

Reactions of Palladium(II) with Organic Compounds. Part III.¹ Reactions of Aromatic Iodides in Basic Media

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Iodobenzene, some monosubstituted iodobenzenes, and 2,5-dimethyliodobenzene couple through the iodine-bearing carbon atom to form biaryls, and also undergo protodeiodination to a small extent, when treated with a catalytic quantity of palladium(II) acetate in triethylamine or tri-*n*-butylamine at 100°; in the latter solvent the corresponding aryl propyl ketones are also formed. It is suggested that biaryl formation involves the interaction of two arylpalladium species, and evidence is adduced that such a species reacts with an intermediate enamine to give a ketone or with adventitious water to yield a protodeiodinated product.

THE coupling of aliphatic and aromatic halides to form dimers has been accomplished with various metals,² including palladium.³ There has been much speculation about the mechanism of the reaction and, in particular instances, both heterolytic⁴ and homolytic⁵ pathways have been demonstrated.

Heck and his co-workers recently reported⁶ that vinylic hydrogen is replaced by an aryl group when an alkene and an aryl or vinyl halide are treated with a catalytic quantity of palladium(II) acetate in the presence of a hindered amine at 100°. We now report that aromatic iodides couple readily when treated with a catalytic quantity of palladium(II) acetate in triethylamine or tri-*n*-butylamine at *ca.* 100°. An arbitrary choice of 2.5 mole % palladium acetate, relative to the iodide, was made, and little starting material remained after 48 h. The major side-reaction was the formation of insoluble, involatile, high molecular weight material, but this could be readily separated by trituration. In most cases protodeiodination also occurred but its extent could be reduced by excluding water from the

system. A further side-reaction occurred when tri-*n*-butylamine was employed as the base (see later).

The yields of products and unchanged starting material from the reactions of a representative series of aromatic iodides are in Table 1; yields are based on the iodide. The efficiency of the coupling reaction is hardly sensitive to the nature of the substituent when this is in the *para*-position but it is significantly reduced when one *o*-Me group is present, and no coupled product could be detected from iodomesitylene. There is no evidence that aryl bromides or chlorides couple under our conditions, for no biphenyl could be detected from bromobenzene, and *p*-chloriodobenzene gave 4,4'-dichlorobiphenyl but no iodine-containing dimer.

Table 2 gives the corresponding details for reaction in tri-*n*-butylamine. The general features shown in Table 1 are also apparent here, and in addition we note the following: the yields of coupled product are usually lower (none could be obtained from *p*-iodonitrobenzene), and a further by-product, the (substituted) butyrophenone, is formed in most cases.

Formation of Biaryls.—The addition of palladium(II)

¹ Part II, F. R. S. Clark, R. O. C. Norman, C. B. Thomas, and J. S. Willson, *J.C.S. Perkin I*, 1974, 1289.

² See, *e.g.*, M. S. Kharasch and O. Reinmuth, 'Grignard Reactions of Non-metallic Substances,' Prentice-Hall, New York, 1954, pp. 117–124; J. P. Morizur, *Bull. Soc. chim. France*, 1964, 1331; J. March, 'Advanced Organic Chemistry: Reactions, Mechanisms, and Structure,' McGraw-Hill, New York, 1968, p. 354; P. E. Fanta, *Chem. Rev.*, 1964, **64**, 613; A. McKillop, L. F. Elsom, and E. C. Taylor, *J. Amer. Chem. Soc.*, 1968, **90**, 2423.

³ M. Julia, M. Duteil, C. Grard, and E. Kuutz, *Bull. Soc. chim. France*, 1973, 2791.

⁴ E. Le Goff, S. E. Ulrich, and D. B. Denney, *J. Amer. Chem. Soc.*, 1958, **80**, 622.

⁵ D. Bryce-Smith, *Bull. Soc. chim. France*, 1963, 1418.

