Acknowledgment. We thank Ronald L. Bassfield and John Naworal for invaluable technical assistance and Dr. E. B. Sanders for helpful discussions. We also acknowledge with gratitude Jim Day and Chuck Nilles for providing the graphic arts and Anne Donathan for continuing secretarial assistance.

Registry No. (*S*)-**1**, 54-11-5; (*S*)-**9**, 2820-55-5; (*S*)-**2**, 77698-47-6; (*S*)-**4**, 13270-57-0; (*S*)-**6**, 13270-56-9; (±)-**11**, 69980-22-9; methyllithium, 917-54-4; methylmagnesium bromide, 75-16-1.

Supplementary Material Available: Table I. ^{13}C NMR resonance of nicotine and nicotine analogues (1 page). Ordering information is given on any current masthead page.

New Method for the Preparation of Activated Nickel and Cobalt Powders and Their Application in Biaryl Synthesis

C. S. Chao, C. H. Cheng,* and C. T. Chang

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300

Received March 24, 1983

An activated nickel powder has been prepared by the procedure of electrolysis of a $NiSO_4$ aqueous solution with Hg as the cathode to form a nickel amalgam followed by the removal of the mercury from the amalgam at 150 °C and 10^{-3} torr. The nickel powder, similar to Cu in Ullmann's biaryl synthesis, has been found to react with aryl iodide and aryl bromide at 140 °C to give biaryls in good yields and with dibromobenzene to yield a number of interesting products including triphenylene, tetraphenylene, and polyphenyls, depending on the relative position of the dibromo groups. In the presence of KI, the powder also induces, unprecedentedly, the homo coupling of an aryl chloride to a biaryl. The activity of the activated nickel powder was further demonstrated by the reaction with benzyl bromide to give 1,2-diphenylethane and with α,α-dichlorotoluene to afford mainly *trans*-stilbene.

Recently, one of us developed a new method for the preparation of uranium metal powder. The procedure involved electrolytic reduction of uranium ions on a mercury electrode to form a uranium amalgam followed by vacuum removal of the mercury from the amalgam.[1] We have successfully extended the amalgam method to the preparations of other highly active metal powders. In this paper we report the procedure for the preparation of nickel and cobalt powders and the results of the application of these powders in the syntheses of biaryls from aryl halides.

Prompted by the success of the application of nickel complexes in biaryl synthesis[2-6] and the great activities of the uranium powder activated by the amalgam method,[1] we have undertaken the present investigation. The results clearly demonstrated that the nickel powder not only reacts with aryl iodides and bromides at a temperature lower than that of the Ullmann's biaryl synthesis[9-11] but also couples, unprecedentedly, with aryl chloride in the presence of KI to give biaryls in good yields. The cobalt powder, briefly examined, shows a similar reactivity toward aryl halide. Two independent groups have reported results on the studies of the homo couplings of aryl halides with nickel powder. Rieke and his co-workers[7a,b] have shown that metallic nickel prepared by reduction of nickel halide with lithium metal in the presence of naphthalene is a convenient reagent for the dehalogenative coupling of aryl iodides and bromides. On the other hand, Klabunde[8] et al. have demonstrated that a Ni/THF slury from codeposition of nickel vapor and THF reacted with iodobenzene to give biphenyl in low yield.

Similar to the preparation of uranium powder, activated nickel powder used in the reactions was prepared by two separated steps. In the first, nickel amalgam was formed from electrolysis of an aqueous nickel sulfate solution by using mercury as a cathode, while in the second, the amalgam was placed in a flask (Figure 1), and the mercury was removed from the amalgam at 150 °C and 10^{-3} torr (see Experimental Section). The resulting black powder, which still contains 5–7% of mercury by weight, starts to burn on exposure to air. The coupling reactions of aryl halides were conducted in the same flask at 140 °C by using a 2.0–1.0:1 ratio of aryl halide to nickel metal. While complete removal of mercury from nickel seems unlikely, it is important to mention that the activity of nickel powder is affected by the amount of mercury remaining in the powder, with the activity decreasing as the relative amount of mercury in the nickel powder increases. In one experiment, nickel amalgam prepared from electrolysis was used directly to react with bromobenzene; no coupling product was detected at the end. The activity of nickel powder is further controlled by the ratio of nickel to mercury used in electrolysis with the most suitable value at ca. 1:6. The use of less mercury would lead to an incomplete dissolution of nickel in the amalgam and a decrement of activity due to the direct formation of metal particles from electrolysis, but the employment of more

