ing point, lit.[20] mp 215–220°. When ether V (5.05 g, 0.015 mol) was substituted for I in this procedure, a 59% yield of the substituted 2-naphthol was obtained. When benzene was used instead of carbon tetrachloride as solvent in the reaction of I with 2-naphthol, the substitution product was still formed in 45% yield despite the presence of the competitive reaction with benzene.

Phthalimidomethylation of 2,4-Dinitrophenol (VII) with N-Chloromethylphthalimide (IX).—To a stirred solution of N-chloromethylphthalimide[21] (1.95 g, 0.01 mol) and VII (1.84 g, 0.01 mol) in liquid sulfur dioxide (50–60 ml) cooled to −40° in a chloroform–Dry Ice bath, silver hexafluoroantimonate (Ozark-Mahoning Co., Tulsa, Okla.) (3.43 g, 0.01 mol) was added in several portions (5–10 min). After the mixture stirred at −25 to −30° for 3-4 hr, the solvent was allowed to evaporate overnight. The residual mixture of product and silver chloride was suspended in water and collected at the filter. The dried mixture (4.71 g) was boiled with 100 ml of stirred dichloroethane for several minutes and filtered hot to remove insoluble silver chloride (1.29 g, 90%). The clear, amber filtrate was concentrated to one-third of its volume and cooled. The product VIII (2.47 g, 72%) crystallized in nearly pure form, mp 210–214°. A number of variations of solvent and temperature were tried with the following results: SO_2, −10°, 67%; $(CH_2)_2Cl_2$, −15°, 59%; $(CH_2)_2Cl_2$, 0°, 40%; $(CH_2)_2Cl_2$, 25°, 26%; CH_3NO_2, 10°, 46%. Clearly, low temperatures favor the desired reaction, presumably by reducing the incidence of side reactions of the carbonium ion VI with solvent. This explanation received further support from an experiment in which IX in nitromethane was treated with the silver salt and allowed to stand for 16 hr at 25° before the phenol VII was added. Under these conditions no VIII could be isolated. The instability of the intermediate ion VI also was suggested by attempts to determine its nmr spectrum. Treatment of the N-chloromethylphthalimide (IX), dissolved in 1,2-dichloroethane, with silver hexafluoroantimonate at room temperature gave the theoretical amount of silver chloride, and the filtrate showed a weak, moderately broad peak at 916 Hz (*vs.* TMS in solution). However, its area relative to that of the aromatic peak (475 Hz) indicated that less than 20% of the material could be in the form of VI (assigning the 916 peak to the $>N^+{=}CH_2$ protons). This downfield peak disappeared immediately on the addition of 2,4-dinitrophenol, and overnight on standing at room temperature. Using silver tetrafluoroborate instead of the antimonate gave a 42% yield of VIII, but with silver trifluoroacetate only the trifluoroacetate of I was formed.

Unsuccessful Attempts to Phthalimidomethylate 2,4-Dinitrophenol (VII) with N-Chloromethylphthalimide (IX).—A stirred mixture of VII (2.21 g, 0.012 mol), IX (2.35 g, 0.012 mol), and stannic chloride (15 ml) was heated at 85° for 5 hr. The stannic chloride was removed by distillation under reduced pressure; the residue was suspended in cold ethanol and collected at the filter. The product (3.85 g, mp 80–100°) was a complex mixture in which none of the desired product VIII could be detected (ir). Similar negative results were obtained using the following conditions: $SnCl_4$, 25°, 16 hr; $SbCl_5$, 25°, 16 hr; $ZnCl_2$-CH_3NO_2, 100°, 5 hr; and $AlCl_3$-CH_3SO_3H-$CHCl_3$, 60°, 18 hr.

Registry No.—I, 118-29-6; VII, 51-28-5; sulfuric acid, 7 664-93-9.

Acknowledgment.—We are indebted to Mrs. Ruth Stanaszek for the nmr spectra, to Mr. William Washburn for the infrared spectra, and to Mr. Paul Sanders for assistance with the statistical analyses.

