shown to be uniformly inversion of configuration at phosphorus.[22] There is an absolute requirement for dications for kinase activity.[9,22] Furthermore, ATP^{3-} is known to hydrolyze via a mechanism analogous to that for DMPG hydrolysis, and it is also known that cation coordination has little effect on the rate of nonenzymic ATP^{3-} hydrolysis.[23] These studies, and the results of this paper indicate that cation coordination has little effect on the rate of phosphoryl donor hydrolyses with significant S_N1 character.

There is evidence for migration of the associated cation during the kinase-catalyzed reaction;[24] kinases may utilize the change in site of cation coordination to catalyze phosphoryl transfer. We find that divalent cations coordinate to the α-, β-, and γ-positions of ATP in solution.[1a,14] Coordination of Mg^{2+} to the α- and β-positions, as well as the transferred phosphoryl moiety, would increase the acidity of the leaving group in both the forward and reverse reactions. Additionally, coordination of a cation would reduce the electrostatic repulsion of the negatively charged substrates. The evidence presented in this paper demonstrates that these rate-enhancing properties of cation coordination at the kinase active site would not be diminished at any rate-inhibiting character intrinsic to cation coordination to a substrate that reacts via a transition state with predominant S_N1 character.

Although the importance of our results is not dependent on whether the mechanism is predominantly dissociative or associative,[8] it is certainly true that the metaphosphate ion is a highly unstable intermediate. As Allen and Haake demonstrated, even in the most reactive metaphosphate precursors, there is a tendency for associative character in the transition state, and we therefore predicted that the enzymic reactions would have some associative character in a predominantly dissociative transition state.

The rate effects of high concentrations of salt are probably related to changes in water structure and therefore solvation of **1**–**3** will be of critical importance to their total energies. With 5 M salt, the structure of water will be greatly altered. If each Cl^- and each Na^+ is solvated by six waters, nearly every water molecule will be tied up with salt solvation, and therefore solvation of **1**–**3** will change. For example, if **1** is solvated less well, its energy will be raised and the rate will increase.

Acknowledgment. We thank Professor Max Tishler for comments and the NIH for a grant.

Registry No. DMPG, 34718-93-9; B-DMPG, 50725-11-6; sodium, 7440-23-5; magnesium, 7439-95-4; guanidinium ion, 25215-10-5; kinase, 9031-44-1.

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Highly Reactive Metallic Nickel: Reductive Homocoupling Reagent for Benzylic Mono- and Polyhalides

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Metallic nickel, prepared by the reduction of nickel halides with lithium in glyme using naphthalene as an electron carrier, was found to be a useful reagent for the homocoupling of benzylic mono- and polyhalides. Benzyl halides reacted with metallic nickel at room temperature to give the corresponding 1,2-diarylethanes in good to high yields and functional groups on the aromatic ring such as methoxy, chloro, bromo, nitro, cyano, and alkoxycarbonyl groups were not affected under the conditions employed. Benzylic monohalides (1-(chloromethyl)- or 2-(bromomethyl)naphthalene, chlorodiphenylmethane, and 9-bromofluorene) also underwent coupling reactions with metallic nickel at room temperature to give the corresponding ethane derivatives. On the other hand, benzylic di- and trihalides such as α,α-dibromotoluene and α,α,α-trichlorotoluene yielded mixtures of cis and trans isomers of substituted ethenes. The intermediate of the reaction, benzylnickel complex, was trapped with electron deficient olefins such as methyl acrylate and acrylonitrile.

Introduction

Recently, transition metals in a low oxidation state have been used extensively as reagents for the reductive homocoupling reaction of benzylic halides. For example, titanium,[1] vanadium,[2] chromium,[3] and tungsten[4] have been employed as reagents for this purpose and were prepared in situ by reducing the appropriate metal halide with lithium aluminum hydride. Nickel(I),[5] cobalt(I),[6] and vanadium(II)[7] complexes or metal carbonyls of nickel,[8,9] cobalt,[10] iron,[11-13] molybdenum,[14] and tungsten[4] as well as

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metallic iron[15-17] have also been found to be useful as low-valent coupling reagents of benzylic mono- and polyhalides.

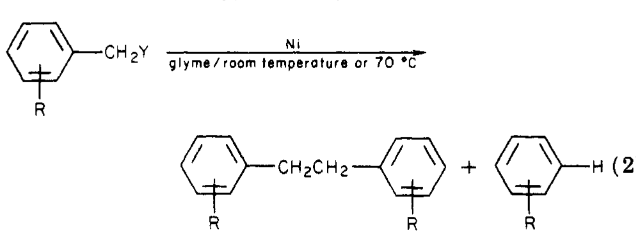
However, low-valent reagents originating from transition metal halides/lithium aluminum hydride have the limitation of not being compatible with functional groups such as cyano and nitro groups. Chlorotris(triphenylphosphine)cobalt(I), dicyclopentadienylvanadium(II), and metallic iron worked well for the coupling of benzyl halides; nevertheless, the examples reported were limited to benzyl halides which did not contain functional groups sensitive to reduction. Although potassium hexacyanodinickelate(I) was applied to 4-(bromomethyl)benzonitrile, the yield of the corresponding homocoupled product was low. Metal carbonyls were generally tried with benzylic polyhalides, and the applicability to benzylic monohalides and the compatibility with functional groups were not made clear.