---

(1) (a) Wang, L. C.; Hung, H. H.; Lee, H. C.; Chang, C. T. *J. Chem. Soc., Chem. Commun.* **1975**, 124. (b) Chang, C. C.; Sung-Yu, N. K.; Hseu, C. S.; Chang, C. T. *Inorg. Chem.* **1979**, *18*, 885. (c) Wang, L. C.; Lee, H. C.; Lai, W. C.; Chang, C. T. *J. Inorg. Nucl. Chem.* **1978**, *40*, 507. (d) Wen, T. C.; Chang, C. C.; Chuang, Y. D.; Chiu, J. P.; Chang, C. T. *J. Am. Chem. Soc.* **1981**, *103*, 4576.

(2) (a) Semmelhack, M. F.; Felquist, P. M.; Jones, L. D. *J. Am. Chem. Soc.* **1971**, *93*, 5909. (b) Semmelhack, M. F.; Helquist, P.; Jones, L. D.; Keller, L.; Mendelson, L.; Ryono, L. S.; Smith, J. G.; Stauffer, R. D. *Ibid.* **1981**, *103* 6460.

(3) Kende, A. S.; Liebeskind, L. S.; Braitsh, D. M. *Tetrahedron Lett.* **1975**, 3375.

(4) Zembayashi, M.; Tamo, K.; Yoshida, J.; Kumada, M. *Tetrahedron Lett.* **1977**, 4089.

(5) (a) Takagi, K.; Hayama, N.; Inokawa, S. *Chem. Lett.* **1979**, 917. (b) Takagi, K.; Hayama, N.; Inokawa, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3691.

(6) Schiavon, G.; Bontempelli, G.; Corain, B. *J. Chem. Soc., Dalton Trans.* **1981**, 1074.

(7) (a) Kavaliunas, A. V.; Rieke, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5945. (b) Matsumoto, H.; Inaba, S.; Rieke, R. D. *J. Org. Chem.* **1983**, *48*, 840. (c) Rieke, R. D.; Bales, S. E. *J. Am. Chem. Soc.* **1974**, *96*, 1775.

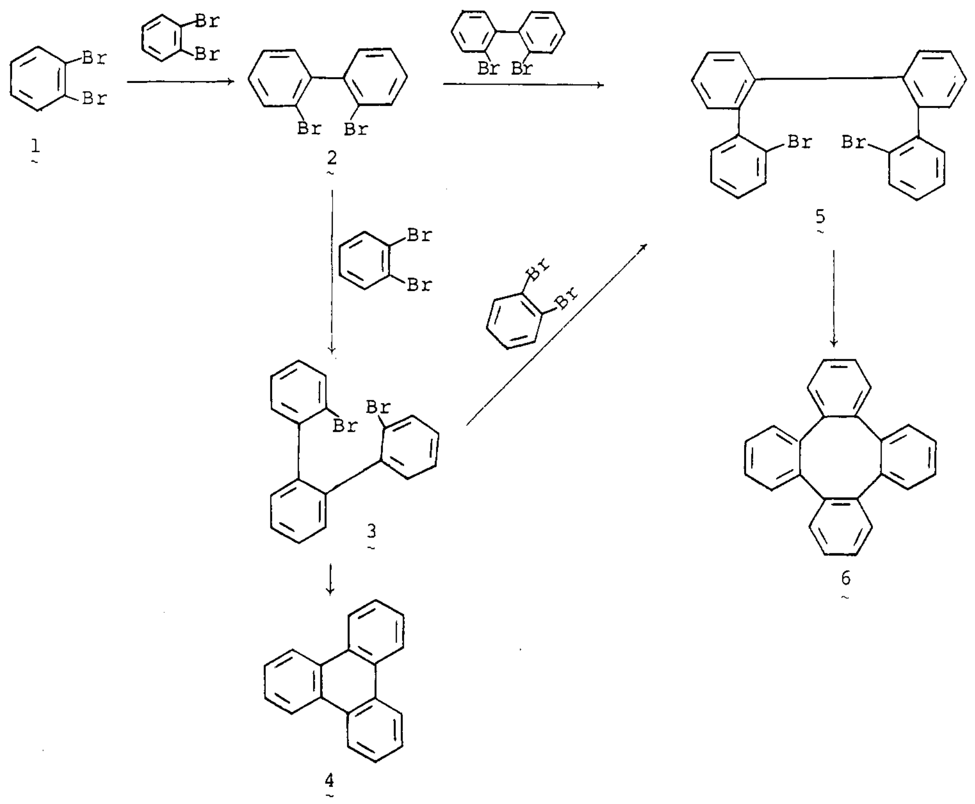
(8) Klabunde, K. J.; Murdock, T. O. *J. Org. Chem.* **1979**, *44*, 3901.

