110. *Homolytic Aromatic Substitution. Part XXI.* The Arylation of Benzotrihalides.*

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Experiments have been carried out on the phenylation and *p*-nitrophenylation of benzotrichloride with benzoyl peroxide and *p*-nitrobenzoyl peroxide respectively. The reaction of benzotrifluoride with benzoyl peroxide has also been investigated. The ratios of the isomeric arylbenzotrihalides obtained in these reactions have been determined with the aid of infrared spectroscopy and gas–liquid chromatography. The results show significant differences from those reported by other workers. In particular, the absence of *ortho*-substitution in the phenylation, and of *para*-substitution in the *p*-nitrophenylation, of benzotrichloride, reported by Dannley and Sternfeld, are not substantiated.

Experiments on the homolytic arylation of benzotrihalides have been reported by two groups of workers. Dannley and Sternfeld[1] investigated the thermal decomposition of benzoyl peroxide in benzotrifluoride, which was found to give negligible reaction at the trifluoromethyl group but gave a mixture of the three isomeric trifluoromethylbiphenyls in 50% yield. The composition of the mixture was reported as *ortho* 18%, *meta* 40%, and *para* 42%. In similar reactions of benzoyl peroxide, *p*-chlorobenzoyl peroxide, and *p*-nitrobenzoyl peroxide with benzotrichloride, these workers reported the total absence of substitution at the *ortho*-position, a decrease in reaction at the side-chain (57, 16, and 0% respectively), and an increase in substitution at the *meta*-position (60, 83, and 100% respectively). The phenylation of benzotrifluoride by means of both benzoyl peroxide and

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* Part XX, *J.*, 1960, 3787.

[1] Dannley and Sternfeld, *J. Amer. Chem. Soc.*, 1954, **76**, 4543.

N-nitrosoacetanilide has also been reported by Rondestvedt and Blanchard[2] and the products from both reactions were reported to have the composition *ortho* 20%, *meta* 40%, and *para* 40%, in good agreement with the results obtained by the earlier workers. In addition, the total rate factor for the phenylation of benzotrifluoride with respect to benzene was shown to be 0·99 by means of competitive experiments with pyridine. More recently Dannley, Weigand, and Pavlos[3] have reported the reactions of *p*-methoxy- and *m*-nitrobenzoyl peroxide with benzotrichloride which gave, respectively, 51% and 62% substitution at the *meta*-position and 49% and 38% substitution at the *para*-position. Again, in neither case was any substitution at the *ortho*-position observed. The above results appeared to show a number of unusual features and for this reason it was considered desirable to re-investigate some of these reactions.

The steric inhibition to free-radical attack at the *ortho*-position with reference to a large substituent has been well recognised,[4,5] but the complete inhibition of reaction at the *ortho*-position with respect to the trichloromethyl group with phenyl, *p*-chlorophenyl, and *p*-nitrophenyl radicals is very surprising. Further, the reported occurrence of 100% substitution at the *meta*-position in the *p*-nitrophenylation of benzotrichloride is a unique observation. The results now reported on the phenylation and *p*-nitrophenylation of benzotrichloride and on the phenylation of benzotrifluoride reveal some marked differences from those reported by the earlier workers.

The reactions of benzoyl peroxide and *p*-nitrobenzoyl peroxide with benzotrichloride were carried out at 80° with a molar ratio of 0·025 : 1 and 0·018 : 1 respectively. Those carried out by Dannley and Sternfeld[1] were conducted at 75° and at 100° with molar ratios of 0·125 and 0·0625 respectively. The reaction with benzotrifluoride was carried out at 80° with a molar ratio of 0·018 : 1. The same experiment was carried out by Dannley and Sternfeld[1] at 75° and at 100° with a molar ratio of 0·0625 : 1 and by Rondestvedt and Blanchard[2] at 80—100° with a molar ratio of 0·030 : 1. The products were worked up by methods similar to those used by the previous investigators. The biaryl products from the reactions with benzotrichloride were hydrolysed to the corresponding arylbenzoic acids, which were then esterified with diazomethane. The mixtures of methyl biphenylcarboxylates were analysed by gas–liquid chromatography and those of the methyl *p*-nitrobiphenylcarboxylates by infrared spectroscopy. The mixtures of trifluoromethylbiphenyls were isolated by distillation and analysed by gas–liquid chromatography. The previous workers used infrared spectroscopy for all their analyses.