In a previous communication, we reported preliminary results showing that metallic nickel powders could provide an alternative tool for the homocoupling of benzylic halides under mild conditions.[18] We wish to report here the detailed applications of metallic nickel as a mild and selective reagent for the reductive coupling reaction of a variety of benzylic halides as well as polyhalides. The mechanistic aspects will be discussed on the basis of the trapping of benzylnickel complexes with electron deficient olefins.

Results and Discussion

Metallic nickel was simply prepared by stirring a mixture of nickel halide and lithium metal (2.3 equiv) with naphthalene (0.1 equiv) as an electron carrier at room temperature for 12 h in 1,2-dimethoxyethane (glyme).

$$\mathrm{NiX_2} \xrightarrow[\text{glyme/room temperature, 12 h}]{\text{Li (2.3 equiv)/}\mathrm{C_{10}H_8}\text{ (0.1 equiv)}} \mathrm{Ni} \qquad (1)$$



(2)

X, Y = I, Br, Cl
R = H, 4-H_3C, 3-CH_3O, 3-F_3C, 4-Cl, 4-Br, 4-O_2N, 4-NC, 4-CH_3OCO

The resulting black powders which slowly settled in a colorless solution after stirring was stopped were used for the reductive homocoupling reaction of benzylic halides.

The results of the reaction of benzyl and substituted benzyl halides with metallic nickel powders are summarized in Table I. Benzyl chloride reacted at room temperature with metallic nickel prepared from nickel chloride to give a mixture of coupled product, bibenzyl (40%), and reduction product, toluene (60%). However, the coupled product was found to be formed mainly when the reaction was run at 70 °C and when the nickel powders used were prepared from nickel iodide. Under these conditions, a yield of 86% bibenzyl was attained. The fact that iodide ion present in the system facilitates the homocoupling reaction may be ascribed to the chlorine–iodine exchange during the reaction.[19] Higher reaction temperatures such as 70 °C may also accerate the exchange reaction.

Table I. Reaction of Benzyl Halides with Metallic Nickel Powders

			product,[b] %	
benzyl halide	NiX_2[a]	conditions[g]	coupling	reduction
$C_6H_5CH_2Cl$	$NiCl_2$	rt, 1 h	40	60
$C_6H_5CH_2Cl$	$NiCl_2$	70 °C, 0.5 h	65	33
$C_6H_5CH_2Cl$	NiI_2	70 °C, 0.5 h	86	10
$C_6H_5CH_2Br$	$NiBr_2$	rt, 1 h	77	23
4-$CH_3C_6H_4CH_2Cl$	$NiCl_2$	rt, 2 h	76	20
4-$CH_3C_6H_4CH_2Cl$	NiI_2	70 °C, 0.5 h	96	4
3-$CH_3OC_6H_4CH_2Cl$	NiI_2	rt, 6 h	69[c]	*d*
3-$F_3CC_6H_4CH_2Cl$	NiI_2	rt, 6 h	75[c]	*d*
4-$ClC_6H_4CH_2Cl$	$NiCl_2$	70 °C, 0.5 h	72	20
4-$ClC_6H_4CH_2Cl$	NiI_2	rt, 3 h	72[c]	*d*
4-$ClC_6H_4CH_2Cl$	NiI_2	70 °C, 0.5 h	85	13
4-$BrC_6H_4CH_2Br$	NiI_2	rt, 6 h	70[c]	*d*
4-$O_2NC_6H_4CH_2Cl$	NiI_2	rt, 1 h	78[c]	*d*
4-$NCC_6H_4CH_2Br$	$NiBr_2$	rt, 1 h	68[c]	*d*
4-$NCC_6H_4CH_2Br$	NiI_2	rt, 1 h	75[c]	*d*
4-$CH_3O_2CC_6H_4CH_2Cl$	NiI_2	rt, 1 h	73[c]	14[c]
4-$HO_2CC_6H_4CH_2Br$	NiI_2	85 °C, 0.5 h	*e*	54[c,f]
$C_6H_5CHBrCO_2H$	NiI_2	rt, 9 h	*e*	80[c]

[a] Nickel halide used for the preparation of nickel powders. [b] Yields were determined by GLPC based on benzyl halides used unless otherwise noted. [c] Isolated yield. [d] Not determined. [e] Not detected. [f] 4-(Iodomethyl)benzoic acid (20%) was also isolated. [g] rt = room temperature.

Similarly, substituted benzyl halides reacted with metallic nickel to afford the corresponding bibenzyls in good to high yields and the use of nickel iodide generally gave more satisfactory results.[19] The aromatic carbon–halogen bond was unreactive toward the nickel in the reaction of 4-chloro- and 4-bromobenzyl halides. When substituents such as methoxy, nitro, cyano, and alkoxycarbonyl groups were used and compatible reaction conditions were employed, the corresponding bibenzyls were obtained in good yields. Benzyl halides having the hydroxycarbonyl group failed to couple with metallic nickel and were reduced to give the corresponding carboxylic acids. For example, α-bromophenylacetic acid was converted to phenylacetic acid in 80% yield. 4-(Bromomethyl)benzoic acid afforded 4-methylbenzoic acid (54%) together with 4-(iodomethyl)benzoic acid (20%). The latter seems to be formed by the halogen–halogen exchange reaction catalyzed by nickel between the substrate and lithium iodide present in the system.

Benzylic monohalides such as 1-(chloromethyl)naphthalene, 2-(bromomethyl)naphthalene, chlorodiphenylmethane, and 9-bromofluorene also underwent a reductive homocoupling reaction at room temperature to afford the corresponding ethane derivatives in 55–76% yields (Table II). The corresponding reduction products were formed as side products in all cases.

