The *in Situ*-generated Nickel(0)-catalyzed Reaction of Aryl Halides with Potassium Iodide and Zinc Powder

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The *in situ*-generated nickel(0) species, presumably atomic nickel, from nickel(II) salt and zinc powder has been proved to be an effective catalyst for the Finkelstein-type displacement reaction of aryl bromides with potassium iodide to give aryl iodides under mild conditions. This species was also effective for the Ullmann-type coupling of bromides or aryl iodides by the use of zinc powder to give biaryls. Furthermore, in the presence of excess nickel(II) salt, the coupling reaction proceeded smoothly, even at an ambient temperature, to give various biaryls in very good yields.

The chemistry of activated metal species has attracted much attention recently from the standpoint of their great affinity for various substrates, including aryl halides.[1] We have found that nickel(II) salt was readily reduced to elemental nickel with zinc powder in the presence of potassium iodide in hexamethylphosphoric triamide (HMPA). On the other hand, if the reaction was conducted in the presence of aryl halides, such as aryl bromides or aryl iodides, aryl iodides and/or biaryls were produced instead of elemental nickel. This implied that not only a Finkelstein-type displacement reaction (Eq. 1),[2] but also an Ullmann-type coupling reaction using zinc powder (Eq. 2)[3] took place, with the aid of the nickel catalyst, with otherwise inert substrates:

$$\mathrm{ArBr} + \mathrm{KI} \xrightarrow{\mathrm{Ni^0}} \mathrm{ArI} + \mathrm{KBr} \quad (1)$$

$$2\mathrm{ArI} + \mathrm{Zn} \xrightarrow{\mathrm{Ni^0}} \mathrm{Ar_2} + \mathrm{ZnI_2} \quad (2)$$

Here in this paper, we will report the detailed results of the facile synthesis of aryl iodides or biaryls from aryl halides by means of *in situ*-generated nickel(0) species.[4]

Results and Discussion

Synthesis of Aryl Iodides from Aryl Bromides. At the beginning of this study, some attempts were made to seek a favorable system for the catalytic displacement reaction of bromobenzene with potassium iodide under mild conditions. The results are shown in Table 1. *In situ*-generated nickel(0) species from nickel(II) salt and zinc powder[5] exhibited a great reactivity among the catalysts examined.[6] Some preformed nickel(0) complexes were also reactive catalysts, but preformed elemental nickel exhibited little reactivity. HMPA was the most suitable solvent. Nickel(II) complexes revealed reactivities only at such an elevated temperature as 140 °C.

The results from various aryl bromides with *in situ*-generated nickel(0) species are listed in Table 2. Aryl bromides containing a meta or para substituent afforded the corresponding aryl iodides in fair yields, accompanied by rather large quantities of biaryls. Aryl bromides containing an ortho electron-withdrawing substituent and aryl chlorides were less reactive, and in such runs elemental nickel soon appeared.

Further investigations were undertaken to improve the selectivity (aryl iodide/(aryl iodide+biaryl) ratio); the results are listed in Table 3 and Fig. 1. Table 3 shows that the selectivity depends on the amount of zinc powder: a decreased amount of zinc powder is favorable, but it simultaneously reduces the conversion. Figure 1 shows that biaryl is produced consecutively from aryl bromide *via* aryl iodide and that the transformation of aryl iodide into biaryl proceeds in preference to the desired transformation of aryl bromide into aryl iodide near the end of the reaction. Therefore, in order to enhance the selectivity, the reaction must be interrupted prior to reaching completion.

From the viewpoint of synthetic utility, a nickel(II)-catalyzed displacement reaction at elevated temperatures might bepreferable to a nickel(0)-catalyzed one, since, in the former case, the resulting product is not contaminated with any biaryl (Runs 39 and 40 and Table 1).

