc. cit.*), was fractionated under reduced pressure. 1 : 4-Di*cyclo*hexylbenzene distilled at 205—220°/17 mm. as a colourless oil (15 g.) which solidified on standing at 0°. On dehydrogenation with bromine (von Braun, *loc. cit.*) and subsequent distillation, *p*-terphenyl was obtained, b. p. 225—235°/17 mm., which separated from alcohol in pearly plates, m. p. and mixed m. p. with an authentic specimen 212°.

4-cyclo*Hexyldiphenyl*.—A solution of diphenyl (15 g.) in tetrachloroethane (50 c.c.) containing aluminium chloride (1·5 g.) was treated with *cyclo*hexyl bromide (16 g.) as described above, but no further addition of aluminium chloride was made. After 45 minutes the reaction was completed by heating at 60° for 1 hour. The product was isolated in the usual manner and 4-*cyclo*hexyldiphenyl distilled at 213—222°/15 mm. (cf. Bodroux, *Ann. Chim.*, 1929, **11**, 527; also Basford, J., 1936, 1593, who gives b. p. 210—230°/7 mm.) as a colourless oil (7 g.). Higher-boiling material was also formed in considerable quantity. A portion of the 4-*cyclo*hexyldiphenyl (7 g.) was heated with selenium (3·5 g.) at 360° for 60 hours, and from the cooled melt hot alcohol (with charcoal) extracted *p*-terphenyl (2 g.).

Reaction of Nitrosoacetanilide with Diphenyl in Presence of Solvent.—Nitrosoacetanilide was prepared by passing nitrous fumes into a solution of acetanilide in glacial acetic acid at 5—10° as described by Grieve and Hey (J., 1934, 1803). To a mixture of diphenyl (25 g.) and benzene (15 c.c.), stirred at 20°, nitrosoacetanilide (15 g.) was gradually added. After 12 hours the mixture was distilled under reduced pressure but, after removal of diphenyl, only a small yield of *p*-terphenyl (1 g.) distilled at 220—240°/17 mm. A similar reaction in dioxan as solvent gave only traces of *p*-terphenyl.

4-*Nitrosoacetamidodiphenyl*.—Nitrous fumes were passed for 5 hours into a stirred solution of 4-acetamidodiphenyl (15 g.) in a mixture of glacial acetic acid (250 c.c.) and acetic anhydride (50 c.c.) cooled to 8°. Dilution of the resultant deep green solution with iced water precipitated the yellow *nitroso*-compound (17 g.), which was filtered off, washed with iced water, and allowed to dry overnight. It melted at 98° with explosive decomposition (Found: N, 11·5. $C_{14}H_{12}O_2N_2$ requires N, 11·7%).

Reaction of 4-*Nitrosoacetamidodiphenyl with Benzene*.—The nitroso-compound (16 g.) was dissolved in benzene (400 c.c.), and the yellow solution stirred for 12 hours at 20°, nitrogen being slowly evolved. After removal of the benzene, the brown residue sublimed at 190—200°/15 mm. as white plates of *p*-terphenyl (7 g.), m. p. 209—212°.

Dinitrosodiacetyl-1 : 4-*phenylenediamine*.—Diacetyl-1 : 4-phenylenediamine (10 g.) (prepared from *p*-aminoacetanilide by acetylation) was warmed with a mixture of glacial acetic acid (200 c.c.) and acetic anhydride (100 c.c.) to obtain partial solution, and cooled with stirring to 8° to give a fine suspension into which nitrous fumes were passed for 5—6 hours with continuous stirring and cooling. The suspended *dinitroso*-compound was filtered from the green solution and repeatedly washed with iced water; the filtrate on dilution gave a further small amount of the dinitroso-compound. It forms small yellow prismatic crystals, m. p. 124—125° with explosive decomposition (Found : N, 22·35. $C_{10}H_{10}O_4N_4$ requires N, 22·4%). Yield, 11·3 g. The addition of phosphoric oxide (2 g. for 10 g. of diacetyl-1 : 4-phenylenediamine) reduces the time required for nitrosation to 1½—2 hours. Dinitrosodiacetyl-1 : 4-phenylenediamine dissolves slowly in aqueous alkali, giving a solution which, after acidification, readily couples with alkaline β-naphthol.