On the other hand, benzylic di- and trihalides afforded substituted ethenes. For example, dichlorodiphenylmethane gave tetraphenylethene in quantitative yield at room temperature, and α,α-dibromotoluene gave predominantly the trans isomer of stilbene (cis/trans = 27/73).

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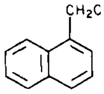
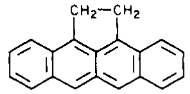
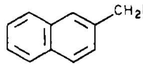
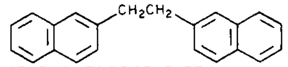
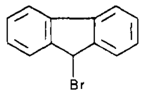
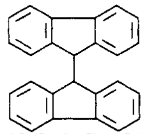
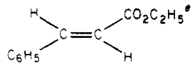
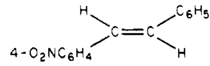
Table II. Reaction of Benzylic Mono- and Polyhalides with Metallic Nickel[a]

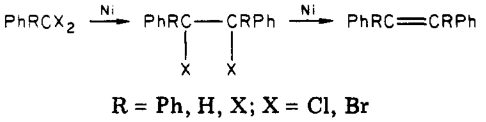
halide	conditions[g]	product	yield,[b] %
	rt, 5 h		55
	rt, 2 h		67
$(C_6H_5)_2CHCl$	rt, 9 h	$(C_6H_5)_2CHCH(C_6H_5)_2$	76
	rt, 1 h		75
$(C_6H_5)_2CCl_2$	rt, 2 h	$(C_6H_5)_2C{=}C(C_6H_5)_2$	99
$C_6H_5CHBr_2$	rt, 1 h	$(C_6H_5)CH{=}CH(C_6H_5)$[c]	65
$C_6H_5CCl_3$	85 °C, 1 h	$(C_6H_5)CCl{=}CCl(C_6H_5)$[d]	71
$C_6H_5CHBrCHBrC_6H_5$ (meso)	rt, 5 h		89
$4\text{-}O_2NC_6H_4CHBrCHBrCO_2C_2H_5$ (erythro)	rt, 1 h		76
$C_6H_5CCl_2CCl_2C_6H_5$	85 °C, 1 h	$(C_6H_5)CCl{=}CCl(C_6H_5)$[f]	97

[a] Metallic nickel prepared by reducing nickel iodide was used. [b] Isolated yield. [c] Ratio of cis/trans determined by GLPC was 27/73. [d] Ratio of cis/trans determined by ^1H NMR was 74/26. [e] Trace amount of *cis*-stilbene was detected by GLPC. [f] Ratio of cis/trans determined by ^1H NMR was 70/30. [g] rt = room temperature.

At 80 °C after 1 h, α,α,α-trichlorotoluene afforded a mixture of *cis*- and *trans*-1,2-dichloro-1,2-diphenylethene with predominantly the cis isomer (cis/trans = 74/26) and a trace amount of diphenylacetylene.

There are two likely mechanistic pathways for the reductive coupling of benzylic polyhalides, either via a carbene or carbene–nickel complex intermediate or via a step-by-step dehalogenation. Coffey[11] suggested a carbene mechanism for the iron pentacarbonyl promoted reaction. Later, carbenoid and carbene–transition metal complex intermediates were suggested on the basis of the trapping of cyclopropane derivatives in the reaction of $Ni(COD)_2$, $Fe(CO)_5$, $Co_2(CO)_8$,[20] or $W(CO)_6$[4] with gem-dihalides. On the other hand, it was suggested that the reaction with $Co(CO)_8$[10] or metallic iron[21] proceeds via a step-by-step mechanism.

The reaction of α,α-dibromotoluene or dichlorodiphenylmethane was carried out in the presence of an excess of cyclohexene or an electron-deficient olefin such as diethyl fumarate in order to try to trap the divalent intermediate. However, the formation of cycloadducts could not be detected. The coupling reaction of α,α,α-trichlorotoluene was then carried out under milder conditions (0 °C for 1 h followed by room temperature for 12 h) and was found to afford 1,2-diphenyl-1,1,2,2-tetrachloroethane in 50% yield. The results suggest that the reaction of benzylic polyhalides proceeds via a stepwise manner such as shown in eq 3.



$$PhRCX_2 \xrightarrow{Ni} \underset{X}{PhRC}{-}\underset{X}{CRPh} \xrightarrow{Ni} PhRC{=}CRPh \qquad (3)$$

$$R = Ph, H, X; X = Cl, Br$$

Dehalogenation of vicinal polyhalides with nickel was then investigated to establish that the second step in eq 3 proceeds as shown. 1,2-Dibromo-1,2-diphenylethane (meso) reacted with metallic nickel at room temperature to yield stilbene (trans) in 89% yield and a trace amount of *cis*-stilbene. Similarly, ethyl 2,3-dibromo-3-(4-nitrophenyl)propanoate (erythro) underwent debromination to give ethyl 4-nitrocinnamate (trans) in 76% yield. Dechlorination of 1,2-diphenyl-1,1,2,2-tetrachloroethane at 85 °C afforded 1,2-dichloro-1,2-diphenylethene (97%, cis/trans = 70/30).

These results show that the second step of eq 3 proceeds smoothly with a variety of vicinal dihalides. Thus, it may be concluded that the reaction of benzylic polyhalides with nickel proceeds via a step-by-step dehalogenation to give ethene derivatives.