Synthesis of Biaryls from Aryl Iodides. The above-mentioned displacement reaction with the aid of *in situ*-generated nickel(0) species was accompanied by a coupling reaction which probably consumed the zinc powder, judging from the results in Table 3. Then, in the presence of an adequate amount of zinc powder,

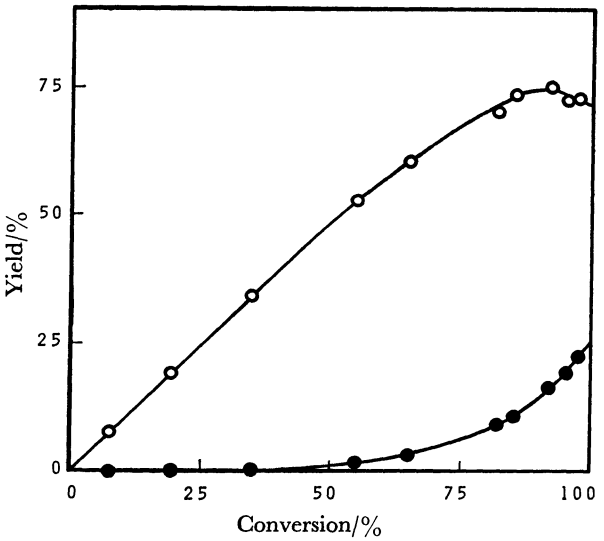

Fig. 1. Plots of conversion of bromobenzene *vs.* yield of iodobenzene or biphenyl.
—○—: Iodobenzene, —●—: biphenyl.

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TABLE 1. EFFECTS OF VARIOUS CONDITIONS ON THE NICKEL-CATALYZED DISPLACEMENT OF BROMOBENZENE WITH POTASSIUM IODIDE[a]

Run	Catalyst	Solvent	Temp °C	Time h	Conv[b] %	Yield[b] %
1	$NiBr_2$	DMF[c]	150	24	38	34(0)
2	$NiBr_2$–PBu_3[d]	DMF	150	3	95	88(0)
3	$NiBr_2$–PEt_3[e]	DMF	150	3	59	51(0)
4	$NiBr_2$–NBu_3[f]	DMF	150	3	57	51(0)
5	$NiBr_2$–PCy_3[g]	DMF	150	3	24	19(0)
6	$NiBr_2$–TMED[h]	DMF	150	3	12	12(0)
7	$NiBr_2$–PBu_3	NMP[i]	150	3	91	89(0)
8	$NiBr_2$–PBu_3	NMP	180	3	89	87(0)
9	$NiBr_2$–PBu_3	NMP	150	1	77	76(0)
10	$NiBr_2$–PBu_3	TMU[j]	150	1	63	58(0)
11	$NiBr_2$–PBu_3	DMAc[k]	150	1	59	56(0)
12	$NiBr_2$–PBu_3	PC[l]	150	1	58	53(0)
13	$NiBr_2$–PBu_3	HMPA	150	1	31	25(0)
14	$NiBr_2$–PBu_3	DGDE[m]	150	1	10	10(0)
15	$NiBr_2$–PBu_3	DMSO[n]	150	1	7	0(0)
16	$NiBr_2$–PBu_3	DMF	140	12	93	89(0)
17	$NiBr_2$–PBu_3	DMF	80	12	—[o]	0(0)
18	Ni[p]	HMPA	50	1.5	96	77(15)
19	Ni	NMP	50	1.5	87	59(30)
20	Ni	DMF	50	1.5	38	36(2)
21	Ni	Pyridine	50	1.5	—[o]	6(0)
22	Ni	THF[q]	50	1.5	—[o]	4(0)
23	Ni	AN[r]	50	1.5	—[o]	1(0)
24	$Ni(COD)_2$	HMPA	50	4	60	52(8)
25	$Ni(PPh_3)_3$	HMPA	50	4	20	10(10)
26	Ni-$[P(OPh)_3]_4$	HMPA	50	4	—[o]	0(0)
27	Ni–PBu_3	HMPA	50	3	80	74(5)
28	Ni-$P(OBP)_3$[s]	HMPA	50	3	35	33(3)

a) The molar ratios of the components were as follows: PhBr/$NiBr_2$/Ligand/KI = 1.0/0.025/0.050/3.0 for Runs 1—17. PhBr/$NiBr_2$/Zn/Ligand(when used)/KI = 1.0/0.02/0.17/0.04/2.5 for Runs 18—23, 27, and 28. PhBr/Ni/KI = 1.0/0.05/2.5 for Runs 24—26. The reactions were carried out on a 0.5—1.0 mmol scale under nitrogen. b) GLC analysis using internal standards. Yields based on bromobenzene. Yields in parentheses were those of biphenyl. c) DMF = *N*,*N*-dimethylformamide. d) PBu_3 = tributylphosphine. e) PEt_3 = triethylphosphine. f) NBu_3 = tributylamine. g) PCy_3 = tricyclohexylphosphine. h) TMED = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine. i) NMP = *N*-methyl-2-pyrrolidone. j) TMU = tetramethylurea. k) DMAc = *N*,*N*-dimethylacetamide. l) PC = propylene carbonate. m) DGDE = diethylene glycol dimethyl ether. n) DMSO = dimethyl sulfoxide. o) Not determined. p) Ni = *in situ*-generated nickel from nickel(II) bromide and zinc powder. q) THF = tetrahydrofuran. r) AN = acetonitrile. s) $P(OBP)_3$ = tris(2-biphenylyl)phosphite.

