Homolytic Aromatic Substitution. Part X. The Phenylation of Pyridine.*

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[Reprint Order No. 6489.]

The proportions of the isomeric phenylpyridines formed in the reaction between pyridine and (*a*) benzoyl peroxide, (*b*) lead tetrabenzoate, (*c*) phenyl iodosobenzoate, (*d*) nitrosoacetanilide, and (*e*) phenylazotriphenylmethane † have been determined. Reactions with (*a*), (*b*), and (*c*) reveal a common mechanism. The reaction with (*e*) gives rise to the formation of a by-product, $C_{30}H_{23}N$, which on infrared spectrometric evidence is regarded as being derived from 2-phenylpyridine. When allowance is made for the disappearance of the 2-isomeride in this manner the results obtained with phenylazotriphenylmethane are quantitatively the same as those obtained with benzoyl peroxide, lead tetrabenzoate, and phenyl iodosobenzoate.

HEY, NECHVATAL, and ROBINSON (*J.*, 1951, 2892) have reviewed the arylation of aromatic compounds by certain diazo-derivatives and aroyl peroxides. These compounds were considered to phenylate by providing free radicals and were divided into five classes. Pyridine has been shown to be phenylated by each class of compound as follows : (*a*) the diazoic acids or diazoates (Mohlau and Berger, *Ber.*, 1893, **26**, 1994; Haworth, Heilbron, and Hey, *J.*, 1940, 349); (*b*) the acylarylnitrosamines (Haworth, Heilbron, and Hey, *J.*, 1940, 372); (*c*) the 1-aryl-3 : 3-dimethyltriazens (Elks and Hey, *J.*, 1943, 441); (*d*) the arylazotriarylmethanes (Wieland, *Annalen*, 1934, **514**, 145; Adams, Hey, Mamalis, and Parker, *J.*, 1949, 3181; Huisgen and Nakaten, *Annalen*, 1954, **586**, 70); and (*e*) the aroyl peroxides (Overhoff and Tilman, *Rec. Trav. chim.*, 1929, **48**, 993; Hey and Walker, *J.*, 1948,

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* Part IX, *J.*, 1955, 1425.

† The well-understood name, phenylazotriphenylmethane, is used here for the compound $PhN{:}N{\cdot}CPh_3$ pending clarification of the nomenclature rules governing this class of compound.

2213; Dannley, Gregg, Phelps, and Coleman, *J. Amer. Chem. Soc.*, 1954, **76**, 445). In addition, Sandin and Brown (*ibid.*, 1947, **69**, 2253) have shown that the decomposition of diphenyliodonium chloride in aqueous alkaline pyridine results in the formation of the three isomeric phenylpyridines. In all of the above reactions a mixture of the isomeric phenylpyridines was isolated from which in some instances one or more of the isomers was isolated, either as such or as a derivative. The only determination of the proportions of each isomer formed on the phenylation of pyridine is that of Dannley *et al.* (*loc. cit.*) who, in the reaction with benzoyl peroxide at 70°, reported 58 ± 3·5% phenylation at the 2-position, 28 ± 3% at the 3-position, and 14 ± 1·5% at the 4-position.

In the present work, five phenylation reactions have been selected for quantitative study, namely, those with benzoyl peroxide, phenylazotriphenylmethane, nitrosoacetanilide, lead tetrabenzoate (Part VI, *J.*, 1954, 2747), and phenyl iodosobenzoate (of which a full discussion is deferred to a later paper). Each of these five compounds has been allowed to decompose in pyridine at 105°, the mixture of isomeric phenylpyridines formed has been isolated quantitatively, and the proportion of the isomers in the mixture determined by means of ultraviolet spectroscopy. The results of these experiments are shown in Table 2 below. Further, the presence of all three isomers in the mixtures obtained from the reactions with lead tetrabenzoate and phenyl iodosobenzoate was demonstrated by conversion of the mixtures into the picrates, fractional crystallisation of which yielded each isomer as its pure picrate (cf. Haworth, Heilbron, and Hey, *loc. cit.*).