EXPERIMENTAL

Preparation of Reagents.—Benzoyl peroxide and nitrobenzene were purified as described in Part II.[6] *p*-Nitrobenzoyl peroxide was prepared by Hey and Walker's method.[7] 1,1,2,2-Tetrachloro-1,2-diphenylethane, m. p. 160—161°, was prepared by Fuson and Ross's method.[8] Benzotrichloride and benzotrifluoride were dried ($CaCl_2$), filtered, and distilled in a 4 ft. helix-packed column fitted with a heating jacket. The former was collected at 96°/18 mm. and the latter at 102·5°/760 mm. 2-, 3-, and 4-Trifluoromethylbiphenyl were supplied by Professor J. C. Tatlow of the University of Birmingham, and had m. p. 15° (b. p. 102—103°/8 mm.), m. p. 26·5°, and m. p. 70° respectively.

Isomeric Methyl Biphenylcarboxylates.—Methyl biphenyl-2-carboxylate was prepared by Grieve and Hey's method,[9] the crude ester being hydrolysed to biphenyl-2-carboxylic acid, m. p. 114°, which was re-esterified with diazomethane. The pure ester had b. p. 96—98°/0·1 mm., n_D^{18} 1·5855 (Found: C, 79·1; H, 5·7. Calc. for $C_{14}H_{12}O_2$: C, 79·3; H, 5·7%). In a similar

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[2] Rondestvedt and Blanchard, *J. Org. Chem.*, 1956, **21**, 229.
[3] Dannley, Weigand, and Pavlos, 136th Meeting Amer. Chem. Soc., Sept., 1959, 18P.
[4] Cadogan, Hey, and Williams, *J.*, 1953, 3412; 1954, 3352.
[5] Hey, Pengilly, and Williams, *J.*, 1956, 1463.
[6] Augood, Hey, and Williams, *J.*, 1952, 2094.
[7] Hey and Walker, *J.*, 1948, 2216.
[8] Fuson and Ross, *J. Amer. Chem. Soc.*, 1933, **55**, 722.
[9] Grieve and Hey, *J.*, 1938, 111.

reaction methyl *m*-aminobenzoate hydrochloride (65 g.) was diazotised and in reaction with benzene gave crude methyl biphenyl-3-carboxylate (7·8 g.) as a yellow oil, b. p. 180—185°/15 mm. After purification on an alumina column with benzene–light petroleum as eluent, the oil (7·5 g.) was hydrolysed with aqueous sodium hydroxide to biphenyl-3-carboxylic acid, m. p. 161° (from benzene). Esterification with diazomethane gave the *methyl ester* (3·41 g.), b. p. 88—89°/0·05 mm., which solidified. Recrystallisation from light petroleum (b. p. 40—60°) gave needles, m. p. 48—49° (Found: C, 79·1; H, 5·8. $C_{14}H_{12}O_2$ requires C, 79·3; H, 5·7%). Methyl biphenyl-4-carboxylate was prepared by two methods: (*a*) 4-Methylbiphenyl, prepared by Gomberg and Pernert's method,[10] was oxidised with potassium permanganate to biphenyl-4-carboxylic acid, m. p. 222° (from ethanol), esterification of which by the Fischer–Speier method gave the methyl ester, m. p. 116·5° (from aqueous methanol). (*b*) Diazotised methyl *p*-aminobenzoate (50 g.) and benzene, as described above for the corresponding reaction with the *ortho*- and *meta*-isomers, gave a crude methyl ester, b. p. 155—165°/20 mm., which solidified. Four recrystallisations from methanol gave the pure ester (10·64 g.), m. p. 116·5° alone and on admixture with the compound prepared by method (*a*) (Found: C, 79·0; H, 5·7%).

Methyl 4′-*Nitrobiphenyl*-2-*carboxylate*.—2-Methyl-4′-nitrobiphenyl (8 g.), kindly supplied by Dr. J. K. Hambling, in 2% aqueous potassium permanganate (600 ml.) was heated with stirring on a steam-bath for 24 hr. Sulphur dioxide was passed into the cooled solution and the precipitated acid was collected, dried, and crystallised from ethanol (7 g.; m. p. 226—227°). Esterification with diazomethane gave methyl 4′-nitrobiphenyl-2-carboxylate, m. p. 78° (from ethanol) (Found: C, 65·3; H, 4·4; N, 5·1. Calc. for $C_{14}H_{11}NO_4$: C, 65·4; H, 4·3; N, 5·4%). Dannley and Sternfeld [1] reported m. p. 75—76°.