(9) Ullman, F.; Bielecki, J. *Chem. Ber.* **1901**, *34*, 2174.

(10) Gibson, H. W.; Bailey, F. C. *J. Org. Chem.* **1976**, *41*, 557.

(11) (a) Normant, J. F. *Synthesis.* **1972**, 63. (b) Fanta, P. E. *Ibid.* **1974**, 9. (c) Fanta, P. E. *Chem. Rev.* **1964**, *64*, 613. (d) Fanta, P. E. *Chem. Rev.* **1946**, *38*, 139.

Scheme I



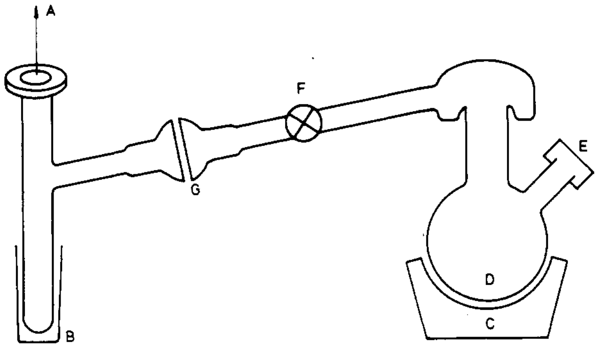
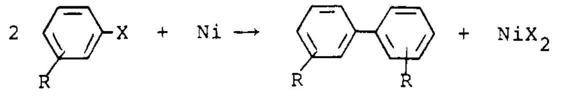


Figure 1. Mercury removal apparatus: A, vacuum; B, liquid nitrogen trap; C, heating mantle; D, flask for amalgam; E, septum; F, Teflon vacuum valve; G, connector.

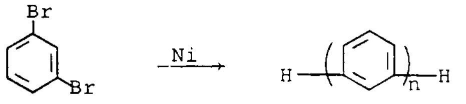
mercury would result in a longer time for mercury removal. It is of interest to note that the mercury removed from amalgam can be reused without further treatment, and therefore mercury is not consumed.

The high activity of the nickel powder prepared by our method was demonstrated in its reaction with bromobenzene in DMF at 140 °C to afford biphenyl in 71% yield (eq 1). In contrast, the commercially available nickel powder did not induce the same coupling under the same reaction conditions. Other substituted aryl bromides and iodides also undergo the same reaction to form the corresponding biaryls (Table I). As depicted in Table I, it is evident that the ortho-substituted aryl halides are much less reactive than the corresponding meta- and para-substituted ones, indicating that steric hindrance has played an important role in the reaction, paralleling the observations in the coupling of aryl halide by a nickel complex such as $Ni(COD)_2$ or $Ni(PPh_4)_4$. The reactivity of the aryl halide is in the order I > Br > Cl, similar to the reactivity pattern with nickel complex or copper metal as the coupling reagent. In contrast with the result that the presence of a nitro group on the ring increases the activity of aryl halide in the Ullmann synthesis, no biaryl product was obtained in the reaction of *p*-bromonitrobenzene with nickel powder. The same result, however, was found in the coupling reaction with $Ni(COD)_2$ as the reagent.



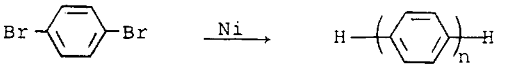
(1)

One of the most intriguing aspects of this chemistry is the one-pot formation of triphenylene (4, 25%) and tetraphenylene 6 (22.5%) from the reaction of 1,2-dibromobenzene with the activated nickel powder. The separation of these two products is readily achieved by using their different solubility properties in cyclohexane in which only the yellow triphenylene can be dissolved. Presumably, the formation of these cyclic compounds is the result of several successive intermolecular couplings and an intramolecular reaction in the last step as shown in Scheme I. The lack of higher molecular weight species other than 4 and 6 indicates that an intramolecular or ring closure reaction is much more favorable than intermolecular couplings for intermediates 3 and 5. The other two dibromo compounds, 1,3-dibromobenzene and 1,4-dibromobenene, however, give noncyclic polyphenyls (eq 2 and 3), identified by mass spectroscopy after reaction with nickel powder.