⁶ (a) R. F. Heck, and J. P. Nolley, jun., *J. Org. Chem.*, 1972, **37**, 2320; (b) H. A. Dieck and R. F. Heck, *J. Amer. Chem. Soc.*, 1974, **96**, 1133.

acetate to the amine-iodide mixture causes it to turn black, a process which appears to be complete after *ca.* 5 min at 100°. Palladium metal is deposited during *ca.* 48 h, appearing either as an amorphous solid or as a mirror on the glass surface of the container. Thus,

TABLE 1

Products (mole %) from the reactions of aryl iodides (20 mmol) and palladium(II) acetate (0.5 mmol) in triethylamine (20 mmol) at 100° after 48 h

Ar	Recovered			Total
	ArI	ArAr	ArH	
Ph	0	54	0	54
<i>p</i> -MeC ₆ H ₄	0	50	3	53
<i>p</i> -MeO·C ₆ H ₄ ^a	7	39	5	51
<i>p</i> -O ₂ N·C ₆ H ₄ ^b	0	54	5	59
<i>p</i> -ClC ₆ H ₄	2	57	9	68
<i>o</i> -MeC ₆ H ₄	11	10	34	55
2,5-Me ₂ C ₆ H ₃	18	3	20	41
2,4,6-Me ₃ C ₆ H ₂	57	0	6	63

^a Yields after 2.5 h. ^b To obtain solution, Et₃N (0.11 mol) was used.

TABLE 2

Products (mole %) from the reactions of aryl iodides (20 mmol) and palladium(II) acetate (0.5 mmol) in tri-n-butylamine (20 mmol) at 100° after 48 h

Ar	Recovered			ArCO· C ₃ H ₇	Total
	ArI	ArAr	ArH		
Ph	0	38	0	7	45
<i>p</i> -MeC ₆ H ₄	1	34	0.3	6	41
<i>p</i> -MeO·C ₆ H ₄	0	25	22	4	51
<i>p</i> -O ₂ N·C ₆ H ₄	0	0	Trace	0	Trace
<i>p</i> -ClC ₆ H ₄	0	67	5	3	75
<i>o</i> -MeC ₆ H ₄	0	1	35	7	43
2,5-Me ₂ C ₆ H ₃	0	Trace	12	17	29
2,4,6-Me ₃ C ₆ H ₂	10	0	29	0	39

Pd^{II} or Pd⁰, either in a solubilised form or as finely divided metal, might be the active species in the formation of biaryls.

A fine suspension of palladium metal was prepared by treating palladium(II) acetate with an excess of methanol at the reflux temperature for 30 min. After removal of the solvent and its oxidation products under reduced pressure, the precipitate was heated with iodobenzene at 118° for 23 h. Biphenyl was formed, but in not more than 2% yield, so that precipitated palladium cannot be the active agent under the conditions of Tables 1 and 2.

When the reaction of iodobenzene under the conditions of Table 2 was repeated in the presence of 2.5 mmol of copper(II) acetate, the yield of biphenyl was reduced to 16% and that of butyrophenone was increased to the same amount: neither product was formed when the palladium salt was omitted. Since Cu^{II} converts Pd⁰ into Pd^{II}, we infer that Pd⁰ is essential in biaryl formation.

Heck has accounted for the phenylation of styrene with palladium(II) acetate in tri-*n*-butylamine at 100° in terms of 'PhPdI' as the active entity.^{6a} Since that reaction is complete in a shorter time than ours, PhPdI and its ring-derivatives, formed from the aryl iodide and Pd⁰, are likely to provide the active entity in our aryl-deiodinations. Moreover, the yields of biaryls from

para-substituted iodobenzenes (obtained in experiments in which a larger amount of triethylamine was used compared with the conditions in Table 1, to ensure that the reaction remained homogeneous) were found to increase with increase in the electron-withdrawing capacity of the substituent (Table 3) paralleling the known ease of formation of ArPd(PPh₃)₂X.⁷

TABLE 3

Yields of biaryls (mole %) from ArI^a

Ar	Yield ArAr
4-ClC ₆ H ₄	6.5
C ₆ H ₅	2.0
4-MeO·C ₆ H ₄	0.9

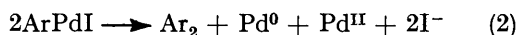
^a ArI (20 mmol), Et₃N (25 ml), and Pd(OAc)₂ (100 mg) heated at the reflux temperature in anhydrous conditions for 24 h.

