Reaction of Diazonium Salts with Transition Metals. Part 13.[1] Palladium-catalyzed Carbonylative Coupling of Arenediazonium Salts with Organotin Reagents to give Aromatic Ketones

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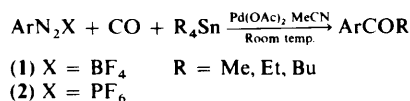
Palladium-catalyzed reactions of arenediazonium salts (ArN_2X; $Ar = Y-Ph$, $Y = H$, 2-, 3-, 4-Me, 2-Ph, 2-, 3-MeO, 2-, 3-, 4-Cl, 4-Br, 4-I, 2-, 3-, and 4-NO_2, $X = BF_4$ and PF_6) with carbon monoxide and organostannanes (R_4Sn, $R =$ Me, Et, and Ph; $RSnMe_3$, $R =$ Ph, 2-, 3-, 4-MeC_6H_4, and 4-ClC_6H_4; $RSnEt_3$, $R = 4-NO_2C_6H_4$; $RSnBu_3$, $R =$ Ph) gave aromatic ketones (ArCOR) in good yields (40—95%) at room temperature.

Replacement of a diazonium group is an effective method for the regioselective introduction of many functional groups into an aromatic ring, copper catalysts having frequently been used to facilitate the process *e.g.*, in Meerwein arylation[2] and Sandmeyer cyanation.[3] Recently, palladium-catalyzed reactions of arenediazonium salts, in which arylpalladium species are assumed to be intermediates, have afforded a simple method for the transformation of the C–N bond to a C–C bond, for processes such as alkenylation,[4] silylalkenylation,[5] carboxylation,[6] alkylation,[7] and formylation.[8] Such reactions have the advantage over conventional copper-catalyzed ones of both higher yields and less restriction of substituents on the two substrates.

In the presence of a palladium catalyst, organostannanes have been shown to be versatile reagents in cross-coupling reactions with organic halides and related electrophiles.[9–13] In a preliminary communication we reported the palladium-catalyzed transformation of a diazonium group to an acetyl group using carbon monoxide and Me_4Sn[14] and here we describe a convenient synthesis of aromatic ketones by the palladium-catalyzed carbonylative coupling of arenediazonium salts with organotin reagents.

Results

Synthesis of Aryl Alkyl Ketones.—The reactions were carried out with arenediazonium tetrafluoroborate (**1**) [or hexafluorophosphate (**2**)] (10 mmol), a tetra-alkyltin reagent (11 mmol), $Pd(OAc)_2$ (0.2 mmol) and carbon monoxide (9 kg/cm²) in acetonitrile (60 ml) at room temperature (20—25 °C) for 0.5 h (Scheme 1).

$$ArN_2X + CO + R_4Sn \xrightarrow[\text{Room temp.}]{\text{Pd(OAc)}_2, \text{ MeCN}} ArCOR$$

(**1**) X = BF_4 R = Me, Et, Bu
(**2**) X = PF_6

Scheme 1.

Carbon monoxide reduced $Pd(OAc)_2$ to a black powder which on addition of (**1**) immediately dissolved to give a pale yellow homogeneous solution. The consumption of (**1**) *i.e.*, the completion of the reaction, was indicated by reappearance of the black powder. Most of the present reactions were completed within 15 min. Both (**1**) and (**2**) were used successfully, whereas

Table 1. Palladium-catalyzed synthesis of aryl alkyl ketones from ArN_2X [(**1**) or (**2**)], carbon monoxide, and R_4Sn (Scheme 1)