Methyl 4′-*Nitrobiphenyl*-3-*carboxylate*.—4′-Nitrobiphenyl-3-carboxylic acid was prepared by two methods: (*a*) Biphenyl-3-carboxylic acid (2·5 g.), prepared as described above, in a mixture of fuming nitric acid (3·5 ml.) and glacial acetic acid (10 ml.), was boiled under reflux for 2 hr. The mixture was cooled to 0° and the solid product was collected, washed with water, and crystallised from ethanol to give 4′-nitrobiphenyl-3-carboxylic acid (0·5 g.), m. p. 232° (Found: N, 5·2. Calc. for $C_{13}H_9NO_4$: N, 5·8%). (*b*) *m*-Toluidine (107 g.) in concentrated hydrochloric acid (185 ml.) and water (50 ml.) was cooled in ice–salt and diazotised with sodium nitrite (70 g.) in water (90 ml.). The resulting solution after filtration was added slowly to stirred nitrobenzene (1000 ml.) and 40% aqueous sodium hydroxide (275 ml.) at 5°. After 3 hr. the temperature was allowed to rise to room temperature and stirring was continued for 48 hr. The nitrobenzene layer was separated, washed with dilute hydrochloric acid and then with water, and dried ($CaCl_2$). Excess of nitrobenzene was removed by distillation and the tarry residue was extracted with light petroleum (b. p. 60—80°; 6 × 100 ml.). Removal of the solvent by distillation left a red oil, which was distilled under reduced pressure. The fraction, b. p. 190—210°/15 mm., was chromatographed on an alumina column and eluted with benzene. Removal of the solvent from the eluate gave a red oil, which was further purified by shaking it in benzene solution with concentrated sulphuric acid (8 × 5 ml.). The resulting yellow solution was washed with water and dried (Na_2SO_4). Removal of the benzene left a yellow oil, which was distilled at 0·05 mm. The main distillate was collected at 98—100° as a pale yellow oil (6·4 g.). A second fraction was collected at 116—118° and solidified (1·85 g.); on recrystallisation from light petroleum (b. p. 60—80°) this gave 3-*methyl*-4′-*nitrobiphenyl* in pale yellow needles, m. p. 55° (Found: C, 73·0; H, 5·4; N, 6·2. $C_{13}H_{11}NO_2$ requires C, 73·2; H, 5·2; N, 6·6%). A further quantity of 3-methyl-4′-nitrobiphenyl (0·4 g.) separated gradually from the main distillate, which consisted of a mixture of the isomeric 3-methylnitrobiphenyls. 3-Methyl-4′-nitrobiphenyl (0·5 g.) in glacial acetic acid (10 ml.) was heated on a steam-bath with stirring and oxidised by the slow addition of chromium trioxide (0·5 g.) in the same solvent (150 ml.). Stirring of the hot solution was continued overnight, after which it was added to water (500 ml.) and cooled to 5°. The precipitated solid was collected, washed with water, and shaken with saturated aqueous sodium hydrogen carbonate (100 ml.). After filtration from unchanged 3-methyl-4′-nitrobiphenyl, acidification of the solution gave 4′-nitrobiphenyl-3-carboxylic acid (0·1 g.), m. p. 230—231° alone and on admixture with the acid prepared by method (*a*) above. A similar oxidation was carried out with aqueous potassium permanganate.

Esterification of the acid with ethereal diazomethane in the normal manner gave the methyl ester, m. p. 116—117° (from ethanol), in 95% yield. Dannley and Sternfeld [1] reported m. p. 112·5—113°.

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[10] Gomberg and Pernert, *J. Amer. Chem. Soc.*, 1926, **48**, 1372.

