1020. *Isomer Ratios for the Mononitration of* p-*Terphenyl in Acetic Acid and Acetic Anhydride.*

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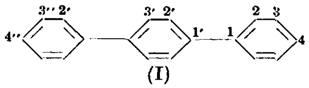
Quantitative data have been obtained for the ratios of the mononitro-isomers (4-, 2-, and 2′-) formed on nitration of *p*-terphenyl in glacial acetic acid at 20° and in acetic anhydride at 0°, 20°, 40°, and 80°. The results and their accuracy are discussed in general terms, and attention is drawn to the greater degree of *ortho*-substitution, *i.e.*, at the 2- and 2′-positions, which occurs in acetic anhydride. Isomer ratios published for the mononitration of biphenyl are reviewed and compared with the present results for *p*-terphenyl

France, Heilbron, and Hey[1] reported that the nitration of *p*-terphenyl in acetic acid with fuming nitric acid at 100° gave a 43% yield of 4,4″-dinitro-*p*-terphenyl, and that nitration in acetic anhydride at 45—50° gave the same product in 68% yield. These authors also obtained a 100% yield of 4,2′,4″-trinitro-*p*-terphenyl by nitrating the hydrocarbon in fuming nitric acid alone. Recently,[2] attempts to reproduce these and other nitrations reported by France, Heilbron, and Hey proved unsuccessful, and qualitative studies showed that there was considerably less nitration at the *para*-positions of *p*-terphenyl than France, Heilbron, and Hey found in their experiments. In fact, a close similarity was indicated between the *ortho* : *para*-isomer ratios for *p*-terphenyl and biphenyl. Quantitative data for the proportions of the isomers formed



(I)

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[1] France, Heilbron, and Hey, *J.*, 1938, 1364.

[2] Culling, Gray, and Lewis, *J.*, 1960, 1547.

on mononitration of the hydrocarbon (I) are now presented (Table 1) in support of these recent findings.

TABLE 1.

Expt.	Nitrating conditions [a]		Proportions of isomers [b] (%)		
			2	2′	4
N 5	HOAc at 20°		25	12	63
N 12	,, ,,		—	—	62
N 14	,, ,,		25	12	63
		Mean	25	12	62·7
N 2	Ac$_2$O at 0°		40	20	40
N 3	,, ,,		42	18	40
		Mean	41	19	40
N 10	Ac$_2$O at 20°		29	17	54
N 13	,, ,,		32	17	51
N 15	,, ,,		32	17	51
		Mean	31	17	52
N 18	Ac$_2$O at 40°		—	—	58
N 24	,, ,,		—	—	52
N 29	,, ,,		29	17	55
N 30	,, ,,		29	18	53
		Mean	29	17·5	54·5
N 28	Ac$_2$O at 80°		31	14	55

[a] For details of the nitrating conditions, see Experimental section. [b] It is shown in the Experimental section under " accuracy of results," that the amount of 3-nitro-*p*-terphenyl is too small for detection. [c] Because of the limited accuracy of these determinations involving three component mixtures, we judge that not more than two significant figures are justified in quoting the individual results.

Table 2 makes possible a comparison between the observed positional order of reactivities for *p*-terphenyl and various theoretically predicted values, allowance being made for the number of positions of each type.

TABLE 2.

	Positional order of reactivity
Found in all cases	$4 > 2 > 2' (\gg 3)$
Reactivity number [a]	$4 = 2 > 2' \gg 3$
Resonance theory	$4 = 2 > 2' >$ or $\gg 3$
Free valence [b]	$2 > 2' > 4 > 3$

[a] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341 *et seq.* [b] Buu-Hoï, Coulson, Daudel, Daudel, Martin, Pullman, and Pullman, *Rev. Sci.*, 1947, **85**, 1041.