ArCOR		Yields[b]	ArCOR		Yields[b]
Ar	R	%	Ar	R	%
Ph	Me	55[c]	2-ClC_6H_4	Me	76
Ph	Et	48[d,e]	3-ClC_6H_4	Me	59
Ph	Et	40[c,d,f]	4-ClC_6H_4	Me	90
Ph	Bu	Trace[g]	4-BrC_6H_4	Me	84
2-MeC_6H_4	Me	63	4-IC_6H_4	Me	79
3-MeC_6H_4	Me	70[h]	2-$NO_2C_6H_4$	Me	93
4-MeC_6H_4	Me	86	3-$NO_2C_6H_4$	Me	70
2-PhC_6H_4	Me	80[j]	3-$NO_2C_6H_4$	Me	66[i]
2-$MeOC_6H_4$	Me	64	4-$NO_2C_6H_4$	Me	85[c]
4-$MeOC_6H_4$	Me	69			

[a] Unless otherwise stated the reactions were carried out with (**1**) (10 mmol), Me_4Sn (11 mmol), $Pd(OAc)_2$ (0.2 mmol), and carbon monoxide (9 kg/cm²) in MeCN (60 ml) at room temperature for 0.5 h. [b] Isolated yields based on (**1**) or (**2**). [c] Reagent (**2**) was used. [d] Et_4Sn was used. [e] The reaction time was 5 h. [f] The reaction time was 6 h. [g] The reaction was carried out with Bu_4Sn in MeCN–Et_2O (50 ml : 50 ml) at 30 °C for 8 h. Most of the Bu_4Sn was recovered. [h] The product was contaminated with small amounts of impurities. [i] Atmospheric pressure of carbon monoxide was used. [j] 2-Phenylacetanilide (<2%) was present as an impurity.

the use of PhN_2Cl led to drastically decreased yields (<10%) and an increased proportion of intractable tarry materials. The isolated yields of ArCOR (R = Me and Et) are summarized in Table 1. Fairly good yields were obtained irrespective of the nature of the substituent on the aromatic ring. Carbon monoxide at atmospheric pressure could also be used and, although a longer reaction time was required, Et_4Sn also gave ArCOEt in this reaction. The reaction with Bu_4Sn did not proceed under the reaction conditions described. The corresponding alkyl arenes could not be detected in all the cases investigated.

Synthesis of Diaryl Ketones.—When $PhSnR_3$ (R = Me, Bu, and Ph) was used in the reaction with (**1**) (Ar = 4-MeC_6H_4), 4-methylbenzophenone was obtained along with small amounts of by-products (Scheme 2). No products derived from the alkyl groups of $ArSnR_3$ were formed in the reactions described in Tables 2 and 3.
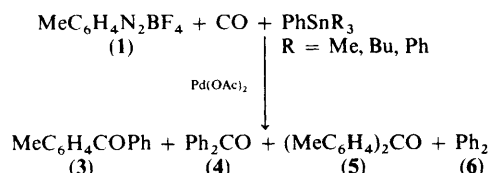
The effects of reaction conditions on the benzoylation are summarized in Table 2. A mixture of (**1**) and $Pd(OAc)_2$ was added to a solution of $PhSnR_3$ in acetonitrile after introduction

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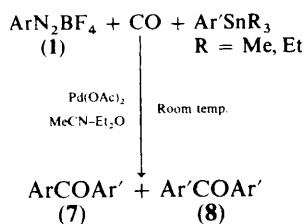
Table 2. Effects of reaction conditions on benzoylation of 4-$MeC_6H_4N_2BF_4$ (Scheme 2)[a]

PhSnR$_3$ R	Method[b]	Solvent	Reaction time (h)	Yields[c] (%)	Products (% ratio)[d]			
					(3)	(4)	(5)	(6)
Ph	A	MeCN	7	92	80	11	0	9
Ph	B	MeCN	7	65	96	1	0	3
Me	B	MeCN	1[e]	73	97	2.5	0.5	0
Me	B	MeCN–Et$_2$O	1[e]	82	98	2	0	0
Me	B	MeCN–THF	1[e]	87	97	2.7	0.3	0
Bu	B	MeCN–Et$_2$O	1[f]	71	97	2.4	0.6	0