Methyl 4'-Nitrobiphenyl-4-carboxylate.—4'-Nitrobiphenyl-4-carboxylic acid, m. p. 338—340°, was prepared (*a*) by the successive nitration and oxidation of 4-methylbiphenyl,[11] and (*b*) by the preparation of 4-methyl-4'-nitrobiphenyl from *p*-toluidine and nitrobenzene followed by oxidation.[11] Esterification of the acid with ethereal diazomethane gave the methyl ester, m. p. 188—189° (from ethanol) (Found: C, 64·8; H, 4·7. Calc. for $C_{14}H_{11}NO_4$: C, 65·4; H, 4·3%). The same ester was prepared as follows: *p*-Nitroaniline (138 g.) in concentrated hydrochloric acid (270 ml.) and water (50 ml.) was diazotised in the normal manner with sodium nitrite (70 g.) in water (150 ml.), and added slowly to cold stirred methyl benzoate (900 ml.). To this vigorously stirred mixture, maintained at 0—5°, was added dropwise a solution of hydrated sodium acetate (320 g.) in water (800 ml.). After 2 hr. the temperature was allowed to rise to room temperature and stirring was continued for 36 hr. The organic layer was separated, washed with hydrochloric acid and with water, and dried (Na_2SO_4). The excess of methyl benzoate was removed by distillation and the residue was distilled at 0·05 mm., to give the following fractions: (*a*) b. p. 40—60° (5 ml.); (*b*) b. p. 155—170° (1·5 g.); and (*c*) b. p. 170—185° (*ca.* 50 g.). Fraction (*a*) consisted of methyl benzoate; fractions (*b*) and (*c*) were red oils, which solidified. Fraction (*c*) was digested with cold acetone and the extract was evaporated to dryness. Crystallisation of the residue from ethanol gave pale yellow methyl 4'-nitrobiphenyl-2-carboxylate (44 g.), m. p. 77—78° alone and on admixture with the compound prepared as above. The infrared spectra were identical. The same product was obtained from fraction (*b*). The residue, which remained after the digestion of fraction (*c*) with cold acetone, was boiled with ethanol and charcoal. After filtration and partial evaporation this solution deposited methyl 4'-nitrobiphenyl-4-carboxylate (5·8 g.), m. p. 188° (from ethanol) alone and on admixture with the compound prepared as above. The infrared spectra of the two samples were identical. The m. p. recorded by Dannley and Sternfeld [1] for the 4-carboxylate is 135—135·5°, and it was for this reason that two independent methods of preparation were undertaken.

Analytical Procedures.—The infrared spectrographic measurements were made on a Grubb–Parsons double-beam spectrometer, equipped with a rock-salt optical system and an automatic pen-recorder. Gas–liquid chromatographic analyses were carried out on a 4' glass column of 4 mm. diameter. Nitrogen was used as eluent and a Martin gas density balance was used as detector. Analysis of the esters was carried out at 245°, over Celite 545 coated with Apiezon grease (type L, 20% w/w). Analysis of the trifluoromethylbiphenyls was carried out at 135° over an Epikote resin (A.C.D.S. 834) as stationary phase. Retention times were measured relative to n-hexadecane.

The Reaction between Benzoyl Peroxide and Benzotrichloride. Preliminary Experiments.—It was shown that benzotrichloride is converted quantitatively into benzoic acid by boiling it under reflux with an excess of 10% aqueous sodium hydroxide for 12 hr. and that the benzoic acid isolated can be converted quantitatively into its methyl ester with diazomethane. The mixtures of isomeric trichloromethylbiphenyls formed in the phenylation of benzotrichloride were boiled under reflux with alkali twice, in order to ensure complete hydrolysis. The quantitative esterification of the acids was established by the conversion of a mixture of benzoic acid and the three biphenylcarboxylic acids into a mixture of the four esters with diazomethane. The methyl benzoate could be distilled at 76—80°/12 mm., whereas the biphenyl esters distilled at 70—80°/0·05 mm. The weights of the two fractions confirmed that the esterifications and separation were quantitative. Examination of the vapour-phase chromatograms showed the absence of methyl methoxybenzoates in the products obtained from the phenylation of benzotrichloride at 80° with benzoyl peroxide, when they were worked up by hydrolysis and esterification. Methyl methoxybenzoates could be formed by hydrolysis and subsequent methylation of the products of benzoyloxylation of benzotrichloride. 1,1,2,2-Tetrachloro-1,2-diphenylethane was shown to be stable to boiling 10% aqueous sodium hydroxide for 14 hr.