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(20) R. Maki, Y. Ishida, K. Satake, and R. Oda, *Kogyo Kagaku Zasshi*, **57**, 44 (1954); *Chem. Abstr.*, **49**, 10907*d* (1955).

(21) H. Böhme, R. Broese, and F. Eiden, *Chem. Ber.*, **92**, 1258 (1959).

Oxidative Coupling of Toluene through Organometallic Intermediates

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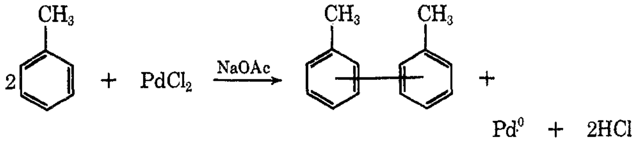
Organomercury compounds have been shown to undergo substitution by palladium salts with subsequent reduction of the palladium(II) to palladium(0) and oxidative coupling of the aromatic rings. The system, toluene–mercuric acetate–palladium acetate, was investigated in detail. A mechanism is proposed based on the isomer distribution of the bitolyls.

van Helden and Verberg[1,2] have shown that palladium chloride in the presence of sodium acetate can oxidatively couple aromatic compounds. Benzene yields biphenyl, while substituted aromatic compounds lead to a mixture of the various possible biaryl isomers.

If toluene is treated with palladium chloride in an acetic acid–sodium acetate medium, a mixture of the six possible isomeric bitolyls is obtained.



The rate of the reaction and the isomer distribution are temperature dependent, the reaction proceeding very slowly at room temperature. Table I shows the isomer distribution at various reaction temperatures. It can be seen that coupling involving an *ortho* position increases with decreasing temperature at the expense of the *meta*- and *para*-derived isomers.

TABLE I

TEMPERATURE DEPENDENCE OF BITOLYL ISOMER DISTRIBUTION IN THE $PdCl_2$–NaOAc SYSTEM

	Amount, mol %						Yield,[a]	
T, °C	*o,o'*	*o,m'*	*o,p'*	*m,m'*	*m,p'*	*p,p'*	%	Time
200[b]	Traces	12.5	12.2	18.8	35.3	21.4	28	2 hr
110	Traces	12.7	13.4	17.2	35.2	21.2	54	3 hr
90	Traces	12.4	17.9	14.5	34.6	20.4	58	6 hr
50	Traces	15.3	27.2	11.6	28.4	17.4	31	4 days
25	Traces	24.5	44.5	5.0	14.9	11.6	16	7 days

[a] Based on $PdCl_2$ charged. [b] Shaker tube run.

The distribution of the bitolyl isomers is not considerably altered by changes in solvent, or by the addition of cocatalysts, buffers, acids, or ligands. One exception was found in that addition of catalytic amounts of perchloric acid resulted in an increase in the rate of the reaction and a shift in the isomer distribution toward *meta*- and *ortho*-derived isomers.

Recently it was shown by Bryant, McKeon, and

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(1) R. van Helden, G. Verberg, and B. Balder, U. S. Patent 3,145,237 (Aug 18, 1964).

(2) R. van Helden and G. Verberg, *Rec. Trav. Chim. Pays-Bas*, **84**, 1263 (1965).

Ream[8] that the ratio of sodium acetate to palladium salt is crucial, since a high level of acetate anion tends to favor benzylic oxidation, particularly to benzyl acetate. The use of palladium chloride, therefore, is preferred over palladium acetate, if oxidative coupling of the aromatic nucleus is the goal. Even so, the yields of bitolyl isomers do not exceed 60%. The benzylic oxidation can also be suppressed by the addition of perchloric acid.[4]

It has now been found that a complete conversion into bitolyls, based on palladium salt charged, can be achieved if mercuric acetate is added to the reaction mixture. Furthermore, the isomer distribution can be changed extensively in favor of the *p,p'*-bitolyl isomer. A detailed study of this system has clearly demonstrated that this reaction proceeds *via* an organomercury intermediate.

