1075. *Homolytic Aromatic Substitution. Part XXIX.* The Photolysis of Triphenylbismuth in Aromatic Solvents.*

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Phenyl radicals have been shown to be formed by the photolysis of triphenylbismuth, and the phenylation of pyridine, toluene, and t-butylbenzene by this method has been studied. Partial rate factors have been measured for these reactions, and the small discrepancies exhibited between these and previous results on the phenylation of these compounds with benzoyl peroxide are discussed.

PHENYL radicals have been shown to be formed by the photolysis of some metal phenyls, namely, diphenylmercury[1,2] and tetraphenyl-lead.[2,3] This method of preparation of phenyl radicals has the advantage over other methods, such as the pyrolysis of benzoyl peroxide, that radicals are formed directly, without free-radical precursors, and it is therefore of interest to compare the results of phenylation of a range of aromatic compounds by this method with the corresponding results obtained by the use of benzoyl peroxide, which have been reported in earlier papers in this series.

Apart from diphenylmercury, tetraphenyl-lead, and, possibly, tetraphenyltin, it was expected that triphenylbismuth should readily undergo homolytic decomposition on photolysis in solution, since it is a typically covalent organometallic compound, and, of all the triphenyl derivatives of the elements of Group V, is the one which would be expected to have the weakest carbon–metal bond. These expectations were confirmed by trial experiments. Triphenylbismuth is an easily prepared crystalline solid which, unlike diphenylmercury, can be distilled without decomposition, and obtained highly pure. It is more soluble in organic solvents than is tetraphenyl-lead, and was therefore chosen as the most convenient metal phenyl on which to conduct a detailed investigation.

The proportions in which the isomeric products of nuclear phenylation are formed, and the relative reactivity of several aromatic compounds towards nuclear phenylation have been measured. It was not possible to use nitrobenzene as the reference compound for the determination of relative rates of phenylation, or indeed, to phenylate nitrobenzene, since triphenylbismuth did not undergo photolysis in solutions containing large quantities of nitrobenzene. This failure is probably attributable to the very strong absorption of ultraviolet light by nitrobenzene, which therefore acted as an internal filter and rendered the amount of light available to the organometallic compound insufficient to effect photodecomposition.

Pyridine was therefore used as the reference compound in competitive experiments, although it suffers from the disadvantage that, unlike nitrobenzene, it does not prevent the formation of appreciable quantities of high-boiling residues in phenylations. The results now reported must therefore be regarded as intrinsically less accurate and reliable than those previously reported on phenylation with benzoyl peroxide, in which nitrobenzene was used as the reference compound and the amounts of high-boiling residue formed were consequently very small.

Before any phenylations were carried out, it was necessary to ascertain the extent of photodecomposition of the aromatic solvents themselves, in the absence of any radical source, and the necessary preliminary experiments were therefore conducted. The only solvent investigated which was appreciably photolysed under the reaction conditions employed was chlorobenzene, and the attempt to study its phenylation was therefore abandoned. Since the presence of pyridine greatly reduced the extent of photolysis of

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* Part XXVIII, preceding paper.

[1] Razuvaev and Ol'dekop, *J. Gen. Chem. U.S.S.R.*, 1949, **19**, 711, 1485; 1951, **21**, 1225.

[2] Blair, Bryce-Smith, and Pengilly, *J.*, 1959, 3174.

[3] Leighton and Mortensen, *J. Amer. Chem. Soc.*, 1936, **58**, 448.

chlorobenzene, the photolysis of other aromatic compounds was carried out mainly in the presence of pyridine. The following systems were found to be suitable for phenylation, and were therefore studied: pyridine, pyridine–benzene, pyridine–toluene, pyridine–t-butylbenzene.

EXPERIMENTAL

Solvents.—Pyridine, benzene, toluene, and chlorobenzene were purified by standard methods as described in earlier papers in this series. t-Butylbenzene was prepared by Kharasch and Brown's method [4] and had b. p. 169°/760 mm. Biphenyl (B.D.H) was crystallised from ethanol and had m. p. 70°.