Reactions with Benzoyl Peroxide.—Experiments 1—6 (see Table 1) were carried out with benzoyl peroxide (6 g.) in benzotrichloride (200 g.) at 80° for 72 hr. The flask was fitted with an air-condenser and calcium chloride guard-tube. The mixture was then extracted with cold saturated aqueous sodium hydrogen carbonate (5 × 50 ml.) to remove free benzoic acid, and the organic layer was washed with water and dried ($CaCl_2$). The aqueous layer was shaken with benzene and these washings were added to the organic layer. The benzoic acid was recovered from the combined alkaline washings by acidification and extraction with ether. The main organic layer was distilled slowly using a 25 cm. helix-packed column surrounded by

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[11] Grieve and Hey, *J.*, 1932, 1891, 1893.

a heating jacket. Benzene was collected at atmospheric pressure and the excess of benzotrichloride at 20 mm. The residue was boiled under reflux twice with 10% aqueous sodium hydroxide for 14 hr. When cold, the mixture was extracted with benzene and the organic layer separated. The alkaline layer was acidified with hydrochloric acid, and the precipitated solid was digested with aqueous sodium hydrogen carbonate until it was alkaline. This mixture was heated to coagulate inorganic matter, cooled, and filtered. The filtrate was acidified and extracted with ether, and the acidic residue obtained on removal of the solvent at room temperature was esterified with an excess of ethereal diazomethane. After removal of ether and excess of diazomethane the residual esters (*ca.* 5 ml.) were transferred to a micro-distillation flask and distillation gave two fractions: (*a*) b. p. 76—80°/12 mm. and (*b*) b. p. 70—80°/0·05 mm. (see Table 1). A small residue was left which did not distil at 150°/0·05 mm.

TABLE 1.

Experiment no.:	1	2	3	4	5	6
Free benzoic acid (g.)	0·49	0·51	—	0·48	—	—
Chlorobenzene (g.)	—	—	2·42	—	2·40	2·45
Tetrachlorodiphenylethane (g.)	2·04	2·28	2·28	2·52	2·25	2·32
Biaryls (g.)	0·756	0·854	0·821	0·721	0·850	0·885
Residue (g.)	0·118	0·121	0·219	0·290	0·219	0·179

The organic layer from the hydrolysis was dried ($CaCl_2$) and the solvents were removed by distillation. The residue was adsorbed on alumina and eluted, first with light petroleum (b. p. 60—80°) which gave an orange solid, secondly with benzene which gave a dark red tar, and thirdly with chloroform which gave a dark tar. Recrystallisation of the orange solid, first, from ethanol and finally from glacial acetic acid gave tetrachlorodiphenylethane, m. p. 155°, which was not depressed on admixture with an authentic specimen (m. p. 160—161°) (Found: C, 52·4; H, 3·2; Cl, 44·3. Calc. for $C_{14}H_{10}Cl_4$: C, 52·5; H, 3·2; Cl, 44·3%). The infrared spectra of the two samples were identical.

In experiments 3, 5, and 6, in which the chlorobenzene formed was estimated, the benzotrichloride was removed by distillation under reduced pressure *without* previous removal of the benzoic acid by extraction with sodium hydrogen carbonate solution. The first 25—30 ml. of benzotrichloride were collected separately and it was assumed that any chlorobenzene formed would be found in this fraction. The fraction was diluted with light petroleum (10 ml.; b. p. 100—120°), and the light petroleum was slowly distilled off. This process was repeated six times and the total distillate was treated with concentrated sulphuric acid and fuming nitric acid to convert any chlorobenzene into 1-chloro-2,4-dinitrobenzene, which was collected and weighed. The method was tested with mixtures of known composition and a small correction factor was applied in order to allow for the non-quantitative nature of the method. The results obtained in Experiments 1—6 are given in Table 1. These results correspond to 66% of side-chain attack and 34% of nuclear attack. The procedure described above does not permit the measurement of the amount of benzoic acid formed by the hydrolysis of esters, since benzotrichloride itself is readily hydrolysed and any benzoic acid formed by the hydrolysis of residual solvent is obtained together with any formed from esters.

Determination of the Isomer Ratios in the Methyl Biphenylcarboxylates derived from the Products of the Phenylation of Benzotrichloride.—(a) *Infrared method.* Examination of the spectra of methyl biphenyl-2-carboxylate as a liquid film and of the 3- and 4-isomers as Nujol mulls led to the selection of the following wavelengths for analytical purposes: *ortho*, 794·9 cm.$^{-1}$, *meta*, 845·2 cm.$^{-1}$, *para*, 863·5 cm.$^{-1}$. Nitromethane was used as solvent but analysis of mixtures of known composition revealed that this method afforded only a determination of the *para*-isomer with any degree of accuracy (±4%). (b) *Gas–liquid chromatographic method.* Retention volumes were determined in turn for n-hexadecane and the three methyl biphenylcarboxylates. Determinations were then made with the products derived from the phenylation of benzotrichloride. The accuracy of the method was determined by its application to the analysis of a typical mixture of known composition. The results obtained are given in Table 2.

