Bridged Polycyclic Compounds. LXXVII. Coupling Reactions of 7-Chlorobenzonorbornadienes with Phenylmagnesium Bromide. Evidence for Carbocationic Intermediates[1,2]

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The syn (1-Cl) and anti (2-Cl) epimers of 7-chlorobenzonorbornadiene have been treated with a variety of organometallic reagents. Neither chloride reacted with phenyllithium or with a variety of organometallic species prepared by the addition of varying amounts of cuprous bromide to phenyllithium. The syn isomer reacted slowly with phenylmagnesium bromide in THF to give *syn*-7-phenylbenzonorbornadiene (1-Ph), while the anti chloride was inert. Additions of cuprous bromide to the Grignard reagent before addition of chloride promoted reaction. Anti chloride was slowly converted to *anti*-7-phenylbenzonorbornadiene (2-Ph), while syn chloride was more rapidly converted to a mixture of *syn*-7-phenylbenzonorbornadiene (1-Ph) and the *endo*-phenylbenzotricycloheptene (3-Ph). Those stereospecific coupling reactions are discussed in terms of ion-pair mechanisms.

The coupling reactions of alkyl halides with organometallic compounds (eq 1) are synthetically useful processes for the preparation of hydrocarbons. For this reason and because of similarities to the second part of the postulated path for the Wurtz-Fittig reaction, the mechanisms of such reactions received considerable early attention.[3-5]

$$\text{R-metal} + \text{R'X} \longrightarrow \text{R-R'} + \text{metal-X} \tag{1}$$

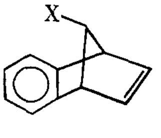
In studies on the reaction of Grignard reagents with allylic halides,[6] Young and his coworkers reported that crotyl chloride (1-chloro-2-butene) and α-methylallyl chloride (3-chloro-1-butene) reacted with phenylmagnesium bromide to give identical mixtures of butenylbenzenes. They proposed that the electrophilic magnesium atom coordinated with the halogen atom of the allylic halide, promoting heterolytic cleavage, to give a mesomeric butenyl cation which became free enough to lose its identity as either a crotyl or an α-methylallyl group before coordination with the phenyl anionoid species. Similar results were reported with phenyllithium and with butyllithium in ether[7] and with phenylsodium in pentane,[8] and analogous rationalizations were offered.

More recently Prevost and coworkers[9] studied coupling of α-methylallyl chloride and *cis*- and *trans*-crotyl chlorides with *n*-butylmagnesium bromide in ether and with *n*-butyllithium and *n*-butylsodium in pentane. Their more precise analytical methods showed that differences existed between product mixtures formed from the three isomers, and that with the organolithium and -sodium compounds, complete retention of geometric isomerism obtained (almost complete with the organomagnesium compound), but that each chloride gave a product mixture rich in the product of coupling at the primary position. They concluded that the mixtures were the result of combinations of cationic processes, direct displacement processes (S_N2), and abnormal allylic displacements (S_N2') or cyclic processes. Wawzonek[10] also studied the reaction of the crotyl chlorides with phenyllithium, phenylsodium, and phenylmagnesium bromide, and noted that the lithium reagent gave some phenylmethylcyclopropanes. All three organometallic reagents gave mixtures of the three butenylbenzenes.

Detailed studies have been reported recently by Magid and his students[11] on the reaction of phenyllithium in ether with a variety of allylic halides. The allylic halides were made isomeric by methyl substitution or by deuterium placement; in one case an optically active substance was used. Their data made it clear that, for some cases at least, a cationic process in which the two ends of the allylic system lose their identity before coordination with the phenyl nucleophile cannot be the sole process.[12] Although these authors do not exclude cationic processes from consideration, they seem to favor competition between cyclic processes involving S_N2-like and S_N2'-like transition states to rationalize their mixture compositions. The effect of structural variations in allylic chloride upon product composition, such that α,α-dimethylallyl chloride and the γ,γ isomer both give almost entirely coupling at the primary carbon atom, and α,γ-dimethylallyl chloride labeled with deuterium or ^{14}C gives complete scrambling, seems to us to argue for the existence of cationic mechanisms in the process mix.