[a] The reactions were carried out wih 2.5 mmol of a PhSnR$_3$, 2.5 mmol of 4-$MeC_6H_4N_2BF_4$, 0.05 mmol of $Pd(OAc)_2$ and carbon monoxide (10 kg/cm^2) in 30 ml of acetonitrile [or acetonitrile-diethyl ether (1:1) (50 ml)] at room temperature. [b] Method A: 4-$MeC_6H_4N_2BF_4$ was added finally. Method B: A mixture of 4-$MeC_6H_4N_2BF_4$ and $Pd(OAc)_2$ was added finally. [c] Isolated total yields of the products based on 4-$MeC_6H_4N_2BF_4$. [d] Determined by g.l.c. analysis of the ether extracts before isolation. [e] The black suspension was appeared within 5 min. [f] The reaction was carried out at 30 °C, and the black suspension appeared after 30 min.

$$MeC_6H_4N_2BF_4 + CO + PhSnR_3$$
$$(1) \qquad\qquad R = Me, Bu, Ph$$

Pd(OAc)$_2$

$$MeC_6H_4COPh + Ph_2CO + (MeC_6H_4)_2CO + Ph_2$$
$$(3) \qquad\qquad (4) \qquad\qquad (5) \qquad\qquad (6)$$

Scheme 2.

of carbon monoxide (method B in Table 2) to obtain compound (**3**) selectively. The 1:1 mixed solvent of acetonitrile and diethyl ether gave the best selectivity. Thus, the mixed solvent system and method B were employed in the following aroylation of (**1**) (Scheme 3).

$$ArN_2BF_4 + CO + Ar'SnR_3$$
$$(1) \qquad\qquad R = Me, Et$$

Pd(OAc)$_2$

MeCN–Et$_2$O Room temp.

$$ArCOAr' + Ar'COAr'$$
$$(7) \qquad\qquad (8)$$

Scheme 3.

The isolated yields of the cross-coupled products (**7**) are summarized in Table 3: no symmetric ketones derived from (**1**) and biaryls were observed in these reactions. In the reactions with PhSnMe$_3$, the black powder formed within a few minutes. Although some reactions with MeC$_6$H$_4$SnMe$_3$ failed to generate black powder during the reaction time described (Table 3), after purging with carbon monoxide, and addition of triethylamine the black powder was precipitated along with a white precipitate of R$_3$SnF. Whereas an electron-withdrawing substituent on (**1**) considerably increased the yield of the homo-coupling products. (**8**), use of 4-NO$_2$C$_6$H$_4$SnEt$_3$ suppressed formation of the latter [even with nitro substituted (**1**)] to give higher yields of compound (**7**).

The unsymmetric ketones bearing a polar substituent were easily isolated in pure form by simple procedures such as

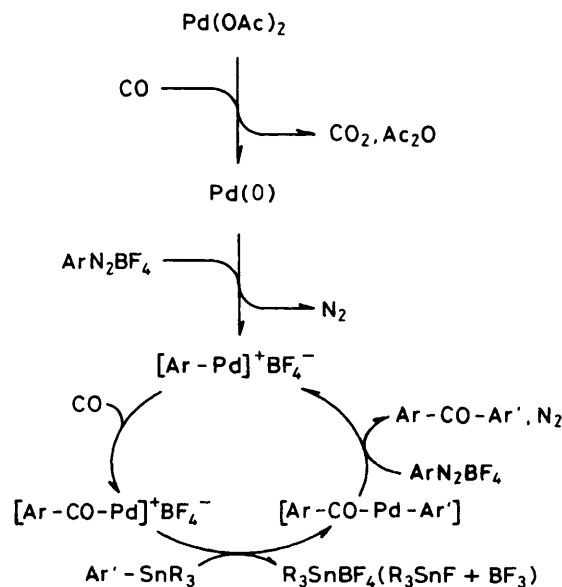**Table 3.** Palladium-catalyzed aroylation of ArN$_2$BF$_4$ (**4**) by carbon monoxide and Ar'SnR$_3$ (Scheme 3)[a]