TABLE 2. CATALYTIC SYNTHESIS OF ARYL IODIDES[a]

Run	X	Y	Time h	Aryl iodide[b] %	Biaryl[b] %
18	Br	H	1.5	77	15
29	Br	4-OCH_3	1.5	78	16
30	Br	4-$COCH_3$	1.5	76	22
31	Br	4-Cl	1.5	81	9
32	Br	4-NO_2	1.5	0	0
33	Br	3-CO_2CH_3	5	81	11
34	Br	2-CH_3	3	66	23
35	Br	2-OCH_3	1.5	47	6
36	Br	2-CO_2CH_3	4	0	9
37	Cl	H	20	0	0
38	Cl	4-$COCH_3$	20	0	0
39	Br	4-OCH_3	2	(80)	
40	Br	4-$COCH_3$	2	(66)	

a) Conditions of Runs 29—38 were same as those of Run 18. Conditions of Runs 39 and 40 were same as those of Run 2, except for the reaction temperature of 153 °C. b) GLC analysis using internal standards. Yields based on aryl halides. Yields in parentheses were isolated ones.

TABLE 3. EFFECT OF ZINC POWDER ON PRODUCT DISTRIBUTION[a]

Run	Zn/$NiBr_2$ molar ratio	Time h	Conv[b] %	PhI/Ph–Ph[b] molar ratio	Ph–Ph[c] %
41	0	12	0	—	—
42	1	12	92	44	100
43	3	12	98	14	100
44	7	5	99	6	86
45	75	3	100	0.15	60

a) Conditions were same as those of Run 18, except for the amount of Zn powder. b) GLC analysis using internal standards. c) Yields based on Zn powder.

the Ullmann-type coupling of aryl iodides by the use of zinc powder (Eq. 2) was considered feasible. Actually, the coupling reaction proceeded smoothly under mild conditions with the aid of *in situ*-generated nickel(0) species.

The results from various aryl iodides are listed in Table 4. The reaction mixture was green during the reaction, but it turned black near the end of the reaction. A stoichiometric amount of zinc powder sufficed for the reaction, but the use of excess zinc powder was desirable. The presence of potassium iodide promoted the reaction efficiently.[7] Preformed elemental nickel exhibited little reactivity for this reaction, either. Aryl iodides containing a meta or para substituent afforded

Table 4. Catalytic synthesis of biaryls[a]

Run	X	Y	Time h	Yield[b] %
46	I	H	3.5	94
47[c]	I	H	3.5	(98)
48[d]	I	H	3.5	(0)
49	I	4-$COCH_3$	3	98
50	I	4-CH_3	10	92
51	I	4-OCH_3	30	87
52	I	4-NO_2	3	0
53	I	3-CO_2CH_3	3	96
54	I	2-CH_3	7	83
55	I	2-Cl	17	(25)[e]
56	I	2-CO_2CH_3	10	(22)[f]
57[g]	Br	H	7	(98)
58	Cl	H	7	(0)

a) Molar ratio of the components was as follows: ArX/Zn/$NiBr_2$/KI = 1.0/1.25—1.85/0.025/1.25. The reaction was carried out on a 0.4—10 mmol scale in HMPA at 50 °C under nitrogen. b) Isolated Yields. Yields in parentheses were determined by GLC. c) PhI/Zn/$NiBr_2$/KI = 1.0/0.6/0.05/1.25. d) KI was not added. e) Chlorobenzene 39%. f) Methyl benzoate 67%. g) Two times as much KI was used.