Organometallic Compounds.—A specimen of tetraphenyltin, kindly supplied by Dr. J. I. G. Cadogan, was crystallised from ethanol (m. p. 226°). Tetraphenyl-lead was prepared from phenylmagnesium bromide and lead chloride by Setzer, Leeper, and Gilman's method [5] (m. p. 228°; lit.,[5] m. p. 226°). Triphenylbismuth was prepared by an analogous method,[6,7] and had m. p. 77—78° (lit.,[6] m. p. 77—78°). It was stored in the dark, and all work with it conducted in a fume cupboard with a good draught in order to avoid its reputed unpleasant physiological effects. Diphenylmercury (B.D.H.) was crystallised from nitromethane after removal of insoluble impurities by filtration (m. p. 126°).

Reference Compounds.—Bibenzyl (Judex) (m. p. 51—52°) was crystallised from methanol. The specimens of 2-, 3-, and 4-phenylpyridine used had been prepared by Hey, Stirling, and Williams,[8] and those of 2-, 3-, and 4-methylbiphenyl by Hey, Pengilly, and Williams.[9]

Photolytic Experiments.—These were carried out by use of the apparatus and technique described previously.[10] Unchanged triphenylbismuth was separated from the phenylation products by distillation at 140°/0·01 mm., since it is much less volatile. The distillate was pure, and could be weighed to give the amount of unchanged triphenylbismuth directly. Neutral and basic portions of biaryl fractions obtained from competitive experiments were separated by acid-extraction as described by Augood, Hey, and Williams.[11] Bismuth-containing products were analysed by evaporation of a small portion to dryness with concentrated nitric acid and ignition of the residue to bismuth trioxide. This was dissolved in concentrated nitric acid and identified qualitatively, or estimated as described below.

Estimation of Bismuth.—Solutions of bismuth nitrate prepared as described above, or by solution of bismuth precipitated during photolytic experiments, in 100 ml. of 29% (w/v) nitric acid and dilution to 1 litre, were analysed by precipitation as the bismuth derivative of 8-hydroxyquinoline.[12] The precipitate was dissolved in concentrated hydrochloric acid and the regenerated 8-hydroxyquinoline quantitatively brominated with an excess of standard bromide–bromate solution. The excess of bromate was estimated iodometrically by addition of potassium iodide and hydrochloric acid, and titration of the liberated iodine with standard sodium thiosulphate. Trial experiments showed that the bromination of 8-hydroxyquinoline was instantaneous, so that the back-titration could be carried out immediately. The accuracy of the method was verified by the estimation of standard solutions of bismuth nitrate.

Photolysis of Solvents.—The solvents, or equimolar mixtures thereof, given in Table 1 (200 ml.) were photolysed under nitrogen. In no case were any condensible gases collected in the liquid-air trap, and the quantities of photo-products formed were very small, except when chlorobenzene was photolysed. With this exception, therefore, these products were not examined further. The distilled products were volatile at temperatures below 180°/0·01 mm.

The product from the photolysis of chlorobenzene was obtained as a black gum (b. p. >300°/0·1 mm.) from which brownish-yellow amorphous solids were obtained (C, 67·7—69·8; H, 3·4—4·5; Cl, 25·2—26·6%).

Attempted Pyrolysis of Organometallic Compounds in Aromatic Solvents.—In every case, the

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[4] Kharasch and Brown, *J. Amer. Chem. Soc.*, 1939, **61**, 2142.
[5] Setzer, Leeper, and Gilman, *J. Amer. Chem. Soc.*, 1939, **61**, 1609.
[6] Pietsch, *Ber.*, 1904, **4**, 4622.
[7] Manulkin and Tatarenko, *Zhur. obshchei Khim.*, 1951, **21**, 93.
[8] Hey, Stirling, and Williams, *J.*, 1955, 3963.
[9] Hey, Pengilly, and Williams, *J.*, 1955, 6.
[10] Hey, Shingleton, and Williams, *J.*, 1963, 1958.
[11] Augood, Hey, and Williams, *J.*, 1952, 2094.
[12] Sutton, " A Systematic Handbook of Volumetric Analysis," 13th Edn., Butterworths, London, 1955.

Table 1.