Additional mechanistic aspects of the homocoupling of benzylic monohalides need to be addressed. Although the oxidative addition of organic halides to transition metal complexes has been well-known,[22] few examples are reported on the corresponding reaction of transition metals in the metallic state under mild conditions.[23-26] Previously we reported that the homocoupling reaction of aromatic halides mediated by metallic nickel proceeds via ArNiX followed by Ar_2Ni intermediates, which were isolated as the phosphine complexes ($Ar = C_6F_5$).[18,27] The benzyl halide reaction seems to occur in a similar way. However, the possibility of a radical mechanism cannot be excluded. Both radical[15] and organoiron[21] intermediates were proposed in the homocoupling reaction of benzylic halides using metallic iron in water.

Organonickel compounds which contain carbon–metal σ bonds are known to add to active unsaturated

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(20) Furukawa, J.; Matsumura, A.; Matsuoka, Y.; Kiji, J. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 829.

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(24) The oxidative addition of aryl halide to palladium black is postulated in the catalytic arylation of olefin with aryl halide. For example: Mizoroki, T.; Mori, K.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 581. Mori, K.; Mizoroki, T.; Ozaki, A. *Ibid.* **1973**, *46*, 1505. Hech, R. F.; Nolley, Jr., J. P. *J. Org. Chem.* **1972**, *37*, 2320.

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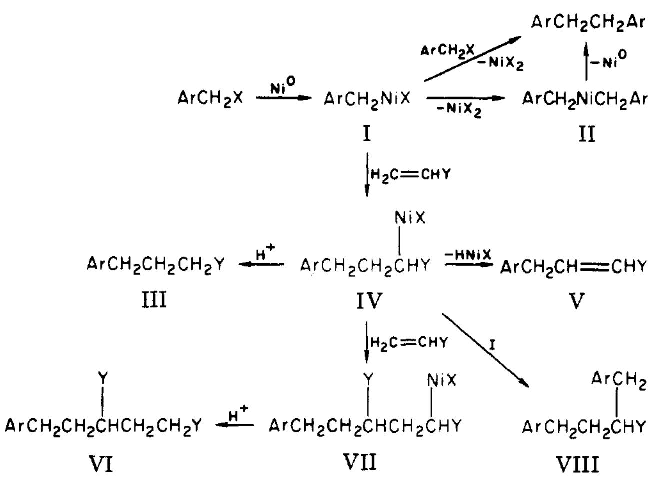
Scheme I[a]



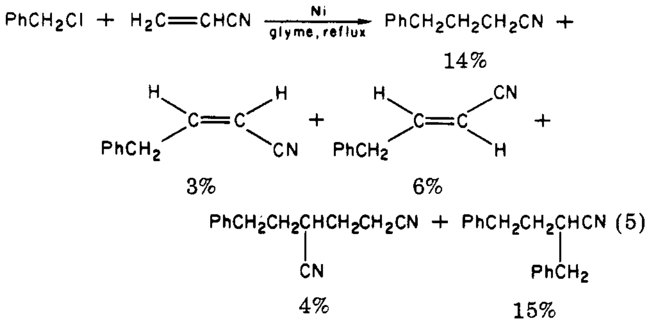
[a] X = halogen; Y = CO_2CH_3 or CN.

bonds.[5,28-33] For example, Hashimoto et al.[5] reported that benzylnickel(II) complex prepared from benzyl bromide and potassium hexacyanodinickelate added to acrylonitrile or ethyl acrylate. The addition reaction of benzyl chloride to electron-deficient olefins mediated by metallic nickel was carried out to help establish the presence of benzylnickel intermediates.

The reaction of benzyl chloride with metallic nickel in the presence of methyl acrylate was carried out at 85 °C and the expected addition product, methyl 4-phenylbutanoate, was formed in 17% yield (eq 4). The reaction

$$PhCH_2Cl + H_2C{=}CHCO_2CH_3 \xrightarrow[\text{glyme, reflux}]{\text{Ni}} \underset{17\%}{PhCH_2CH_2CH_2CO_2CH_3} \quad (4)$$

with acrylonitrile gave 4-phenylbutanenitrile in 14% yield together with *cis*- and *trans*-4-phenyl-2-butenenitriles, 4-cyano-6-phenylhexanenitrile, and 2-benzyl-4-phenylbutanenitrile (eq 5). The results suggest the presence of



a benzylnickel(II) chloride complex (I), which could have been formed by the oxidative addition of benzyl chloride to the metallic nickel (Scheme I). The complex (I) would then be expected to add to the electron-deficient olefins affording the addition product (III) via intermediate complex (IV). The formation of *cis*- and *trans*-4-phenyl-2-butenenitrile (V) is reasonably explained by the reductive elimination of nickel hydride from intermediate (IV), which is analogous to the substitution reaction of olefins with alkylpalladium compounds[34] and to the addition–elimination reaction of bis(triphenylphosphine)phenylnickel(II) bromide with methyl acrylate to yield methyl cinnamate.[28] Furthermore, intermediate (IV) seems to add another molecule of acrylonitrile to give the 1:2 adduct, 4-cyano-6-phenylhexanenitrile (VI). 2-Benzyl-4-phenylbutanenitrile (VIII) would be formed by the metathesis of complex IV and the benzylnickel chloride (I).

Thus, the homocoupling reaction might be reasonably explained by the smooth oxidative addition of benzyl halide to nickel in the metallic state, which gives benzylnickel(II) halide complex (I). The metathesis of the complex (I) would afford dibenzylnickel(II) complex (II) which could undergo reductive elimination to yield coupled product, 1,2-diarylethane. The formation of 1,2-diarylethane could also possibly result from the reaction of benzylnickel halide (I) with benzyl halide.