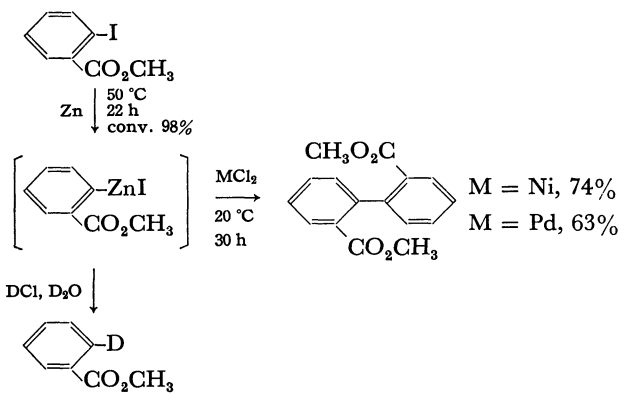
Table 5. Biaryl synthesis at ambient temperature[a]

Run	Y	Z	Time h	Yield[b] %
59	H	H	8	100
60	2-CO_2CH_3	H	6	95
61[c]	2-CO_2CH_3	H	7	28
62	2-CO_2CH_3	4-CH_3	28	(98)
63	2-$COCH_3$	H	6	96(68)[d]
64[e]	2-Cl	H	3.5	84(59)[f]
65[e]	2-CF_3	H	6	75(29)[g]

a) Molar ratio of the components was as follows: ArI/$NiCl_2$/Zn/KI = 1.0/1.1/1.0/1.25. The reactions were carried out on a 0.4—8 mmol scale in HMPA at 20 °C under nitrogen. b) GLC analysis using internal standards. Yields in parentheses were isolated ones. c) $PdCl_2$ was used in the place of $NiCl_2$. d) Reaction for 16 h. e) Reaction at 35 °C. f) Reaction at 20 °C for 18 h. g) Reaction at 20 °C for 100 h.

the corresponding biaryls in good yoelds. Biaryls were also produced from aryl bromides under conditions almost identical with those in aryl iodides: this is clearly due to the rapid formation of aryl iodide from aryl bromide under this catalyst system.

Aryl iodides containing an ortho electron-withdrawing substituent afforded large quantities of dehaloprotonated products, which probably arose from organozinc compounds,[8] by-products of the combination of aryl iodides and zinc powder, upon an aqueous workup. The addition of palladium(II) or nickel(II) salt to a prepared mixture including organozinc compounds afforded the biaryls containing electron-withdrawing substituents at the 2,2′-positions, presumably *via* the well-known transfer of organo groups from zinc(II) to palladium(II) or nickel(II).[9,10] A convenient



batch method could be used for the system. That is, in the presence of excess nickel(II) salt, the coupling reaction proceeded smoothly even at an ambient temperature to give various biaryls in very good yields. The results are shown in Table 5. The intermediate use of organozinc compounds in these reactions was, however, omitted on the basis of the fact that the reaction between aryl iodides and zinc powder was by far slower than the present coupling reaction.[11]

Reaction Path. The results and discussion presented above lead to the following equations as the most plausible sequences of the reaction. The atomic nickel which comes from nickel(II) salt and zinc powder (Eq. 3) readily reacts with aryl halide (bromide or iodide) to give an oxidative-addition adduct, **1** or **2** (Eqs. 4 and 6).

$$NiX_2 + Zn \longrightarrow Ni + ZnX_2 \quad (3)$$

$$Ni + ArBr \rightleftharpoons \underset{\mathbf{1}}{Ar\text{-}Ni\text{-}Br} \quad (4)$$

$$Ar\text{-}Ni\text{-}Br + KI \rightleftharpoons \underset{\mathbf{2}}{Ar\text{-}Ni\text{-}I} + KBr \quad (5)$$

$$Ar\text{-}Ni\text{-}I \rightleftharpoons ArI + Ni \quad (6)$$

$$2Ar\text{-}Ni\text{-}I \rightleftharpoons \underset{\mathbf{3}}{Ar\text{-}Ni\text{-}Ar} + NiI_2 \quad (7)$$

$$Ar\text{-}Ni\text{-}Ar \longrightarrow Ar_2 + Ni \quad (8)$$

In a catalytic displacement reaction, the metathetical replacement of **1** with potassium iodide produces another organonickel(II) species **2** (Eq. 5), which subsequently yields aryl iodide and regenerates the atomic nickel to ensure the catalytic reaction (Eq. 6). This is the well-known sequence of oxidative addition, metathesis, and reductive elimination in transition metal chemistry.[12] It is noteworthy that the equilibrium in Eq. 5 is presumed to lie so far to the right, because the concentration of potassium iodide is much higher than that of potassium bromide in our solvent (see Experimental).[13]

In a coupling reaction, the disproportionation of **2** takes place to give nickel(II) salt and a diorganonickel(II) species, **3** (Eq. 7), which subsequently yields biaryl (Eq. 8). This type of decomposition is well-established and is not catalytic by nature.[14] To ensure the catalytic

cycle, the original atomic nickel must be regenerated from the nickel(II) salt thus formed, and then zinc powder in at least a stoichiometric quantity is required.