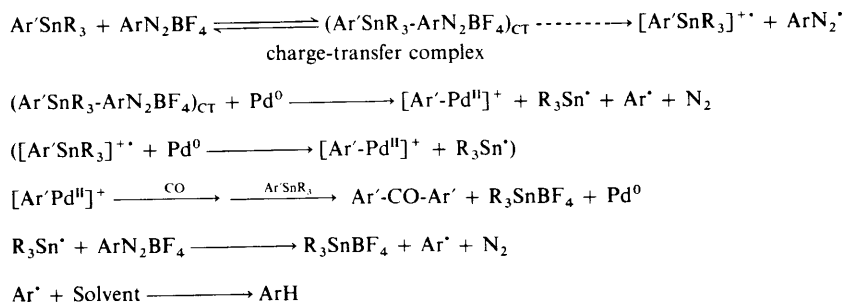| ArN$_2$BF$_4$ Ar	Ar'SnR$_3$ Ar'	R	Reaction time, h	Yields[b] %	Products (% ratio)[c] (7):(8)
4-MeC$_6$H$_4$	Ph	Me	1[d]	82[f]	98:2
4-BrC$_6$H$_4$	Ph	Me	1[d]	71	90:10
4-IC$_6$H$_4$	Ph	Me	1[d]	75	81:19
4-NO$_2$C$_6$H$_4$	Ph	Me	1[d]	72	78:22
2-MeC$_6$H$_4$	2-MeC$_6$H$_4$	Me	3[e]	72	—
3-MeC$_6$H$_4$	2-MeC$_6$H$_4$	Me	3[e]	76[f]	>99:Trace
3-ClC$_6$H$_4$	2-MeC$_6$H$_4$	Me	2[e]	69[f]	98:2
2-MeC$_6$H$_4$	3-MeC$_6$H$_4$	Me	2[e]	86[f]	99:1
3-MeC$_6$H$_4$	3-MeC$_6$H$_4$	Me	1	76	—
3-ClC$_6$H$_4$	3-MeC$_6$H$_4$	Me	2[e]	83[f]	95:5
4-NO$_2$C$_6$H$_4$	4-ClC$_6$H$_4$	Me	1	61	75:25
Ph	4-NO$_2$C$_6$H$_4$	Et	2.5	88	100:0
4-IC$_6$H$_4$	4-NO$_2$C$_6$H$_4$	Et	2	87	100:0
3-NO$_2$C$_6$H$_4$	4-NO$_2$C$_6$H$_4$	Et	4	96	100:0
4-NO$_2$C$_6$H$_4$	4-NO$_2$C$_6$H$_4$	Et	2.3	85	—

[a] The reactions were carried out with (1) (2.5 mmol), Ar'SnR$_3$ (2.5 mmol), $Pd(OAc)_2$ (0.05 mmol) and carbon monoxide (9 kg/cm^2) in a mixture of CH$_3$CN (25 ml) and Et$_2$O (25 ml) at room temperature. [b] Unless otherwise stated isolated yields of pure (7) based on (1). [c] Determined by g.l.c. analysis of the ether extracts before isolation. [d] The black suspension appeared within 5 min. [e] The black suspension did not appear. [f] The product was contaminated with a small amount of (8) (<2%).

column chromatography (silica gel–CCl$_4$/CHCl$_3$) and/or recrystallization.