Solvent	Period of illumination (hr.)	Temp.	Colour of solvent after photolysis	Photo-products (g.)	
				Distilled	Undistilled
Pyridine[1]	14	100°	Dark red	0·042	0·003
Pyridine	4	100	Pale yellow	0·006	0·003
Chlorobenzene	10	80	Dark brown	0	1·920
Pyridine–chlorobenzene	10	80	Brown	0	0·428
Pyridine–benzene	5	80	Very pale yellow	0·084	0·038
Pyridine–toluene	10	80	,, ,,	0·026	0·083
Pyridine–t-butylbenzene	10	80	,, ,,	0·017	0·056
t-Butylbenzene	10	80	Bright yellow[2]	0·000	0·041

[1] Photolysed under air. [2] The colour was removed by the action of bromine in carbon tetrachloride.

organometallic compound was recovered unchanged after solutions of tetraphenyltin, tetraphenyl-lead, triphenylbismuth, and diphenylmercury in benzene, nitrobenzene, chlorobenzene, and pyridine had been boiled under reflux for 16—30 hr.

Preliminary Experiments on the Photolysis of Organometallic Compounds in Aromatic Solvents.—Solutions of the organometallic compound (4·0 g.) in the solvent (200 ml.) were photolysed for 6 hr. at 80°. The results are given in Table 2.

Table 2.

Photolysis of organometallic compounds in aromatic solvents.

Expt. no.	Organometallic compd.	Solvent	Products
1	Ph_4Sn	Pyridine	A little tin
2	Ph_3Bi	Nitrobenzene	No reaction
3	Ph_2Hg	,,	,,
4	Ph_4Pb	Pyridine	Lead; phenylpyridines
5	Ph_3Bi	,,	Bismuth; phenylpyridines
6	Ph_2Hg	,,	Mercury; phenylpyridines
7	Ph_2Hg	Benzene	Mercury; biphenyl

In Expts. 4, 5, and 6 the mixtures of 2-, 3-, and 4-phenylpyridine were obtained as colourless semi-solids (b. p. 68°/0·01 mm.). The elementary analyses and molecular weights agreed with those calculated for $C_{11}H_9N$. The biphenyl obtained in Expt. 7 had m. p. and mixed m. p. 70°, and an infrared spectrum identical with that of an authentic specimen.

Photolysis of Triphenylbismuth in Pyridine (100°).—In Expts. 8 and 9 triphenylbismuth (2·856 g.) was photolysed in pyridine (200 ml.) for 10 and 20 hr., respectively. The results are given in Table 3. The "precipitated residue" was the solid which separated from the residual liquid obtained after removal of the solvent. The undistilled residue consisted of material which was not volatile at 200°/0·01 mm. These two fractions were very similar; they were brown, amorphous, high-melting, bismuth-containing solids. The "precipitated residue" had m. p. 300° (Found: C, 18·6; H, 1·6; N, 3·7; Bi, 60·7%).

Table 3.

Photolysis of triphenylbismuth in pyridine.

Expt. no.	8	9	Expt. no.	8	9
Ph_3Bi decomposed (g.)	2·25	2·27	Precipitated residue (g.)	0·113	0·000
Ph_3Bi recovered (g.)	0·261	0·345	Benzene (g.)	0·232	*
Phenylpyridines (g.)	1·280	1·318	Liberated phenyl radicals accounted for as phenylpyridines (%)	54	55
Undistilled residue (g.)	0·772	0·574			

* Not estimated.

Benzene was present in the forerun to the main pyridine fraction in the first distillation. This fraction was analysed by gas–liquid chromatography with a Perkin-Elmer model 116 vapour fractometer and catharometer detector. The peak areas obtained were compared with those predicted from a calibration curve obtained by gas–liquid chromatography of standard solutions of benzene in pyridine, under precisely the same conditions.

The proportions of the 2-, 3-, and 4-isomers present in the phenylpyridine fractions were determined by ultraviolet spectrophotometry as described by Hey, Stirling, and Williams,[8] and the results are accurate to ±2%. The extinction coefficients of the mixtures from Expts. 8 and 9 were almost identical, and the mean values were therefore used in the calculations. The results are given in Table 4.

TABLE 4.

Composition of mixtures of isomeric phenylpyridines.