Adding to the confusion is the suggestion[13] that coupling of Grignard reagents with allyl bromide involves free-radical intermediates. Similar suggestions[14] involving radical or radical ion intermediates have been made by Eastham, by Ward and Lawler, by Lepley, by Russell, and by others, and it appears particularly clear, from both electron-spin resonance and chemically induced dynamic nuclear polarization experiments, that radical intermediates can intervene in these reactions, particularly with organolithium compounds.

In view of these recent developments, which raise serious doubts regarding the existence of a reaction path involving carbocations in such coupling reactions, we decided to turn our attention to this problem again. We obviously needed a system where radical, direct displacement, and cationic paths would give different products, and where cyclic paths perhaps could also be noted and/or excluded. One such system is the 7-chlorobenzonorbornadiene system, where syn (1-Cl) and anti (2-Cl) isomers are available,[15] and they or their bromine analogs have been subjected to a variety of ionic and radical reactions.



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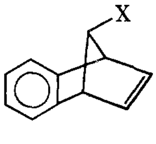

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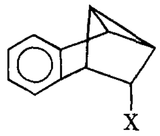

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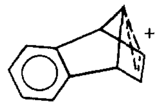

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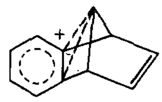

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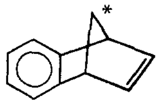


6

1-Cl upon acetolysis yields 1-OAc, and 2-Cl yields only 2-OAc, both reactions occurring with complete retention.[15b] Similarly 1-Cl and 2-Cl undergo methanolysis with retention,[16] and 1-Br[17] and 2-Br[18] also suffer hydrolysis with retention.

The methanolysis of 1-Cl in the presence of sodium methoxide is diverted to give substantial amounts of *endo*-2-methoxy-4-benzotricyclo[4.1.0.0^{3,7}]heptene (3-OCH$_3$) as well as 1-OCH$_3$.[16,19] These data have been bases for the conclusion that the nonclassical carbonium ions **4** and **5** intervene in solvolytic reactions of **1** and **2**, respectively. Furthermore, the rate enhancement due to double-bond participation in **1** is much greater than that of the aromatic π system in **2**. Thus 1-Cl acetolyzes about 10^3 times as fast as 2-Cl in acetic acid,[15b] and by a factor of about 10^5 when return from solvent-separated ion pairs is excluded.[20] Similarly, 1-Br solvolyzes in 80% ethanol 4×10^4 times as fast as 2-Br.[17]

While carbocation reactions of **1** and **2** show large rate and product differences, neither of these effects is true for radical reactions. Thus 1-Br and 2-Br in reduction with tri-*n*-butyltin deuteride (initiated with azoisobutyronitrile) give identical mixtures of 1-*d* and 2-*d*.[21] When an equimolar mixture of 1-Br and 2-Br was treated with approximately one half the amount of tri-*n*-butyltin hydride required for complete reaction, the remaining starting material was, within the limits of pmr analysis, half 1-Br and half 2-Br. Thus tributyltin radical shows no kinetic preference for either of these bromides.[21b] These data make it clear that the radical **6** is identical with either **1** or **2** and is classical (although not necessarily planar).

The stereochemical results described above are those of a radical chain process and may not follow for geminate pair recombination. However, for a high degree of stereoselectivity, steric interference with recombination of the radicals must be low. For example, the thermal decomposition of (*S*)-1,1′-diphenyl-1-methylazomethane proceeds with a maximum of 17% retention of configuration with only a nitrogen molecule intervening between the members of the radical pair.[22] It thus seems unlikely that complete retention of configuration in the organometallic couplings could be due to cage radical combination. Rather it seems reasonable to assume that, if a cationic intermediate is involved, each epimer would react with complete retention of configuration (or perhaps 1-Cl might give 3-Ph), while a free-radical intermediate would lead to mixing.

