Registry No.—Naphthalene, 91-20-3; mercuric acetate, 1600-27-7; 1-acetatomercurinaphthalene, 32049-36-8; 2-acetatomercurinaphthalene, 38487-16-0.

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Coupling of Nonequivalent Aromatic Rings by Soluble Nickel Catalysts. A General Route to the 1,8-Diarylnaphthalenes[1a]

Roger L. Clough,[1b] Pierre Mison,[1c] and John D. Roberts*

Contribution No. 5122 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91125

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A facile route to the 1,8-diarylnaphthalene derivatives is described. The parent compound, 1,8-diphenylnaphthalene, can be prepared in two steps with 35% overall yield from the commercial 1,8-diaminonaphthalene. The key step in these preparations is the direct joining of two nonequivalent aromatic molecules by an organonickel-catalyzed Grignard–aryl halide coupling reaction at −15 °C. The coupling reaction is regiospecific with respect to the position of substitution of both aromatic halves. The yields of this coupling reaction are high, even though the 1,8-diarylnaphthalenes are sterically crowded. The efficiency of the reaction under a variety of conditions is evaluated. The order of reactivity of aryl halides is found to be I > Br > Cl, and it is possible to effect coupling preferentially at an iodo group in the presence of a chloro group, the latter being available for further synthetic functionalization.

The 1,8-diarylnaphthalenes are of interest because of their unusual geometry and their inherent strain due to steric overcrowding. The crowded peri-aryl rings are constrained to face each other.[2] Adjacent parallel π systems are also a feature of the extensively studied[3a] paracyclophanes, though the phenyl rings of the latter are substantially warped from planarity,[3b] while the aryl rings of the diarylnaphthalenes, which are not bound together at both ends, retain their planarity.[2] Many unusual properties have been observed with the paracyclophanes and these have been related to the closely held parallel aromatic ring geometries.[3a]

The 1,8-diarylnaphthalenes have, at the same time, π systems which are nearly perpendicular, because the naphthyl and peri-aryl ring planes are restricted from approaching coplanarity. The barrier to a 180° rotation about a naphthyl–aryl bond has been measured[4] as ~15 kcal which seems surprisingly low judging from examination of molecular models. The distance between atoms 1 and 8 in naphthalene is 2.44 Å, while the van der Waals separation between parallel π systems is 3.4 Å.[5] Thus, substantial repulsive interactions must exist between the peri-aryl substituents.[2]

We have undertaken a series of investigations of the conformational, thermodynamic, spectroscopic, and chemical properties of 1,8-diarylnaphthalene derivatives, which necessitated development of a convenient and efficient general synthesis for this class of compounds.[2b,6–9] The most straightforward approach envisioned was a direct joining of aryl and naphthyl groups, but preparative techniques for effecting carbon–carbon bond formation between two aromatic rings are notably lacking. Major classical methods for aromatic arylation are outlined below.

I Ullman reaction[2a,10] $2\mathrm{ArI} \xrightarrow{\mathrm{Cu}} \mathrm{Ar{-}Ar}$

II Scholl reaction[11] $2\mathrm{ArH} \xrightarrow[\mathrm{H^+}]{\mathrm{AlCl_3}} \mathrm{Ar{-}Ar}$

III Radical-mediated coupling[12]

$$\left.\begin{array}{l} [\mathrm{Ar{-}N_2}]^+ \\ \mathrm{Ar{-}N{=}N{-}Ar} \\ [\mathrm{Ar{-}CO_2}]_2 \\ \mathrm{Ar{-}I},\ h\nu \\ \text{or other radical source} \end{array}\right\} + \mathrm{Ar'H} \longrightarrow \mathrm{Ar{-}Ar'}$$

IV Benzyne-mediated coupling[13]

$$\begin{array}{c} \mathrm{Ar{-}X} \\ + \\ \mathrm{Ar'{-}Li} \end{array} \longrightarrow \begin{array}{c} \text{benzyne} \\ \text{(from Ar—X)} \\ \big\downarrow{\scriptstyle \mathrm{Ar'Li}} \\ \mathrm{Ar{-}Ar'} \end{array}$$

V Grignard homo coupling and aryllithium homo coupling[14] $2ArMgX \xrightarrow{\text{catalyst}} Ar{-}Ar$

$2ArLi \xrightarrow{\text{catalyst}} Ar{-}Ar$ (catalysts include $TlBr$, $CoBr_2$, $CrCl_3$, $CuCl_2$)