Wavelength (mμ)		252, 278	254, 276	256, 280	262, 282	258, 280	
Isomer (%)	2-	48·3	48·6	48·1	48·2	48·1	Mean 48
	3-	31·6	29·5	30·3	30·7	30·8	Mean 31
	4-	20·1	21·9	21·6	21·1	21·2	Mean 21

Competitive Phenylation of Benzene and Pyridine.—In Expts. 10 and 11, triphenylbismuth (2·856 g.) was photolysed in an equimolar mixture (200 ml.) of benzene and pyridine at 80° for 10 and 9 hr., respectively. The results are given in Table 5.

TABLE 5.

Competitive phenylation of benzene and pyridine with triphenylbismuth.

Expt. no.	10	11	Expt. no.	10	11
Ph_3Bi decomposed (g.)	2·13	1·78	Liberated phenyl radicals accounted for as biaryls (%)	48	50
Ph_3Bi recovered (g.) [1]	0·162	0·356			
Biphenyl (g.) [2]	0·485	0·438			
Phenylpyridines (g.) [3]	0·593	0·502	${}^{C_5H_5N}_{PhH}K$	1·22	1·14
Total residue (g.)	1·035	1·066	Mean	1·18	

[1] M. p. and mixed m. p. 77—78°. [2] M. p. and mixed m. p. 69° (Found: C, 93·0; H, 6·6. Calc. for $C_{12}H_{10}$: C, 93·4; H, 6·6%). [3] B. p. 68°/0·01 mm. (Found: C, 85·1; H, 5·9; N, 9·2. Calc. for $C_{11}H_9N$: C, 85·1; H, 5·9; N, 9·0%).

Competitive Phenylation of Toluene and Pyridine.—In Expts. 12 and 13, triphenylbismuth (5·713 g.) was photolysed in an equimolar mixture of toluene and pyridine (200 ml.) at 80° for 10 hr. The results are given in Table 6.

TABLE 6.

Competitive phenylation of toluene and pyridine with triphenylbismuth.

Expt. no.	12	13	Expt. no.	12	13
Ph_3Bi decomposed (g.)	3·31	3·20	Undistilled residue (g.)	1·239	1·128
Ph_3Bi recovered (g.) [1]	1·333	1·488	Liberated phenyl radicals accounted for as biaryls (%)	45	46
Methylbiphenyl fraction (g.) [2]	1·065	1·070			
Phenylpyridine fraction (g.) [3]	0·589	0·574			
Precipitated residue (g.) [4]	0·254	0·231	${}^{PhCH_3}_{C_5H_5N}K$	1·67	1·72
			Mean	1·69	

[1] M. p. and mixed m. p. 77—78°. [2] B. p. 90—95°/0·01 mm. (Found: C, 92·6; H, 7·3. Calc. for $C_{14}H_{14}$: C, 92·3; H, 7·7%). [3] B. p. 70°/0·02 mm. (Found: C, 85·0; H, 6·0; N, 8·7. Calc. for $C_{11}H_9N$: C, 85·1; H, 5·9; N, 9·0%). [4] M. p. >300° (Found: C, 35·5; H, 2·9; N, 2·6; Bi, 55·4%).

Rondestvedt and Blanchard,[13] and Hey, Pengilly, and Williams [9] obtained 15% and 13%, respectively, of bibenzyl from the products of the reaction of benzoyl peroxide with toluene by crystallisation from light petroleum (b. p. 40—60°) at −80°. Bibenzyl could not, however, be obtained by this method from the neutral products of Expts. 12 and 13. Although peaks due to 3- and 4-methylbiphenyl and bibenzyl could not be completely separated by gas–liquid chromatography, analysis of synthetic mixtures of known composition showed that $\nless 4\%$ of bibenzyl could be detected. Examination of the neutral products of Expts. 12 and 13 by this method provided no evidence for the presence of bibenzyl. The peak due to 2-methylbiphenyl was, however, well separated, and, by the use of synthetic mixtures of 2-, 3-, and 4-methylbiphenyl, it was shown that the amount of 2-methylbiphenyl present in mixtures containing all three isomers together with bibenzyl, could be accurately determined. The method of internal normalisation, with biphenyl as internal standard, was used.