Some aryl halides, such as aryl chlorides, or aryl bromides and aryl iodides containing an ortho electron-withdrawing substituent, do not undergo either reaction. Presumably, these aryl halides can not trap a generated atomic nickel efficiently; consequently, they condense to form a slurry that no longer exhibits rcactivity, even for reactive aryl halides, as has been described above.

Experimental

All reagents were used directly as obtained commercially, unless otherwise noted. The solvents were distilled under nitrogen and were dried over a molecular sieve (3A). The $RhCl(PPh_3)_3$[15] and $Ni[P(OPh)_3]_4$[16] were prepared by previously reported methods. Some aryl iodides were prepared according to a procedure in the literature.[17] The ^1H NMR spectra were obtained on JOEL PMX 60 apparatus. A Hitachi 160 gas chromatograph was used for the GLC analyses.

Reduction of Nickel(II) Chloride by Zinc Powder. A mixture of zinc powder (65 mg, 1.0 mmol), nickel(II) chloride (38 mg, 0.3 mmol), potassium iodide (83 mg, 0.5 mmol), and HMPA (0.5 ml) was evacuated, flushed with nitrogen, and kept at 20 °C with stirring. The initial blue-green solution gradually turned black. After 10 h, the resulting black solid was filtered off and washed with aqueous ammonia and water until the wash was free of the nickel(II) ion. The amount of elemental nickel was determined by the dimethylglyoxime method, which showed that 93% of the nickel(II) chloride had been reduced to elemental nickel.

Preparation of Aryl Iodides. *Preparation of* p-*Iodoanisole*: A mixture of *p*-bromoanisole (0.32 ml, 2.5 mmol), potassium iodide (2.07 g, 12 mmol), a 0.17 mol dm^{-3}-DMF solution of nickel(II) bromide (0.59 ml, 0.10 mmol), tributylphosphine (0.059 ml, 0.20 mmol), and DMF (1.90 ml) was heated to reflux for 2 h with stirring under nitrogen. To the resulting mixture, aqueous sodium chloride (20 ml) was added, and the organic materials, extracted with three 10-ml portions of pentane, were washed successively with three 5- ml portions of concd hydrochloric acid, aqueous sodium chloride (15 ml), aqueous sodium carbonate (15 ml), and aqueous sodium thiosulfate (15 ml), and then dried over anhydrous sodium sulfate. The evaporation of the solvent gave 0.52 g of crude *p*-iodoanisole (87%). Recrystalization from hexane gave the pure iodide. Mp 47—48 °C (lit,[18] 51—52 °C). Found: C, 35.68; H, 3.04%. Calcd for C_7H_7IO: C; 35.92; H, 3.01%. p-*Iodoacetophenone*: Mp 83.5—84 °C (lit,[19] 85 °C). Found: C, 39.21; H, 2.88%. Calcd for C_8H_7IO: C, 39.05; H 2.87%.

Preparation of Biaryls. *Preparation of Dimethyl 3,3'-Biphenyldicarboxylate*: A mixture of methyl *m*-iodobenzoate (524 mg, 2 mmol), a 0.17 mol dm^{-3}-DMF solution of nickel(II) bromide (0.30 ml, 0.05 mmol), zinc powder (164 mg, 2.5 mmol), potassium iodide (415 mg, 2.5 mmol), and HMPA (2.2 ml) was frozen at −78 °C, evacuated, flushed with nitrogen, and then kept at 50 °C for 3 h with stirring. To the resulting mixture, dilute hydrochloric acid (0.4 mol dm^{-3}, 16 ml) was added, and the organic materials, extracted with 15-ml portions of ether–dichloromethane (7 : 1), were washed with aqueous sodium sulfite (15 ml) and three 15-ml portions of aqueous sodium chloride, and dried over anhydrous sodium sulfate. The subsequent evaporation of the solvent gave 260 mg of crude dimethyl 3,3'-biphenyldicarboxylate (96%). Recrystalization from ether gave the pure biaryl. Mp 103—103.5 °C (lit,[20] 104 °C). Found: C, 70.93; H, 5.13%. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22%.