Discussion

The present carbonylative coupling of (**1**) with organostannanes can be reasonably described by the catalytic cycle shown in Scheme 4.[6,15] Carbon monoxide readily reduces $Pd(OAc)_2$ to palladium(0), which reacts with (**1**) to give the arylpalladium species under very mild conditions.[16] The absence of direct coupling products (Ar–R) suggests that the carbon monoxide

$$Pd(OAc)_2$$

$$CO \longrightarrow \qquad \longrightarrow CO_2, Ac_2O$$

$$Pd(0)$$

$$ArN_2BF_4 \longrightarrow$$
$$\longrightarrow N_2$$

$$[Ar-Pd]^+BF_4^-$$

$$CO \qquad\qquad Ar-CO-Ar', N_2$$

$$\qquad\qquad ArN_2BF_4$$

$$[Ar-CO-Pd]^+BF_4^- \qquad [Ar-CO-Pd-Ar']$$

$$Ar'-SnR_3 \qquad R_3SnBF_4(R_3SnF + BF_3)$$

Scheme 4.

$$Ar'SnR_3 + ArN_2BF_4 \rightleftharpoons (Ar'SnR_3\text{-}ArN_2BF_4)_{CT} \dashrightarrow [Ar'SnR_3]^{+\cdot} + ArN_2^{\cdot}$$
$$\text{charge-transfer complex}$$

$$(Ar'SnR_3\text{-}ArN_2BF_4)_{CT} + Pd^0 \longrightarrow [Ar'\text{-}Pd^{II}]^+ + R_3Sn^{\cdot} + Ar^{\cdot} + N_2$$

$$([Ar'SnR_3]^{+\cdot} + Pd^0 \longrightarrow [Ar'\text{-}Pd^{II}]^+ + R_3Sn^{\cdot})$$

$$[Ar'Pd^{II}]^+ \xrightarrow{\text{CO}} \xrightarrow{Ar'SnR_3} Ar'\text{-CO-}Ar' + R_3SnBF_4 + Pd^0$$

$$R_3Sn^{\cdot} + ArN_2BF_4 \longrightarrow R_3SnBF_4 + Ar^{\cdot} + N_2$$

$$Ar^{\cdot} + \text{Solvent} \longrightarrow ArH$$

Scheme 5.

Table 4. Effects of reaction conditions on benzoylation of 4-$NO_2C_6H_4N_2BF_4$[a]

PhSnR$_3$	Solvent	Additive	Yields[b] (%)	Products (% ratio)[c] (7):(4)	PhNO$_2$[d] %
Me	MeCN–Et$_2$O		72 (97)	78:22	—
Me	MeCN–Et$_2$O	DBP[e]	62 (88)	77:23	—
Me	DME[f]		9[g] (45)	20:80	32
Me	MeCN		62 (88)	80:20	—
Bu	MeCN–Et$_2$O		35[g] (50)	70:30	58

[a] The reactions were started by addition of a mixture of 4-$NO_2C_6H_4N_2BF_4$ (2.5 mmol) and Pd(OAc)$_2$ (0.05 mmol) to a solution of PhSnR$_3$ (2.5 mmol) under 10 kg/cm^2 of carbon monoxide at room temperature for 1 h. [b] Unless otherwise noted, isolated yields of (7) based on (1). The values in parenthesis are total yields of (4) and (7). [c] Determined by g.l.c. before isolation. [d] G. l.c. yields based on (1). [e] 2,6,-Di-t-butylphenol (10 mol%). [f] 1,2-Dimethoxyethane. [g] G.l.c. yields of (7) based on (1).

is firmly bound into the Ar–Pd bond. The high reactivity of (1) with palladium(0) and that of organostannanes with palladium(II) are responsible for the selective formation of the cross-coupling products.