In the infrared spectrum 3- and 4-methylbiphenyl have discrete absorption bands at 797 and 829 cm.$^{-1}$, respectively, and bibenzyl is transparent at these frequencies. The amounts

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[13] Rondestvedt and Blanchard, *J. Amer. Chem. Soc.*, 1955, **77**, 1769.

of these isomers present in mixtures containing them can therefore be obtained directly by infrared spectroscopy. The characteristic absorption band of 2-methylbiphenyl at 777·5 cm.$^{-1}$ coincides with absorption bands due to the other isomers, and cannot, therefore, be used for the estimation of this compound. The concentration of 2-methylbiphenyl can, however, be obtained by difference, provided the amount of bibenzyl present is known (*e.g.*, from the amount obtained by crystallisation at $-80°$). This method was used for the analysis of mixtures such as these by Hey, Pengilly, and Williams.[9] The proportion of 2-methylbiphenyl present in a mixture of the 2-, 3-, and 4-isomers can, however, now be measured separately, as described above, by gas–liquid chromatography. If, therefore, such a mixture is examined by both this and the infrared method, the two values obtained for the proportion of the 2-isomer present should agree only if bibenzyl is absent. Moreover, use of the value obtained by gas–liquid chromatography for the proportion of 2-methylbiphenyl enables the accuracy of the measurement of the proportions of the 3- and 4-isomers by infrared spectroscopy to be improved, since no parameter has then to be obtained by difference. These conclusions were verified by the use of a synthetic mixture of known composition which, together with the mixtures obtained from Expts. 12 and 13, were analysed as described. The results, which are given in Table 7, demonstrate that bibenzyl, if it occurs at all, is present to an extent of $\ngtr 3\%$.

TABLE 7.

Composition of mixtures of isomeric methylbiphenyls.

			Isomer (%)	
Mixture	Method	2-	3-	4-
Synthetic	Known composition	58·3	27·5	14·2
	i.r. alone	54·5	29·3	16·3
	g.l.c. alone	58·3	—	—
	i.r. + g.l.c.	58·3	27·4	14·3
Expt. 12	i.r. alone	60·1	24·8	15·1
	g.l.c. alone	57·0	—	—
	i.r. + g.l.c.	57·0	27·2	15·8
Expt. 13	i.r. alone	59·4	23·6	17·0
	g.l.c. alone	56·2	—	—
	i.r. + g.l.c.	56·2	27·0	16·8
Mean of Expts. 12 and 13	i.r. + g.l.c.	56·6	27·1	16·3

Competitive Phenylation of t-Butylbenzene and Pyridine.—In Expts. 14, 15, and 16, triphenylbismuth (5·715 g.) was photolysed in an equimolar mixture (200 ml.) of t-butylbenzene and pyridine at 80° for 5 hr. The results are given in Table 8.

TABLE 8.

Competitive phenylation of t-butylbenzene and pyridine with triphenylbismuth.

Expt. no.	14	15	16
Ph$_3$Bi decomposed (g.)	2·84	2·64	3·01
Ph$_3$Bi recovered (g.) [1]	2·012	2·220	2·152
t-Butylbiphenyls (g.) [2]	0·902	0·786	0·937
Phenylpyridines (g.) [3]	0·670	0·652	0·713
Undistilled residue (g.) [4]	1·048	1·279	1·039
Liberated phenyl radicals accounted for as biaryls (%)	45	44	44
$K^{\text{PhBu}}_{\text{C}_5\text{H}_5\text{N}}$	0·99	0·89	0·97
Mean	0·95		

[1] M. p. and mixed m. p. 77—78°. [2] B. p. 100°/0·1 mm. (Found: C, 91·3; H, 8·9. Calc. for $C_{16}H_{18}$: C, 91·4; H, 8·6%). [3] B. p. 66°/0·01 mm. (Found: C, 85·0; H, 6·1; N, 8·9. Calc. for $C_{11}H_9N$: C, 85·1; H, 5·9; N, 9·0%). [4] B. p. >280°/0·01 mm. Contained N and Bi.

TABLE 9.

Composition of neutral fractions from Expts. 14—16.