No treatment predicts that the 4-position should be more reactive than the 2- or 2′-positions, and it is probable that this discrepancy arises from steric factors which prevent the *ortho*-positions from being attacked as easily as the exposed *para*-positions. The difference (0·05) between the reactivity numbers for the equally sterically affected 2- and 2′-positions corresponds to a two-fold difference in the rates of nitration at these positions (cf. 0·38 unit of reactivity number in phenanthrene corresponds to a seven-fold change in the rate of nitration [3]). On this basis, no substitution would be expected, and none was found, at the 3-position of *p*-terphenyl.

Turning to a consideration of the results themselves, the main feature is the increase in the ratio of *ortho*(2- + 2′)- to *para*(4)-substitution obtained on changing the solvent from acetic acid to acetic anhydride. The 63% yield of 4-nitro-*p*-terphenyl obtained by nitration in acetic acid at 20° is in good agreement with the preparative yield [2] of 52—54% for nitration in this solvent at 111°. If equation 39 of Augood and Williams [4] is used, a 63% yield of the 4-isomer will fall to 52% at 111°. If this equation 39 and the results for nitration in acetic anhydride at 0° are used, the calculated *ortho*(2- + 2′)- to *para*-ratio

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[3] Dewar and Warford, *J.*, 1956, 3570.

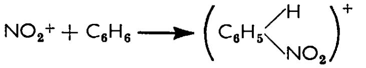
[4] Augood and Williams, *Chem. Rev.*, 1957, 123.

should be 63 : 37 at 40°. In fact the results show a large decrease to a ratio of 48 : 52 at 20°, and to one of 46·5 : 54·5 at 40°. These changes cannot therefore be caused by the temperature differences, and nitrations at 80° were attempted to obtain more results. Unfortunately the products obtained were brown, indicating that the nitration products were undergoing further reaction at this high temperature. The single result obtained does, however, suggest that the ratio (45 : 55) is virtually the same as that at 40°.

Whilst it is reasonably well established that aromatic nitrations by solutions of nitric acid in acetic acid proceed by a mechanism involving the nitronium ion, there remains uncertainty in the case of nitrations in acetic anhydride. Paul[5] found that the nitration of benzene by nitric acid in acetic anhydride at 25° was approximately of the second order with respect to the nitric acid. The fact that the reaction is strongly suppressed by added nitrate ion led Paul to reject the idea that nitration was occurring by means of the ion pair $NO_2^+NO_3^-$ or molecular N_2O_5, and to favour instead attack by the nitronium ion:

$$HNO_3 + H^+ \rightleftharpoons H_2NO_3^+ \qquad \text{(i)}$$

$$H_2NO_3^+ + Ac_2O \rightleftharpoons NO_2^+ + 2AcOH \qquad \text{(ii)}$$



$$NO_2^+ + C_6H_6 \longrightarrow \left(C_6H_5\begin{smallmatrix}H\\NO_2\end{smallmatrix}\right)^+ \qquad \text{(iii)}$$

Nitration at oxygen centres by nitric acid in acetic acid containing a small amount of acetic anhydride is also of second order with respect to the nitric acid.[6] Bonner interprets this in terms of nitration by N_2O_5, and more recently Norman and Radda[7] have explained the high *ortho* : *para*-ratio obtained on nitration of methyl phenethyl ether by acetyl nitrate in terms of displacement of nitrate ion from covalent dinitrogen pentoxide by the oxygen of the ether, forming an intermediate, $Ph{\cdot}CH_2{\cdot}CH_2{\cdot}O^+(Me){\cdot}NO_2$, which rearranges to the usual transition state for *ortho*-substitution. This apparently conflicting evidence for the nature of the attacking species in nitrations in acetic anhydride could be reconciled if in fact nitration in acetic anhydride proceeds by different mechanisms under different conditions. Indeed, the change in the isomer ratios for nitration of *p*-terphenyl in acetic anhydride at 0° and 20° was at first thought to support this idea.