The Reaction between p-*Nitrobenzoyl Peroxide and Benzotrichloride.*—In experiments 7—10 *p*-nitrobenzoyl peroxide (6 g.) was allowed to decompose in benzotrichloride (200 g.) at 80° for 72 hr. as in the preceding experiments. The mixture was extracted with aqueous sodium hydrogen carbonate (6 × 50 ml.) and acidification of the extract gave *p*-nitrobenzoic acid,

m. p. 235—236°. Excess of benzotrichloride was removed under reduced pressure from the dried ($CaCl_2$) organic layer, and the residue was boiled under reflux twice with 10% aqueous sodium hydroxide (100 ml.) for 12 hr. The alkaline layer was separated, diluted, acidified with hydrochloric acid, and redigested with sodium hydrogen carbonate solution, after which it was boiled (to coagulate inorganic matter), cooled, and filtered. Acidification of the filtrate gave a precipitate, which was extracted with ether and then with chloroform to remove all the 4′-nitrobiphenyl-4-carboxylic acid. Evaporation of the combined extracts left a light-brown solid, which was dried *in vacuo* and then dissolved in a large excess of ether to which was added an excess of ethereal diazomethane. After 14 hr. at room temperature the solution was concentrated to small bulk (10—15 ml.) and then distilled. Two main fractions were collected: (*a*) b. p. 76—80°/12 mm. and (*b*) b. p. 80—100°/0·05 mm. Fraction (*a*) consisted of methyl benzoate. Fraction (*b*) contained the biaryls, the final traces of which had to be removed from the stem of the distillation flask by means of a small flame. The solid which came over at this stage was identified as methyl 4′-nitrobiphenyl-4-carboxylate, m. p. 186—188° (from acetone) (mixed m. p. and infrared spectrum). There was a small residue which did not distil at 150°/0·05 mm. The organic layer from the hydrolysis was dried ($CaCl_2$) and evaporated, and the residue was chromatographed as described above for the corresponding reaction with benzoyl peroxide. The product was an orange-red tar (1·5 g.), from which no solid could be obtained. The results obtained in experiments 7—10 are given in Table 3.

TABLE 2.

Mixture		*ortho*-Isomer (%)	*meta*-Isomer (%)	*para*-Isomer (%)	*para*-Isomer by infrared analysis (%)
3		11·9	48·2	39·9	36·0
4		11·7	49·5	38·8	44·0
Mean		11·8	48·8	39·3	40·0
Synthetic mixture	Known	10·1	60·5	29·3	29·3
	Found	11·5	56·9	31·6	28·0

TABLE 3.

Experiment no.:	7	8	9	10
Free *p*-nitrobenzoic acid (g.) ...	2·05	2·22	2·02	1·99
Biaryls (g.)	2·06	1·97	2·10	1·97
Residue (g.)	0·094	0·084	0·079	0·106

Determination of the Isomer Ratios in the Methyl Nitrobiphenylcarboxylates derived from the p-*Nitrophenylation of Benzotrichloride.*—Examination of the spectra of the three isomeric 4-nitro-esters as Nujol mulls suggested the following wavelengths for analytical purposes: *ortho* 701·3 cm.$^{-1}$, 800·0 cm.$^{-1}$; *meta* 763·4 cm.$^{-1}$, 843·7 cm.$^{-1}$; *para* 778·1 cm.$^{-1}$. Dimethylormamide was used as the solvent. The spectra of the mixtures of nitro-esters did not reveal the presence of any bands other than those known to be due to the isomers. Examination of the spectra of mixtures of known composition showed that the concentration of the *ortho*-isomer in the reaction mixtures could not have been greater than 3%, and that difficulties would be encountered in the analysis of the content of the *meta*-isomer. Accordingly, determinations were made of the content of the *para*-isomer, as previously carried out for the methyl biphenylcarboxylates, and the content of the *meta*-isomer was calculated by difference on the assumpton that 3% of the *ortho*-isomer was present. In this manner the values obtained for the *para*-isomer formed in experiments 7, 8, 9, and 10 were found to be 34·2, 29·5, 35·2, and 31·5% (mean 32·5%). These results are considered to be accurate only to ±4%. The isomer ratios resulting from the attack of *p*-nitrophenyl radicals on benzotrichloride may therefore be represented as follows: *ortho* $\ngtr$3%; *meta* 64·5% (±4); *para* 32·5% (±4).