Reaction of Dinitrosodiacetyl-1: 4-*phenylenediamine with Benzene*.—A mixture of the dry dinitroso-compound (11 g.) and benzene (300 c.c.) was stirred at 35° for 12 hours, during which the solid passed into solution with evolution of nitrogen. The brown residue obtained on removal of solvent was distilled at 110—120°/10^{-3} mm., giving *p*-terphenyl (7 g.). In some experiments a small insoluble residue of diacetyl-1 : 4-phenylenediamine was removed from the reaction mixture.

Dinitrosodiformyl-1 : 4-*phenylenediamine*.—Nitrous fumes were passed for about 1 hour into a stirred solution of diformyl-1 : 4-phenylenediamine (5 g., m. p. 205—207°), prepared from *p*-phenylenediamine and formic acid as described by Wundt (*Ber.*, 1878, **11**, 828), in a mixture of glacial acetic acid (100 c.c.) and acetic anhydride (50 c.c.) cooled to 8°, to which phosphoric oxide (2 g.) had been added. *Dinitrosodiformyl*-1 : 4-*phenylenediamine* (5 g.) separated from solution as a yellow microcrystalline powder, which was filtered off and washed with water. When dry, it decomposed violently at 132° (Found : N, 25·8. $C_8H_6O_4N_4$ requires N, 25·2%).

Reaction of Dinitrosodiformyl-1 : 4-*phenylenediamine with Benzene*.—The dry dinitroso-compound (6 g.) was stirred with benzene (800 c.c.) and warmed gradually to 50—55°, a brisk evolution of nitrogen then starting. The mixture was maintained at this temperature for 2 hours, after which it was boiled under reflux for ¼ hour and filtered from a dark brown residue (3 g., m. p. 88—90°, with decomp.) (Found : N, 15·5%), which was not further investigated. Excess benzene was removed from the filtrate, and the residue on distillation at 140°/10^{-3} mm. yielded *p*-terphenyl (1 g.), which after crystallisation from glacial acetic acid melted at 210—212°, both alone and on admixture with an authentic specimen.

Dinitrosodi-n-*propionyl*-1 : 4-*phenylenediamine*.—A mixture of *p*-phenylenediamine (10 g.) and propionic anhydride (50 c.c.) was heated for ½ hour on the steam-bath. *Di*-n-*propionyl*-1 : 4-*phenylenediamine*, which separated on addition of water, was filtered off, washed with water, dried, and crystallised first from nitrobenzene and then from 95% ethyl alcohol, being obtained in almost colourless prisms, m. p. 289—291° (10 g.) (Found : C, 65·4; H, 6·9. $C_{12}H_{16}O_2N_2$ requires C, 65·5; H, 7·3%). Nitrous fumes were passed for 4 hours into a stirred suspension of the foregoing compound (8 g.) in a mixture of glacial acetic acid (150 c.c.) and acetic anhydride (70 c.c.) cooled to 8°. The insoluble yellow microcrystalline *dinitrosodi*-n-*propionyl*-1 : 4-*phenylenediamine* was filtered off, washed with water, and dried. It detonated at 110° (Found : N, 19·5. $C_{12}H_{14}O_4N_4$ requires N, 20·1%).

Reaction of Dinitrosodi-n-*propionyl*-1 : 4-*phenylenediamine with Benzene*.—A suspension of the dinitroso-compound (8 g.) in benzene (800 c.c.) was stirred at 45° for 2 hours. Nitrogen was evolved, and the suspended solid passed into solution. After 10 minutes' boiling under reflux and subsequent filtration from a small insoluble residue, the excess benzene was removed by distillation. The dark brown residue (6 g.) on distillation at 140°/10^{-3} mm. gave *p*-terphenyl (3·5 g.), which after crystallisation from glacial acetic acid melted at 210—212°, both alone and on admixture with an authentic specimen.