However, semi-quantitative data (see Experimental section) show that the nitration of *p*-terphenyl is strongly retarded by added nitrate ion for both acetic acid and acetic anhydride media at 0° and 20°. Corresponding experiments conducted with added perchlorate ion showed that there was no retardation of the nitration, and the conclusion must be reached that the nitronium ion is the attacking species in all these experiments.

A comparison of the isomer ratios for nitration of *p*-terphenyl and biphenyl shows features of considerable interest (Table 3).

The results, for both *p*-terphenyl and biphenyl, fall into two distinct groups, although there is a considerable variation of the ratios within each set. Thus, in an acetic anhydride medium, a high *ortho* : *para*-ratio is obtained, whilst various other media result in a low *ortho* : *para*-ratio. de la Mare and Hassen[8,9] have commented that the isomer ratio obtained on nitration of biphenyl is dependent on the conditions of reaction, and indeed, the available data for the nitration of this hydrocarbon support the present results for *p*-terphenyl and demonstrate that a change from a high to a low *ortho* : *para*-ratio occurs on changing the nitrating medium from acetic anhydride to acetic acid.

It is, of course, well established[10] that higher proportions of *ortho*-substitution occur

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[5] Paul, *J. Amer. Chem. Soc.*, 1958, **80**, 5329.

[6] Bonner, *J.*, 1959, 3908.

[7] Norman and Radda, *Proc. Chem. Soc.*, 1960, 423.

[8] de la Mare and Hassen, *J.*, 1957, 3004.

[9] de la Mare and Hassen, *J.*, 1958, 1519.

[10] Griffiths, Walkey, and Walker, *J.*, 1934, 631; Halvarson and Melander, *Arkiv Kemi*, 1957, **11**, 77; Holleman, *Chem. Rev.*, 1925, **1**, 187; Arnall and Lewis, *J. Soc. Chem. Ind.*, 1929, **48**, 159T.

TABLE 3.

	Ratio (%) *	
Nitrating conditions	*ortho-*	*para-*
Biphenyl, Ac_2O–HNO_3 (*d* 1·38) at 53° (87%) [a]	58	42
,, ,, (*d* 1·5) 0° [b]	68	32
,, ,, ,, ,, [c]	67	33
,, ,, ,, ,, [d]	77	23
p-Terphenyl, ,, ,, ,,	60	40
Biphenyl, HOAc–HNO_3 (*d* 1·5) at 70—90° (*ca.* 77%) [e]	36	64
,, H_2SO_4–HNO_3 (*d* 1·5)–H_2O at 35—40° (91%) [f]	37	63
,, HNO_3 (*d* 1·448) at *ca.* 50° [g]	53	47
,, liquid N_2O_4 at room temp.[h]	35	65
p-Terphenyl, HOAc–HNO_3 (*d* 1·5) at 20°	37	63

* In these cases for which the isomer ratios have been normalised to 100%, the actual yields recovered are given in parentheses.

[a] Hayashi, Inana, and Ishikawa, *J. Pharm. Soc. Japan*, 1959, **79**, 972. [b] Simamura and Mizuno, *Bull. Chem. Soc. Japan*, 1957, **30**, 196. [c] Warford, Ph.D. Thesis, London University, 1956. [d] Dewar, Mole, Urch, and Warford, *J.*, 1956, 3572. [e] Bell, Kenyon, and Robinson, *J.*, 1926, 1239. Jenkins, McCullough, and Booth, *Ind. Eng. Chem.*, 1930, **22**, 31. [g] Gull and Turner, *J.*, 1929, 491. [h] Shorygin, Topchiev, and Ananina, *J. Gen. Chem.* (*U.S.S.R.*), 1938, **8**, 981.

when acetanilide and anisole are nitrated with acetyl nitrate than with nitric acid or mixed acid, and Paul[11] considers that the *ortho* : *para*-ratios for certain substitutions can be changed by the influence of the dielectric constant of the medium on the polar character of a substituent in the aromatic substrate. Since, however, biphenyl and *p*-terphenyl are both non-polar, Paul's hypothesis can hardly be applied to the substitution of these hydrocarbons, and the change in the isomer ratios when the solvent is changed.