VI Lithium diarylcuprate and aryl iodides[9,15] $Ar{-}X + LiAr_2Cu \longrightarrow Ar{-}Ar$

These techniques suffer from various problems, including primary limitation to preparation of symmetric biphenyls (I, II, and V), lack of regiospecificity with respect to both reactants resulting in mixtures of isomeric products (II, III, and IV), rather severe reaction conditions, and often low yields. The investigation described here had two parallel goals, establishment of a convenient general synthesis for 1,8-diarylnaphthalenes and development of an efficient technique for the direct coupling of nonequivalent aromatic systems.

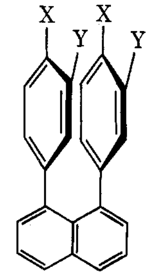
Results and Discussion

It has long been known that reaction of aryl halides with magnesium to form Grignard reagents is often accompanied by formation of a small amount of diaryl compound. The coupling of Grignards with activated alkyl halides is also well known.[16] We have observed that under forcing conditions, some mixed aryl coupling may be effected, though this reaction probably has little preparative value. Thus, on refluxing phenylmagnesium bromide with 1-iodonaphthalene for 48 h in toluene, a yield of about 45% of 1-phenylnaphthalene was obtained. Naphthalene and biphenyl were also identified in the product mixture, along with unreacted 1-iodonaphthalene. An attempt to prepare the internally crowded 1,8-diphenylnaphthalene by this technique was completely unsuccessful.

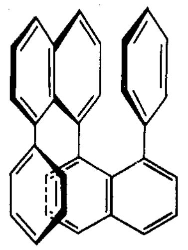
It has been reported that some transition-metal compounds, especially of copper, iron, nickel, and silver, may catalyze the reaction between certain Grignard reagents and organohalides, though reports have concentrated almost exclusively on cross-couplings of the type alkyl–alkyl, alkyl–vinyl, alkyl–aryl, and vinyl–aryl.[17] We have employed catalytic amounts of soluble organonickel complexes to effect aryl Grignard–aryl halide coupling in high yield under very mild conditions, to provide a direct route to the 1,8-diarylnaphthalenes. Experiments with two organonickel compounds, nickel(II) acetylacetonate [$Ni(acac)_2$] and dichloro[1,2-bis(diphenylphosphino)ethane]nickel(II),[18] indicated that both complexes were highly active in inducing heteroaryl coupling, and that the relative effectiveness of the two was essentially the same. The former, a readily available commercial compound, was selected for use in further experiments. Reactions were found to proceed smoothly with a molar ratio of nickel catalyst:aryl halide of 1:100 (ratio of catalyst molecule:halide substituent 1:200).

1,8-Dihalonaphthalenes were prepared for use in the coupling reaction from the commercial 1,8-diaminonaphthalene using the Sandmeyer technique. The best success was obtained when the reactions were run at −30 °C.[2b] The yields follow: 1,8-diiodonaphthalene, 49%; 1,8-dibromonaphthalene, 17%; 1,8-dichloronaphthalene, 15%. A description of a preparation of 1,8-diphenylnaphthalene is given below, followed by a discussion of results obtained under other conditions.

An eightfold excess of phenylmagnesium iodide in ether was slowly added to a solution of 1,8-diiodonaphthalene and a catalytic amount of nickel acetylacetonate in ether–benzene at −15 to −10 °C. The solution turned to a bright red which faded to brown during the course of the reaction. Pure 1,8-diphenylnaphthalene (**1a**) was obtained in a yield of 70% based on diiodonaphthalene; the reaction was repeated several times to give yields reproducible to within several percent.



1a, X = Y = H
b, X = CH_3, Y = H
c, X = H, Y = OCH_3
d, X = H, Y = Cl



2

Biphenyl and 1-phenylnaphthalene were also isolated, and gas chromatography–mass spectral analysis provided evidence for the presence of small amounts of **2**.