	Biphenyl (%) [1]	Isomeric t-butylbiphenyls (%) [2]		
Expt. no.		2-	3-	4-
14	2·8	10·1	62·7	27·2
15	2·8	9·8	61·6	28·6
16	2·0	11·4	63·2	25·4
Mean	2·5	10	63	27

[1] Calc. on total hydrocarbon fractions. [2] Calc. on total t-butylbiphenyls.

In these experiments, the excess of pyridine was removed by distillation at atmospheric pressure, and that of t-butylbenzene by distillation at 15 mm. In order to ensure the complete removal of the latter solvent, in the final distillation, the flask was maintained at 50°/0·01 mm. for a long period before the biaryls were distilled. Examination of these fractions by gas–liquid chromatography showed them to contain a little biphenyl as well as the expected t-butylbiphenyls. Their composition, as determined by gas–liquid chromatography, is given in Table 9.

DISCUSSION

Photolysis of Aromatic Solvents.—The only solvent which was found to undergo appreciable photodecomposition under the conditions employed was chlorobenzene. It is known that the carbon–halogen bonds in chlorobenzene, bromobenzene, and iodobenzene are susceptible to homolytic cleavage, and the spectra of these compounds display continuous absorption in this region.[14] Moreover, phenyl radicals are known to be formed by the photolysis of iodobenzene.[2,15] The observed high degree of stability of aromatic hydrocarbons towards ultraviolet light is expected from the low intensity of their absorption in the region 2300—2700 Å and from the fact that they fluoresce quite strongly under such irradiation. Thus, irradiation of toluene, mesitylene, ethylbenzene, isopropylbenzene, and t-butylbenzene in the liquid and the vapour phase is known to give hydrogen with a quantum yield of only $\sim 10^{-4}$, and even less methane and ethane.[16] The yellow colours developed by the alkylbenzenes on photolysis are probably due to the formation of small amounts of fulvene derivatives, as shown by Blair and Bryce-Smith.[17] Some of the observations made by these workers have been verified in the present work. Pyridine appears to inhibit the formation of fulvene derivatives, just as it reduces the extent of the photodecomposition of chlorobenzene, and probably for the same reasons.

The Photodecomposition of Triphenylbismuth.—The decomposition of triphenylbismuth, induced by ultraviolet light, in the solvents studied, clearly proceeds by a homolytic mechanism, liberating metallic bismuth, and giving organic products consistent with the intermediate formation of phenyl radicals. The aromatic solvents are phenylated in about 45% yield, and benzene is formed. The phenyl radicals formed in this reaction appear to behave in a manner essentially similar to those derived by the thermal decomposition of the several other well-established sources of these radicals.[18] The relatively high yield of biaryls and the formation of benzene are consistent with the simplest mechanism for the formation of biaryls, that is by addition of about half of the available phenyl radicals to the aromatic nuclei to give substituted phenylcyclohexadienyl radicals; these are then oxidised to biaryls by the remainder of the phenyl radicals, which are reduced to benzene.

The presence of nitrogen in the high-boiling residues formed in experiments in which pyridine was a solvent indicates that solvent molecules are incorporated in them to some extent. However, these residues obviously do not consist mainly of derivatives of tetrahydroquaterphenyl (formed by dimerisation of substituted phenylcyclohexadienyl radicals), as do those formed when benzoyl peroxide is used as the phenylating agent,[19] since they contain a high proportion of bismuth in addition to nitrogen.

It seems probable that the three phenyl radicals are liberated from triphenylbismuth in a stepwise manner, so that the radical $\cdot BiPh_2$, and the diradical $:BiPh$ are both present as intermediates during the photolysis. Organobismuth compounds of the type $R_2Bi\cdot BiR_2$ are unknown, and dimerisation of the diphenylbismuth radicals is therefore unlikely. However, a polymer $(BiPh)_n$ containing ~73% bismuth might be formed from the phenylbismuth diradicals. The bismuth content of this material could become reduced by

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[14] Semenova and Tsikunov, *Zhur. fiz. Khim.*, 1944, **18**, 311.

[15] Szwarc, *Chem. Rev.*, 1950, **47**, 75; Jaquis and Szwarc, *Nature*, 1952, **170**, 312.