We considered several possible reaction pathways. First, ArPdI might undergo homolysis, the resulting aryl radicals yielding biaryls by coupling or by homolytic substitution in ArI or ArPdI. However, this is *a priori* unlikely; high yields of coupled product would be improbable given the other possible fates for the very reactive aryl radicals, namely, abstraction of hydrogen from the amine and replacement of hydrogen in the aromatic compound. Protiodination is generally a minor reaction which dominates only when steric hindrance is pronounced at the reaction site. Further, the extent of protiodination shows a marked dependence on the amount of water present in the solution (see later).

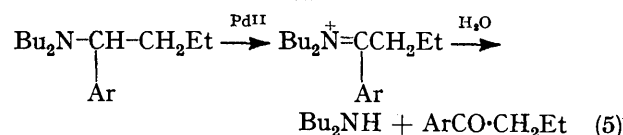
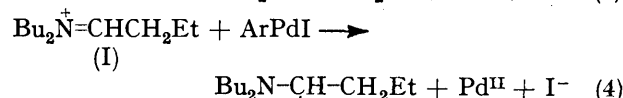
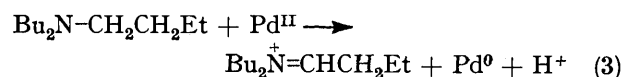
We next considered the possibilities that two ArPdI species might couple, with extrusion of the two PdI units, or that ArPdI might effect substitution in an aryl iodide. (At first sight, the latter would appear to be incompatible with the reported failure of alkyl iodides to undergo reaction;^{6a} however, this almost certainly stems from the fact that alkyl, unlike aryl or vinyl, iodides are converted into quaternary ammonium salts under the reaction conditions.) To investigate further, we heated PhPd(PPh₃)₂I⁷ in air-free benzene at 75° under nitrogen in the presence of an equivalent of 4-iodotoluene, and obtained biphenyl (63%), 4-methylbiphenyl (7%), and a trace of 4,4'-bitolyl. The formation of the tolyl-containing products shows that reaction cannot consist only of the coupling of two phenylpalladium species, but the results are consistent either with this reaction superimposed on at least partial equilibration of PhPd(PPh₃)₂I and 4-MeC₆H₄I to give 4-MeC₆H₄Pd(PPh₃)₂I and PhI, or with this equilibration together with substitution [ArPd(PPh₃)₂I + Ar'I → ArAr' + Pd(PPh₃)₂I₂]. Now, treatment of a mixture of iodobenzene and 4-iodotoluene with palladium(II) acetate in triethylamine at 100° gave biphenyl, 4-methylbiphenyl, and 4,4'-bitolyl in 19, 9, and 10% yield, respectively. Since phenylpalladium(II) iodide is expected to be formed more rapidly than 4-tolyl-

⁷ P. Fitton and E. A. Rick, *J. Organometallic Chem.*, 1971, **28**, 287.

palladium(II) iodide (ref. 7 and Table 3), the fact that the yield of biphenyl is only about twice that of the bitolyl would require, if substitution were to occur, that 4-tolylpalladium(II) iodide reacts with 4-iodotoluene either faster than, or hardly slower than, phenylpalladium(II) iodide reacts with iodobenzene. However, this cannot be reconciled with the results from reaction of the phosphine complex; the substitution mechanism could only lead to a 63% yield of biphenyl if there were extensive equilibration, and in that case a substantial amount of 4-tolylpalladium(II) iodide and thence of 4,4'-bitolyl would be expected, contrary to observation.* On the other hand, the data are compatible with the coupling of two arylpalladium(II) species; the overall sequence suggested for biaryl formation is then as in reactions (1) and (2) (ligands associated with Pd⁰ are not specified). As we show in the following section, Pd⁰ is likely to owe its origin to reduction of Pd^{II} by the amine, accounting for its requirement in only catalytic amount.