In conclusion, a very convenient method is presented for the reductive coupling of benzylic mono-, di-, and trihalides. The procedure involves the use of highly reactive nickel in the metallic state simply prepared by the lithium reduction of anhydrous nickel halides. The yields are good to high and the system is compatible with a wide variety of substituents on the aromatic ring including nitro, cyano, alkoxycarbonyl, methoxy, bromo, and chloro groups. Because of the ease of preparation of the highly reactive nickel powders and of the mild conditions, this procedure should prove to be a convenient and general method for carrying out reductive coupling of benzylic halides.

Experimental Section

Melting points and boiling points are uncorrected. The infrared spectra were taken on a Perkin-Elmer 283 spectrophotometer using samples as KBr disks or neat liquids. The nuclear magnetic resonance spectra were obtained on a Varian EM 390 spectrometer with Me_4Si as the internal standard. Mass spectra were recorded on a Kratos MS80 spectrometer. Analytical gas chromatography was carried out on a Hewlett-Packard 5702A using a column packed with Silicone SE-30 (10%) or OV-17 (3%) on Chromosorb P or W.

Benzylic halides were commercially available and were used as received. 1,2-Dimethoxyethane (glyme) was distilled prior to use from sodium potassium alloy under argon. Anhydrous nickel halides were purchased from Cerac, Inc. and were used as received.

Preparation of metallic nickel powders and their reaction with benzylic halides were carried out in an atmosphere of argon and a typical procedure is as follows. Coupling and reduction products were identified by the comparison of their physical and spectral properties with those of commercially available authentic samples or reported values. Yields of products were determined by GLPC using an appropriate internal standard calibrated against the pure samples or by isolation with recrystallization or silica gel chromatography.

Preparation of Metallic Nickel Powders and Their Reaction with 4-Nitrobenzyl Chloride. A 50-mL two-neck flask was equipped with a magnetic stirrer, rubber septum, and a condenser topped with argon inlet. The flask was charged with nickel iodide (4.53 g, 14.5 mmol), freshly cut lithium (0.232 g, 33.4 mmol), naphthalene (0.186 g, 1.45 mmol), and glyme (30 mL), and the mixture was stirred vigorously at room temperature for 12 h. The nickel powders were precipitated as bulky black slurries in colorless clear solution after the stirring was stopped. Lithium metal was completely consumed.[52]

To the nickel powders 4-nitrobenzyl chloride (1.97 g, 11.5 mmol) in glyme (10 mL) was added and stirred at room temperature for

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1 h. The reddish-brown colored reaction mixture formed was poured into 3% hydrochloric acid solution (100 mL) and was extracted with chloroform twice (150 mL). The extracts were washed with water (50 mL) and the aqueous phase was extracted with chloroform. The chloroform solution was dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was washed with pentane twice (15 mL) to give pale yellow needles (mp 176–179 °C). Recrystallization from ethanol gave 1,2-bis(4-nitrophenyl)ethane (1.22 g, 78%): mp 182–183 °C (lit.[35] mp 183–184 °C); NMR ($CDCl_3$) δ 3.10 (s, CH_2, 4 H), 7.30 (d, J = 9 Hz, Ar, 4 H), 8.10 (d, J = 9 Hz, Ar, 4 H); IR (KBr disk) 1505 and 1335 cm^{-1} (NO_2).

The reaction of 4-nitrobenzyl chloride (3.37 g, 19.6 mmol) with nickel prepared from nickel iodide (3.86 g, 12.4 mmol) proceeded smoothly at room temperature for 2 h and gave 1,2-bis(4-nitrophenyl)ethane in 76% yield.

All other coupling reactions were carried out using the reagents in the ratio of metallic nickel/one halogen for coupling = 1/0.8 to optimize the yield and to shorten the reaction time.

1,2-Bis(4-methylphenyl)ethane: mp 83–84 °C (ethanol) (lit.[5] mp 82 °C); NMR ($CDCl_3$) δ 2.27 (s, CH_3, 6 H), 2.83 (s, CH_2, 4 H), 7.03 (s, Ar, 8 H).

1,2-Bis(3-methoxyphenyl)ethane: bp 136–138 °C (0.35 mmHg) (product was an oil and failed to crystallize, lit.[36] mp 61–62 °C, lit.[37] mp 40 °C); NMR ($CDCl_3$) δ 2.87 (s, CH_2, 4 H), 3.73 (s, CH_3O, 6 H), 6.57–6.83 (m, Ar, 6 H), 7.00–7.27 (m, Ar, 2 H); mass spectrum, *m/e* 242.1306; calcd for $C_{16}H_{18}O_2$, 242.1306.

1,2-Bis(3-(trifluoromethyl)phenyl)ethane: mp 77–78 °C (hexane); NMR ($CDCl_3$) δ 2.95 (s, CH_2, 4 H), 7.13–7.62 (m, Ar, 8 H); mass spectrum, *m/e* 318.0837; calcd for $C_{16}H_{12}F_6$, 318.0843.

1,2-Bis(4-chlorophenyl)ethane: mp 98.5–99.5 °C (ethanol) (lit.[38] mp 98–99 °C); NMR ($CDCl_3$) δ 2.81 (s, CH_2, 4 H), 7.00 (d, J = 9 Hz, Ar, 4 H), 7.21 (d, J = 9 Hz, Ar, 4 H).

1,2-Bis(4-bromophenyl)ethane: mp 114–115 °C (hexane/carbon tetrachloride) (lit.[39] 114 °C); NMR ($CDCl_3$) δ 2.81 (s, CH_2, 4 H), 7.00 (d, J = 9 Hz, Ar, 4 H), 7.37 (d, J = 9 Hz, Ar, 4 H).