The formation of (8) can be explained by different reaction sequences. The withdrawing groups of (1) relative to Ar'SnR$_3$ suggest that electron transfer is from Ar'SnR$_3$ to (1) and it is known that arene-diazonium salts form charge-transfer complexes with various aromatic compounds.[17] On addition of PhSnMe$_3$ to an acetonitrile solution of 4-$NO_2C_6H_4N_2BF_4$ the yellow colour deepened and the mixture showed the charge-transfer absorption signal near 400 nm, the absorption maximum of which was indistinct. Since the spontaneous reaction of (1) with Ar'SnR$_3$ is very slow in the absence of a palladium catalyst, palladium(0) may react with the charge-transfer complex to yield the Ar'Pd^{II} species via electron transfer as shown in Scheme 5. The effects of different reaction conditions on the formation of compounds (4) and (8) from 4-$NO_2C_6H_4N_2BF_4$ and PhSnR$_3$ (R = Me and Bu) are given in Table 4. The reaction with PhSnMe$_3$ or PhSnBu$_3$ in dimethoxyethane (DME) produced considerable amounts of nitrobenzene and decreased the yield of ketone products, the former arising from the 4-nitrophenyl radical (Ar·). The larger alkyl groups on PhSnR$_3$ may not affect the formation of charge-transfer complexes but may depress the transmetallation from tin to palladium. The reactions of organostannanes are liable to include radical species,[18] and reduction of ArN$_2$X by R$_3$SnH proceeds via a radical process.[19] Protons on DME which may be used to effect isomerization are readily abstracted by radical species. Addition of 2,6-di-t-butylphenol (DBP), which is an effective inhibitor of isomerization in the palladium-catalyzed reactions of alkenylstannanes,[12] did not affect the formation of (4). This observation need not necessarily imply the absence of

radical species but only suggests the absence of a radical chain reaction. Since trialkylstannyl radicals easily abstract iodine from aryl iodides,[20] the presence of (4) in the benzoylation of 4-$IC_6H_4N_2BF_4$ (Table 3) can be explained by the iodine abstraction from 4-iodobenzophenone by the trimethylstannyl radical. The formation of (3) in the carbonylative coupling of 4-$IC_6H_4N_2BF_4$ with 4-$MeC_6H_4SnMe_3$ also explains the presence of the trimethylstannyl radical (Scheme 6).

$$ArN_2BF_4 + Ar'SnMe_3 + CO$$
$$(Ar = 4\text{-}IC_6H_4, \ Ar' = 4\text{-}Me\text{-}C_6H_4)$$
$$\downarrow \begin{array}{c} Pd(OAc)_2 \\ MeCN\text{-}Et_2O \end{array} \quad \begin{array}{c} \text{Room temp.} \\ 1 \text{ h} \end{array}$$
$$ArCOAr' + Ar'COAr' + PhCOAr' + PhI$$
$$\quad (7) \qquad \quad (5) \qquad \quad (3)$$
$$\quad 81\% \qquad \quad 7\% \qquad \quad 2\% \qquad 14\%$$
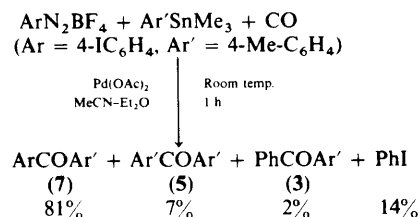
Scheme 6.

The fair to excellent yields obtained irrespective of the type of substituents on both (1) and the organotin reagent supports the use of the carbonylative coupling procedure in synthetic organic chemistry. The procedure overcomes the problem of highly variable or low yields, such as those obtained in the arylation of oximes,[2] and also allows selective formation of ortho-and meta-substituted ketones which cannot be produced by more general methods such as Friedel-Crafts acylation.

The present reaction is closely related to the recently described palladium-catalyzed carbonylative coupling of aromatic halides with organostannanes and carbon monoxide.[11,21] Because of the high reactivity of the diazonium group, halogeno substituted, and especially iodo substituted aromatic ketones can be prepared chemoselectively from halogeno substituted (1). Furthermore, some of the aryl halides are commonly prepared from ArN$_2$X. The palladium-catalyzed coupling of acyl halides with organostannanes is another valuable method in organic synthesis.[2]