B. *Nitro- and Amino-derivatives.*

Nitration of p-*Terphenyl*.—(i) A solution of *p*-terphenyl (2 g.) in glacial acetic acid (100 c.c.) was treated with fuming nitric acid (*d* 1·5, 12 c.c.). No apparent reaction took place in the cold, but on heating to 100°, nitrous fumes were evolved and yellow needles commenced to separate. After 15 minutes the mixture was cooled, and the crude solid, crystallised from nitrobenzene, gave 4 : 4''-*dinitro*-p-*terphenyl* (1·2 g.) in yellow needles, m. p. 272—273° both alone and on admixture with the synthetic specimen prepared as below (Found : C, 67·6; H, 3·7. $C_{18}H_{12}O_4N_2$ requires C, 67·5; H, 3·75%). On dilution of the original filtrate with water, 4 : 2' : 4''-*trinitro*-p-*terphenyl* (0·9 g.) was obtained, which separated from alcohol or acetic acid in pale yellow needles, m. p. 193—194° both alone and mixed with the synthetic specimen described below (Found : C, 59·3; H, 3·0. $C_{18}H_{11}O_6N_3$ requires C, 59·2; H, 3·0%).

(ii) *p*-Terphenyl (2 g.) was stirred with acetic anhydride (20 c.c.) at 0°, and fuming nitric acid (*d* 1·5, 0·9 c.c.) added dropwise during 30 minutes. Stirring was continued at 0° for a further 30 minutes. The temperature was allowed to rise to 20°, and then maintained at 45—50°

for 1 hour. The separated 4 : 4″-dinitro-*p*-terphenyl (1·9 g.) gave yellow needles, m. p. 272—273°, from nitrobenzene.

(iii) *p*-Terphenyl (2 g.) was gradually added at room temperature to fuming nitric acid (*d* 1·5, 15 c.c.). A vigorous reaction occurred with considerable rise of temperature. The crude 4 : 2′ : 4″-trinitro-*p*-terphenyl, which was deposited in quantitative yield on cooling, separated from alcohol in yellow needles, m. p. 193—194°.

(iv) *p*-Terphenyl (4 g.) was added to a mixture of concentrated nitric acid (3 c.c.), concentrated sulphuric acid (6 c.c.), and water (1·5 c.c.), and the whole rapidly stirred at 45—50° for 5 hours. No appreciable solution occurred, and the insoluble material was filtered off, washed, and crystallised from alcohol, 4 : 2′ : 4″-trinitro-*p*-terphenyl, m. p. 193—194° (3·2 g.), again being obtained.

Reaction of 4-*Nitrosoacetamidodiphenyl with Nitrobenzene.*—A solution of the nitroso-compound (10 g.) in nitrobenzene (250 c.c.) was kept for 48 hours at 20°. The excess nitrobenzene was removed by distillation in steam, and the residue extracted with chloroform. After removal of solvent from the dried solution, the residue distilled at 140°/10^{-3} mm. as a yellow solid distillate. On crystallisation from acetic acid 4-nitro-*p*-terphenyl separated in yellow platelets (2·5 g.), m. p. 211—212°, undepressed by admixture with authentic specimens prepared either as described below, or as described by Grieve and Hey (this vol., p. 112). Concentration of the mother-liquor gave 2-nitro-*p*-terphenyl (2·9 g.), which separated from acetic acid in yellow platelets, m. p. and mixed m. p. with an authentic specimen, prepared as described below, 127—128°.