The high *ortho* : *para*-ratios which have been obtained by other workers[7,11] for certain nitrations in acetic anhydride have, therefore, been explained by the influence of the dielectric properties of the medium on the polarity of a ring-substituent bond, or by the attack of dinitrogen pentoxide at an oxygen centre in a side chain attached to the aromatic ring. Neither explanation can be applied to the high *ortho* : *para*-ratios for nitrations of biphenyl and *p*-terphenyl in acetic anhydride and, further, it is clear that this high ratio for *p*-terphenyl is obtained under conditions which involve the nitronium ion, not dinitrogen pentoxide, as the electrophilic reagent. The rapid decrease in the *ortho* : *para*-ratio for the nitration of *p*-terphenyl in acetic anhydride to approximately 1 : 1 when the temperature is raised from 0° to 20° is also of considerable interest, but further work is necessary before an explanation of these effects can be proposed.

EXPERIMENTAL

Materials and Media.—Fuming nitric acid (*d* 1·504), acetic anhydride, and acetic acid ("AnalaR") were commercial products used without further purification. *p*-Terphenyl (Light and Co. Ltd.), after two crystallisations from nitrobenzene, had m. p. 207—209·5°.

3-*Nitro*-p-*terphenyl.*—4-Amino-3-nitro-*p*-terphenyl was prepared as described by Sawicki and Ray,[12] but with the following modifications. 4-Amino-*p*-terphenyl (18 g.) was *N*-propionylated by adding propionic anhydride (36 ml.), containing concentrated sulphuric acid (1 drop), to a boiling solution of the amine in propionic acid (360 ml.). The crude *product* (94%), m. p. 282—284·5°, was satisfactory for nitration. A sample (Found: C, 83·6; H, 6·6; N, 4·75. $C_{21}H_{19}NO$ requires C, 83·7; H, 6·35; N, 4·65%) separated from nitrobenzene or ethylene glycol monomethyl ether as a poorly crystalline solid, m. p. 282—285°. Fuming nitric acid (12 ml.; *d* 1·5) in acetic acid (75 ml.) was added during 2 min. to a stirred suspension of 4-propionamido-*p*-terphenyl (15 g.) in acetic acid (225 ml.) at 70°. After a total reaction time of 15 min., the mixture was cooled and the solid filtered off. The residue (92%), m. p. 197·5—198·5°, was satisfactory for deacylation. A sample (Found: C, 72·7; H, 5·4; N, 7·9. Calc. for $C_{21}H_{18}N_2O_3$: C, 72·9; H, 5·2; N, 8·1%) crystallised from acetic acid in yellow needles, m. p. 198·5—199°. In view of the discrepancy (27°) between this m. p. for 3-nitro-4-propionamido-*p*-terphenyl and that reported by Sawicki and Ray[12] (m. p. 171—172°), the constitution

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[11] Paul, *J. Amer. Chem. Soc.*, 1958, **80**, 5332.

[12] Sawicki and Ray, *J. Org. Chem.*, 1954, **19**, 1903.

of the material above was proved by nitrating it in acetic acid, using the method for preparing 4,4″-dinitro-*p*-terphenyl from *p*-terphenyl.[2] The crude 3,4″-dinitro-4-propionamido-*p*-terphenyl (11%), isolated by dilution of the reaction mixture with a little water, was deacylated with boiling alcoholic sodium hydroxide, yielding 4-amino-3,4″-dinitro-*p*-terphenyl, m. p. 217·5—219°. A mixed m. p. with an authentic specimen [13] of the dinitro-amine was not depressed.