Experimental

Materials.—Acetonitrile was distilled from phosphorus pentaoxide (twice) and calcium hydride under nitrogen. Diethyl ether, 1,2-dimethoxyethane, and tetrahydrofuran were distilled from sodium metal or sodium benzophenone ketyl. ArN$_2$BF$_4$ (1)[22] and ArN$_2$PF$_6$ (2)[23] were prepared by the literature methods and stored under nitrogen in a refrigerator. Palladium acetate was prepared by the published method.[24] Ph$_4$Sn and Bu$_4$Sn were used as received. Organotin reagents except for 4-$NO_2C_6H_4SnEt_3$ were prepared by the reactions of Grignard reagents with SnCl$_4$ or R$_3$SnCl.[25] 4-Nitrophenyltriethyltin was prepared by the palladium-catalyzed reaction of 4-$NO_2C_6H_4I$ with (Et$_3$Sn)$_2$.[26]

General Procedure for the Synthesis of Aryl Alkyl Ketones.—A mixture of R$_4$Sn (11 mmol), Pd(OAc)$_2$ (0.2 mmol), and

acetonitrile (60 ml) was placed in a glass autoclave. Reagent ArN$_2$X (**1**) or (**2**) (10 mmol) wrapped in polyethylene film was held loosely to a stirring rod and added to the reaction mixture by rotating the stirring rod after introduction of carbon monoxide (9 kg/cm^2). The fine black powder formed by the introduction of carbon monoxide disappeared on mixing the ArN$_2$X with the solution. The mixture was then stirred for 0.5 h. The completion of reaction was easily discerned by reappearance of the black suspension. Carbon monoxide was released and the reaction mixture was refluxed for 1 h. When this procedure was omitted, unidentified impurities remained in the products even after distillation. After removal of acetonitrile, the residue was diluted with ether, neutralized by aqueous sodium carbonate and vacuum distilled and/or column chromatographed to yield the pure ketones. The introduction of chloride ion in the isolation procedure, *e.g.* washing by brine or hydrochloric acid, must be avoided, as it is difficult to remove R$_3$SnCl once formed.

Acetophenone, propiophenone, and valerophenone. The i.r. and n.m.r. spectra, and retention time on g.l.c. of the products were identical to those of commercial compounds. M.p., $\nu_{max.}$ (C=O), and δ(Me) (relative to Me$_4$Si) are shown in parentheses.

2'-Methylacetophenone (liq.; 1 680 cm^{-1}; 2.45, 6 H). 3'-Methylacetophenone (liq.; 1 675 cm^{-1}; 2.40, 2.55). 4'-Methylacetophenone (liq.; 1 680 cm^{-1}; 1.92, 2.08). 2'-Methoxyacetophenone (liq.; 1 670 cm^{-1}; 2.45, 3.22). 4'-Methoxyacetophenone [37.0—37.2 °C (lit.,[27] 38—39 °C); 1 665 cm^{-1}; 2.35, 3.7]. 2'-Phenylacetophenone (liq.; 1 690 cm^{-1}; 1.90). 2'-Chloroacetophenone (liq.; 1 700 cm^{-1}; 2.50). 3'-Chloroacetophenone (liq.; 1 690 cm^{-1}; 2.40). 4'-Chloroacetophenone [liq. (lit.,[27] 20 °C); 1 685 cm^{-1}; 2.10]. 4'-Bromoacetophenone [49.5—51.0 °C (lit.,[27] 50—51 °C); 1 690 cm^{-1}; 2.52]. 4'-Iodoacetophenone [84.8—85.8 °C (lit.,[28] 83—84 °C); 1 675 cm^{-1}; 2.52]. 2'-Nitroacetophenone [liq. (lit.,[28] 24.5 °C); 1 705 cm^{-1}; 2.50]. 3'-Nitroacetophenone [78.0—79.0 °C (lit.,[27] 80—81 °C); 1 690 cm^{-1}; 2.65]. 4'-Nitroacetophenone [78.8—80.0 °C (lit.,[28] 78—80 °C); 1 690 cm^{-1}; 2.64].