Mercuric salts are uniquely capable of direct metalation of aromatic compounds, resulting in a stable C–Hg bond.[5,6] Furthermore, substitution in the *para* position is generally favored. The isomer distribution of the tolylmercuric acetates, formed by the mercuration of toluene at room temperature, was found to be 20% *ortho*, 10% *meta*, and 70% *para*. The rate of mercuration of toluene is greatly increased by the addition of perchloric acid.[7] If one adds palladium acetate to mercurated toluene in acetic acid solution, palladium metal is slowly precipitated with the formation of a mixture of bitolyl isomers. The isomer distribution shows a high percentage of *para* isomers, suggesting that organomercury compounds may be intermediates (Table II). The isomer distributions of the tolylmercuric acetates and the bitolyls are temperature dependent. An increase in the relative amount of *para* isomers with decreasing temperature is observed, particularly for the *p,p'*-bitolyl isomer.

TABLE II

TEMPERATURE DEPENDENCE OF BITOLYL ISOMER DISTRIBUTION

	Amount, mol %					
T, °C	*o,o'*	*o,m'*	*o,p'*	*m,m'*	*m,p'*	*p,p'*
90	...	10.1	11.8	16.9	41.5	30.6
50	...	1.6	3.2	2.3	35.2	60.0
0	...	0.7	6.7	0.9	25.4	67.5

Perchloric acid considerably increases the rate of the mercuration of toluene. This has been explained in the case of benzene by Perrin and Westheimer[8] as a removal of the solvated water from the mercury ion with the aid of the perchlorate ion. Perchloric acid also has a strong influence on the isomer distribution in the present reaction. This can be seen in Figure 1 where the *p,p'*-bitolyl/*m,p'*-bitolyl isomer ratio has been plotted against increasing perchloric acid concentration. The selectivity of the reaction for the production of the *para* isomer increases with increasing amount of perchloric acid.

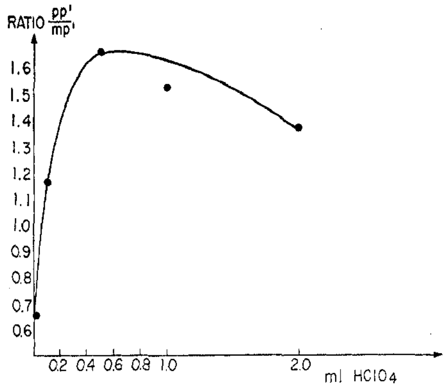

Figure 1.—Ratio of *p,p'*-/*m,p'*-bitolyl as a function of perchloric acid concentration [$PdCl_2$–$Hg(OAc)_2$].

With the further addition of perchloric acid, the reaction becomes so rapid that the isomer distribution approaches statistical values. This is reflected in a decline of the selectivity for the *p,p'*-bitolyl isomer. A similar effect can be seen when water is added to the reaction mixture (Figure 2). Here the effect of the perchloric acid is immediately weakened and with increasing amount of water present in the system one observes a steady decline for the selectivity of the *p,p'*-bitolyl isomer.

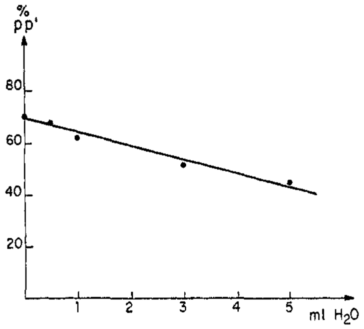

Figure 2.—Effect of water on the distribution of *p,p'*-bitolyl.

By changing the Hg/Pd ratio and following the isomer distribution, it is possible to observe a gradual shift from a pure palladium oriented coupling of toluene, where no mercury salt is added, to a predominantly mercury derived isomer distribution where mercury is in excess of palladium. In Figure 3 the amount of palladium acetate has been held constant and the mercuric acetate has been varied, while in Figure 4, mercuric acetate has been held constant and the palladium acetate varied. With no mercuric acetate present, Figure 3, the distribution is controlled by the palladium acetate alone, resulting in the familiar distribution pattern of only 20% *p,p'*-bitolyl. With increasing mercuric acetate a maximum of 70% *p,p'*-bitolyl is reached at a mercuric acetate–palladium acetate ratio of 2:1.