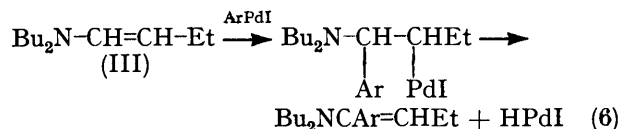
Formation of Butyrophenones.—Tri-*n*-butylamine is readily oxidised by manganese dioxide to Bu₂N·CHO, *via* the enamine Bu₂N·CH:CH₂Et, under conditions in which triethylamine is unaffected.⁸ It is therefore likely that the formation under our conditions of butyrophenones from tri-*n*-butylamine but not of acetophenones from triethylamine is associated with the ease of oxidation of the amine by palladium(II). One possibility is that the iminium ion (I) formed by such oxidation yields the butyrophenone *via* reactions (4) and (5). If so, PhCHMe·NBu₂, which is structurally related to the suggested intermediate (II), would be expected to yield acetophenone under our reaction conditions; however, it failed to do so.



We next considered the possibility that the enamine (III) derived from the iminium ion (I) is arylated in a manner similar to that suggested by Heck⁶ for olefins [reaction (6)], with hydrolysis of the resulting enamine

* It might be argued that there is no *a priori* reason why the phosphinepalladium complex should behave in the same way as our labile unphosphinated species. However, Heck has shown that in a similar system the phosphine ligand does not appreciably alter the nature of the products.^{6b}

during work-up to give the butyrophenone. Consistent with this suggestion, we found that when the enamine (III) was included in the reaction of iodobenzene with palladium(II) acetate in tri-*n*-butylamine, the yield of butyrophenone rose from 7 to 20%; and when triethylamine was used in place of the butylamine, butyrophenone was formed in 17% yield in a reaction taken to 100% conversion in 2 h.



Conversion of ArI into ArH.—We investigated this process by studying iodomesitylene. This was found to be free of mesitylene, to the limits of g.l.c. detection, and not to give mesitylene on treatment with 2*M*-hydrochloric acid in the manner of the work-up procedure (>99% of the iodo-compound was recovered). A possible origin of the incorporated hydrogen atom is the water present in the hygroscopic amine, and evidence that this is at least one source was obtained by finding that the yield of mesitylene under the conditions of Table 2 was decreased by drying the amine. Moreover, when reaction was carried out in the presence of D₂O, a deuterium atom was incorporated into the aromatic ring in place of iodine (Table 4). [That not all the mesitylene contained deuterium is not exceptional since, for example, the HPdI liberated in reaction (6) may serve as a source of protons.]

TABLE 4
Formation of mesitylene from iodomesitylene^a

Amine	Water content	Iodomesitylene recovery (%)	Mesitylene (%)
Bu ₂ N	<i>b</i>	10	29
Bu ₂ N ^c	<i>d</i>	30	4
Bu ₂ N ^e	D ₂ O ^e	92	3 ^f

^a Under the conditions of Table 2. ^b No attempt to remove water. ^c Under N₂. ^d The amine was dried over Al₂O₃. ^e Molarity equivalent to that of the amine. ^f Me₃C₆H₃: Me₃C₆H₂D = 1:1.8.

We found that iodomesitylene arylates styrene in the presence of palladium(II) acetate and tri-*n*-butylamine to give *cis*- and *trans*-2,4,6-trimethylstilbene (37%), implying that it can yield the mesitylpalladium derivative ArPdI (*cf.* ref. 6). Thus, since the replacement of iodine by hydrogen under the conditions of Tables 1 and 2 becomes increasingly important relative to biaryl formation as first one and then two methyl groups are introduced *ortho* to the iodine substituent, we infer that ArPdI is strongly sensitive to steric hindrance in the latter reaction.