Substituents at C-7 in norbornanes or unsaturated analogs are generally inert toward S$_N$2 displacements, and this is true for 2-Br as well.[15a,23] While derivatives of **1** have not been studied, one would guess that these also would be unreactive. In any case, such reactions would proceed with inversion, **1** giving **2** and vice versa.

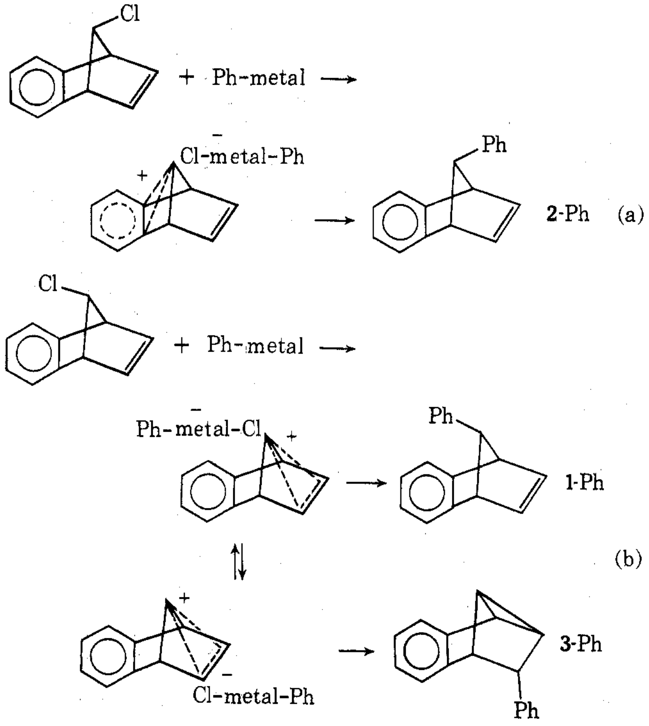
When 1-Cl was treated with phenylmagnesium bromide in tetrahydrofuran (THF) for 5 days at reflux, all of the chloride reacted and 27% of 1-Ph was obtained. No lines in the pmr spectrum attributable to 2-Ph were observed, nor was 3-Ph present. The formation of 1-Ph from 1-Cl was therefore stereospecific.[24]

When 2-Cl was treated with phenylmagnesium bromide in ethyl ether or in THF under more severe conditions than those which succeeded with 1-Cl, it was recovered unchanged. As reactions of organometallic compounds are often irreproducible, a competition reaction was run between 1-Cl and 2-Cl with an excess of phenylmagnesium bromide. All of the 1-Cl was consumed, and, besides the dimeric product, only 1-Ph and 2-Cl were recovered. Clearly then, 1-Cl was substantially more reactive than 2-Cl.

Although these results were interesting and fit the carbocation theory, we were somewhat confused by the failure of 2-Cl to react, as it had been reported[25] that 2-Ph was produced by reaction of 2-Cl with phenylmagnesium bromide in ether fairly rapidly, albeit in poor yield. As Battiste's paper dealt with copper(I)-catalyzed reactions of peroxides with 1-H, we guessed that their success might be attributable to copper catalysis of the Grignard coupling.[26] We were therefore pleased to find that addition of cuprous bromide to the Grignard reagent before addition of 2-Cl led to a slow coupling reaction. After 9 days of reflux in ether, 13% of 2-Ph (no 1-Ph) was obtained and 85% of 2-Cl was recovered. Even more interesting was the fact that analogous treatment of 1-Cl (for 4 days) gave 36% of 1-Ph and 29% of 3-Ph (no 1-Cl was recovered and no 2-Ph or exo epimer of 3-Ph was formed).