When the reaction was followed by gas chromatography, a transient peak was observed having a retention time between that of the starting diiodo compound and 1,8-diphenylnaphthalene, and for this, mass spectroscopy gave a molecular weight of 330, as expected for the monophenylmonoiodonaphthalene.[2b] The rates of coupling of the first and second phenyl groups were of similar magnitude, the first step being slightly more rapid. Interruption of the reaction and use of monoarylmonoiodonaphthalene as an intermediate in preparation of 1,8-diarylnaphthalenes having different aryl groups should be possible, as has been done with the lithium diarylcuprate couplings,[2b] though low overall yields would be anticipated. The reaction was seen to be essentially complete 4 h after Grignard addition was begun, when the reaction temperature was −15 to −10 °C. Use of a higher temperature gave enhanced reaction rate but decreased yields. The gradual color change during the course of the reaction suggested the possibility that the catalyst was slowly destroyed, and that the yield might be improved by periodic addition of catalyst. However, addition of catalyst at 45-min intervals, beginning at the start of the Grignard addition, resulted in no change in yield.

The use of excess Grignard reagent is necessary to give good results. Use of 7:1 Grignard:diiodonaphthalene (3.5 mol Grignard/mol iodo substituent) was found to be an ample excess. Higher Grignard:halide ratios did not improve matters, while use of only 3:1 Grignard:diiodonaphthalene resulted in incomplete conversion of the diiodonaphthalene. The product was then largely the 1-phenyl-8-iodonaphthalene intermediate.

The $Ni(acac)_2$ catalyst was found to cause some homo-Grignard coupling. When two portions of phenylmagnesium iodide, one of which contained added $Ni(acac)_2$, were stirred overnight at 0 °C, the solution containing the catalyst was found to contain a significantly larger amount of biphenyl. Analysis of the freshly prepared Grignard solution showed that it contained some biphenyl but no iodobenzene.

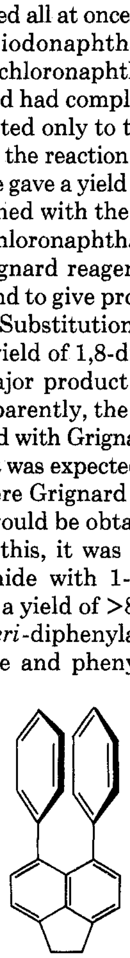
Approximately 20% of the initial 1,8-diiodonaphthalene was converted to 1-phenylnaphthalene under the conditions of the coupling reaction. It seemed possible that this unwanted side reaction might have proceeded by Grignard exchange between the phenylmagnesium iodide and the iodo compound. This would also cause some loss of phenylmagnesium iodide. For each molecule exchanged, two molecules of phenylmagnesium iodide would be converted to one molecule of biphenyl. That such an exchange is in fact facile was demonstrated when 1,8-diiodonaphthalene was combined with excess phenylmagnesium iodide at 0 °C and kept overnight in the absence of catalyst. After hydrolysis, the reaction mixture was found to contain large quantities of 1-iodonaphthalene and iodobenzene in equimolar amounts, along with some remaining

1,8-diiodonaphthalene. This exchange between an aryl Grignard reagent and an aryl halide is quite unusual. Earlier attempts at effecting such exchanges have been unsuccessful.[19] It seems likely that the driving force for the reaction in this system may stem from the high overcrowding of the peri-iodo substituents. Consistent with the observed Grignard–halide exchange, it was found that the yield of 1,8-diphenylnaphthalene was critically dependent on the rate of Grignard addition. Thus, when the phenylmagnesium iodide was added all at once, a substantial increase in 1-phenylnaphthalene was found in the product mixture. Apparently the nickel catalyst becomes saturated, and Grignard exchange is enhanced more than coupling by the presence of a large amount of Grignard reagent.

The reactivities of aryl halides in this system toward $Ni(acac)_2$-catalyzed coupling with Grignard reagent was found to be $I > Br \gg Cl$. Thus, when a 7-molar excess of phenylmagnesium iodide was added all at once to $Ni(acac)_2$-containing solutions of 1,8-diiodonaphthalene, 1,8-dibromonaphthalene, and 1,8-dichloronaphthalene at 0 °C after 30 min the diiodo compound had completely reacted, while the dibromo compound reacted only to the extent of 50%. With 1,8-dichloronaphthalene, the reaction was 30% complete after 4 h. Dibromonaphthalene gave a yield of diphenylnaphthalene equivalent to that obtained with the diiodo compound. The yield was lower with dichloronaphthalene.