Reaction of Dinitrosodiacetyl-1 : 4-*phenylenediamine with Nitrobenzene.*—The product of reaction between dinitrosodiacetyl-1 : 4-phenylenediamine (5 g.) and nitrobenzene, carried out in the usual manner at 25°, was purified by distillation in a high vacuum, 4 : 4″-dinitro-*p*-terphenyl being isolated in small yield (0·5 g.). It forms yellow needles from nitrobenzene, m. p. 272—273°, identical with the compound produced by the direct nitration of *p*-terphenyl (see above). No other pure product could be isolated.

Oxidation of 4 : 4″-*Dinitro*-p-*terphenyl.*—The dinitro-compound (0·7 g.), oxidised in boiling acetic acid solution with excess of chromic anhydride in the usual way, gave *p*-nitrobenzoic acid (0·5 g.). The theoretical requirement is 0·7 g. for two *p*-nitrophenyl groups.

2-*Nitro*-p-*terphenyl.*—2-Nitro-4′-aminodiphenyl was prepared by the partial reduction of 2 : 4′-dinitrodiphenyl by Guglialmelli and Franco's method (*Anal. Asoc. Quim. Argentina*, 1929, **17**, 340) for 4-nitro-4′-aminodiphenyl. 2-*Nitro*-4′-*acetamidodiphenyl*, obtained in the usual manner, separated from alcohol in yellow hexagonal plates, m. p. 152—153° (Found : C, 66·0; H, 4·4. $C_{14}H_{12}O_3N_2$ requires C, 65·7; H, 4·7%); and when it (8 g.) was dissolved in a mixture of acetic acid (200 c.c.) and acetic anhydride (50 c.c.) and nitrosated in the usual way, it gave 2-*nitro*-4′-*nitrosoacetamidodiphenyl* (4 g.) as a yellow solid, m. p. 85—87° (decomp.) (Found : N, 14·9. $C_{14}H_{11}O_4N_3$ requires N, 14·7%). The nitroso-compound was allowed to react with benzene for 24 hours at 20°, and the product purified by distillation at 100°/10^{-3} mm. Crystallisation of the solid distillate from alcohol gave 2-*nitro*-p-*terphenyl* in yellow plates, m. p. 127—128° (Found : C, 78·4; H, 5·1. $C_{18}H_{13}O_2N$ requires C, 78·5; H, 4·7%).

Oxidation of 2-*Nitro*-p-*terphenyl.*—To a solution of the nitro-compound (0·25 g.) in hot glacial acetic acid (30 c.c.), a solution of chromic anhydride (0·83 g.) in glacial acetic acid (20 c.c.) was added dropwise. After 4 hours' boiling under reflux, the product was precipitated with water, filtered off, dissolved in ether, and extracted with alkali. Acidification of the alkaline solution precipitated 2-nitrodiphenyl-4′-carboxylic acid (0·17 g.), which crystallised from alcohol in plates, m. p. 246—248°, undepressed by admixture with an authentic specimen (Grieve and Hey, J., 1932, 1892).

2-*Amino*-p-*terphenyl.*—A hot solution of stannous chloride (20 g.) in concentrated hydrochloric acid (20 g.) was added to a hot solution of 2-nitro-*p*-terphenyl (2·5 g.) in alcohol (30 c.c.) and the whole boiled gently for 6 hours. After treatment with excess alkali, the free base was extracted with ether. Evaporation of the ethereal solution, which showed a marked violet fluorescence, gave in almost quantitative yield 2-*amino*-p-*terphenyl*, which crystallised from alcohol in colourless needles, m. p. 159—160° (Found : C, 88·3; H, 6·3. $C_{18}H_{15}N$ requires C, 88·2; H, 6·1%). Acetylation in the normal manner gave 2-*acetamido*-p-*terphenyl*, which separated from benzene–light petroleum (b. p. 60—80°) in plates, m. p. 125—126° (Found : C, 83·3; H, 5·8. $C_{20}H_{17}ON$ requires C, 83·6; H, 5·9%).