The Reaction between Benzoyl Peroxide and Benzotrifluoride.—Reactions 11—14 were carried out with benzoyl peroxide (6 g.) in benzotrifluoride (200 g.) at 80° for 72 hr. as described above for the reactions with benzotrichloride. Free benzoic acid was removed by extraction with aqueous sodium hydrogen carbonate as previously described, and the excess of benzotrifluoride was removed by distillation at atmospheric pressure. The residue was boiled under reflux with 10% aqueous sodium hydroxide (100 ml.) for 14 hr. and extracted as previously described. The alkaline layer was acidified and the liberated acid was extracted with ether. The organic layer from the hydrolysis was dried (Na_2SO_4) and after removal of benzene (wash-liquid) at atmospheric pressure the residue was distilled to give three fractions: (*a*) b. p. 20°/15 mm.; (*b*) b. p. 102—120°/10 mm. (*ca.* 4·5 g.); and (*c*) b. p. 70—90°/0·05 mm. (*ca.* 1·5 g.). Fraction (*a*) was benzotrifluoride. Fraction (*b*) contained the trifluoromethylbiphenyls. Fraction (*c*) solidified to a glass which was dissolved in benzene and chromatographed. Only a small quantity of solid (0·1 g.; m. p. 50—70°) was, however, recovered. The products obtained in these reactions are given in Table 4. The weight of benzoic acid formed by the hydrolysis of esters is included in this Table since, unlike benzotrichloride, benzotrifluoride is not readily hydrolysed under the conditions employed.

TABLE 4.

Experiment no.:	11	12	13	14
Free benzoic acid (g.)	0·74	0·65	0·71	0·67
Benzoic acid from esters (g.)	0·20	0·22	0·17	0·24
Trifluoromethylbiphenyls (g.)	4·605	4·617	4·801	4·129
Higher-boiling fraction (g.)	1·511	1·359	0·969	1·658
Residue (g.)	1·004	0·833	1·164	1·145

TABLE 5.

Mixture	*ortho*-Isomer (%)	*meta*-Isomer (%)	*para*-Isomer (%)
11	32·2	37·6	30·2
12	36·0	37·4	26·6
13	36·4	35·3	28·3
14	31·0	37·7	31·3
Mean	33·9	37·0	29·1
Synthetic mixture Known	40·3	40·9	18·8
Synthetic mixture Found	37·2	42·2	20·6

TABLE 6.

Mixture	*ortho*-Isomer (%)	*meta*-Isomer (%)	*para*-Isomer (%)
12	29·4	41·2	29·4
13	29·4	41·0	29·6
Mean	29·4	41·1	29·5

Determination of the Isomer Ratios in the Trifluoromethylbiphenyls obtained from the Phenylation of Benzotrifluoride.—(a) *Infrared method.* 2-Trifluoromethylbiphenyl was examined as a liquid film and the 3- and 4-isomerides as Nujol mulls. The following wavelengths were chosen for analytical purposes: *meta* 819·7 cm.$^{-1}$, 809·8 cm.$^{-1}$; *para* 842·2 cm.$^{-1}$. Nitromethane was used as solvent and analyses were carried out on the products of the four reactions and on a synthetic mixture of known composition. The results are given in Table 5.

(b) *Gas–liquid chromatographic method.* For details see above. The results are given in Table 6. The presence of a fourth component of unknown identity in these mixtures was revealed by the chromatograms, which contained a small extra peak. This is probably the explanation of the slight discrepancy between the results of the infrared and gas–liquid chromatographic analyses. The latter method is the more reliable, since each isomer is estimated separately and the result is therefore unaffected by the presence of impurities. In the infrared method, however, the amount of *ortho*-isomer is obtained by difference and the result may therefore be high, as it also includes the impurities. For this reason, the results obtained by the chromatographic method are accepted as the more accurate.