3-Nitro-4-propionamido-*p*-terphenyl (9 g.) in boiling ethylene glycol monoethyl ether (450 ml.) was treated with potassium hydroxide (3·6 g.) in water (4 ml.). After boiling for 2 min., the solution was cooled. Bright red crystals of 4-amino-3-nitro-*p*-terphenyl (89%), m. p. 269·5—271° (Found: C, 74·7; H, 5·1; N, 9·3. Calc. for $C_{18}H_{14}N_2O_2$: C, 74·5; H, 4·9; N, 9·65%), were obtained. Sawicki and Ray [12] report m. p. 271—272°. 4-Amino-3-nitro-*p*-terphenyl (6·37 g.) in acetic acid (45 ml.) was deaminated by the method described [13] for the preparation of 3,4″-dinitro-*p*-terphenyl. The orange paste was set aside for 60 min. before the addition of the hypophosphorous acid, after which the whole was kept at about 4° for 5 days and then at 20° for 12 hr. To isolate the 3-nitro-*p*-terphenyl, the filtrate from a suspension of the crude, dry product in benzene (300 ml.) was passed down a column of alumina (120 g.). The filter cake from the suspension was washed with benzene, and the washings were also placed on the column. The nitro-compound (4·5 g.) was eluted first (benzene eluate, 450 ml.). After crystallisation from a mixture of alcohol (400 ml.) and acetone (130 ml.), *3-nitro-*p*-terphenyl* (3·84 g.) had m. p. 174—175°. The crystallisation liquors yielded a further 0·6 g. of material, m. p. 174°, a total yield of 74%. A sample (Found: C, 78·6; H, 4·5; N, 5·4. $C_{18}H_{13}NO_2$ requires C, 78·5; H, 4·8; N, 5·1%) crystallised from acetone as irregular, pale yellow plates, m. p. 176—176·5°.

Proof of the constitution. 3-Nitro-*p*-terphenyl (0·3 g.) was nitrated in acetic acid according to the method [2] used to prepare 4,4″-dinitro-*p*-terphenyl from *p*-terphenyl. Water (1 ml.) was added at the end of the reaction and crude 3,4″-dinitro-*p*-terphenyl (32%), m. p. 156·5—157·5°, was precipitated on cooling of the mixture. Crystallisation from benzene and then from acetic acid raised the m. p. to the constant value of 159—160·5°. A mixed m. p. with 3,4″-dinitro-*p*-terphenyl,[13] m. p. 161—162°, gave no depression.

Amines.—The most convenient means of preparing *small* amounts of 2-, 3-, and 4-amino-*p*-terphenyls is by the catalytic reduction of the nitro-compounds, as described below for reduction of the mixture of products obtained on mononitration of *p*-terphenyl. After removal of the ethyl acetate, the crude amines, obtained in almost quantitative yields, crystallised from alcohol. Pure 2′-nitro-*p*-terphenyl,[2] however, was incompletely reduced by the catalytic method after a reaction time of 3 hr. But, it should be noted that the catalytic reduction procedure was applied successfully to the quantitative reduction of mixtures of the nitro-compounds containing 2′-nitro-*p*-terphenyl. The success in these cases is explained by the low concentration of the 2′-nitro-isomer used in the synthetic mixtures chosen to simulate actual nitration products.

The pure 2′-isomeride (49%) was prepared by stannous chloride reduction of the nitro-compound.