4-*Nitro*-p-*terphenyl.*—4-Nitro-4′-acetamidodiphenyl (cf. Willstätter and Kalb, *Ber.*, 1906, **39**, 3479) was prepared from 4 : 4′-dinitrodiphenyl by partial reduction to 4-nitro-4′-aminodiphenyl (Guglialmelli and Franco, *loc. cit.*) followed by acetylation. The acetyl derivative

(10 g.) was nitrosated in the usual manner and gave 4-*nitro*-4′-*nitrosoacetamidodiphenyl* (8 g.) as a light yellow powder, m. p. 106° with explosive decomposition (Found: N, 15·15. $C_{14}H_{11}O_4N_3$ requires N, 14·7%). Reaction with benzene at 20° in the usual way yielded 4-nitro-*p*-terphenyl in yellow plates from alcohol, m. p. and mixed m. p. 211—212° (Found: C, 78·7; H, 4·5. Calc. for $C_{18}H_{13}O_2N$: C, 78·5; H, 4·7%).

4-*Amino*-p-*terphenyl*.—Reduction of 4-nitro-*p*-terphenyl with stannous chloride, as described above for 2-nitro-*p*-terphenyl, gave 4-amino-*p*-terphenyl, m. p. 197—198° (cf. Pummerer, Binapfl, Bittner, and Schuegraf, *loc. cit.*; Pummerer and Bittner, *loc. cit.*).

Nitration of 4-*Nitro*-p-*terphenyl*.—A solution of the nitro-compound (0·7 g.) in a mixture of glacial acetic acid (50 c.c.) and fuming nitric acid (*d* 1·5, 3 c.c.) was heated at 100° for 1 hour. The yellow crystalline substance (0·5 g.) which separated in yellow needles (m. p. 272—273° from nitrobenzene) was shown to be identical with 4 : 4″-dinitro-*p*-terphenyl.

Nitration of 4 : 4″-*Dinitro*-p-*terphenyl*.—A suspension of the dinitro-compound (0·5 g.) in glacial acetic acid (25 c.c.) and fuming nitric acid (*d* 1·52; 1 c.c.) was heated at 100° for 15 minutes. Addition of water precipitated 4 : 2′ : 4″-trinitro-*p*-terphenyl, which crystallised from alcohol in pale yellow needles, m. p. 193—194°, undepressed on admixture with the trinitro-compound obtained by direct nitration of *p*-terphenyl.

4 : 3′-*Dinitro*-p-*terphenyl*.—Nitrous fumes were passed for 7 hours into a suspension of 3 : 4′-dinitro-4-acetamidodiphenyl (4 g.) (cf. Scarborough and Waters, J., 1927, 1139), prepared from 3-nitro-4-acetamidodiphenyl (Fichter and Sulzberger, *Ber.*, 1904, **37**, 881), in a mixture of glacial acetic acid (150 c.c.) and acetic anhydride (40 c.c.) at 8° with continuous stirring. No nitroso-compound could be detected in solution, and the solid in suspension was unchanged starting material. The mixture was therefore left overnight at 15°, and from the green solution decanted from unchanged material, iced water precipitated a yellow nitroso-compound. This was allowed to react with benzene at 20° in the usual way, and the product purified by distillation at 175°/10^{-3} mm. Crystallisation of the solid distillate from alcohol gave yellow needles of 4 : 3′-*dinitro*-p-*terphenyl*, m. p. 174—175° (Found: C, 67·5; H, 3·6. $C_{18}H_{12}O_4N_2$ requires C, 67·5; H, 3·75%).

Nitration of 4 : 3′-*Dinitro*-p-*terphenyl*.—A solution of the dinitro-compound (0·2 g.) in glacial acetic acid (10 c.c.) was heated with fuming nitric acid (*d* 1·5, 0·5 c.c.) at 100° for 2 hours. The solid which separated on dilution with water crystallised from alcohol or acetic acid in pale yellow needles, m. p. 193—194°, both alone and mixed with the trinitro-compound obtained by direct nitration of *p*-terphenyl.