1,2-Bis(4-cyanophenyl)ethane: mp 199–200 °C (ethanol) (lit.[5] mp 200–201 °C); NMR ($CDCl_3$) δ 3.00 (s, CH_2, 4 H), 7.21 (d, J = 9 Hz, Ar, 4 H), 7.58 (d, J = 9 Hz, Ar, 4 H); IR (KBr disk) 2215 cm^{-1} (CN).

1,2-Bis(4-(methoxycarbonyl)phenyl)ethane: mp 118–119 °C (carbon tetrachloride) (lit.[40] 118.5–119 °C); NMR ($CDCl_3$) δ 2.97 (s, CH_2, 4 H), 3.87 (s, CH_3O, 6 H), 7.17 (d, J = 8 Hz, Ar, 4 H), 7.87 (d, J = 8 Hz, Ar, 4 H); IR (KBr disk) 1730 cm^{-1} (CO).

4-(Iodomethyl)benzoic acid: mp 234–235 °C (acetone) (lit.[41] 235 °C); NMR (acetone-d_6) δ 3.43 (broad s, OH, 1 H), 4.63 (s, CH_2, 2 H), 7.55 (d, J = 8.5 Hz, Ar, 2 H), 7.91 (d, J = 8.5 Hz, Ar, 2 H); IR (KBr disk) 1670 cm^{-1} (CO).

1,2-Bis(1-naphthyl)ethane: mp 160–161 °C (ethanol/ethyl acetate) (lit.[17] mp 161–162 °C); NMR ($CDCl_3$) δ 3.48 (s, CH_2, 4 H), 7.16–8.30 (m, Ar, 14 H).

1,2-Bis(2-naphthyl)ethane: mp 183–184 °C (ethanol/ethyl acetate) (lit.[42] mp 185–186 °C); NMR ($CDCl_3$) δ 3.17 (s, CH_2, 4 H), 7.27–7.93 (m, Ar, 14 H).

1,1,2,2-Tetraphenylethane: mp 208–209 °C (ethanol) (lit.[43] mp 208–209 °C); NMR ($CDCl_3$) δ 4.75 (s, CH, 2 H), 6.87–7.31 (m, Ar, 20 H).

9,9′-Bifluorene: mp 243–243.5 °C (chloroform) (lit.[44] mp 245–246 °C); NMR ($CDCl_3$) δ 4.83 (s, CH, 2 H), 6.85–7.40 (m, Ar, 12 H), 7.55–7.75 (m, Ar, 4 H).

1,2-Dichloro-1,2-diphenylethene (cis isomer): mp 64–66 °C (pentane) (lit.[45] mp 67–68 °C); NMR ($CDCl_3$) δ 7.18 (s, Ar, 10 H). Trans isomer: mp 140–141 °C (ethanol) (lit.[45] mp 142–143 °C); NMR ($CDCl_3$) δ 7.30–7.75 (m, Ar, 10 H).

1,2-Diphenyl-1,1,2,2-tetrachloroethane: To the nickel powders prepared from nickel iodide (3.52 g, 11.3 mmol), lithium (0.180 g, 25.9 mmol), and naphthalene (0.144 g, 1.13 mmol) was added α,α,α-trichlorotoluene (3.98 g, 20.4 mmol) at 0 °C. After 1 h, the reaction mixture was warmed to room temperature and was stirred for 12 h. The reaction mixture was treated in the same manner as described above and the crude solid was chromatographed on silica gel upon elution with carbon tetrachloride to give 1,2-diphenyl-1,1,2,2-tetrachloroethane (1.62 g, 50%): mp 160–161 °C (lit.[46] mp 160–161 °C); NMR ($CDCl_3$) δ 6.90–7.67 (m, Ar, 10 H).

***trans*-Ethyl 4-nitrocinnamate**: mp 135.5–136.5 °C (ether) (lit.[47] mp 136 °C). *erythro*-Ethyl 2,3-dibromo-3-(4-nitrophenyl)propanoate (mp 115–116 °C (lit.[48] mp 116–117 °C)) as a reactant was prepared by the bromination of *trans*-ethyl 4-nitrocinnamate.[48]

Reaction of Benzyl Chloride with Methyl Acrylate in the Presence of Metallic Nickel. Metallic nickel powders were prepared from nickel iodide (4.71 g, 15.1 mmol), lithium (0.240 g, 34.7 mmol), and naphthalene (0.193 g, 1.51 mmol) in glyme (30 mL) as described above. The metallic nickel in glyme was heated to reflux and a mixture of benzyl chloride (1.40 g, 11.1 mmol) and methyl acrylate (1.30 g, 15.1 mmol) in glyme (10 mL) was added dropwise for 30 min and additional heating was continued for 30 min. After cooling, the reaction mixture was poured into 3% hydrochloric acid solution (100 mL) and was extracted with chloroform. The chloroform solution was washed with water and the aqueous phase was extracted with chloroform. The combined extracts were dried over anhydrous sodium sulfate and concentrated. The crude oil was chromatographed on silica gel eluted with chloroform. Methyl 4-phenylbutanoate (0.326 g, 17%): bp 123–124 °C (13 mmHg); NMR ($CDCl_3$) δ 1.73–2.13 (m, CH_2, 2 H), 2.00–2.45 (m, CH_2CO, 2 H), 2.63 (t, J = 7.5 Hz, CH_2, 2 H), 3.63 (s, CH_3O, 3 H), 7.00–7.43 (m, Ar, 5 H); NMR spectral data were consistent with those reported;[49] IR (neat) 1730 cm^{-1} (C=O); mass spectrum, *m/e* 178.0993; calcd for $C_{11}H_{14}O_2$, 178.0993.