DISCUSSION

Dannley and Sternfeld[1] attributed the complete absence of substitution at the *ortho*-position with reference to the trichloromethyl group in the arylation of benzotrichloride to steric hindrance. A similar argument was put forward to account for the low yield (18%) of the *ortho*-isomer in the phenylation of benzotrifluoride. It has been shown that in the phenylation of t-butylbenzene the *ortho*-isomer constitutes some 24% of the mixture of t-butylbiphenyls.[4] In view of the comparative sizes of the groups $\cdot CMe_3$ and $\cdot CCl_3$, it would seem that the total absence of substitution at the *ortho*-position in benzotrichloride on steric grounds alone would be most improbable and the value now reported of 12% *ortho*-substitution appears more reasonable. The existence and concentration of this isomer in the product of the phenylation of benzotrichloride was established by means of gas–liquid chromatography on the mixture of isomeric methyl biphenylcarboxylates obtained from the trichloromethylbiphenyls by hydrolysis and esterification. The concentration of peroxide and of benzotrichloride employed (0·025 : 1) ensures that very little of the biphenylcarboxylic acids is formed by phenylation of the free benzoic acid resulting from the decomposition of the peroxide. The low yield reported for the *ortho*-isomer in the phenylation of benzotrifluoride by both Dannley and Sternfeld[1] (18%) and Rondestvedt and Blanchard[2] (20%), also attributed to steric hindrance, is again not in keeping with the values reported for *ortho*-substitution in t-butylbenzene[4] (24%), isopropylbenzene[5] (31%), and toluene[5] (66%). The higher figure now reported for phenylation at the *ortho*-position in benzotrifluoride, namely, 29·4%, seems to be more realistic. This figure was obtained by gas–liquid chromatography and is supported by the results of infrared analysis.

TABLE 7. *The arylation of benzotrihalides.*

X in Ph·CX$_3$	Radica	Ratio of isomers (%) *ortho*	*meta*	*para*	Method of analysis	Reference
F	Ph·	18	40	42	IR	Dannley & Sternfeld[1]
F	Ph·	20	40	40	IR	Rondestvedt & Blanchard[2]
F	Ph·	29·4	41·1	29·5	GLC	This work
Cl	Ph·	0	60	40	IR	Dannley & Sternfeld[1]
Cl	Ph·	12	49	39	GLC	This work
Cl	p-NO$_2$·C$_6$H$_4$·	0	100	0	IR	Dannley & Sternfeld[1]
Cl	p-NO$_2$·C$_6$H$_4$·	$\not> 3$	64·5 ± 4	32·5 ± 4	IR	This work

The extent of substitution at the *meta*-position in the arylation of benzotrichloride would be expected to be greater for *p*-nitrophenylation than for phenylation, as a result of the electrophilic character of the *p*-nitrophenyl radical. This increase was observed by Dannley and Sternfeld[1] and is confirmed in the present work. However, the exclusive *meta*-substitution reported by Dannley and Sternfeld[1] appears highly improbable, and the existence of appreciable simultaneous substitution at the *para*-position has now been established beyond doubt by the isolation of methyl 4′-nitrobiphenyl-4-carboxylate by hydrolysis and methylation of the product obtained from the *p*-nitrophenylation of benzotrichloride. These results are summarised in Table 7.

Side-chain attack in the arylation of benzotrichloride is important in phenylation (66% by weight of the total binuclear products), but appears to be absent in *p*-nitrophenylation. This is in agreement with earlier observations on the *p*-nitrophenylation of toluene.[12] No identifiable products were obtained from reaction at the side-chain in the phenylation of benzotrifluoride. Attempts to prepare 1,1,2,2-tetrafluorodiphenylethane gave, instead, 1,2-diphenyl-1,2-difluoroethylene, which might be susceptible to polymerisation. This may in fact account for the resinous material formed in the phenylation of benzotrifluoride. Dannley and Sternfeld[1] have, however, reported the isolation of very small quantities of difluorodiphenylmethane and fluorobenzene from the products of the phenylation of benzotrifluoride. Difluorodiphenylmethane in fact may be present in the eluates containing the *ortho*- and *meta*-phenylbenzotrifluorides reported in the present work, because a small additional peak was observed in the gas–liquid chromatogram.

Partial rate factors for the phenylation of benzotrifluoride may be calculated from the isomer ratios reported in this paper coupled with the value for ${}^{\mathrm{PhCF_3}}_{\mathrm{PhH}}K = 0{\cdot}99$ reported by Rondestvedt and Blanchard.[2] Thus:

$$F_o = 3 \times 0{\cdot}99 \times 0{\cdot}294 = 0{\cdot}87$$

$$F_m = 3 \times 0{\cdot}99 \times 0{\cdot}411 = 1{\cdot}21$$

$$F_p = 6 \times 0{\cdot}99 \times 0{\cdot}295 = 1{\cdot}76$$

[12] Augood and Williams, *Chem. Rev.*, 1957, **57**, 171.

On the other hand, partial rate factors for the phenylation of benzotrichloride are not available because the high incidence of side-chain attack renders an accurate determination of the rate ratio very difficult.

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