2-Amino-*p*-terphenyl melted at 161—161·5°, agreeing with the m. p. of 159—160° reported by France, Heilbron, and Hey.[1] 2′-Amino-*p*-terphenyl (Found: C, 88·5; H, 6·75; N, 6·1. Calc. for $C_{18}H_{15}N$: C, 88·2; H, 6·2; N, 5·7%) had m. p. 175·5—176°. The benzoyl derivative (Found: C, 85·9; H, 5·4; N, 4·2. Calc. for $C_{25}H_{19}NO$: C, 85·9; H, 5·5; N, 4·0%), crystallised from alcohol, had m. p. 150°. Ames and Davey [14] report m. p.s of 171—172° and 148°, respectively, for these compounds. *3-Amino-*p*-terphenyl* (79%) melted at 177—178° (Found: C, 88·2; H, 6·1; N, 5·8%). The amine (0·1 g.), acetic acid (2 ml.), and acetic anhydride (2 ml.) were refluxed for 15 min. Dilution with water gave *3-acetamido-*p*-terphenyl*, m. p. 214—215° (from benzene) (Found: C, 83·6; H, 5·9; N, 4·9. $C_{20}H_{17}NO$ requires C, 83·6; H, 6·0; N, 4·9%). 4-Amino-*p*-terphenyl melted at 197—198°, giving a dark, misty melt. France, Heilbron, and Hey [1] report the same m. p. The acetyl derivative, from acetic acid, had m. p. 293—295° (lit.,[15] m. p. 294°).

Outline of Method of Analysis of Nitration Products.—Complete mononitration of *p*-terphenyl gave a product contaminated with dinitro-compounds. Conditions were therefore chosen so

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[13] Gray and Lewis, *J.*, 1961, 1069.

[14] Ames and Davey, *J.*, 1957, 3480.

[15] Pummerer and Bittner, *Ber.*, 1924, **57**, 84.

that only about 50% of the *p*-terphenyl underwent substitution. Since *p*-terphenyl yields the 2-, 2′-, and 4-isomerides on nitration,[2] such conditions result in the formation of a quaternary mixture. Nitration at the 3-position is discussed below.

Analyses of quaternary mixtures (prepared from the pure components) of known composition, by column chromatography on alumina, were unsatisfactory. It was also impracticable to use infrared (650—4000 cm.$^{-1}$) or near-infrared (1—2·8 μ) spectroscopy for the analyses as there were insufficient differences between the individual spectra. Furthermore, *p*-terphenyl and 4-nitro-*p*-terphenyl have extremely low solubilities in solvents suitable for infrared studies.

An ultraviolet spectrophotometric method was therefore developed. The instruments used were a Beckman DK-2 instrument equipped with an automatic pen recorder and a single-beam Uvispek instrument. Absorption spectra for the four compounds are shown in Fig. 1, and it is obvious that there is little opportunity of distinguishing between 2- and 2′-nitro-*p*-terphenyl. However, it was possible to calculate the amounts of the hydrocarbon, 4-nitro-*p*-terphenyl, and (2 + 2′)-nitro-isomers present. The nitro-compounds were then reduced, and the quaternary mixture was digested with dilute hydrochloric acid. Basification of the extract yielded only the free amines which were analysed as a binary mixture of 2- and 2′-amino-*p*-terphenyl, since 4-amino-*p*-terphenyl hydrochloride has an extremely low solubility and the extract contained only traces of this isomer, for which a small correction was then applied.

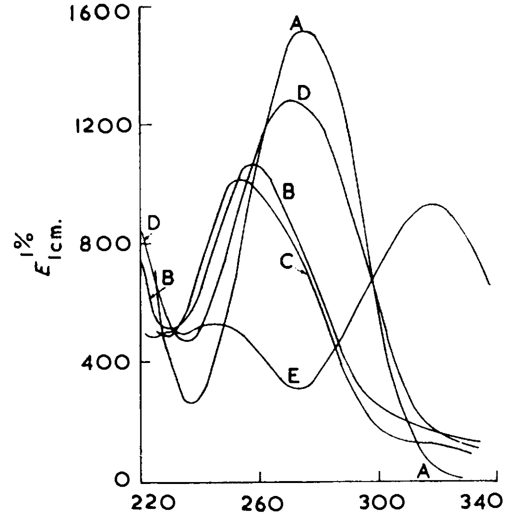

FIG. 1.