Reaction of Benzyl Chloride with Acrylonitrile in the Presence of Metallic Nickel. A mixture of benzyl chloride (2.24 g, 17.7 mmol) and acrylonitrile (1.19 g, 22.5 mmol) in glyme (10 mL) was added dropwise to nickel powders, prepared from nickel iodide (3.52 g, 11.3 mmol), lithium (0.180 g, 25.9 mmol), and naphthalene (0.144 g, 1.13 mmol), in refluxing glyme (30 mL) for 30 min and heating was continued for an additional 30 min. The reaction mixture was cooled, poured into 3% hydrochloric acid solution (100 mL), and extracted with chloroform twice. The extracts were washed with water and the aqueous phase was extracted with chloroform. The combined chloroform solution was dried over anhydrous sodium sulfate and concentrated. The crude oil was submitted on silica gel chromatography upon elution with carbon tetrachloride. 4-Phenylbutanenitrile (0.336 g, 14%): bp 139–140 °C (14 mmHg) (lit.[50] bp 130–131 °C (10 mmHg)); NMR ($CDCl_3$) δ 1.73–2.13 (m, CH_2, 2 H), 2.26 (t, J = 7 Hz, CH_2, 2 H), 2.75 (t, J = 7 Hz, CH_2, 2 H), 7.00–7.47 (m, Ar, 5 H); IR (neat) 2250 cm^{-1} (CN); mass spectrum, *m/e* 145.0889; calcd for $C_{10}H_{11}N$, 145.0891. *cis*-4-Phenyl-2-butenenitrile (0.081 g, 3%): oil; NMR ($CDCl_3$) δ 3.74 (d of d, J = 8 and 1 Hz, CH_2, 2 H), 5.38 (d of t, J = 11 and 1 Hz, CHCN, 1 H), 6.60 (d of t, J = 11 and 8 Hz, CH, 1 H) 7.07–7.50 (m, Ar, 5 H); NMR spectral data were consistent with those reported;[51] IR (neat) 2210 (CN) and 1615 cm^{-1} (C=C); mass spectrum, *m/e* 143.0744; calcd for $C_{10}H_9N$, 143.0735. *trans*-4-Phenyl-2-butenenitrile (0.148 g, 6%): bp 135 °C (13 mmHg); NMR ($CDCl_3$) δ 3.50 (d of d, J = 6.5 and 1.8 Hz, CH_2, 2 H), 5.24 (d of t, J = 16.5 and 1.8 Hz, CHCN, 1 H), 6.84 (d of t, J = 16.5 and 6.5 Hz, CH, 1 H), 7.03–7.50 (m, Ar, 5 H); NMR

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spectral data were consistent with those reported;[51] IR (neat) 2210 (CN) and 1625 cm^{-1} (C=C); mass spectrum, *m/e* 143.0736; calcd for $C_{10}H_9N$, 143.0735. 4-Cyano-6-phenylhexanenitrile (0.137 g, 4%): bp 154 °C (0.38 mmHg); NMR ($CDCl_3$) δ 1.73–2.15 (m, CH_2, 4 H), 2.33–3.07 (m, $ArCH_2$, CHCN, and CH_2CN, 5 H), 7.03–7.47 (m, Ar, 5 H); IR (neat) 2230 cm^{-1} (CN); mass spectrum, *m/e* 198.1168; calcd for $C_{13}H_{14}N_2$, 198.1158. 2-Benzyl-4-phenylbutanenitrile (0.315 g, 15%): bp 150 °C (0.6 mmHg); NMR ($CDCl_3$) δ 1.70–2.03 (m, CH_2, 2 H), 2.50–3.10 (m, $ArCH_2$ and CHCN, 5 H), 7.03–7.46 (m, Ar, 10 H); IR (neat) 2230 cm^{-1} (CN); mass spectrum, *m/e* 235.1370; calcd for $C_{17}H_{17}N$, 235.1362.