When equimolar amounts of 4-iodochlorobenzene and 4-iodotoluene were treated at 100° with catalytic palladium(II) acetate in triethylamine and water (2 equiv. each), for a time (4 h) sufficient for <1% reaction, chlorobenzene and toluene were formed in the molar ratio 2.9:1. Since a hydrogen atom in water can be

⁸ H. B. Henbest and M. J. W. Stratford, *Chem. and Ind.*, 1961, 1170.

electrophilic but not nucleophilic, so that reaction (7) should be facilitated when Ar = *p*-tolyl compared with Ar = *p*-chlorophenyl, we suggest that the initial step, $\text{ArI} + \text{Pd}^0 \longrightarrow \text{ArPdI}$, is retarded by electron-releasing groups, as has been found in other conditions for very similar species.⁷



It is interesting to note that Dieck and Heck^{6b} observed biphenyl as a by-product from the arylation of methyl acrylate with 2-bromobiphenyl. This is consistent with our observation that *ortho*-substitution favours protiodehalogenation.

EXPERIMENTAL

G.l.c. analyses were carried out with a Pye instrument (series 104, model 24), with flame-ionisation detection and nitrogen as carrier gas, fitted with 5 ft \times 1/4 in glass columns containing either 10% SE30 or 10% Carbowax 20M on Celite. Products were identified by comparison with authentic materials of both retention times and mass spectra, the latter being measured with an A.E.I. MS12 spectrometer which was attached to the g.l.c. column *via* a heated stainless steel capillary.

Materials.—Palladium(II) acetate was a Johnson–Matthey reagent. This, iodobenzene, 4-iodotoluene, 4-iodonitrobenzene, tri-*n*-butylamine, biphenyl (all B.D.H.), 4-iodoanisole (Koch–Light), triethylamine, and copper(II) acetate monohydrate (both Fisons) were used without further purification. 2-Iodotoluene was made by the method of Datta and Mitter⁹ and had b.p. 84° at 14 mmHg (lit.,¹⁰ 211° at 760 mmHg); 2,5-dimethyliodobenzene, b.p. 100–102° at 15 mmHg (lit.,¹¹ 217–218° at 760 mmHg), and 2,4,6-trimethyliodobenzene, m.p. 29–30° (lit.,¹¹ 30°), were prepared by the method of Datta and Chatterjee;¹¹ 4-iodochlorobenzene was prepared by the iodination of chlorobenzene and had m.p. 51–51.5° (lit.,¹² 56°).

4,4'-Bitolyl was prepared by cobalt(II) chloride-initiated coupling of the *p*-tolyl Grignard reagent and had m.p. 118–119° (lit.,¹³ 121°). 4,4'-Dichlorobiphenyl, prepared by chlorinating biphenyl,¹⁴ had m.p. 146–147.5° (lit.,¹⁴ 148–149°). Butyrophenone was obtained from treatment of benzene with *n*-butyryl chloride and aluminium chloride and had b.p. 227–230° (lit.,¹³ 228–229°). 4-Methylbutyrophenone, prepared from toluene in carbon disulphide in a like manner, had b.p. 246–248° (lit.,¹³ 251.5°); the 4-methoxy-derivative, prepared analogously, had b.p. 149–152° at 13 mmHg and partly solidified on standing (lit.,¹⁵ m.p. 21°); the 4-chloro-derivative, from chlorobenzene, butyryl chloride, and aluminium chloride, with dry nitrogen passed through the solution, had m.p. 35.5–37° (lit.,¹⁶ 36°). 2-Methylbutyrophenone, prepared from the tolyl Grignard reagent and butyryl chloride, had b.p. 118–126° at 15 mmHg (lit.,¹⁷ 92.5° at 5 mmHg). 2,5-Dimethylbutyrophenone, prepared by adding butyryl chloride

⁹ R. L. Datta and H. K. Mitter, *J. Amer. Chem. Soc.*, 1919, **41**, 287.

¹⁰ 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.

¹¹ R. L. Datta and N. R. Chatterjee, *J. Amer. Chem. Soc.*, 1917, **39**, 435.

¹² R. L. Datta and N. R. Chatterjee, *J. Amer. Chem. Soc.*, 1919, **41**, 292.

¹³ 'Handbook of Chemistry and Physics,' 49th edn., The Chemical Rubber Co., Cleveland, 1968.