(2)

n = 2~8



(3)

n = 2~6

Although the activated nickel powder does not react with aryl chloride alone, in the presence of KI the reaction proceeds well and gives the biaryl product in an excellent

Table I. Results of the Coupling of Aryl Halides by Nickel Powder[a]

expt	aryl halide	temp, °C/time, h	biaryl,[b] %
1	iodobenzene	120/19	73
2	bromobenzene	140/21.5	71
3	chlorobenzene	130/60	0
4	*p*-bromotoluene	140/23	71
5	*m*-bromotoluene	140/22	68
6	*o*-bromotoluene	140/21.5	27[c]
7	*p*-bromoanisole	140/20	68
8	*p*-bromoacetophenone	140/23	77
9	4-iodo-*o*-xylene	140/23	70
10	4-iodo-*m*-xylene	140/78	54
11	3-iodo-*p*-xylene	140/53	42
12	*p*-bromonitrobenzene	140/20	0
13	*p*-chlorotoluene	140/58	<2[c]
14	*p*-chlorotoluene/KI	140/28	83
15	*m*-chlorotoluene/KI	140/30	72
16	*p*-chloroacetophenone/KI	140/22	85
17	chlorobenzene/KI	130/60	90[c]

[a] For expt 1-13, each reaction solution contains 1.59 g (0.027 mol) of nickel powder, 0.0405 mol of aryl halide, and 10 mL of DMF, while for expt 14-17, the reaction solution consists of 1.20 g (0.020 mol) of nickel powder, 0.025 mol of aryl chloride, 4.0 g (0.024 mol) of KI, and 15 mL of DMF at the beginning of the reaction. [b] Isolated yield except if otherwise mentioned. [c] Yield determined by GC.

yield (Table I). This striking result provides us the advantage of using the most readily available aryl chlorides as the reagents in the biaryl synthesis. In the Ullmann reactions, only the most activated aryl chloride undergoes the coupling reactions,[11c] while in the biaryl synthesis using nickel complexes as the reagent, no successful example by using aryl chloride as the reagent has been reported.[2-6] Analysis of the mixture during the coupling reaction of aryl chloride indicates that aryl iodide was rapidly formed. Thus, the enhancement of the rate of aryl chloride coupling with KI present may be attributed at least partly to the facile chloride–iodide exchange that leads to the formation of more reactive aryl iodide. Similar halide–halide exchange reactions catalyzed by nickel metal or complexes were observed previously.[5,7]

The effects of solvents on the coupling reactions are summarized in Table II. A low yield of biphenyl was obtained in the absence of solvent or on using mesitylene as the solvent, whereas a much better yield was observed in DMF, Me_2SO, or pyridine. It thus appears that a solvent with coordinating ability is required for an effective coupling. If the reaction is conducted in ethylene glycol, no biphenyl but benzene was detected, indicating that dehalogenation of the aryl halide occurred. Dehalogenation of aryl halide was also observed in protic medium using a Cu metal or nickel(0) complex as the coupling reagent.[2,11]

An additional evidence for the high reactivity of the nickel powder can be seen in its reaction with benzyl bromide to afford a 91% yield of 1,2-diphenylethane and, more interestingly, with α,α,-dichlorotoluene in the presence of KI to give *trans*- and *cis*-stilbene in 93% and 5% yields, respectively. A detailed understanding of the mechanism regarding the formation of the interesting products has not yet been obtained and awaits further investigation.

The cobalt powder prepared by the amalgam method shows a similar activity toward aryl halide as the nickel powder. Our result indicates that the reaction of cobalt powder with bromobenzene also leads to the formation of biphenyl in a 71% yield.