The ratios of isomerides obtained in the experiments with benzoyl peroxide, lead tetrabenzoate, and phenyl iodosobenzoate are in good agreement (Table 2) and it is clear that the mechanism of the decomposition, which comprises an initial breakdown to benzoyloxy-radicals and hence, by loss of carbon dioxide, to phenyl radicals, is common to each reaction.

From the reaction of phenylazotriphenylmethane with pyridine a compound, $C_{30}H_{23}N$, m. p. 215°, was isolated in 28% yield in addition to the phenylpyridines and tri- and tetraphenylmethane. Huisgen and Nakaten (*loc. cit.*) also isolated this compound in the same yield from the products of this reaction and suggested that it was a triphenylmethyl-substituted phenylpyridine. Oxidation of this compound with acid and with alkaline permanganate (cf. Tschitschibabin, *Ber.*, 1904, **37**, 1373; Skraup and Cobenzl, *Monatsh.*, 1883, **4**, 436) yielded no information. The infrared spectrum of the compound showed a band at 842 cm.$^{-1}$, characteristic of a *para*-disubstituted benzene nucleus (cf. earlier papers in this series), and bands at 1272 and 1185 cm.$^{-1}$. Absorption at these wavelengths has been reported in compounds containing a triphenylmethyl group (Pinchas and Samuel, *J.*, 1954, 863). The latter pair of bands was, however, shown also to be present in the spectra of 2-, 3-, and 4-phenylpyridine. Each band in the spectrum of the compound, m. p. 215° (except for that at 842 cm.$^{-1}$), could be accounted for by taking the spectrum of 2-phenylpyridine in conjunction with that of tetraphenylmethane, whereas this result could not be achieved (see Experimental section) by substituting the spectrum of either 3- or 4-phenylpyridine for that of the 2-isomer. The ratio of isomerides was therefore recalculated (Table 2) on the assumption that the phenylpyridine consumed in the formation of the compound, m. p. 215°, was the 2-isomer. The corrected values for the ratio of isomerides are found to be close to those obtained with benzoyl peroxide, lead tetrabenzoate, and phenyl iodosobenzoate.

The foregoing evidence suggests that the compound, m. p. 215°, may be *p*-2-pyridyltetraphenylmethane. An attempt to synthesise *p*-2-pyridyltetraphenylmethane by a Wurtz–Grignard reaction between 2-*p*-bromophenylpyridine and triphenylchloromethane failed, as 2-*p*-bromophenylpyridine did not react with magnesium. A second attempt was made by a route analogous to that used for the synthesis of 2-phenylpyridine (Ziegler and Zeiser, *Ber.*, 1930, **63**, 1847). *p*-Triphenylmethylphenyl-lithium was prepared by the reaction of *n*-butyl-lithium with *p*-bromotetraphenylmethane. The product, on treatment with pyridine and subsequent heating at 110°, yielded a compound $C_{30}H_{23}N$, m. p. 215°, which, however, depressed the melting point of the compound of the same melting point isolated from the reaction of phenylazotriphenylmethane with pyridine. The possibility that the compound synthesised was the 1 : 2-dihydro-derivative was rejected because the compound was unaffected on treatment with palladium on charcoal. In spite of the failure to synthesise the compound obtained from the phenylazotriphenylmethane reaction, the spectral evidence, which shows that it is the 2-phenylpyridine which is consumed in the formation of the compound, $C_{30}H_{23}N$, is considered to justify the correction made to the ratio of isomerides.

In the reaction with nitrosoacetanilide only 47% of the starting material was accounted for, and much intractable tar was formed. It is probable that side reactions affecting individual isomers account for the anomalous values of the isomer ratio which are obtained, and little significance is attached to them. The ratios of isomerides obtained in the reactions of pyridine with benzoyl peroxide, lead tetrabenzoate, and phenyl iodosobenzoate are, however, the same within the limits of the accuracy of the determination, and moreover, that obtained in the phenylazotriphenylmethane reaction, after correction for the effect of a subsequent reaction on the 2-phenylpyridine, has a similar value. In a detailed investigation of the kinetics of the decomposition of phenylazotriphenylmethane, Huisgen and Nakaten (*loc. cit.*) have been able to distinguish between (*a*) a simple dissociation into free radicals, (*b*) a free-radical chain decomposition, and (*c*) the formation of a complex with the solvent before dissociation, followed by a directed radical reaction. Their results, which favour mechanism (*a*), taken in conjunction with the results that we have obtained, make it seem likely that the phenylating agent is the same in all these reactions, and that it is, in fact, the phenyl radical.