At higher ratios, this value decreases to level out at about 57% *p,p'*-bitolyl. *m,p'*-Bitolyl is the other isomer present in significant amounts at this point, while the *ortho*-derived isomers decrease to less than 10%. This isomer distribution is approximately the starting point in Figure 4, where at a low palladium acetate concentration about 55% *p,p'*- and 30% *m,p'*-bitolyl are found. In all isomer distribution curves, there is a drastic change between Pd/Hg ratios of 1:2 to 2:1.

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(3) D. R. Bryant, J. E. McKeon, and B. C. Ream, *Tetrahedron Lett.*, 3371 (1968).

(4) J. M. Davidson and C. Triggs, *Chem. Ind.* (London), 457 (1966).

(5) R. M. Schramm, W. Klapproth, and F. H. Westheimer, *J. Phys. Colloid Chem.*, **55**, 843 (1951).

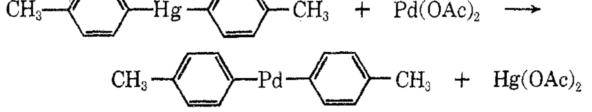
(6) H. C. Brown and C. W. McGary, Jr.; *J. Amer. Chem. Soc.*, **77**, 2300 (1955).

(7) H. C. Brown and C. W. McGary, *ibid.*, **77**, 2306 (1955).

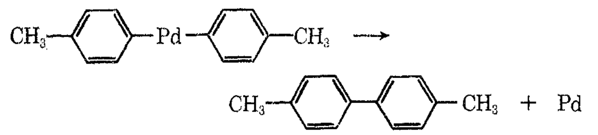
(8) C. Perrin and F. H. Westheimer, *ibid.*, **85**, 2773 (1963).

Apparently, the distribution changes from Pd-controlled to a Hg-controlled reaction in this range.

To obtain more insight into the reaction mechanism, the reaction was investigated using preformed mercury compounds such as *p*-tolylmercuric acetate and *p,p'*-bitolyl mercury. If tolylmercuric acetate is treated with palladium acetate at room temperature, no immediate reaction occurs. At 90°, the reaction proceeds slowly with the formation of palladium metal. If perchloric acid is added, however, the rate is increased considerably so that the reaction is complete even at room temperature in a matter of hours. On the other hand, perchloric acid is not necessary in the case of bitolylmercury, which reacts instantaneously with palladium salts in acetic acid solution. The reaction does not proceed *via* a simple metal substitution reaction, such as sequence 1 and 2, since 1 mol of bitolylmercury should then produce 1 mol of bitolyl.

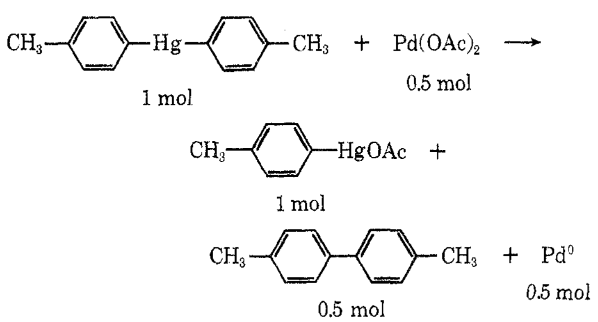


(1)



(2)

However, it has been shown that even excess palladium acetate produces only 0.5 mol of bitolyl from 1 mol of bitolylmercury if no perchloric acid is added. The mercury has been found to be present as tolylmercuric acetate in the reaction products and not as mercuric acetate. Quantitative measurement of all reactants and products has given the stoichiometry in reaction 3.