Table II. Effects of Solvents on the Coupling of Bromobenzene by Nickel Powder[a]

expt	solvent	temp, °C/time, h	biphenyl, %
1	DMF	140/21.5	71[b]
2	Me_2SO	140/20	99[c,d]
3	pyridine	115/10	71[c]
4	mesitylene	140/21.5	24[c]
5	*e*	140/23.5	23[c]
6	ethylene glycol	140/23.5	*f*

[a] Except otherwise mentioned, each solution contains 1.59 g (0.027 mol) of nickel powder, 4.27 mL (0.0405 mol) of bromobenzene, and 10 mL of solvent; Ni/PhBr ratio of 1:1.5. [b] Isolated yield. [c] The yield calculated from GC peak areas. [d] The solution contains 1.59 g (0.027 mol) of nickel powder, 2.85 mL (0.027 mol) of bromobenzene, and 10 mL of Me_2SO; Ni/PhBr ratio of 1:1. [e] No solvent is used. [f] Benzene is the major product.

In conclusion, preparation of very active nickel and cobalt powders can be achieved by using the amalgam method described above. The activated nickel powder reacts with a variety of aryl halides including the most inert aryl chlorides to give biaryls in good yields and with dibromobenzene to afford cyclic phenylenes and noncyclic polyphenyls, depending on the relative position of the two bromo groups. It also exhibits high activity toward benzyl bromide and α,α-dichlorotoluenes, yielding bibenzyl and *trans*-stilben, respectively.

Experimental Section

Infrared spectra were measured on Perkin-Elmer 710B or JASCO A-100 spectrometers. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-100 spectrometer. Gas chromatographic analyses were performed on a Shimadzu Model GC-7AG gas chromatography by using a 5% SE-30 column. Melting points were determined on a Fisher-Johns apparatus and were uncorrected.

4-Iodo-*m*-xylene, 3-iodo-*p*-xylene, 4-iodo-*o*-xylene were prepared according to previous methods,[12] while the other aryl halides (Tokyo Chemical), $NiSO_4 \cdot 6H_2O$, and mercury (Wako) were used as purchased. All reactions were conducted under 1 atm of nitrogen and in a well-ventilated hood.

Preparation of Activated Nickel Powder. An electrolyzer with a platinum plate as the anode and 30 g of Hg as the cathode was filled with 100 mL of an aqueous solution containing 0.25 M $NiSO_4$. Electrolysis was conducted at an applied voltage of 5 V and a current of 0.8–0.9 A for a period of ca. 6 h until the solution was colorless. The nickel amalgam formed was first broken to small pieces, then washed with 3% hydrochloric acid, distilled water, and acetone, and finally transfered to a specially designed flask (Figure 1) to distill off the mercury at 150 °C (10^{-3} torr). During distillation, the mercury in the amalgam was evaporated to the top of flask and condensed. The stopcock was opened from time to time to allow the condensed mercury to drop into the trap. This removing process continued until no further mercury came out of the amalgam. Black nickel powder containing 5–7% of Hg as determined by the weighing method was thus obtained. The time required for the distillation was about 7 h.

The method can also be used to prepare cobalt powder.

General Procedures for the Reaction of Aryl Halides with the Activated Nickel Powder. Example 1. To the nickel powder (0.025 mol) prepared by the amalgam method were added through the septum (Figure 1) 10 mL of DMF and 4.25 mL (0.040 mol) of bromobenzene. The mixture was then heated at 140 °C with stirring for 21.5 h. During the reaction, the powder was gradually dissolved and a dark green color developed. At the end of the reaction, 70 mL of 3% hydrochloric acid and 20 mL of

---

(12) (a) Datta, R.. L.; Chatterjee, N. R. *J. Am. Chem. Soc.* **1917**, *39*, 435. (b) *Ibid.* **1919**, *41*, 292.

chloroform were added to the mixture. The unreacted nickel powder was filtered off, and the organic phase was separated from the aqueous layer. The latter was further extracted twice with 10 mL of chloroform. The combined chloroform solution was then concentrated to afford the desired crude product. Recrystallization from ethanol gave 2.2 g biphenyl: 2.2 g (71%); mp 68–71 °C (lit.[13] mp 71 °C); mass spectral mol wt 154, calcd for $C_{12}H_{10}$ 154.

The reaction conditions and the isolation methods of other aryl halides except those described below are similar to the above procedures. Yields of the biaryls are presented in Table I. In a few cases, such as the reaction of iodoxylene with nickel powder, where some starting material was left unreacted in the crude product, separation of the starting material from the desired biaryls was performed by column chromatography (SiO_2). The melting points and important spectral data of the biaryls are as follows.