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Registry No. Ni, 7440-02-0; $C_6H_5CH_2Cl$, 100-44-7; $C_6H_5CH_2Br$, 100-39-0; 4-$CH_3C_6H_4CH_2Br$, 104-82-5; 3-$CH_3OC_6H_4CH_2Cl$, 824-98-6; 3-$F_3CC_6H_4CH_2Cl$, 705-29-3; 4-$ClC_6H_4CH_2Cl$, 104-83-6; 4-$BrC_6H_4CH_2Br$, 589-15-1; 4-$O_2NC_6H_4CH_2Cl$, 100-14-1; 4-$NCC_6H_4CH_2Br$, 17201-43-3; 4-$CH_3O_2CC_6H_4CH_2Cl$, 34040-64-7; 4-$HO_2CC_6H_4CH_2Br$, 6232-88-8; $C_6H_5CHBrCO_2H$, 4870-65-9; $C_6H_5CH_2CH_2C_6H_5$, 103-29-7; $(4\text{-}CH_3C_6H_4CH_2)_2$, 538-39-6; $(3\text{-}CH_3OC_6H_4CH_2)_2$, 1657-55-2; $(3\text{-}F_3CC_6H_4CH_2)_2$, 72390-22-8; $(4\text{-}ClC_6H_4CH_2)_2$, 5216-35-3; $(4\text{-}BrC_6H_4CH_2)_2$, 19829-56-2; $(4\text{-}O_2NC_6H_4CH_2)_2$, 736-30-1; $(4\text{-}NCC_6H_4CH_2)_2$, 4381-02-6; $(4\text{-}CH_3O_2CC_6H_4CH_2)_2$, 797-21-7; $C_6H_5CH_3$, 108-88-3; 4-$CH_3C_6H_4CH_3$, 106-42-3; 4-$ClC_6H_4CH_3$, 106-43-4; 4-$CH_3O_2CC_6H_4CH_3$, 99-75-2; 4-$HO_2CC_6H_4CH_3$, 99-94-5; $C_6H_5CH_2CO_2H$, 103-82-2; $(C_6H_5)_2CHCl$, 90-99-3; $(C_6H_5)_2CCl_2$, 2051-90-3; $C_6H_5CHBr_2$, 618-31-5; $C_6H_5CCl_3$, 98-07-7; *meso*-$C_6H_5CHBrCHBrC_6H_5$, 13440-24-9; *erythro*-4-$O_2NC_6H_4CHBrCHBrCO_2C_2H_5$, 41441-00-3; $C_6H_5CCl_2CCl_2C_6H_5$, 13700-81-7; $(C_6H_5)_2CHCH(C_6H_5)_2$, 632-50-8; $(C_6H_5)_2C{=}C(C_6H_5)_2$, 632-51-9; *cis*-$(C_6H_5)CH{=}CH(C_6H_5)$, 645-49-8; *trans*-$(C_6H_5)CH{=}CH(C_6H_5)$, 103-30-0; *cis*-$(C_6H_5)CCl{=}CCl(C_6H_5)$, 5216-32-0; *trans*-$(C_6H_5)CCl{=}CCl(C_6H_5)$, 951-86-0; *trans*-4-$O_2NC_6H_4CH{=}CHCO_2C_2H_5$, 24393-61-1; NiI_2, 13462-90-3; Li, 7439-93-2; methyl acrylate, 96-33-3; methyl 4-phenylbutanoate, 2046-17-5; acrylonitrile, 107-13-1; 4-phenylbutanenitrile, 2046-18-6; *cis*-4-phenyl-2-butenenitrile, 20067-97-4; *trans*-4-phenyl-2-butenenitrile, 20067-98-5; 4-cyano-6-phenylhexanenitrile, 89873-49-4; 2-benzyl-4-phenylbutanenitrile, 89873-50-7; (iodomethyl)benzoic acid, 31719-79-6; 1-(chloromethyl)naphthalene, 86-52-2; 2-(bromomethyl)naphthalene, 939-26-4; 9-bromofluorene, 1940-57-4; 1,2-bis(1-naphthyl)ethane, 15374-45-5; 1,2-bis(2-naphthyl)ethane, 21969-45-9; 9,9′-bi-9*H*-fluorene, 1530-12-7.

Reactions of *tert*-Butyllithium with α,ω-Dihaloalkanes. Evidence for Single-Electron-Transfer-Mediated Metal–Halogen Interchange Involving Alkyl Radical–Halide Ion Adducts

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The reactions of *tert*-butyllithium (*t*-BuLi) with primary α-iodo-ω-haloalkanes and α,ω-dibromoalkanes have been investigated in experiments conducted at −23 °C in *n*-pentane–diethyl ether (3:2 by volume) solution. It has been found that production of an α-lithio-ω-haloalkane (1) by metal–halogen interchange at one end of a 1,3-, 1,4-, or 1,5-dihalide results in intramolecular coupling to give cycloalkanes in high yield. As the chain length of the dihalide is increased beyond five carbon atoms the production of an α,ω-dilithio species by interchange at both ends of the dihalide ceases to be excluded by cyclization of 1 and a precipitous drop in the yield of cycloalkane was found to occur in reactions of 1,6-diiodoalkanes with *t*-BuLi. Metal–halogen interchange was the exclusive process observed in reactions of α,ω-dihalides with *t*-BuLi provided at least one halogen of the substrate was an iodine. By contrast, similar treatment of α,ω-dibromoalkane provided only minor amounts of product attributable to metal–halogen interchange. Under conditions that provide an essentially quantitative yield of carbocyclic product from reductive cyclization of 1 generated from 1,5-diiodo-3,3-dimethylpentane, the corresponding 1,5-dibromide was converted to a mixture composed of cycloalkane, products from Wurtz-type coupling with *t*-BuLi, and quantities of parent alkane from formal reduction of the dihalide. The mechanism of the metal–halogen interchange was further probed by using 6-halo-1-hexene substrates. Observation of cyclized product from the reaction of *t*-BuLi with 6-bromo- and 6-iodo-1-hexene demonstrated that the interchange between *t*-BuLi and primary alkyl bromides and iodides occurs predominantly via a single-electron-transfer (SET) process. Incorporation of alkyl radical–halide ion adducts with halogen dependent lifetimes as intermediates following SET from alkyllithium to alkyl halide serves to explain the disparate behavior of alkyl bromides and iodides when treated with *t*-BuLi. A unified SET-mediated mechanism for metal–halogen interchange and Wurtz coupling is presented.

The exchange of halogen and lithium atoms in the reaction of an organic halide with an organolithium is known as the metal–halogen interchange. The reaction, discovered independently and virtually simultaneously by the groups of Gilman[2] and Wittig,[3] has attracted considerable attention over the past forty years[4] and the vast literature on this topic has been extensively reviewed.[5-10] Despite continued interest in the metal–halogen interchange as a

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