[16] Hentz and Burton, *J. Amer. Chem. Soc.*, 1951, **73**, 532; Sworski, Hentz, and Burton, *ibid.*, p. 1998.

[17] Blair and Bryce-Smith, *Proc. Chem. Soc.*, 1957, 287.

[18] Gibson, Blake, and Kalm, *J. Chem. Phys.*, 1953, **21**, 1000; Leach and Migirdicyan, *Compt. rend.*, 1959, **248**, 1805.

[19] (*a*) DeTar and Long, *J. Amer. Chem. Soc.*, 1958, **80**, 4742; (*b*) Hey, Perkins, and Williams, unpublished work.

incorporation of solvent molecules in the growing polymer, or by termination of chains by combination with phenyl or substituted phenylcyclohexadienyl radicals. A very similar polymerisation of diphenyltin is known. This material, although monomeric when freshly prepared, rapidly polymerises to $(SnPh_2)_n$, where $n \geqslant 5$.[20] It is assumed, therefore, that the residues consist partly of polymeric bismuth-containing material, and partly of tetrahydroquaterphenyl derivatives. This has the important consequence that some of the substituted phenylcyclohexadienyl radicals intermediate in the phenylation process may be lost by incorporation in both components of the residue.

Partial Rate Factors for Phenylation with Triphenylbismuth.—Relative rates of phenylation of toluene and t-butylbenzene can be calculated from the results of the competitive experiments reported, by the use of the relation:

$${}^{\mathrm{PhX}}_{\mathrm{PhH}}K = {}^{\mathrm{PhX}}_{\mathrm{C_5H_5N}}K \times {}^{\mathrm{C_5H_5N}}_{\mathrm{PhH}}K,$$

and partial rate factors can be derived from these quantities taken together with the proportions in which the isomeric products of nuclear phenylation are formed. These quantities, with the corresponding quantities for phenylation with benzoyl peroxide, are given in Table 10. All the measurements were at 80°, except where otherwise stated. The possible error involved in the use of quantities measured at slightly different temperatures is probably not serious, as ratios of isomers are known not to be very sensitive to change in temperature. Some of the ratios of isomers were measured with mixtures obtained from competitive experiments in which pyridine was also present. No error is thought to be involved in this procedure as homolytic arylation reactions have been shown not to be subject to solvent effects of this kind.[21]

TABLE 10.

Partial rate factors for homolytic phenylation.

Solvent	Radical source	Rel. rate †	Isomers (%) 2-	3-	4-	Partial rate factors F_o or F_α	F_m or F_β	F_p or F_γ
Pyridine	Ph_3Bi	1·18	48 *	31 *	21 *	1·7	1·1	1·5
	$(PhCO{\cdot}O)_2$ [a,b]	1·04	54 §	32 §	14 §	1·7	1·0	0·9
Toluene	Ph_3Bi	1·99 ‡	57	27	16	3·4	1·6	1·9
	$(PhCO{\cdot}O)_2$ [c]	1·23	66·5	19·2	14·3	2·5	0·71	1·0
t-Butylbenzene	Ph_3Bi	1·12	10	63	27	0·3	2·1	1·8
	$(PhCO{\cdot}O)_2$ [c]	0·64	24	49	27	0·46	0·94	1·0

* Measured at 100.° † Relative rate of phenylation. ‡ It being assumed that there is no side-chain attack. § Measured at 105°.

[a] Ref. 11. [b] Ref. 8. [c] Hey, Orman, and Williams, *J.*, 1961, 565.

It is seen from Table 10 that there is an approximate correlation between the values of the various quantities obtained with the two sources of phenyl radicals. The characteristic features of homolytic phenylation reactions are displayed, including the previously observed steric hindrance to substitution at the *ortho*-position of t-butylbenzene.[22] There can be little doubt, therefore, that phenyl radicals are formed by the photolysis of triphenylbismuth, and that they effect substitution of hydrogen in the nuclei of aromatic solvents.