4,4′-Dimethoxybiphenyl: mp 182–183 °C (lit.[14] mp 176–178 °C); ^1H NMR ($CDCl_3$) δ 3.83 (s, 6 H), 6.93 (d, J = 9 Hz, 4 H), 7.46 (d, J = 9 Hz, 4 H); mass spectral mol wt 214, calcd for $C_{14}H_{14}O_2$ 214.

4,4′-Diacetylbiphenyl: mp 190–192 °C (lit.[15] mp 191–192 °C); ^1H NMR ($CDCl_3$) δ 2.63 (s, 6 H), 7.67 (d, 4 H), 8.02 (d, 4 H); mass mol wt 238, calcd for $C_{16}H_{14}O_2$ 238.

3,3′-Dimethylbiphenyl: mp 8–9 °C (lit.[16] mp 9.0–9.5 °C; ^1H NMR ($CDCl_3$) δ 2.25 (s, 6 H), 7.1 (m, 8 H); mass spectral mol wt 182, calcd for $C_{14}H_{14}$ 182.

3,3′,4,4′-Tetramethylbiphenyl: mp 74–75 °C (lit.[14] mp 76–77 °C); ^1H NMR ($CDCl_3$) δ 2.28, 2.31 (s, 12 H), 7.18 (m, 6 H); mass spectral mol wt 210, calcd for $C_{10}H_{18}$ 210.

2,2′,4,4′-Tetramethylbiphenyl: mp 37–39 °C (lit.[17] mp 41 °C); ^1H NMR ($CDCl_3$) δ 2.00 (s, 6 H), 2.33 (s, 6 H), 6.96 (m, 6 H); mass spectral mol wt 210, calcd for $C_{16}H_{18}$ 210.

2,2′,5,5′-Tetramethylbiphenyl: mp 50–51 °C (lit.[18] mp 53–54 °C); ^1H NMR ($CDCl_3$) δ 1.98 (s, 6 H), 2.25 (s, 6 H), 6.93 (m, 6 H); mass spectral mol wt 210, calcd for $C_{16}H_{18}$ 210.

Reaction of a Commercially Available Nickel Powder with Bromobenzene. Nickel powder (5.87 g, 100 mesh) was first washed with dilute hydrochloric acid and acetone and dried in vacuo. To the powder were added 10 mL of DMF and 3.5 mL (0.033 mol) of bromobenzene. The mixture was then heated at 140 °C with stirring for 80 h. Separation of the reacted mixture by the same procedures as in example 1, followed by analysis of the organic phase by GC, indicated that 2.9% of biphenyl was formed. The rest of the bromobenzene was unreacted.

Reaction of Aryl Chloride with Activated Nickel Powder in the Presence of KI. Example 2. To the nickel powder (1.20 g, 0.020 mol) freshly prepared from nickel amalgam were added 4.0 g (0.024 mol) of KI and a solution consisting of 2.9 mL (0.025 mol) of *p*-chlorotoluene and 15 mL of DMF. The system was then heated at 140 °C with stirring for 28 h. 4,4′-Dimethylbiphenyl was obtained in 83% yield after the same workup as described in example 1: mp 122–123 °C (lit.[5b] mp 121 °C); ^1H NMR ($CDCl_3$) δ 2.35 (s, 3 H), 7.12 (d, J = 8 Hz, 2 H), 7.38 (d, J = 8 Hz, 2 H); mass spectral mol wt 182, calcd for $C_{14}H_{14}$ 182.

The reactions of other aryl chlorides with nickel powder were conducted under the same conditions, and the yields are shown in Table I.