The value for the ratio of isomerides obtained in the benzoyl peroxide reaction, taken in conjunction with the rate of substitution relative to benzene (Augood, Hey, and Williams, *J.*, 1952, 2094), gives the following partial rate factors for the phenylation of pyridine: 2-position, 1·69; 3-position, 1·0; 4-position, 0·87. Yvan's calculation (*Compt. rend.*, 1949, **229**, 622) of what are termed " potential barriers " for radical substitution in pyridine are in qualitative agreement with these values (cf. Hey and Williams, *Discuss. Faraday Soc.*, 1953, **14**, 216).

EXPERIMENTAL

Reagents.—Pyridine (Hopkins and Williams, AnalaR) was dried (KOH) and fractionally distilled (b. p. 115·5°/750 mm.). It was redistilled from anhydrous barium oxide immediately before use. 5-Ethyl-2-methylpyridine (Light) was fractionally distilled and collected at 78°/22 mm. (picrate, m. p. 167°). Benzoyl peroxide (May and Baker) was purified according to the procedure described by Augood, Hey, and Williams (*loc. cit.*).

Reactions in Pyridine.—The following series of reactions was carried out in duplicate in a thermostat maintained at 105° ± 0·1°. The method used was that of Augood, Hey, and Williams (*loc. cit.*). In each case the concentration of the phenylating agent was 1 mole per 55 moles of pyridine. In each of the first three reactions the reagent was added rapidly to the pyridine at 105°. The mixtures were removed from the thermostat after 20 hr. except in the case of phenyl iodosobenzoate, when heating was continued for 60 hr.

(a) *With benzoyl peroxide* (5·25 g./100 ml. of pyridine). After the reaction was complete, pyridine was removed by distillation through a 25-cm. helix-packed column, and esters in the residue were hydrolysed by boiling for 4 hr. with 2N-sodium hydroxide (100 ml.). The unsaponifiable material was thoroughly extracted with benzene (5 × 30 ml.). The benzene extracts were then extracted with 7N-hydrochloric acid (3 × 50 ml.), and the acid extracts were neutralised by the addition of excess of concentrated aqueous sodium hydroxide. The alkaline solution was extracted with benzene (5 × 30 ml.), and the extracts dried ($CaCl_2$). Benzene was removed by distillation through a 25-cm. helix-packed column and the residue was distilled at reduced pressure to give an oil (2·08 g.), b. p. 139—141°/12 mm., which partly solidified. The residue weighed 0·27 g.

(b) *With lead tetrabenzoate* (Hey, Stirling, and Williams, *loc. cit.*; 18·0 g./120 ml. of pyridine). The working procedure was that described for benzoyl peroxide, except that, after the removal of pyridine, lead benzoate was precipitated by the addition of light petroleum (b. p. 60—80°; 100 ml.) and filtered off. Light petroleum was removed from the filtrate by distillation and the residue was treated with sodium hydroxide as before. The final distillation yielded an oil (1·65 g.), b. p. 140—144°/12 mm., and a residue (0·080 g.).

(c) *With phenyl iodosobenzoate* (14·49 g./150 ml. of pyridine). The preparation of this compound, m. p. 159·5—160·5° (Found: C, 53·8; H, 3·3%; equiv., 223. Calc. for $C_{20}H_{15}O_4I$: C, 53·8; H, 3·4%; equiv., 223) from iodosobenzene by a modification of Arbuzov's method (*J. prakt. Chem.*, 1931, **131**, 357) will be described fully in a later paper. The working-up procedure was the same as for the benzoyl peroxide reaction. Iodobenzene was isolated in almost quantitative yield from the benzene extracts of the mixture after treatment with sodium hydroxide and removal of the basic components by acid extraction. The final distillation gave an oil (1·17 g.), b. p. 138°/10 mm., and a residue (0·084 g.).