(3)

The most likely mechanism seems to be an electrophilic attack of palladium acetate on the Hg–C bond, resulting in two metalated rings (eq 4). The Hg–C bond is stable and the tolylmercuric acetate, being much less reactive than bitolylmercury, will not take part in a further reaction and can be found as such in the reaction mixture. Tolylpalladium acetate, on the other hand, is a highly unstable species and will react with more bitolylmercury to produce 1 more mol of tolylmercuric acetate. The Pd–C bond is broken with the formation of bitolyl and reduction of the palladium (eq 5). Starting with *p,p'*-bitolylmercury, the only bitolyl isomer observed was *p,p'*-bitolyl.

$$\text{R–Hg–R} + \text{PdAc}_2 \longrightarrow \text{R–HgAc} + \text{R–PdAc} \qquad (4)$$

$$\text{R–PdAc} + \text{R–Hg–R} \longrightarrow \text{R–R} + \text{Pd} + \text{R–HgAc} \qquad (5)$$

$$2\text{R–Hg–R} + \text{PdAc}_2 \longrightarrow 2\text{R–HgAc} + \text{R–R} + \text{Pd} \qquad (6)$$

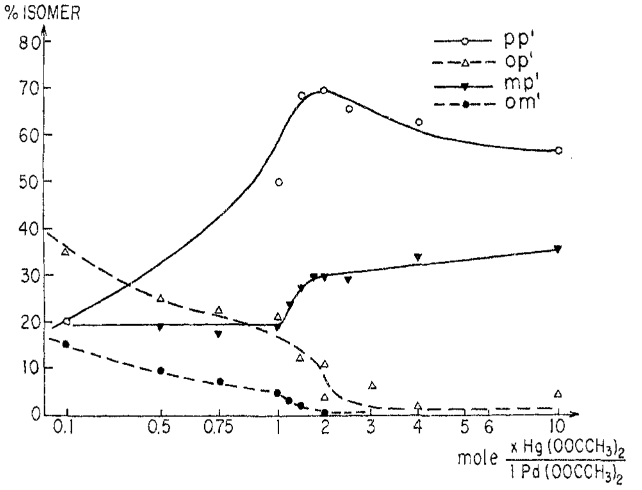


Figure 3.—Isomer distribution of bitolyls, $Pd(OAc)_2$–$Hg(OAc)_2$ system with $Pd(OAc)_2$ held constant.

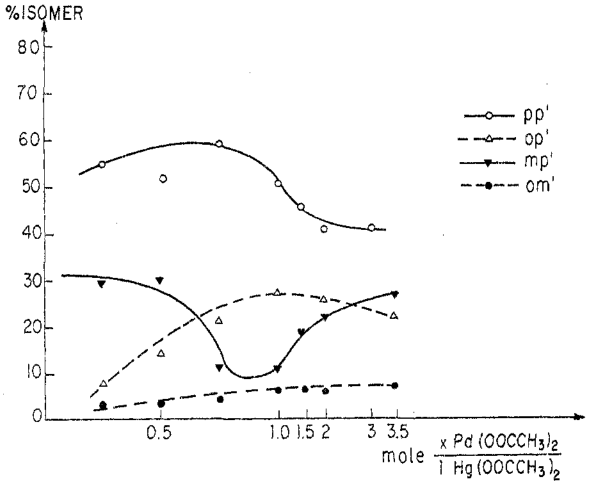


Figure 4.—Isomer distribution of bitolyls, $Pd(OAc)_2$–$Hg(OAc)_2$ system with $Hg(OAc)_2$ held constant.

Davidson and Triggs[9] in a recent paper also postulate a phenylpalladium(II) complex as an intermediate in the oxidative coupling of benzene with palladium acetate–perchloric acid. However, they have evidence that a bimolecular decomposition of this complex may result only in a partial reduction of the palladium to palladium(I). If the same palladium(I) complex should be formed in our system it probably would react with even greater ease with the organomercury compound than a palladium(II) complex and the end result would be the same, namely, complete reduction to palladium(0).