Reaction of 1,2-Dibromobenzene with Activated Nickel Powder. To 2.79 g (0.0475 mol) of freshly prepared nickel powder was added 3.5 mL (0.029 mol) of 1,2-dibromobenzene in 10 mL of DMF. The system was then heated at 140 °C with stirring for 56 h. Addition of dilute hydrochloric acid to the reaction mixture, followed by extraction with chloroform several times, and concentration of the organic phase led to a solid mixture. Further treatment of the solid with cyclohexane separated it into two parts. The undissolved solid was then recrystallized from ethyl acetate to give tetraphenylene: 0.50g (22.5%); mp 237–239 °C (lit.[19] mp 237–239 °C); ^1H NMR ($CDCl_3$) δ 7.21 (m, 6 H); ^{13}C NMR $CDCl_3$) δ 141.3 (s), 128.8 (d), 127.0 (d); IR (KBr) 3030 (m), 1470 (s), 1430 (s), 1265 (m), 1115 (m), 1005 (m), 945 (m), 770 (s), 755 (s), 740 (s), 730 cm^{-1} (s); mass spectral mol wt 304, calcd for $C_{24}H_{16}$ 304. Evaporation of the solution part followed by recrystallization from methanol afforded triphenylene: 0.55g (25%); mp 197–198 °C (lit.[20] mp 199 °C); ^1H NMR ($CDCl_3$) δ 7.50 (q, 6 H), 8.60 (q, 6 H); mass spectral mol wt 228, calcd for $C_{18}H_{12}$ 228.

Reaction of α,α-Dichlorotoluene with Activated Nickel Powder. To 1.11 g (0.019 mol) of freshly prepared nickel powder was added 6.0 g (0.036 mol) of KI and a solution containing 1.5 mL (0.0117 mol) of α,α-dichlorotoluene in 15 mL of DMF. The system was heated at 140 °C with stirring for 10 h. Isolation of the product by using the same procedures as described in example 1 gave a mixture of *trans*- (93%) and *cis*-stilbene (5%). The relative amount of these two isomers was determined from the relative peak areas at δ 7.02 (trans) and 6.53 (cis) of the NMR spectrum of the mixture. Recrystallization of the mixture from methanol afforded pure trans stilbene: mp 124–125 °C (lit.[21] mp 124 °C); ^1H NMR ($CDCl_3$) δ 7.02 (s, 2 H), 7.30 (m, 10 H); mass spectral mol wt 180, calcd for $C_{14}H_{12}$ 180.

Acknowledgment. We thank the National Science Council of the Republic of China for support of this research.

Registry No. Ni, 7440-02-0; Co, 7440-48-4; iodobenzene, 591-50-4; bromobenzene, 108-86-1; chlorobenzene, 108-90-7; *p*-bromotoluene, 106-38-7; *m*-bromotoluene, 591-17-3; *o*-bromotoluene, 95-46-5; *p*-bromoanisole, 104-92-7; *p*-bromoacetophenone, 99-90-1; 4-iodo-*o*-xylene, 31599-61-8; 4-iodo-*m*-xylene, 4214-28-2; 3-iodo-*p*-xylene, 1122-42-5; *p*-bromonitrobenzene, 586-78-7; *p*-chlorotoluene, 106-43-4; *m*-chlorotoluene, 108-41-8; *p*-chloroacetophenone, 99-91-2; biphenyl, 92-52-4; 4,4′-dimethylbiphenyl, 613-33-2; 3,3′-dimethylbiphenyl, 612-75-9; 2,2′-dimethylbiphenyl, 605-39-0; 4,4′-dimethoxybiphenyl, 2132-80-1; 4,4′-diacetylbiphenyl, 787-69-9; 3,3′,4,4′-tetramethylbiphenyl, 4920-95-0; 2,2′,4,4′-tetramethylbiphenyl, 3976-36-1; 2,2′,5,5′-tetramethylbiphenyl, 3075-84-1; tetraphenylene, 212-74-8; 1,2-dibromobenzene, 583-53-9; *trans*-stilbene, 103-30-0; triphenylene, 217-59-4; α,α-dichlorotoluene, 98-87-3.

---

[13] Gomberg, M.; Bachmann, W. E. *J. Am. Chem. Soc.* **1924**, *46*, 2343.

[14] McKillop, A.; Elson, L. F.; Taylor, E. C. *Tetrahedron* **1970**, *26*, 4041.

[15] Sloan, G. J.; Vaughan, W. R. *J. Org. Chem.* **1957**, *22*, 750.

[16] Johnson, E. A. *J. Chem. Soc.* **1957**, 4155.

[17] Snyder, L. R. *J. Phys. Chem.* **1961**, *65*, 246.

[18] Fujiwara, Y. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 863.

[19] Xing, Y. D.; Huang, N. Z. *J. Org. Chem.* **1982**, *47*, 140.

[20] Heaney, H.; Millar, I. T. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 295.

[21] Mitchell, R. H. *J. Chem. Soc., Chem. Commun.* **1974**, 990.