(d) *With nitrosoacetanilide* (France, Heilbron, and Hey, *J.*, 1940, 369; 3·56 g./100 ml. of pyridine). The reagent was dissolved in pyridine (25 ml.) which had previously been cooled to −20°, and the solution was added dropwise to the remainder of the pyridine at 105°. The working-up procedure was the same as for the benzoyl peroxide reaction, and final distillation gave a yellow oil (1·59 g.), b. p. 137°/10 mm., from which the colour was not removed by chromatography, and a residue (0·48 g.).

(e) *With phenylazotriphenylmethane* (Wieland, Hove, and Börner, *Annalen*, 1926, **446**, 31; 12·55 g./166 ml. of pyridine). The reagent was dissolved in 161 ml. of pyridine at room temperature and the solution was added dropwise during 2 hr. to the remainder of the pyridine at 105°. After 20 hr. the pyridine was removed by distillation and chloroform (100 ml.) was added to the residue. The chloroform solution was extracted with 7N-hydrochloric acid (4 × 15 ml.), washed with water, and dried ($CaCl_2$). The acid extracts were worked up in the manner described for the benzoyl peroxide reaction, yielding an oil, b. p. 130°/8 mm. (2·20 g.), and residue (0·06 g.). The chloroform solution was evaporated to dryness and the residue (10·22 g.), after extraction successively with (*a*) boiling light petroleum (b. p. 40—60°; 50 ml.) and (*b*) ether (60 ml.), left a pale-brown residue (*c*). Both extracts were evaporated to dryness and the three residues were chromatographed on alumina. Residue from (*a*) (7·00 g.) yielded triphenylmethane (4·6 g.), m. p. and mixed m. p. 92°, and a compound, $C_{30}H_{23}N$ (m. p. 215°; 0·49 g.) (see below). Residue from (*b*) (1·70 g.) yielded chiefly the compound, m. p. 215° (1·14 g.), and a small amount of tetraphenylmethane (0·10 g.), m. p. and mixed m. p. 275°. Residue (*c*) (1·32 g.) yielded the compound, m. p. 215° (1·12 g.), and tetraphenylmethane (0·04 g.). In this way 75% of the neutral residue was accounted for. The compound, m. p. 215°, is believed to be isolated quantitatively as a result of its very sparing solubility in light petroleum (b. p. 40—60°).

The other products isolated from this series of reactions are listed in Table 1. Benzoic acid, which was formed in the first three reactions, was isolated by the following procedure. The alkaline extracts obtained after the hydrolysis stage of the working-up procedure were made just acid with concentrated hydrochloric acid, neutralised by the addition of solid sodium hydrogen carbonate, and filtered. The filtrate was extracted with methylene chloride and acidified with concentrated hydrochloric acid, and the precipitated benzoic acid was quantitatively extracted with methylene chloride (4 × 30 ml.). The aqueous layer was rejected and the combined methylene chloride extracts, after being dried (Na_2SO_4), were evaporated at room temperature. The residual benzoic acid had m. p. and mixed m. p. 117—119°. In this series of reactions no identifiable products could be isolated from the residues obtained after distillation of the phenylpyridines. They probably consisted mainly of higher phenylated products. They have not been included in the calculations of the proportions of the phenyl radicals accounted for in each reaction.

TABLE 1. *Products obtained in reactions with pyridine at* 105°

Reagent	$Ph{\cdot}CO_2H$, mol.*	$Ph{\cdot}C_5H_4N$, mol.*	% Ph accounted for
Benzoyl peroxide	0·89	0·62	76
Lead tetrabenzoate	1·16	0·42	78
Phenyl iodosobenzoate	1·66	0·23	95
Nitrosoacetanilide	—	0·47	47
Phenylazotriphenylmethane	—	0·40	61

* Per mol. (mean) of reagent.

The isomer ratios of the products formed in these reactions were determined by ultraviolet spectrophotometry with the aid of a " Unicam S.P. 500 " quartz spectrometer. The method of calculation previously described (Cadogan, Hey, and Williams, *J.*, 1954, 794) was used. The solvent was ethanol.