The relative reactivities of 1-Cl and 2-Cl and the products obtained seem to us to be consistent only with the idea that the alkyl halides are transformed to the cations **4** or **5** during the reaction course. As our data offer no evidence regarding the complex question of the nature of the Grignard reagent or of the copper-promoted reagent, we can say very little about the nature of the ion paired with **4** or **5**. What can be confidently stated is proposed in Scheme I, where the organometallic compound is simply described as Ph–metal.

Scheme I



With the anti chloride (a) the gegenion need only rotate to be in a position to donate the nucleophilic phenyl group to the cationic center, and a similar scheme is proposed for the Grignard reagent reacting as in b. However, with the copper-promoted reagent, one must assume that the lifetime of the ion pair is large, that is, that coordination of the cation with the phenyl anionoid species is slow enough to allow competitive migration of the anion to a position from which phenyl can be donated to the opposite face of the cation to give 3-Ph. The postulated longer lifetime is reasonable, as the enhanced reactivity over the simple Grignard reagent speaks for a more stable ion pair. The fact that *no* mixing of **1** and **2** species occurs even in the copper-promoted reactions speaks against the idea of radical intermediates, as it seems impossible to make any reasonable argument involving geminate recombination, considering the stereochemistry noted. Obviously S$_N$2 mechanisms are also excluded.

Although these Grignard reactions proceeded, neither **1**-Cl nor **2**-Cl reacted with phenyllithium, with CuBr-promoted phenyllithium, with lithium diphenylcuprate,[27] or with phenylcopper[28] prepared from phenyllithium with excess cuprous bromide, that is, with phenyllithium recipes containing either excess phenyllithium or excess copper species. In each case substantially all of the starting chloride was recovered. Apparently these reagents are not electrophilic enough to promote ionization of the halide. Pentafluorophenylcopper is reported to couple with iodobenzene, methyl iodide, 1-bromoadamantane, and benzyl bromide,[29a] and with 7-chloronorbornadiene,[29b] and the authors suggest that cationic intermediates are involved in the latter three cases. It would thus appear that the electron-attracting fluorine substituents increase the electrophilicity of the copper atom enough to produce ionic intermediates. It would clearly be of interest to study the reaction of **1** and **2** with pentafluorophenylcopper.

Experimental Section

Coupling of *syn*-7-Chlorobenzonorbornadiene (1-Cl) with Phenylmagnesium Bromide. In 5 ml of THF, 198 mg (8 mmol) of Mg shavings was stirred in a sealed flask under N_2. Bromobenzene (0.84 ml, 8 mmol) was added *via* a syringe. The mixture was heated until all the magnesium had reacted. To the cooled flask 707 mg (4.00 mmol) of **1**-Cl[30] in 15 ml of THF was added *via* syringe. The mixture was heated at reflux for 5 days. Water was then added, and the mixture was extracted with ether. The ethereal layer was washed twice with saturated sodium chloride solution. The ether layer was then dried ($MgSO_4$). Evaporation of the solvent left 816 mg of a dark oil whose pmr spectrum indicated that none of the starting chloride was present. Chromatography on an alumina column gave, upon elution with hexane, 223 mg (27%) of a solid identified as *syn*-7-phenylbenzonorbornadiene (**1**-Ph), whose pmr spectrum indicated that no **2**-Ph was present. Recrystallization from hexane gave white needles (150 mg, 18%, mp 98.5–99°) with a pmr spectrum ($CDCl_3$) characteristic of the syn 7-substituted derivative, δ 6.75–7.35 (m, 11 H), 4.13 (q, J = 2 Hz, 2 H), 4.01 (m, 1 H).

Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.34; H, 6.60.

Further elution of the column with benzene and finally with ether gave 303 mg (54%) of a dark oil whose pmr spectrum indicated a mixture of the 7,7′ dimers of benzonorbornadiene[15a] which were not readily separable by further column chromatography.