¹⁴ F. R. Shaw and E. E. Turner, *J. Chem. Soc.*, 1932, 285.

to *p*-xylene in carbon disulphide in the presence of aluminium chloride, had b.p. 246–250° (lit.,¹⁸ 119° at 7 mmHg). *NN*-Dimethyl-1-phenylethylamine was prepared from 1-phenylethylamine with formaldehyde and formic acid¹⁹ and had b.p. 73–74° at 15 mmHg (lit.,¹⁹ 71° at 11 mmHg). *NN*-Dibutylbut-1-enylamine was obtained by the dropwise addition of dibutylamine to butanal²⁰ and had b.p. 86–96° at 18 mmHg, ν_{max} . 950 and 1650 cm^{-1} (lit.,²⁰ b.p. 62° at 0.5 mmHg, ν_{max} . 930 and 1640 cm^{-1}). The following substituted biphenyls were available in this laboratory: 4-Me, 4-OMe, 4-Cl, 4,4'-(OMe)₂, 4,4'-(NO₂)₂, 2,2'-Me₂, and 2,2',4,4',6,6'-Me₆.

Reactions of Aryl Iodides with Palladium(II) Acetate and a Tertiary Amine.—The typical procedure was as follows. A mixture of the iodide (20 mmol), amine (20 mmol), and palladium(II) acetate (0.5 mmol) was heated on an oil-bath at 100 \pm 10° with magnetic stirring; a drying-tube was fitted to the reflux condenser. In some cases the reaction was followed by the periodic removal of 25 μ l aliquot portions which were quenched with dichloromethane and 2M-HCl before analysis by g.l.c. When reaction was complete, the cooled solution was diluted with dichloromethane (100 ml), washed with 2M-HCl (4 \times 100 ml) and water (300 ml), and dried (K₂CO₃).

Reaction of Iodobenzene with Palladium Metal.—A mixture of palladium(II) acetate (1.10 mmol) and methanol (20 ml) was heated to reflux for 30 min, after which time the palladium was reduced to a fine black powder. Iodobenzene (20 mmol) was added and methanol and its volatile oxidation products were removed under vacuum. The flask was fitted with a reflux condenser and drying-tube and heated for 23 h at 118° with magnetic stirring. Ether (50 ml) was added to the cooled mixture and this was filtered through a pad of powdered MgSO₄ to remove the palladium. Removal of the solvent gave a light yellow oil which, by g.l.c., contained biphenyl (24.5 mg, 1.6%).

Reaction of 4-Iodotoluene with Iodo(phenyl)bis(triphenylphosphine)palladium(II).—A homogeneous solution of 4-iodotoluene (0.30 mmol), iodo(phenyl)bis(triphenylphosphine)palladium(II) (0.30 mmol), and benzene (nitrogen-flushed; 20 ml) was stirred under nitrogen at 75°. After 41 h the mixture was cooled, diluted with pentane, filtered, and the filtrate concentrated to give a solid which by g.l.c. analysis contained biphenyl (0.094 mmol; 63% on Pd), 4-methylbiphenyl (0.012 mmol, 7%), and a trace of 4,4'-bitolyl.

Reactions of Iodobenzene and 4-Iodotoluene with Palladium(II) Acetate.—A mixture of iodobenzene (20 mmol), 4-iodotoluene (20 mmol), palladium(II) acetate (0.48 mmol), and triethylamine (20 mmol) was stirred for 48 h at 110–120°. Water was added and the ether extract was washed with 2M-HCl and water, and dried (K₂CO₃). Removal of solvent gave an orange oil which by g.l.c. analysis contained biphenyl (1.93 mmol; 19% on iodide), 4-methylbiphenyl (1.81 mmol, 9%), and 4,4'-bitolyl (0.98 mmol, 10%).

¹⁵ N. M. Cullinane, S. J. Chard, and D. M. Leyshon, *J. Chem. Soc.*, 1952, 376.

¹⁶ G. T. Morgan and W. J. Hickinbottom, *J. Chem. Soc.*, 1921, 1879.

¹⁷ J. L. Maxwell, M. J. Brownlee, and M. P. Holden, *J. Amer. Chem. Soc.*, 1961, **83**, 589.