The absorption curves of the isomeric phenylpyridines have been recorded by Gillam, Hey, and Lambert (*J.*, 1941, 366). The pure isomers for the calibration spectra were obtained from their picrates (cf. Haworth, Heilbron, and Hey, *loc. cit.*). The picrates of 2- and 3-phenylpyridine (m. p. 176° and 160°, respectively) were chromatographed on alumina in methylene chloride solution. Removal of methylene chloride from the eluates, and distillation of the residue gave 2-phenylpyridine, b. p. 127°/8 mm., n_D^{20} 1·6227, and 3-phenylpyridine, b. p. 141°/12 mm., n_D^{20} 1·6143. 4-Phenylpyridine (plates, m. p. 73°, from water) was obtained by treatment of the pure picrate, m. p. 197°, with 10% aqueous sodium hydroxide.

The extinction coefficients of the mixtures from the duplicate reactions with benzoyl peroxide, phenyl iodosobenzoate, lead tetrabenzoate, and nitrosoacetanilide differed only slightly from each other, and mean values were used for purposes of calculation. The mixtures from the phenylazotriphenylmethane reactions were treated separately. As the method of calculation is valid only for mixtures which contain only the three isomers, the nitrogen content of each mixture was determined (Calc. for $C_{11}H_9N$: N, 9·05%). The compositions of the mixtures thus obtained are given in Table 2, the overall error in each determination being ±2%.

TABLE 2 *Ratios of isomerides obtained in the phenylation of pyridine at* 105°

Reagent	Isomers, % 2-	3-	4-	N, %
Benzoyl peroxide	54	32	14	(1) 9·35, (2) 9·00
Lead tetrabenzoate	52	32·5	15·5	(1) 9·15, (2) 8·80
Phenyl iodosobenzoate	58	28	14	(1) 9·18, (2) 9·25
Nitrosoacetanilide	46	43	11	(1) 8·90, (2) 9·35
Phenylazotriphenylmethane	(1) 29·3	47	23·7	8·94
,,	(2) 30·6	46·4	23	9·20
,, (corrected)	53	31	16	—

The compound, m. p. 215° (Found : C, 90·6; H, 5·9; N, 3·35%; *M*, 342. Calc. for $C_{30}H_{23}N$: C, 90·7; H, 5·8; N, 3·5%; *M*, 397). Huisgen and Nakaten (*loc. cit.*) reported m. p. 213° for this compound. Attempted oxidation with alkaline permanganate resulted in the recovery of starting material in almost quantitative yield. Acid permanganate was decolorised and only part of the starting material was recovered, but no identifiable oxidation products could be isolated.

Infrared Spectra.—The instrument used was a Grubb-Parsons single-beam infrared spectrometer. 2- and 3-Phenylpyridine and 5-ethyl-2-methylpyridine were used as capillary films, and the other compounds investigated as crystalline powders in Nujol mulls, all between rock-salt plates. The spectra of 2-, 3-, and 4-phenylpyridine, 2-*p*-bromophenylpyridine, tetraphenylmethane, *p*-2-pyridyltetraphenylmethane, and the compound of m. p. 215° isolated from the phenylazotriphenylmethane reaction, were taken between 1320 cm.$^{-1}$ and 780 cm.$^{-1}$. Apart from a weak band at 944 cm.$^{-1}$ all the bands in the spectrum of the compound, m. p. 215°, are accounted for by bands in the spectra of 2-phenylpyridine, 2-*p*-bromophenylpyridine or tetraphenylmethane. On the other hand, the spectra of 3- and 4-phenylpyridine show strong absorption bands at 810 and 826 cm.$^{-1}$, respectively, while there is no band in the spectrum of the compound, m. p. 215°, which corresponds to either of these bands. Further, the spectra of these two isomers show no absorption at 1290 and 1089 cm.$^{-1}$, whereas at these wavelengths there are bands of medium intensity in the spectrum of the compound, m. p. 215°. The presence of a band at 844 cm.$^{-1}$ in the spectrum of 2-*p*-bromophenylpyridine confirms that this absorption is characteristic of a *para*-disubstituted benzene nucleus. No band is present at 844 cm.$^{-1}$ in the spectrum of 5-ethyl-2-methylpyridine. This absorption is therefore not due to the presence of a 2 : 5-disubstituted pyridine derivative. A very weak band at 840 cm.$^{-1}$ in the spectrum of tetraphenylmethane is probably due to a trace of *p*-ethoxytetraphenylmethane, formed as a by-product in the preparation of this compound. These results are tabulated in Table 3.