In a quantitative sense, however, there are differences between the two sets of figures both in the relative rates of arylation and in the ratios of isomers. Two reasons for these differences may be advanced: (*a*) the possibly selective removal of the differently substituted phenylcyclohexadienyl radicals (σ-complexes), which are intermediates in the various phenylation processes, by incorporation in the high-boiling residues, as suggested

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[20] Chambers and Scherer, *J. Amer. Chem. Soc.*, 1926, **48**, 1054.

[21] Dannley, Gregg, Phelps, and Coleman, *J. Amer. Chem. Soc.*, 1954, **76**, 445; Dannley and Gregg *ibid.*, p. 2997; Hey, Saunders, and Williams, unpublished observations; Cadogan, private communication.

[22] Cadogan, Hey, and Williams, *J.*, 1954, 3352.

by Blair, Bryce-Smith, and Pengilly,[2] and (*b*) the possibility that phenyl radicals formed by photolysis may contain an excess of vibrational energy, or may be formed in an electronically excited state, since the quanta of energy of the incident radiation may be considerably in excess of the dissociation energy of the C–Bi bonds in triphenylbismuth or the intermediates, $\cdot BiPh_2$ and $:BiPh$.

The relative rates of phenylation of toluene and t-butylbenzene with benzoyl peroxide were determined by means of competitive experiments in which nitrobenzene was the reference solvent and all the solvent mixtures phenylated therefore contained nitrobenzene. The amounts of high-boiling material formed in these experiments was very small, a circumstance which has often been found to be associated with the presence of nitrobenzene. There is therefore very little possibility that these results are subject to errors arising from the selective removal of σ-complexes. Although the ratios of isomers formed in the phenylation of these compounds with benzoyl peroxide were measured in experiments in which residues were formed, it has recently been shown [19b] that, in analogous cases, these ratios are unchanged when the formation of residues is inhibited by the presence of nitrocompounds. It is probable, therefore, that it is the results obtained with triphenylbismuth, rather than those obtained with benzoyl peroxide, that are subject to these errors. This is reasonable with benzoyl peroxide, since benzoyloxy-radicals and molecular benzoyl peroxide,[23] both of which are strong oxidising agents, are available for the oxidation of σ-complexes to biaryls, whereas with triphenylbismuth, the only oxidising agent available (apart from the solvent) is the phenyl radical, whose stationary concentration must be small. It is therefore very likely that, in the latter case, some of the σ-complexes partake in residue-forming side-reactions. It is also reasonable that, for steric reasons, σ-complexes leading to *ortho*-substitution should be oxidised with the most difficulty, and may therefore become incorporated in the residue more rapidly than their *meta*- and *para*-analogues. It is noteworthy in this connection that, with all three compounds studied, the proportion of the 2-isomers formed is lower with triphenylbismuth than with benzoyl peroxide. It is possible, therefore, that selective removal of σ-complexes in side-reactions may be at least partly responsible for the observed differences.

The second possible interpretation, namely, that " hot radicals " are involved in the phenylation reaction, was considered improbable by Blair, Bryce-Smith, and Pengilly,[2] because the direction of the effects observed by these workers was inconsistent with this hypothesis. The present results do not provide any clear-cut evidence one way or the other.

The present results on the phenylation of toluene differ from those previously reported on its phenylation with benzoyl peroxide [24] in one other respect. With benzoyl peroxide, 13% (by weight) of the binuclear products consisted of bibenzyl, the product of attack in the side-chain, whereas with triphenylbismuth no bibenzyl could be detected in the products. Agreement between the two sets of results in this respect is, however, hardly to be expected since Foster and Williams [23] have shown that part, at least, of the attack on the side-chains of alkylbenzenes in their reactions with benzoyl peroxide is due to benzoyloxy-radicals, which are absent from reactions with triphenylbismuth. Variations in the extent of side-chain attack on a given alkylbenzene within a series of organometallic compounds have also been observed.[2,25]

The authors are indebted to Dr. D. Bryce-Smith for helpful discussion, and to the Ministry of Education for the award of a grant to D. A. S.

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[*Received, December 29th*, 1962.]

[23] Foster and Williams, *J.*, 1962, 2862.
[24] Hey, Pengilly, and Williams, *J.*, 1956, 1463.
[25] Hey, Shingleton, and Williams, unpublished observations.