A similar experiment with **2**-Cl[15a] for 60 hr gave 95% recovery of **2**-Cl and after 30 days gave, upon chromatography, only **2**-Cl (plus some biphenyl from the Grignard preparation).

Competition Reaction of *syn*- (1-Cl) and *anti*-7-Chlorobenzonorbornadiene (2-Cl) with Phenylmagnesium Bromide. The reaction was run as described above with ether as solvent and the following reagents: 195 mg (8 mmol) of magnesium, 0.84 ml (8 mmol) of bromobenzene, 353 mg (2 mmol) of **2**-Cl, and 353 mg (2 mmol) of **1**-Cl. After 5 days the reaction mixture was worked up as usual, yielding a yellow oil which when chromatographed on an alumina column yielded 240 mg of the mixture of dimers noted in the reaction with **1**-Cl (0.85 mmol, 42% based on **1**-Cl and **2**-Cl) and 476 mg of a mixture of **1**-Ph, **2**-Cl, and biphenyl. This mixture was then chromatographed on an activated silica gel column which separated the biphenyl from the remaining two products. Pmr analysis of the remaining mixture (329 mg) indicated a 1:4.5 molar ratio of **1**-Ph to **2**-Cl (0.4 mmol of **1**-Ph, 10%; 1.8 mmol of **2**-Cl, 45%).

Cuprous Bromide Catalyzed Reaction of 2-Cl with Phenylmagnesium Bromide. Cuprous bromide (300 mg, 2 mmol) was added in 2 ml of ether to the Grignard reagent prepared from 194 mg (8 mmol) of Mg and 0.84 ml (8 mmol) of bromobenzene in 2 ml of ether. The solution immediately turned dark red, then black. The mixture was then heated at reflux for 20 min, and 707 mg (4 mmol) of **2**-Cl in 20 ml of ether was then added. After 9 days the solution as worked up in a manner similar to that for the noncatalyzed reaction, yielding 714 mg of a yellow liquid whose pmr spectrum indicated a ratio of **2**-Cl:**2**-Ph of 5.7:1 (3.4 mmol of **2**-Cl, 85%, and 0.52 mmol of **2**-Ph, 13%).

Chromatography on alumina gave 412 mg (2.3 mmol, 58%) of **2**-Cl upon elution with hexane. Further elution with benzene and finally with ether gave 195 mg (0.48 mmol, 12%) of a solid with a pmr spectrum similar to that reported[25] for *anti*-7-phenylbenzonorbornadiene (**2**-Ph). The **2**-Ph was recrystallized out of hexane, yielding a white solid (mp 87–88°) with the following pmr spectrum ($CDCl_3$): δ 7.04–7.33 (m, 9 H), 6.58 (t, J = 2 Hz, 2 H), 4.15 (q, 2 H), 3.96 (broad s, 1 H). Pmr absorption attributable to **1**-Ph was found in neither the crude product nor the eluted products.

Cuprous Bromide Catalyzed Reaction of 1-Cl with Phenylmagnesium Bromide. The reaction was run as with the anti epimer using 353 mg (2 mmol) of **1**-Cl, 0.42 ml (4 mmol) of bromobenzene, 97 mg (4 mmol) of Mg, and 150 mg (1 mmol) of CuBr. After 4 days of reflux in ether the mixture was worked up and yielded 430 mg of a yellow oil whose pmr spectrum indicated a mixture identified as biphenyl (1.0 mmol), **1**-Ph (0.72 mmol, 36%), and **3**-Ph (0.57 mmol, 29%). Chromatography on an alumina column gave 120 mg (27%) of *endo*-2-phenyl-4-benzotricyclo[4.1.0.0^{3,7}]-heptene (**3**-Ph), mp 87.5–88°, upon elution with hexane. Recrystallization from hexane gave an analytical sample characterized by the following pmr spectrum ($CDCl_3$):[31] δ 6.5–7.4 (m, aromatic, 9 H), 4.10 (1 H, d of d, H-3, J = 8.3 Hz), 3.75 (1 H, d of t, H-2, J = 8.3, 2.5 Hz), 3.22 (1 H, d of t, H-1, J = 5.5, 3 Hz), 2.62 (1 H, t, H-6, J = 5 Hz), and 2.26 (1 H, m, H-7, J = 5.5, 3, 2.5 Hz).

Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.30; H, 6.22.

Further elution of the column with 1% benzene in hexane gave 100 mg (25%) of **1**-Ph.

Photorearrangement of 1-Ph. A 100-mg portion of **1**-Ph was dissolved in 0.5 ml of ether and placed in a Pyrex nmr tube with 0.06 ml (60 mg) of distilled acetophenone. Irradiation (20 hr) with a Hanovia 450-W Model L mercury arc lamp, followed by evaporation of the solvent, gave 145 mg of a yellow oil whose pmr spectrum, after correction for acetophenone, was identical with that of the other sample of **3**-Ph. This material was not separated or purified, but we judge that this would be a useful preparation of **3**-Ph, if **1**-Ph is available.

Attempted Coupling of *anti*-7-Chlorobenzonorbornadiene (2-Cl) with Phenyllithium. To a solution of 177 mg (1 mmol) of *anti*-7-chlorobenzonorbornadiene (**2**-Cl) in 5 ml of anhydrous ether (under nitrogen) was added 1.0 ml of 1.9 *M* phenyllithium (Alfa) *via* syringe. The mixture was heated at reflux for 3 days. Water was then added and the solution was washed with two 20-ml portions of water. The ether layer was concentrated, yielding a yellow liquid. The crude product was purified on a column of alumina, yielding 164 mg (93%) of the starting chloride. A similar experiment was performed in distilled THF with a reaction time of 22 days and gave only the starting chloride. A third experiment was also performed with freshly prepared phenyllithium and a reaction time of 7 days in ether resulted in 85% recovery of the starting chloride.

Attempted Coupling of *syn*-7-Chlorobenzonorbornadiene (1-Cl) with Phenyllithium. In freshly distilled THF, 528 mg (3 mmol) of **1**-Cl and 4.5 ml (2 *M*, 9 mmol) of freshly prepared phenyllithium were refluxed for 7 days. Work-up similar to that used for the reactions of **2**-Cl yielded 835 mg of a yellow oil whose pmr spectrum indicated a ratio of 1:13:11 for **1**-Br:**1**-Cl:Ph_2 and recovery of 2.56 mmol (85%) of **1**-Cl and 0.20 mmol (6.7%) of **1**-Br. The formation of **1**-Br is apparently due to capture of **4** by lithium bromide.[32]

Attempted Cuprous Bromide Catalyzed Coupling of *anti*-7-Chlorobenzonorbornadiene (2-Cl) with Phenyllithium. To 4 ml (2 *M*, 8 mmol) of freshly prepared phenyllithium was added 300 mg (2 mmol) of CuBr under nitrogen. After 20 min, 707 mg (4 mmol) of **2**-Cl was added in ether, making a total volume of 20 ml. The solution was heated at reflux for 7 days, after which time the solution had turned yellow. Work-up similar to that for the uncatalyzed phenyllithium reactions yielded 1.15 g of a dark oil whose pmr spectrum indicated recovery of 3.9 mmol (98%) of the starting chloride (**2**-Cl), as well as biphenyl.

Attempted Coupling of Lithium Diphenylcuprate with *anti*-7-Chlorobenzonorbornadiene (2-Cl). Lithium diphenylcuprate was prepared[27] by adding 12 ml (2 *M*, 24 mmol) of freshly prepared phenyllithium to 1.72 g (12 mmol) of CuBr which was in ether solution under nitrogen at 0°. The ice bath was removed and to this solution 707 mg (4 mmol) of **2**-Cl was added in 20 ml of ether. The mixture was heated slowly and as the ether evaporated 25 ml of distilled THF was added. This mixture was heated at reflux for 3 days. Aqueous ammonium chloride was added with additional ether, and the ether layer was washed three times with a saturated NaCl solution and one time with water. The aqueous layer had a deep blue color which faded to a clear solution by the final washing. The ether layer was then dried over $MgSO_4$ and evaporated to yield 1.84 g of a yellow oil whose pmr spectrum indicated quantitative recovery of the starting chloride (**2**-Cl) in addition to 7 mmol of biphenyl.