Tetraphenylmethane, m. p. 276°, was prepared by the deamination of *p*-aminotetraphenylmethane by Ullmann and Munzhuber's method (*Ber.*, 1903, **36**, 404).

2-p-*Bromophenylpyridine* (cf. Butterworth, Heilbron, and Hey, *J.*, 1940, 355).—A solution of *p*-bromo-*N*-nitrosoacetanilide (60 g.), prepared by the method of Hey, Stuart-Webb, and Williams (*J.*, 1952, 4657) in anhydrous pyridine (550 ml.), was warmed on the water-bath until the evolution of nitrogen slackened, and was thereafter boiled under reflux for 3 hr. Pyridine was distilled off and the residue dissolved in benzene (150 ml.). The benzene solution was extracted with 7N-hydrochloric acid (5 × 40 ml.). The acid extracts were made alkaline by the addition of excess of aqueous sodium hydroxide and extracted with ether (3 × 100 ml.). Evaporation of the extracts and distillation of the residue yielded a mixture of the isomeric *p*-bromophenylpyridines (19·6 g.), b. p. 135—165°/0·5 mm. This mixture was converted into the mixture of picrates (46 g.), fractional crystallisation of which from acetone yielded 2-*p*-bromophenylpyridine picrate (4·0 g.), m. p. 164°. This picrate was chromatographed in acetone solution on alumina. Evaporation of the eluates and crystallisation of the residue from light petroleum (b. p. 40—60°) gave 2-*p*-bromophenylpyridine, m. p. 61—62°, in white flakes (1·25 g.). 2-*p*-Bromophenylpyridine did not appear to react with magnesium and from an attempt to couple it with triphenylchloromethane, by Schoepfle and Trepp's method (*J. Amer. Chem. Soc.*, 1932, **54**, 4059), starting material was obtained in quantitative yield.

TABLE 3. *Infrared absorption bands* (*cm.*$^{-1}$).

(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)	(*g*)
1318 m	—	—	—	1308 w	1308 w	1309 w
—	1303 m	—	—	—	—	—
1298 m	—	—	1290 m	—	—	—
1272 m	1275 w	—	1265 w	1273 w	1273 vw	1265 w
1237 w	—	—	1234 vw	1235 vw	1228 vw	—
1185 s	1190 s	1185 m	1183 w	1190 m	1190 vw	1190 w
1153 m	1155 m	—	1150 m	1157 vw	1160 vw	1165 m
—	1121 w	—	—	1123 w, 1105 w	1100 w	1125 w
1089 m	1089 m	—	1092 w	—	—	1103 m
1075 m	—	1075 m	—	1075 m	1070 m	1075 m
—	1065 w	—	1063 m	—	—	—
—	—	—	—	1051 vw	—	—
1038 s	1038 s	—	—	—	1040 vw	1038 w
—	—	1030 m	—	—	—	—
1020 m	1020 s	—	1020 m	1020 s	—	—
—	—	—	—	—	—	1010 m
1002 m	1000 m	995 m	—	1002 vs	995 w	—
990 w	990 w	980 w	985 m	990 m	985 w	990 m
—	—	—	—	—	962 vw	—
944 w	944 w	—	—	948 vw	—	—
934 w	—	935 w	—	—	—	—
921 w	—	—	916 w	—	915 m	—
—	—	—	—	909 m	—	—
893 m	893 m	889 w	882 vw	—	—	—
—	—	855 vw	—	—	865 vw	—
842 vs	840 s	840 vw	—	—	—	844 s
—	—	—	—	810 vs	826 vs	—
—	—	—	796 m	—	—	—
781 m	—	—	—	—	—	—