Interestingly, the Grignard reagents of iodobenzene and bromobenzene were found to give pronounced differences in the coupling reaction. Substitution of phenylmagnesium bromide decreased the yield of 1,8-diphenylnaphthalene by more than half. The major product of the reaction was 1-phenylnaphthalene. Apparently, the rate of coupling is relatively less rapid compared with Grignard exchange in the case of the bromo Grignard. It was expected that for reactions with noncrowded halides where Grignard exchange would not be a problem, good yields would be obtained with a bromo Grignard. Consistent with this, it was found that reaction of phenylmagnesium bromide with 1-iodonaphthalene gives 1-phenylnaphthalene in a yield of >85%.

We have prepared *peri*-diphenylacenaphthene (3) from *peri*-diiodoacenaphthene and phenylmagnesium iodide at −15 °C with $Ni(acac)_2$ in 78% yield using the procedure described for 1,8-diphenylnaphthalene. 1,8-Bis(*p*-tolyl)naphthalene (**1b**) and 1,8-bis(3-methoxyphenyl)naphthalene (**1c**) were also prepared by this method from 1,8-diiodonaphthalene in yields of 53 and 49% by use of the respective Grignard reagents, *p*-tolylmagnesium iodide and *m*-methoxyphenylmagnesium iodide.



3

The differences in reactivities of halides toward coupling with Grignard reagent suggested the possibility of coupling with an iodide in the presence of a chloro substituent. The substituent could serve as a site for further chemical functionalization of the aromatic product. This possibility has been realized. Thus, when a 5-molar excess of *m*-chlorophenylmagnesium iodide was added to 1,8-diiodonaphthalene and $Ni(acac)_2$ at −20 °C and the reaction mixture hydrolyzed immediately after it was judged to be complete by gas chromatography, 1,8-bis(3-chlorophenyl)naphthalene (**1d**) was obtained in 52% yield, based on diiodonaphthalene. Use of higher temperature or larger excess of Grignard gave lower yields. When the reaction was allowed to continue for a longer time, the yield of the product decreased, presumably because of a slow reaction of the chloro substituent.

Experimental Section

^1H NMR spectra were taken with a Varian Associates A-60 or T-60 spectrometer. All spectra were obtained using deuteriochloroform as a solvent, with Me_4Si as an internal standard. Infrared absorption spectra were obtained on a Perkin-Elmer Model 257 infrared spectrometer. Mass spectra were run on an EAI Quad 300 quadrupolar mass spectrometer under the control of an SCC 4700 computer. Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich. GLC separations were carried out on a Hewlett-Packard Model 5750 gas chromatograph with a flame ionization detection system, utilizing a 6 ft × 0.125 in. column packed with 3% SE-30 on 40–60 mesh Chromasorb P. Injections were made at an oven temperature of 90 °C, and the instrument was programmed to raise the column temperature to 300 °C at 20 °C per minute. The observed peaks were catalogued in accord with the oven temperature at which they began to appear.

Uncatalyzed Grignard–Halide Coupling. A solution of 0.01 mol of phenylmagnesium iodide from 2.04 g of iodobenzene and 0.24 g of magnesium in 20 ml of ether was added to 2.54 g (0.01 mol) of 1-iodonaphthalene in 15 ml of toluene. The excess ether was distilled and the mixture was allowed to reflux for 48 h. After hydrolysis with 10% HCl, gas chromatographic analysis showed 45% conversion of iodonaphthalene to 1-phenylnaphthalene. Biphenyl and naphthalene were also present. The products were identified by retention times in the gas chromatograph. The 1-phenylnaphthalene was isolated by chromatography on silica gel with hexane eluent and its identity confirmed by comparison of the infrared spectrum with that of a commercial sample. When phenylmagnesium bromide was substituted for phenylmagnesium iodide in the above procedure, the gas chromatogram showed that, after 69 h at reflux, the conversion was only 25% complete. When 0.02 mol of phenylmagnesium iodide was heated to reflux with 0.01 mol of 1,8-diiodonaphthalene for 96 h, no 1,8-diphenylnaphthalene was formed.