Nitrosation of 2-*Nitrodiacetyl*-1 : 4-*phenylenediamine*.—2-Nitrodiacetyl-1 : 4-phenylenediamine (7 g.), prepared by nitration of diacetyl-1 : 4-phenylenediamine (Ladenburg, *Ber.*, 1884, **17**, 148), was nitrosated in a mixture of glacial acetic acid (100 c.c.) and acetic anhydride (25 c.c.) in the usual manner. When the liquid was poured into iced-water, the nitroso-derivative separated as a yellow oil, which was extracted with benzene (400 c.c.). After standing overnight, the benzene was removed, and the residue distilled at 140°/10^{-3} mm. The solid distillate crystallised from methyl alcohol in yellow needles (2·4 g.), m. p. 132—133°, both alone and admixed with an authentic specimen of 3-nitro-4-acetamidodiphenyl (Found: C, 65·4; H, 4·8. Calc. for $C_{14}H_{12}O_3N_2$: C, 65·6; H, 4·7%).

C. Halogeno-derivatives.

Reaction of 4-*Nitrosoacetamidodiphenyl with Chlorobenzene*.—The nitroso-compound (6 g.) was dissolved in chlorobenzene (180 c.c.) at 20°, the subsequent procedure being as described above for the reaction with nitrobenzene. The solid distillate obtained at 150°/10^{-3} mm. was fractionally crystallised from acetic acid and gave finally three distinct crops of crystals in the following order: (i) 4-Chloro-*p*-terphenyl, in colourless plates from alcohol, m. p. 220—221° (1·2 g.) (Found: C, 81·7; H, 4·9. Calc. for $C_{18}H_{13}Cl$: C, 81·7; H, 4·9%); (ii) 3-*chloro*-p-*terphenyl*, in colourless leaflets from alcohol, m. p. 136—137° (0·5 g.) (Found: C, 81·7; H, 5·0%); (iii) 2-*chloro*-p-*terphenyl*, in colourless needles from alcohol, m. p. and mixed m. p. with an authentic specimen (see below) 110—111° (0·8 g.) (Found: C, 81·6; H, 4·9%).

2-*Chloro*-p-*terphenyl*.—2-Amino-*p*-terphenyl (1·2 g.) was diazotised by warming with a mixture of concentrated hydrochloric acid (5 c.c.) and water (2 c.c.), cooling rapidly to obtain a fine suspension, and adding sodium nitrite (0·4 g.) in small amounts below 10°. An orange precipitate was produced which remained unchanged on addition of excess sodium nitrite and hydrochloric acid but dissolved in excess water. An ice-cold solution of cuprous chloride (prepared from 1 g. of copper sulphate) was added gradually with shaking to the diazo-solution, and the mixture boiled. The dark oil which formed was extracted with ether, and after removal of solvent the residue was dissolved in hot alcohol (with charcoal). From the filtered solution 2-chloro-*p*-terphenyl separated, m. p. 110—111° both alone and on admixture with the compound of similar m. p. obtained as above.

2 : 5 : 2′′ : 5′′-*Tetrachloro*-p-*terphenyl*. Dinitrosodiacetyl-1 : 4-phenylenediamine (5 g.) was added gradually with stirring to molten *p*-dichlorobenzene (200 g.) maintained at 50—55°. Nitrogen was freely evolved, and after 1 hour the temperature was raised to 90° for 2 hours. The resulting mixture was diluted with benzene and filtered from a small insoluble residue. After removal of benzene and excess *p*-dichlorobenzene by distillation, first at atmospheric pressure and finally under reduced pressure, the residue was distilled at 185—195°/20 mm. The oily distillate rapidly solidified, and on crystallisation from glacial acetic acid 2 : 5 : 2′′ : 5′′-*tetrachloro*-p-*terphenyl* (0·5 g.) separated in almost colourless prisms, m. p. 203—204° (Found : 59·0; H, 2·9. $C_{18}H_{10}Cl_4$ requires C, 58·7; H, 2·7%).