(*a*) Compound, m. p. 215°, isolated from phenylazotriphenylmethane reaction. (*b*) *p*-2-Pyridyltetraphenylmethane. (*c*) Tetraphenylmethane. (*d*) 2-Phenylpyridine. (*e*) 3-Phenylpyridine. (*f*) 4-Phenylpyridine. (*g*) 2-*p*-Bromophenylpyridine.

w = weak. m = medium. s = strong. v = very.

p-*Bromotetraphenylmethane*.—*p*-Aminotetraphenylmethane (25 g.), prepared by Ullmann and Munzhuber's method (*loc. cit.*) was heated to boiling with glacial acetic acid (150 ml.). The suspension was cooled and constant-boiling (48%) hydrobromic acid (12 ml.) was added. Amyl nitrite (18 ml.) was added dropwise to the vigorously stirred suspension of the hydrobromide. After 2 hr. the mixture was filtered and ether (1 l.) was added to the filtrate. The pale grey diazonium bromide was filtered off, dried *in vacuo* (17 g.), and added in portions, with stirring, to a boiling solution of cuprous bromide (17 g.) in 48% hydrobromic acid (200 ml.). The mixture was diluted with water to 1 l. and filtered. The residue was washed with 48% hydrobromic acid (50 ml.), water, and methyl alcohol (200 ml.). The crude *p*-bromotetraphenylmethane (17 g.), after purification by chromatography in benzene solution on alumina, had m. p. 245°. Schoepfle and Trepp (*loc. cit.*) reported m. p. 246° for this compound.

p-2-*Pyridyltetraphenylmethane*.—A solution of *n*-butyl-lithium (Gilman, Beel, Brannen, Bullock, Dunn, and Miller, *J. Amer. Chem. Soc.*, 1949, **71**, 1499) was prepared from lithium (0·8 g.) and *n*-butyl bromide (6·8 g.) in anhydrous ether (30 ml.). *p*-Bromotetraphenylmethane (4 g.) and anhydrous ether (50 ml.) were then added to the ethereal solution of *n*-butyl-lithium. The resulting suspension was boiled for 2 hr., the bromo-compound having then dissolved to give a clear solution. Anhydrous pyridine (15 ml.) in toluene (60 ml.) was added with stirring and cooling to the solution of *p*-triphenylmethylphenyl-lithium. The mixture was distilled until the boiling point reached 110° and was then stirred at 110° for 8 hr. After the mixture had cooled to room temperature, water (150 ml.) was cautiously added and the mixture was filtered. The organic layer was separated and chloroform (150 ml.) was added. The solution was extracted with 5N-hydrochloric acid (120 ml.), washed with water, and dried ($CaCl_2$). Chloroform was removed and the residue was chromatographed in benzene solution on alumina. The eluates yielded p-2-*pyridyltetraphenylmethane* (2·9 g.), m. p. 215°, in needles from benzene–light petroleum (b. p. 80—100°) (Found: C, 90·5; H, 6·1. $C_{30}H_{23}N$ requires C, 90·7; H, 5·8%). This compound was unaffected by boiling a nitrobenzene solution for 1 hr. and was recovered quantitatively. A solution of 1 g. of the compound in *p*-cymene (100 ml.), to which 5% palladium on charcoal (1·5 g.) was added, was distilled until the reflux temperature reached 175° and heating was continued under reflux for 2 hr. (cf. Walker, *J. Amer. Chem. Soc.*, 1954, **76**, 3999). The hot mixture was filtered and a further 1·5 g. of catalyst was added. The mixture was again distilled until the boiling point rose to 175°, and was boiled for a further 2 hr. The catalyst was filtered off and *p*-cymene was removed by steam-distillation. Recrystallisation of the residue from benzene–light petroleum (b. p. 80—100°) gave starting material (m. p. and mixed m. p. 215°).

One of us (C. J. M. S.) thanks the Department of Scientific and Industrial Research for the award of a Maintenance Grant. Thanks are also due to Dr. W. C. Price for helpful discussion on the infrared spectra.

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[*Received, June 8th*, 1955.]