1,8-Diphenylnaphthalene (1a). Magnesium turnings (0.59 g, 24 mmol) were placed in a three-necked round-bottomed flask equipped with a reflux condenser, and the system purged with nitrogen for 5 min while the flask and metal turnings were heated with a heat gun. To the cooled flask was added 3 ml of ether. Approximately 10% of a solution of iodobenzene (4.9 g, 24 mmol) in 20 ml of ether was drawn off from an addition funnel, and the mixture was heated to initiate the reaction. The remaining iodobenzene solution was added just rapidly enough to maintain a gentle reflux (about 45 min). The resulting Grignard reagent was pipetted through glass wool (to prevent contamination with small, unreacted slivers of magnesium) into an addition funnel and then added slowly (during 2 h) to a solution of 1.14 g (3 mmol) of 1,8-diiodonaphthalene and 0.005 g (0.027 mmol) of nickel(II) acetylacetonate[20] in 25 ml of a 1:1 mixture of ether and benzene, which was kept stirring in a dry ice–acetone bath at −15 to −10 °C. The mixture was stirred for an additional 2 h at this temperature, at which time gas chromatographic analysis showed that all starting diiodo compound had reacted. The flask was left stirring overnight at room temperature, the mixture hydrolyzed with concentrated NH_4Cl solution, the aqueous layer extracted once with ether, and the combined organic fractions dried over Na_2SO_4. The 2.4 g of crude mixture remaining after evaporation of the solvent was subjected to chromatography on silica gel with hexane as eluent to yield 0.59 g (70% based on diiodonaphthalene) of pure 1,8-diphenylnaphthalene (mp 147–148 °C, lit.[7] mp 149–150 °C). The ^1H NMR spectrum showed a singlet at δ 6.9 (10 H) and a multiplet at δ 7.2–7.9 (6 H) at 60 MHz. The early chromatographic fractions contained 0.8 g of a white, crystalline solid which was identified as biphenyl by its melting point (69 °C) and by comparison of its infrared spectrum with that of an authentic sample. Several fractions collected between those containing biphenyl and those containing the diphenylnaphthalene were found to contain 0.14 g of a clear, viscous liquid which was identified as 1-phenylnaphthalene by comparison of its infrared spectrum with that of an authentic sample.

A series of reactions analogous to the above was performed with one or more reaction conditions varied as described in the Discussion. Other parameters were held constant during these runs. Results were evaluated using gas chromatography retention times, and by isolation of products using column chromatography.

1,8-Bis(*p*-tolyl)naphthalene (1b) was prepared as described for 1,8-diphenylnaphthalene. From 3 mmol of 1,8-diiodonaphthalene and 25 mmol of *p*-tolylmagnesium iodide, 1.59 mmol (53% based on diiodonaphthalene) of **1b** was obtained, following column chromatography with hexane as eluent (mp 175–177.5 °C): ^{1}H NMR δ 2.17 (s, 6 H), 6.77 (m, 8 H), 7.2–8.0 (m, 6 H); mass spectrum *m/e* 308.

Anal. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.36; H, 6.59.

The early chromatographic fractions were found to contain naphthalene and *p,p′*-bitolyl, identified by comparison of the NMR spectra with those of commercial samples.

1,8-Bis(3-methoxyphenyl)naphthalene (1c) was prepared similarly to 1,8-diphenylnaphthalene, employing 3 mmol of 1,8-diiodonaphthalene and 26 mmol of 3-methoxyphenylmagnesium iodide. Column chromatography with 5% ether in hexane as eluent gave 1.46 mmol of **1c** (49% based on diiodonaphthalene) as a viscous liquid: ^{1}H NMR δ 3.62 (s, 6 H), 6.2–7.2 (m, 8 H), 7.2–8.1 (m, 6 H).

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.78; H, 6.00.

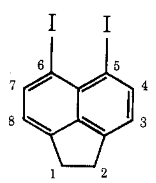
Early chromatographic fractions contained naphthalene and 3,3′-dimethoxybiphenyl, identified by comparison of the NMR spectra with those of commercial samples.

1,8-Bis(3-chlorophenyl)naphthalene (1d). The best yield of 1,8-bis(3-chlorophenyl)naphthalene was obtained when a smaller excess (~5:1) of Grignard reagent and somewhat lower temperature than that used for the 1,8-diphenylnaphthalene synthesis was employed, with the reaction carefully monitored by gas chromatography and stopped immediately at completion. Thus, 15 mmol of *m*-chlorophenylmagnesium iodide, which formed readily on addition of 3.6 g (15 mmol) of *m*-chloroiodobenzene in 18 ml of ether to 0.36 g (15 mmol) of magnesium turnings, was added dropwise to a stirred solution of 1.14 g (3 mmol) of 1,8-diiodonaphthalene and 0.02 g (0.1 mmol) of nickel acetylacetonate in 15 ml of benzene and 12 ml of ether. The reaction vessel was held in a −15 to −20 °C bath during the 2-h Grignard addition. This temperature was maintained and the mixture stirred as the reaction was allowed to continue. During this time, the gas chromatograms of successive aliquots showed disappearance of the diiodo compound (210 °C peak) while a new peak (240 °C) grew and then disappeared at the expense of a higher peak (260 °C). At the end of 4 h, the reaction was seen to be essentially complete. Hydrolysis with saturated ammonium chloride solution followed by column chromatography on silica gel with pentane as the eluent gave 0.53 g (52%) of 1,8-bis(3-chlorophenyl)naphthalene (mp 95–97 °C, lit.[21] mp 97–98.5 °C): mass spectrum parent peaks *m/e* 248, 250, 252, with expected ratio for two chlorine atoms.