Reaction of 4-*Nitrosoacetamidodiphenyl with Bromobenzene.*—The nitroso-compound (6 g.) was allowed to react with bromobenzene (180 c.c.) at 20° and the product worked up as described above. Fractional crystallisation from acetic acid resulted eventually in the isolation of three distinct crops of crystals in the following order : (i) 4-Bromo-*p*-terphenyl, in colourless plates from alcohol, m. p. and mixed m. p. with a synthetic specimen (see below) 231—232° (1·4 g.); (ii) 2-*bromo*-p-*terphenyl*, in colourless plates from alcohol, m. p. 86—88° (0·9 g.) (Found : C, 70·0; H, 4·3. $C_{18}H_{13}Br$ requires C, 69·9; H, 4·2%) ; (iii) 3-*bromo*-p-*terphenyl*, in colourless needles from alcohol, m. p. 147—148° (0·4 g.) (Found : C, 69·9; H, 4·2%).

Oxidation of 2-*Bromo*-p-*terphenyl.*—The bromo-compound, m. p. 86—88° (0·25 g.), was oxidised by boiling with chromic anhydride (0·75 g.) in glacial acetic acid (35 c.c.) for 1 hour. The acid, obtained by precipitation with water, crystallised from acetic acid in white needles, m. p. 240—241°, undepressed by admixture with 2-bromodiphenyl-4′-carboxylic acid prepared and characterised as described below.

4-*Bromo*-p-*terphenyl.*—4-Bromo-4′-acetamidodiphenyl was prepared from 4-nitrodiphenyl by successive bromination, reduction, and acetylation (Le Fèvre and Turner, J., 1926, 2045). Nitrosation was effected in the usual way, and 4-*bromo*-4′-*nitrosoacetamidodiphenyl* obtained as a yellow powder, m. p. 91—92° (decomp.) (Found : N, 9·1. $C_{14}H_{11}O_2N_2Br$ requires N, 9·1%). Reaction with benzene at 30° gave 4-bromo-*p*-terphenyl, which separated from alcohol in colourless plates, m. p. 231—232° (Found : C, 69·5; H, 4·4%).

Bromination of p-*Terphenyl.*—Bromine (4·5 g.) was added to a hot solution of *p*-terphenyl (2 g.) in glacial acetic acid (200 c.c.) containing a trace of iodine. The solution was maintained at 100° for 1 hour, during which little hydrogen bromide was evolved, but, on boiling for 5—6 hours under reflux, evolution of hydrogen bromide was vigorous. After cooling, the separated solid was filtered off and repeatedly extracted with hot alcohol, whereby 4-bromo-*p*-terphenyl (0·9 g.) was removed, m. p. and mixed m. p. with a synthetic specimen 231—232°. Crystallisation of the alcohol-insoluble residue gave 4 : 4′′-dibromo-*p*-terphenyl, which separated from nitrobenzene in colourless prisms, m. p. 309—311° (cf. von Braun, Irmisch, and Nelles, *loc. cit.*).

4-*Iodo*-p-*terphenyl.*—4-Iodo-4′-aminodiphenyl was obtained by reduction with stannous chloride of 4-iodo-4′-nitrodiphenyl, prepared by the method of Guglialmelli and Franco (*Anal. Asoc. Quím. Argentina*, 1931, **19**, 5). The *acetyl* derivative, obtained in the normal manner, separated from nitrobenzene in small needles, m. p. 246—247° (Found : C, 50·0; H, 3·8. $C_{14}H_{12}ONI$ requires C, 49·85; H, 3·6%). Nitrosation of 4-iodo-4′-acetamidodiphenyl (5 g.), suspended in a mixture of glacial acetic acid (150 c.c.) and acetic anhydride (50 c.c.), in the usual way, gave 4-*iodo*-4′-*nitrosoacetamidodiphenyl* as a yellow microcrystalline solid, m. p. 90—91° (decomp.) (Found : N, 7·6. $C_{14}H_{11}O_2N_2I$ requires N, 7·65%). The nitroso-compound was added to benzene (600 c.c.), the mixture being stirred while the temperature was slowly raised from 40° to boiling during 2 hours. After removal of benzene, the residue was purified by distillation at 200°/10^{-2} mm. Crystallisation of the solid distillate from xylene gave 4-iodo-*p*-terphenyl in colourless plates, m. p. 246—247° (Found : C, 60·5; H, 3·8. Calc. for $C_{18}H_{13}I$: C, 60·7; H, 3·7%) (cf. Pummerer and Bittner, *loc. cit.*).