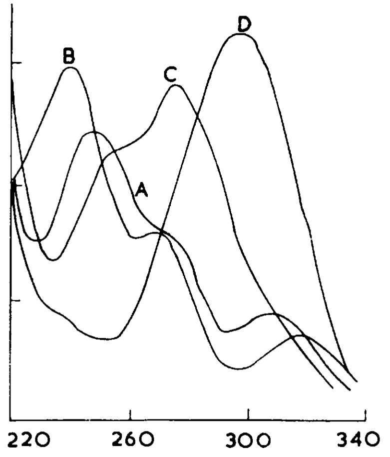

FIG. 2.

FIG. 1. Ultraviolet spectra (A) *p*-terphenyl and its (B) 2-, (C) 2′-, (D) 3-, and (E) 4-nitro-derivative in cyclohexane.

FIG. 2. Ultraviolet spectra of (A) 2-, (B) 2′-, (C) 3-, and (D) 4-amino-*p*-terphenyl in cyclohexane.

Calculation of the Isomer Ratios.—The method given by Friedel and Orchin [16] was used to calculate the isomer ratios from the spectroscopic data. For a quaternary nitration mixture, the optical density of a solution (7—8 × 10^{-4}% w/v) in cyclohexane was measured at 254, 275, and 318 mμ (the wavelengths at which the 2′-nitro-isomer, the hydrocarbon, and the 4-nitro-isomer give strong absorption maxima). The composition of the binary amine mixture was similarly solved by measuring the optical density of a solution (7—8 × 10^{-4}% w/v) in cyclohexane at 230 and 260 mμ, and using the calibration spectra shown in Fig. 2.

Accuracy of Results.—The accuracy of the isomer ratios in Table 1 was checked in three ways.

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[16] Friedel and Orchin, " Ultra-violet Spectra of Aromatic Compounds," Chapman and Hall, London, 1951, p. 29.

(i) Quaternary mixtures of known composition, prepared from the pure components, were treated as if they were nitration products. Table 4 summarises the results obtained from these synthetic mixtures.

TABLE 4.

Expt.		Proportions of isomers (%) 2	2′	4
	Theor.	26·7	13·3	60·0
S 5	Found	23	13	64
S 6	,,	25	14	61
	Mean	24	13·5	62·5
	Theor.	40·0	20·0	40·0
S 2	Found	35	20	45
S 3	,,	40	21	39
S 4	,,	37	20	43
	Mean	37·3	20·3	42·3

The two sets of synthetic mixtures in Table 4 may be considered as typical products from nitration in acetic acid at 20° and in acetic anhydride at 0° respectively. From the limited range of results available, it is indicated that a correction of 5% is required for the *ortho* (2- + 2′-) and *para* (4-) percentage compositions. The normalised percentage compositions of the 2- and 2′-isomers would then require a correction of 2%. If these corrections were justifiable on a statistical basis and were made to the results in Table 1, the general picture as regards the ratios of substitution at the *ortho*- and the *para*-positions in the molecule of *p*-terphenyl, under the various conditions of nitration, would not however be significantly changed.

(ii) The results from actual nitration mixtures (and synthetic mixtures) were also checked by determining the recovery, *i.e.*, the ratio of the sum of the calculated weights of the components in a mixture to the known weight of the mixture used. Quaternary and amine mixtures gave, respectively, recoveries of 95·2 and 100·2% (standard deviation 1·2 and 1·2).

(iii) The results were tested in the manner described by Cadogan, Hey, and Williams.[17] Amine mixtures gave a considerable error (about 8%) in the calculated absorption in the region of 295 mμ. This error was caused by an average of about 2% of 4-amino-*p*-terphenyl. The presence of this compound had not been considered in the initial calculation, and recalculation allowing for this isomer then gave a curve (X) having only a small scatter about the arithmetical mean of the percentage errors. Some typical results for the arithmetical mean are given: N 3, +1·7; N 14, +0·6; S 2, −0·7. Standard deviations were 0·7, 1·1, and 0·8, respectively. Any 3-nitro-*p*-terphenyl formed on nitration would arise as the free base in the amine mixture, and if present, should have been readily detected in curve X, especially in the region 270—300 mμ (cf. Fig. 2). Since there was no evidence for extraneous material, it can be taken that the amount of 3-nitro-*p*-terphenyl formed on nitration of *p*-terphenyl is too small for detection. The percentage error–wavelength curves were equally satisfactory for the quaternary mixtures. Some arithmetic means are quoted: N 2, −1·0; N 5, +2·4; S 5, +2·4. Standard deviations were 0·8, 2·1, and 2·2, respectively. The 3-nitro-isomer would in this case be more difficult to detect (cf. Fig. 1), since unchanged hydrocarbon might mask its presence.