Anal. Calcd for $C_{22}H_{14}Cl_2$: C, 75.66; H, 4.04; Cl, 20.30. Found: C, 75.57; H, 4.14; Cl, 19.93.

When the reaction was run with a 10-molar excess of Grignard reagent at −10 to −5 °C for 6 h, or at −4 °C for 12 h, the gas chromatograms showed that the 1,8-bis(3-chlorophenyl)naphthalene peak reached a maximum and then slowly decreased.

***peri*-Diiodoacenaphthene (7)** was prepared in four steps from acenaphthene by a sequence essentially in accord with that described previously.[22,23] The reaction of 40 g (0.24 mol) of acenaphthene with 62 g of iodine and 90 g of mercuric iodide in refluxing ethanol gave 50.1 g (46%) of 5-iodoacenaphthene (**4**), which crystallized as white needles from methanol (mp 62–64 °C, lit.[22] mp 65 °C; picrate mp 97–99 °C, lit.[22] mp 100 °C). In the nitration of **4** (13.5 g, 0.48 mol) with 5 ml of fuming HNO_3 in 140 ml of glacial acid at room temperature, gas chromatography showed that the reaction was complete after 4 days. The 10 g of crude product which had precipitated was a mixture of isomers. Nine successive recrystallizations from glacial acetic acid gave 2.5 g (16%) of 5-iodo-6-nitroacenaphthene (**5**) as yellow needles (mp 175–178 °C, lit.[22] mp 179–180 °C). Reduction of 10 g (31 mmol) of **5** by refluxing with 80 g of $SnCl_2$ in a solution containing 800 ml of concentrated HCl and 140 ml of ethanol gave 2.6 g (28%) of light yellow 5-iodo-6-aminoacenaphthene, **6** (mp 104–107 °C, lit.[22] mp 107–108 °C). Diazotization of **6** (2.6 g, 8.8 mmol) was accomplished by treatment with 0.75 g of $NaNO_2$ in 55 ml of 10% H_2SO_4 at −4 °C for 40 min. Addition of a solution of 2.5 g of KI in 10 ml of water precipitated the diazonium iodide, which was decomposed by refluxing in acetone for 1 h. The black solid product was treated with $Na_2S_2O_3$ and subjected to chromatography on silica gel with ligroin as eluent to give 1.7 g (48%) of white crystalline 5,6-diiodoacenaphthene (*peri*-diiodoacenaphthene, **7**) (mp 156–158 °C, lit.[22] mp 159–160°C): NMR ($CDCl_3$) δ 3.30 (s,4H), (ABq,4H).



7

***peri*-Diphenylacenaphthene (3)** was prepared using the same conditions described earlier for preparation of 1,8-diphenylnaphthalene. Addition of 8 mmol of phenylmagnesium iodide to 0.41 g (1 mmol) of **6** at −14 to −10 °C during a 2-h period, followed by a 2.5-h period at −10 °C and 1 h of slow warming to room temperature, afforded, after column chromatography on silica gel with ligroin as eluent, 0.24 g (78% based on diiodoacenaphthene) of pure **3** (mp 156–157 °C): NMR δ 3.43 (s, 4 H), 6.87 (s, 10 H), 7.30 (s, 4 H); mass spectrum 306.1410 (calcd for $C_{24}H_{18}$, 306.1408).

Registry No.—**1a**, 1038-67-1; **1b**, 58541-18-7; **1c**, 58541-19-8; **1d**, 7731-47-7; **3**, 57620-87-8; **6**, 58541-20-1; **7**, 55143-88-9; nickel(II) acetylacetonate, 18918-08-6; acenaphthene, 83-32-9.

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