Reaction of Diazotised o-*Bromoaniline with Toluene in Presence of Alkali.*—An ice-cold solution of *o*-bromoaniline (24·5 g.) in concentrated hydrochloric acid (43 c.c.) was diazotised by the slow addition of a slight excess of a solution of sodium nitrite (10 g.) in water (25 c.c.). Toluene (400 c.c.) was added, and the vigorously stirred mixture treated dropwise with a 40% aqueous solution of sodium hydroxide until just alkaline, the temperature being maintained at 5° by addition of ice. Stirring was continued at room temperature overnight. The toluene layer was separated, excess toluene removed, and the tarry residue distilled with superheated steam. The distillate, a mixture of 2-bromo-2′- and -4′-methyldiphenyl, was redistilled, and the oil collected at 120—170°/17 mm.

Oxidation of the mixture of bromomethyldiphenyls. The above oil (6 g.) was oxidised by boiling with chromic anhydride (15 g.) in glacial acetic acid solution for 12 hours, and the resultant bromodiphenylcarboxylic acids precipitated with water and extracted with ether. Alkaline extraction of the ethereal solution and subsequent acidification precipitated the mixture of acids (1·5 g.). Separation of 2-bromodiphenyl-4′- from 2-bromodiphenyl-2′-carboxylic acid was effected by heating the mixed acids with concentrated sulphuric acid (9 c.c.) at 45—50° for 15 minutes, whereby the 2′-carboxylic acid was converted into 4-bromofluorenone. The deep red solution was poured on ice, and the yellow solid which separated was extracted with ether; the ethereal solution was washed with dilute alkali to remove the unchanged 2-bromodiphenyl-4′-carboxylic acid, which was reprecipitated on acidification. Crystallisation from glacial acetic acid (charcoal) gave 2-bromodiphenyl-4′-carboxylic acid in needles, m. p. 240—241° (0·5 g.) (cf. Gomberg and Pernert, *loc. cit.*). 4-*Bromofluorenone*, isolated from the ethereal solution, separated from glacial acetic acid in yellow needles, m. p. 127—128° (0·9 g.) (Found: C, 60·4; H, 2·9. $C_{13}H_7OBr$ requires C, 60·2; H, 2·7%).

Reaction of Diazotised p-*Toluidine with Bromobenzene in the Presence of Alkali.*—*p*-Toluidine (22 g.) was diazotised, and allowed to react with bromobenzene in the presence of alkali exactly as described in the preceding preparation (cf. Gomberg and Pernert, *loc. cit.*). The mixture of 2-bromo- and 4-bromo-4′-methyldiphenyl so obtained was separated by fractional distillation into the former, b. p. 300—305°/760 mm. (2·5 g.), and the latter, b. p. 310—315°/760 mm., m. p. 131—132°.

Oxidation of 2-Bromo-4′-methyldiphenyl.—Oxidation carried out with chromic anhydride in glacial acetic acid solution as previously described gave the corresponding carboxylic acid in small needles, m. p. 240—241° (from acetic acid), undepressed on admixture with the 2-bromodiphenyl-4′-carboxylic acid obtained above from *o*-bromoaniline and toluene.

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