Nitration Procedure and Reduction of the Nitro-compounds to the Amines.—The total volume of the nitration mixture, after addition of the fuming nitric acid to *p*-terphenyl (0·25 g.) dissolved in the appropriate solvent, was 385 ml. With acetic acid as solvent, nitration at 20° required 30 ml. of nitric acid, added as a solution of 1 part by vol. of nitric in 1 part of acetic acid (1 in 2 dilution). With acetic anhydride as solvent, nitration at 0°, 20°, 40°, and 80° required respectively, 1·0, 0·5, 0·3, and 0·4 ml. of nitric acid, added as a solution of 1 part of acid in 9 parts by vol. of acetic anhydride (1 in 10 dilution). After 24 hr., water (2·7 l.) was added and the suspension was placed in a refrigerator for 12 hr. in order to precipitate all the material. The product was then filtered off. For nitration in acetic anhydride, the addition of water gave two layers. This inhomogeneous mixture was set aside for 1 hr., then agitated to achieve a homogeneous aqueous phase which was then placed in a refrigerator. With either solvent, successful nitrations, *i.e.*, resulting in about 50% nitration of the *p*-terphenyl, gave a product having an upper m. p. of about 180°. A small portion was retained for spectroscopic determination of the ratio of nitration at the 4- and combined 2- and 2′-positions. The remainder (*ca.* 0·2 g.), dissolved in ethyl acetate (50 ml.), was reduced with

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[17] Cadogan, Hey, and Williams, *J.*, 1954, 794.

hydrogen for 3—4 hr. at room temperature in the presence of Adams catalyst (0·01—0·015 g.). The catalyst was then filtered off and the fluorescent filtrate evaporated to dryness on a water bath. The residue was boiled for 30 min. with 1·2N-aqueous hydrochloric acid (25 ml.), and the suspended material filtered off while the mixture was hot. The filtrate was just neutralised with 2N-sodium hydroxide, and the precipitated amines (0·02—0·05 g.) were filtered off and washed once with water.

Effect of Added Salts.—(1) *Sodium nitrate.* *p*-Terphenyl was nitrated in acetic anhydride as described above, but the nitric acid, before dilution, contained dissolved anhydrous sodium nitrate. It was possible to correlate in a semiquantitative way the *upper* m. p. of a nitration product with the degree of nitration achieved. On use of nitric acid containing, before dilution, 0·0165M-nitrate, the products recovered from nitrations at 0° and 20° were both virtually unchanged *p*-terphenyl. Two experiments with nitric acid containing 0·000165M-nitrate gave, at 0°, products having upper m. p.s of 197° and 194°, *i.e.*, equivalent to about 22% nitration; and similarly at 20° the products had upper m. p.s of 204° and 200°, *i.e.*, equivalent to about 12% nitration. Nitration in acetic acid at 20° was similarly retarded by 0·000165M-nitrate (m. p. of product 197°).

(2) *Sodium perchlorate.* The m. p. of a product from a nitration in acetic anhydride or acetic acid which has resulted in about 50% nitration is 180—182°. On addition of 0·000165M-perchlorate to nitrations in acetic acid at 20°, acetic anhydride at 0°, and acetic anhydride at 20°, the m. p.s of the products were 181°, 180°, and 183°, *i.e.*, the degree of nitration was unaltered by the presence of the neutral salt.

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