As mentioned above, the rate of reaction of bitolylmercury with palladium acetate is much faster than that of tolylmercuric acetate with palladium acetate. Obviously, R–Hg–R easily undergoes substitution by palladium where the mercury is being held by two covalent bonds, whereas the partial positive charge in $RHg^{+}X^{-}$ makes an electrophilic substitution of the C–Hg bond more difficult. Addition of perchloric acid may have the effect of creating a more positively charged species from palladium acetate [*e.g.*, $Pd(ClO_4)_2$] which can compete better with mercury for the electron pair.

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[9] J. M. Davidson and C. Triggs, *J. Chem. Soc., A*, 1324 1331 (1968).

If tolyl mercuric acetate is treated with palladium acetate in the absence of perchloric acid, the only isomer formed, though very slowly at room temperature, is *p,p'*-bitolyl. In the presence of perchloric acid, the rate increases and the resulting product contains about 70% *p,p'*-bitolyl, while the rest is mainly *o,p'*- and *m,p'*-bitolyl. The absence of *m,m'*- and *o,o'*-bitolyl shows that *p*-tolylmercuric acetate reacts with palladium acetate to form *p*-tolylpalladium acetate. This step is slow and rate controlling. If no perchloric acid is present, tolylpalladium acetate apparently is stable to the degree that it can react with more tolylmercuric acetate, resulting in *p,p'*-bitolyl. However, in the presence of perchloric acid, tolylpalladium acetate will react as soon as it forms, not only with *p*-tolylmercuric acetate, but possibly also with toluene itself, which then results in the *ortho*, *para'*, *meta*, *para'*, and *para*, *para'* isomer mixture. In a formal way, the overall reaction can thus be written as

$$\text{R-HgX} + \text{PdX}_2 \longrightarrow \text{R-PdX} + \text{HgX}_2 \qquad (7)$$

$$\text{R—PdX} + \text{RH} \longrightarrow \text{R-R} + \text{Pd} + \text{HX} \qquad (8)$$

$$\text{R-PdX} + \text{R-HgX} \longrightarrow \text{R-R} + \text{Pd} + \text{HgX}_2 \qquad (9)$$

It would therefore seem that the action of palladium salt on a mercurated aromatic nucleus is an extension of a general electrophilic substitution reaction, where instead of metal for hydrogen, or metal for boron,[4] a metal for metal substitution takes place.

A very similar reaction is observed when a platinum salt rather than a palladium salt is added to mercurated toluene. The reduction of Pt(IV) occurs in two distinct steps, which are dependent on the amount of perchloric acid present in the system. In particular the reduction of Pt(II) to Pt(0) is only possible in a strongly acidic medium. Figure 5 shows the dependence of the conversion on the amount of perchloric acid added. Bitolyl (2 mol) was found for each mole of Pt(IV). Again, the highly charged Pt(IV) can easily displace mercury in an electrophilic substitution reaction. However, Pt(II) does not react further unless perchloric acid is added. The addition of perchloric acid probably increases the electrophilicity of Pt(II), either by transforming $PtCl_2$ to $Pt(ClO_4)_2$, which may be more dissociated, or by simply increasing the dielectric constant of the reaction medium thereby aiding the salt to dissociate to produce the more highly charged and reactive cation.

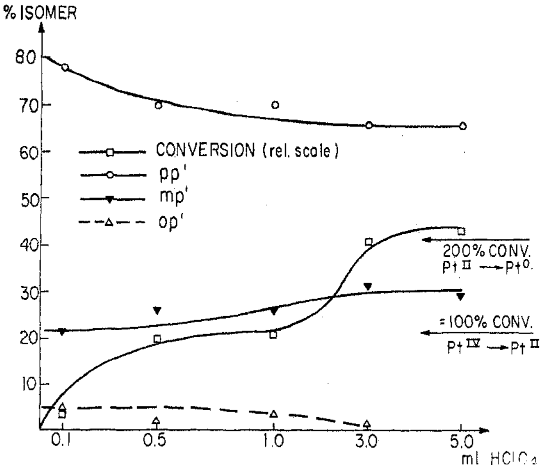

Figure 5.—Isomer distribution and conversion into bitolyl isomers as a function of $HClO_4$ concentration in the $Hg(OAc)_2$–$PtCl_4$ system.