¹⁸ C. T. Lester and E. C. Suratt, *J. Amer. Chem. Soc.*, 1949, **71**, 2262.

¹⁹ A. C. Cope, T. T. Foster, and P. H. Towle, *J. Amer. Chem. Soc.*, 1949, **71**, 3929.

²⁰ H. B. Henbest and M. J. W. Stratford, *J. Chem. Soc.*, 1964, 711.

Reaction of Iodobenzene with NN-Dimethyl-1-phenylethylamine, Tri-n-butylamine, and Palladium(II) Acetate.—Iodobenzene (20 mmol), *NN*-dimethyl-1-phenylethylamine (20 mmol), tri-*n*-butylamine (20 mmol), and palladium(II) acetate (0.5 mmol) were heated as before at 104° for 45 h. Work-up as before, but with 6*M*-HCl as the acidic wash, gave a dark CH₂Cl₂ solution which, by g.l.c., contained biphenyl (3.82 mmol, 38%) and butyrophenone (1.86 mmol, 19%). Neither iodobenzene nor acetophenone was detected.

Reaction of Iodobenzene with NN-Dibutylbut-1-enylamine, a Tertiary Amine, and Palladium(II) Acetate.—Iodobenzene (10 mmol), *NN*-dibutylbut-1-enylamine (10 mmol), tri-*n*-butylamine (10 mmol), and palladium(II) acetate (0.25 mmol) were heated at *ca.* 120° for 3 h. Work-up as in the reaction above and g.l.c. analysis showed the presence of biphenyl (1.14 mmol, 23%) and butyrophenone (2.05 mmol, 20%).

When triethylamine (10 mmol) replaced tri-*n*-butylamine, reaction was complete in 2 h. G.l.c. analysis showed biphenyl (1.41 mmol, 28%) and butyrophenone (1.67 mmol, 17%) to be present.

Reaction of Iodomesitylene with Palladium(II) Acetate in the Presence of Water and Deuterium Oxide.—Iodomesitylene (20 mmol), tri-*n*-butylamine (distilled from MeMgI and stored over molecular sieve under N₂; 20 mmol), deuterium oxide (20 mmol), and palladium(II) acetate (0.43 mmol) were stirred under N₂ at 85° for 49 h. G.l.c. analysis of the cooled solution showed that it contained

iodomesitylene (18.4 mmol, 92%) and (deuteriated) mesitylene (0.55 mmol, 3%). The ratio Me₃C₆H₃:Me₃C₆H₂D (1:1.8) was estimated by observing the mass spectrum of the mesitylene peak by g.l.c.-mass spectrometry; the height of the peak at *m/e* 120 relative to that at *m/e* 121, suitably corrected for the *M* - 1 and *M* + 1 peak heights, gave this ratio directly.

Reaction of Iodomesitylene with Styrene in the Presence of Tri-n-butylamine and Palladium(II) Acetate.—The iodide (10 mmol), styrene (10 mmol), tri-*n*-butylamine (10 mmol), and palladium(II) acetate (0.25 mmol) were stirred at 120° for 2 h. Work-up as above gave an orange oil which was found by g.l.c. to contain mesitylene (1.53 mmol, 15%), iodomesitylene (3.78 mmol, 38%), *cis*-2,4,6-trimethylstilbene (0.30 mmol, 3%), and its *trans*-isomer (3.4 mmol, 34%).²¹

Reaction between 4-Iodochlorobenzene, 4-Iodotoluene, and Palladium(II) Acetate in Triethylamine and Water.—4-Iodochlorobenzene (10 mmol), 4-iodotoluene (10 mmol), triethylamine (20 mmol), water (20 mmol), and palladium(II) acetate (0.24 mmol) were stirred at 100° for 4 h. Normal work-up, followed by g.l.c. analysis, showed that less than 1% reaction had occurred to give chlorobenzene and toluene, and that the ratio of the amounts of these two products was 2.9:1.

[4/1811 Received, 2nd September, 1974]

²¹ R. C. Fuson, J. J. Denton, and C. E. Best, *J. Org. Chem.*, 1943, **8**, 64.