Diaryl Ketones.—A mixture of (**1**) (2.5 mmol) and Pd-(OAc)$_2$ (0.05 mmol) was added to a solution of Ar'SnMe$_3$ (2.5 mmol) in acetonitrile (25 ml) and diethyl ether (25 ml) after introduction of carbon monoxide (9 kg/cm^2) at room temperature. The solution was purged with carbon monoxide, triethylamine (0.5 ml) was added to precipitate R$_3$SnF and the resulting white precipitate was filtered off and washed with ether (3 × 30 ml). The combined filtrate and washings were analyzed by g.l.c. (Silicone SE-30) to determine the products ratio. After removal of solvent, the residue was purified with column chromatography.

4-Methylbenzophenone, m.p. 58—59 °C (lit.,[28] 59—60 °C), $\nu_{C=O}$ 1 650 cm^{-1}, δ(Me) 2.30. 4-Iodobenzophenone, m.p. 99.7—100.0 °C (lit.,[28] 100—101 °C), $\nu_{C=O}$ 1 630. 4-Bromobenzophenone, m.p. 75 °C (lit.,[28] 79—80 °C), $\nu_{C=O}$ 1 640 cm^{-1}. 4-Nitrobenzophenone, m.p. 135.5—136.0 (lit.,[28] 136—138 °C), $\nu_{C=O}$ 1 640 cm^{-1}. 2,2'-Dimethylbenzophenone, m.p. 69 °C (lit.,[29] 70—70.5 °C), $\nu_{C=O}$ 1 660 cm^{-1}, δ(Me) 2.4. 2,3'-Dimethylbenzophenone, liq. (m.p. of 2,4-dinitrophenylhydrazone, 203—204 °C), $\nu_{C=O}$ 1 650 cm^{-1}, δ(Me) 2.20, 2.25 (Found: C, 85.45; H, 6.95. Calc. for C$_{15}$H$_{14}$O: C, 85.65; H, 6.71%). 4-Chloro-4'-nitrobenzophenone, m.p. 97—98 °C (lit.,[28] 98 °C), $\nu_{C=O}$ 1 650 cm^{-1}. 3'-Chloro-2-methylbenzophenone, liq. (m.p. of 2,4-dinitrophenylhydrazone, 208—210 °C), $\nu_{C=O}$ 1 660 cm^{-1}, δ(Me) 2.30, (Found: C, 73.05; H, 5.10. Calc. for C$_{14}$H$_{11}$OCl: C, 72.89; H, 4.81%). 3'-Chloro-3-methylbenzophenone, m.p. 65—66 °C, $\nu_{C=O}$ 1 660 cm^{-1}, δ(Me) 2.40 (Found: C, 72.90; H, 5.05. Calc. for C$_{14}$H$_{11}$OCl: C, 72.89; H, 4.81%). 3,3'-Dimethylbenzophenone, m.p. 44.5—45.5 °C (lit.,[29] 48—49 °C), $\nu_{C=O}$

1 650 cm^{-1}, δ(Me) 2.40. 3,4'-Dinitrobenzophenone, m.p. 174—176.5 °C (lit.,[28] 175 °C), $\nu_{C=O}$ 1 650 cm^{-1}. 4,4'-Dinitrobenzophenone, m.p. 188—191.5 °C (lit.,[28] 189 °C), $\nu_{C=O}$ 1 650 cm^{-1}. 4-Iodo-4'-nitrobenzophenone, m.p. 132.5—134.5 °C, $\nu_{C=O}$ 1 650 cm^{-1}, (Found: C, 44.40; H, 2.30; N, 4.06. Calc. for C$_{13}$H$_8$NO$_2$I: C, 44.20; H, 2.30; N, 3.95%). 4-Iodo-4'-methylbenzophenone, m.p. 157.5—158.0 °C, $\nu_{C=O}$ 1 635 cm^{-1}, δ(Me) 2.40 (Found: C, 52.2; H, 3.45. Calc. for C$_{14}$H$_{11}$OI: C, 52.20; H, 3.44%).

The formation of minor homo-coupling products were confirmed by the comparison of their retention time with that of authentic samples on g.l.c. The minor products were not isolated.

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