Experimental Section

Coupling of Toluene with $PdCl_2$.—A 100-ml, three-necked flask was charged with 1.8 g (0.01 mol) of $PdCl_2$, 4.0 g (0.049 mol) of sodium acetate, 10.0 g (0.10 mol) of toluene, and 40.0 g (0.668 mol) of acetic acid. The mixture was blanketed with nitrogen and heated to 200° with an oil bath. In other experiments, the temperature was kept at 110, 90, 50, and 25°. The initially red mixture gradually turned black due to the formation of metallic palladium. The reaction was followed by gc analysis, using a 20 ft 5% Apiezon M on Chromosorb R column (200°, 150 ml of He/min). The relative retention times of the bitolyl isomers were as follows: *o,o'*-, 1.00; *o,m'*, 1.14; *o,p'*-, 1.31; *m,m'*-, 2.03; *m,p'*-, 2.17; *p,p'*-, 2.31. The mole percentage of each isomer present was determined by quantitative comparison to standard samples (see Table I). Best yield obtained at 90° for all isomers combined, based on $PdCl_2$ charged, was 58%.

Coupling of Toluene with $PdCl_2$ through an Organomercury Intermediate.—Mercuric acetate (3.1 g, 0.01 mol) was added at 25° to a mixture of 9.2 g (0.1 mol) of toluene and 6 g (0.1 mol) of acetic acid. On addition of 1.25 ml of $HClO_4$, the mercuration took place rapidly and was complete in 5 min. Then 0.44 g (0.0025 mol) of $PdCl_2$ was added. After 30 min the palladium metal was filtered off, washed, and dried. About 95% of the theoretical amount could be obtained. Gc analysis gave 1.6% *o,m'*-, 3.2% *o,p'*-, 2.3% *m,m'*-, 35.2% *m,p'*-, and 60% *p,p'*-bitolyl. Using excess mercuric acetate, close to theoretical yields of 1 mol of bitolyl for 1 mol of palladium acetate can be obtained.

Coupling of Toluene with $Hg(OAc)_2$-$Pd(OAc)_2$ (Experiments for Figures 3 and 4).—A series of experiments was run, where (1) the amount of palladium acetate was held constant at 0.001 mol and the mercuric acetate was varied from 0 to 0.01 mol (Figure 3), and (2) the amount of mercuric acetate was held constant at 0.001 mol and the $Pd(OAc)_2$ was varied from 0 to 0.01 mol (Figure 4).

Case 1.—Palladium acetate (0.224 g, 0.001 mol), 5 ml of toluene, 2 ml of acetic acid, and 0.2 ml of $HClO_4$ were charged to a 20-ml flask at room temperature. The appropriate amount of mercuric acetate was added. The mixture was shaken on a wrist-action shaker for 30 hr, followed by gc analysis. Results are shown in Figure 3.

Case 2.—The same procedure was followed as in case 1, charging 0.320 g (0.001 mol) of mercuric acetate, 5 ml of toluene, 2 ml of acetic acid, 0.2 ml of $HClO_4$, and the appropriate amount of palladium acetate. Results are shown in Figure 4.

Coupling of Toluene with $Hg(OAc)_2$-H_2PtCl_6 (Experiments for Figure 5).—To a mixture of 3.18 g (0.001 mol) of mercuric acetate, 0.5 g (0.0012 mol) of H_2PtCl_6, 6 ml of acetic acid, and 10 ml of toluene was added in separate experiments 0.1, 0.5, 1, 3, or 5 ml of $HClO_4$. The mixture was stirred at room temperature for 5 hr and then analyzed by gc for the various bitolyl isomers. Results are shown in Figure 5.

Registry No.—Toluene, 108-88-3; $PdCl_2$, 7647-10-1; $Hg(OAc)_2$, 1600-27-7; $Pd(OAc)_2$, 3375-31-3; H_2PtCl_6, 16941-12-1.