Biphenyl: Mp 68—69 °C (lit,[21] 71 °C). Found: C, 92.90; H, 6.48%. Calcd for $C_{12}H_{10}$: C, 93.46; H, 6.54%.

4,4'-Dimethylbiphenyl: Mp 117.5—119 °C (lit,[22] 121 °C). Found: C, 91.96; H, 7.85%. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74%.

4,4'-Dimethoxybiphenyl: Mp 169—171 °C (lit,[23] 173 °C). Found: C, 78.36; H, 6.60%. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59%.

4,4'-Diacetylbiphenyl: Mp 191—192 °C (lit,[24] 192 °C). Found: C, 80.62; H, 5.91%. Calcd for $C_{16}H_{14}O_2$: C, 80.65, H, 5.92%.

2,2'-Dimethylbiphenyl: Bp 69 °C/67 Pa (lit,[25] 258 °C/98400 Pa). Found: C, 92.31; H, 7.79%. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74%.

Preparation of Dimethyl 4,4'-Dimethyl-2,2'-biphenyldicarboxylate: A mixture of methyl 2-iodo-5-methylbenzoate (1.32 ml, 8 mmol), nickel(II) chloride (1.16 g, 9 mmol), zinc powder (1.04 g, 16 mmol), potassium iodide (1.66 g, 10 mmol), and HMPA (10 ml) was evacuated, flushed with nitrogen, and kept at 20 °C for 28 h with stirring. To the resulting mixture, aqueous sodium chloride (80 ml) was added, and the organic materials, extracted with two 60-ml portions of ether, were washed with four 120-ml portions of aqueous sodium chloride and then dried over anhydrous sodium sulfate. The subsequent evaporation of the solvent gave a crude dimethyl 4,4'-dimethyl-2,2'-biphenyldicarboxylate, which was triturated with a small amount of hexane to leave 1.10 g of the pure biaryl (98%). Mp 90—91 °C. Found: C, 72.29; H, 6.00%. Calcd for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08%.

2,2'-Dichlorobiphenyl: Mp 54—55 °C (lit,[26] 59 °C). Found: C, 64.52; H, 3.45%. Calcd for $C_{12}H_8Cl_2$: C, 64.60; H, 3.61%.

2,2'-Diacetylbiphenyl: Mp 90.5—91.°C (lit,[27] 93—94 °C). Found: C, 80.57; H, 5.79%. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92%.

2,2'-Bis(trifluoromethyl)biphenyl: Bp 119—121 °C/2130 Pa (lit,[28] 236—237 °C). NMR: 7.1—7.9 (*m*).

Reaction of Methyl o-*Iodobenzoate with Zinc Powder.* A mixture of methyl *o*-iodobenzoate (0.059 ml, 0.4 mmol), zinc powder (52 mg, 0.8 mmol), potassium iodide (83 mg, 0.5 mmol), and HMPA (0.5 ml) was stirred at 50 °C for 22 h under nitrogen. To the resulting mixture, dilute hydrochloric acid was added, and the organic materials were extracted with ether. Subsequent analysis by GLC revealed the presence of 53 mg (0.39 mmol) of methyl benzoate. Atmospheric oxygen inhibited the reaction completely. A similar work-up by means of deuterium oxide–hydrochloric acid-d_1 gave methyl benzoate-d_1. NMR: 7.85—8.07 (*m*, 1H), 7.15—7.62 (*m*, 3H), 3.87 (s, 3H). Found: C, 69.97; H, 5.91%. Calcd for $C_8H_7DO_2$: C, 70.06; H, 5.84%.

An alternative treatment of the resulting mixture with palladium(II) chloride (177 mg, 1.0 mmol) at 20 °C for 30 h under nitrogen, followed by GLC analysis, gave 35 mg (0.13 mmol) of dimethyl 2,2'-biphenyldicarboxylate (63%) and 16 mg (0.12 mmol) of methyl benzoate (30%).

Solubility of Potassium Iodide or Potassium Bromide in HMPA–DMF. After a suspension of potassium iodide (9.0 g, 54 mmol) or potassium bromide (6.4 g, 54 mmol) in HMPA–DMF (22 : 3, 10 ml) has been stirred at 50 °C for 1.5 h, the concentration of the iodide ion or the bromide ion in the solution was determined by the Mohr method. One liter of mixed solvents dissolved about 0.11 mol of potassium iodide or 0.001 mol of potassium bromide respectively.

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