Attempted Coupling of Lithium Diphenylcuprate with *syn*-7-Chlorobenzonorbornadiene (1-Cl). The reaction was run as with the anti epimer using 528 mg (3 mmol) of **1**-Cl, 9 ml (2 *M*, 18 mmol) of phenyllithium, and 1.29 g (9 mmol) of CuBr. After 4 days at reflux in THF, work-up as described for the **2**-Cl reaction yielded 1.97 g of a yellow oil whose pmr spectrum indicated biphenyl and recovery of 432 mg (2.46 mmol, 82%) of **1**-Cl and 90 mg (0.41 mmol, 13%) of **1**-Br. The products were identified by pmr absorption of the bridge protons with the **1**-Cl absorption at δ 4.33–4.41 (t) and the **1**-Br at δ 4.45–4.51.

Phenylcopper. As described by Costa,[28] 4 ml (2 *M*, 8 mmol) of freshly prepared phenyllithium was added to a solution of CuBr (1.15 g, 8 mmol) in 30 ml of ether under nitrogen at 0°. The white solution turned yellow-brown gradually and finally a white precipitate of phenylcopper formed.

Attempted Coupling of Phenylcopper with *anti*-7-Chlorobenzonorbornadiene (2-Cl). To a suspension of 8 mmol of phenylcopper at 0° in 30 ml of ether, 707 mg (4 mmol) of **2**-Cl was added in 10 ml of ether. The ice bath was removed and the solution was stirred for 7 days. The solution had a green color and water was added. The ether layer was washed two times with a saturated NaCl solution and the combined aqueous layers were reextracted with ether. The combined ether layers were then washed with an ammonium chloride solution and dried over $MgSO_4$. Evaporation yielded 1.65 g of a light yellow oil whose pmr spectrum indicated a 1:1 ratio of biphenyl and **2**-Cl (660 mg, 94%).

To a suspension of 6 mmol of phenylcopper at 0°, 5 ml of dry pyridine was added, giving a dark-colored solution. After approximately 5 min, 707 mg (4 mmol) of **2**-Cl was added in 10 ml of pyridine. The solution was heated at 45° for 5 days and then approximately 50 ml of 1 *M* HCl was added with 50 ml of ether. The ether layer was washed two times with 1 *M* HCl, one time with a saturated NaCl solution, one time with an ammonium chloride solution, and finally with water. The ether layer was then dried over $MgSO_4$ and evaporated, yielding 753 mg of a yellow oil whose pmr spectrum indicated a 92% recovery of the starting chloride.

Attempted Coupling of Phenylcopper with *syn*-7-Chlorobenzonorbornadiene (1-Cl). Using the same procedure as with **2**-Cl, **1**-Cl (528 mg, 3 mmol) was heated for 5 days with 6 mmol of phenylcopper in approximately 15 ml of pyridine. Work-up yielded 730 mg of a yellow oil whose pmr spectrum indicated recovery of 2.15 mmol (72%) of the starting chloride (**1**-Cl). Biphenyl was the only other product in the mixture.

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Registry No. **1**-Cl, 14518-75-3; **1**-Ph, 42880-72-8; **2**-Cl, 10239-89-1; **2**-Ph, 10239-94-8; **3**-Ph, 42880-74-0; phenyl bromide, 108-86-1; phenyllithium, 591-51-5; lithium diphenylcuprate, 23402-69-9; phenylcopper, 3220-49-3.

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