Ph, R′ = H (2.18 mmol) in *N*,*N*-dimethylacetamide (50 mL) instead of benzene. Workup gave **6**, R = Ph, R′ = H, in 16% yield.

Reaction of 2-Phenylazirine with 1:1 CO/H_2 Catalyzed by $Pd(PPh_3)_4$. A 1:1 carbon monoxide–hydrogen gas mixture was bubbled through a benzene (50 mL) solution containing **5**, R = Ph, R′ = H (0.531 g, 4.54 mmol), and $Pd(PPh_3)_4$ (0.58 mmol). Workup in the usual manner (silica gel chromatography) gave 0.15 g (25%) of **6**, R = Ph, R′ = H, and 0.024 g (4.5%) of 4,5-diphenylpyrimidine.

Reaction of *N*-*n*-Butyl-2-phenylaziridine with CO and $Pd(PPh_3)_4$. The heterocycle (0.602 g, 3.44 mmol) and $Pd(PPh_3)_4$ (0.403 g, 0.349 mmol) in benzene (50 mL) were stirred under an atmosphere of carbon monoxide at 40 °C for 2 days. Workup gave recovered starting material.

Reaction of 4,5-Diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (13) with CO and $Pd(PPh_3)_4$. Starting material was recovered when a mixture of 4,5-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (0.207 g, 0.884 mmol) and $Pd(PPh_3)_4$ (0.117 g, 0.102 mmol) in benzene (50 mL) was exposed to carbon monoxide for 2 days at 40 °C.

(Dimethyl acetylenedicarboxylate)bis(triphenylphosphine)palladium-Catalyzed Carbonylation of 2-Phenylazirine (5, R = Ph, R′ = H). A benzene (50 mL) solution of **5**, R = Ph, R′ = H (0.510 g, 4.36 mmol), and the palladium catalyst (0.337 g, 0.436 mmol) was stirred overnight at 40 °C under a CO atmosphere. Workup gave 0.20 g (35%) of **6**, R = Ph, R′ = H.

General Procedure for the $Pd(dba)_2$-Catalyzed Carbonylation of Azirines. This reaction was effected in a manner identical with that described for the $Pd(PPh_3)_4$ reaction, except for the change in catalyst. The vinyl isocyanate (**14**) can be isolated by distillation[19] of the oil obtained after rotary evaporation. The following procedure was used to obtain pure carbamate ester (**15**): hexane (20–80 mL) was added to the oil, and the solution was filtered. Excess (10–20 mL) methanol was added to the filtrate, and the solution was stirred at room temperature for approximately 2 h. After removal of hexane–methanol (rotary evaporation), the residue was chromatographed on silica gel. The product yields are listed in Table III.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council for support of this research. We thank Dr. John Krause and Raj Capoor for recording mass and carbon-13 magnetic resonance spectra, respectively.

Registry No. 5 (R = *p*-$CH_3C_6H_4$, R′ = H), 32687-33-5; **5** (R = Ph, R′ = H), 7654-06-0; **5** (R = *p*-ClC_6H_4, R′ = H), 32687-35-7; **5** (R = *p*-BrC_6H_4, R′ = H), 17631-26-4; **5** (R = Ph, R′ = CH_3), 16205-14-4; **6** (R = *p*-$CH_3C_6H_4$, R′ = H), 77329-86-3; **6** (R = Ph, R′ = H), 77329-87-4; **6** (R = *p*-ClC_6H_4, R′ = H), 77329-88-5; **6** (R = *p*-BrC_6H_4, R′ = H), 77329-89-6; **6** (R = Ph, R′ = CH_3), 77329-90-9; **13**, 36879-67-1; **14** (R = *p*-$CH_3C_6H_4$, R′ = H), 79152-64-0; **14** (R = Ph, R′ = H), 4737-17-1; **14** (R = *p*-ClC_6H_4, R′ = H), 79152-65-1; **14** (R = *p*-BrC_6H_4, R′ = H), 72328-09-7; **14** (R = Ph, R′ = CH_3), 60995-85-9; **15** (R = *p*-$CH_3C_6H_4$, R′ = H), 79152-66-2; **15** (R = Ph, R′ = H), 72328-04-2; **15** (R = *p*-ClC_6H_4, R′ = H), 79152-67-3; **15** (R = *p*-BrC_6H_4, R′ = H), 72328-10-0; **15** (R = Ph, R′ = CH_3), 79152-68-4; $Pd(PPh_3)_4$, 14221-01-3; $Ni(PPh_3)_4$, 15133-82-1; $Pt(PPh_3)_4$, 14221-02-4; $Pd(PPh_3)_2(COOCH_3C{\equiv}CCOOCH_3)$, 15629-88-6; $Pd(dba)_2$, 32005-36-0; $Pd(diphos)_2$, 31277-98-2.

Mercury in Organic Chemistry. 22. Carbon–Carbon Bond Formation via Organocopper–Organomercury Cross-Coupling Reactions

Richard C. Larock* and Douglas R. Leach

Department of Chemistry, Iowa State University, Ames, Iowa 50011

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Aryl-, alkenyl-, and alkylmercurials undergo carbon–carbon bond formation with primary and secondary alkyl- and alkenylcuprate reagents to give fair to excellent yields of cross-coupled products. The reaction tolerates certain functional groups and proceeds stereospecifically with retention. Mixed diorganocuprates appear to be intermediates in these reactions as evidenced by their ability to add 1,4 to α,β-unsaturated ketones.

Cross-coupling reactions of organometallic reagents have become an increasingly important tool in the formation of carbon–carbon bonds. Attention has recently focused on the development of mild, new chemo-, regio-, and stereoselective organometallic reagents for application in organic synthesis. The ability of organomercurials to accommodate essentially all important organic functional groups and the ease with which they undergo a variety of mild carbon–carbon bond forming reactions make organomercurials increasingly attractive as synthetic intermediates in organic synthesis. Of late, a variety of synthetically interesting reactions of these compounds have been reported.[1]

Unfortunately, the direct alkylation of organomercurials is not easily effected. In general, organomercurials are inert toward alkyl halides. Only under forcing conditions[2–5] or in the presence of aluminum bromide[6] can low to modest yields of cross-coupled products be obtained. We have recently observed that organorhodium(III) compounds can be employed to effect cross-coupling of alkenyl-, alkynyl-, and arylmercurials and that the reaction can even be carried out by using only catalytic amounts of rhodium (eq 1).[7] However, the catalyst turnover is generally quite low.

$$CH_3I \xrightarrow{ClRh(PPh_3)_3} CH_3RhI_2(PPh_3)_2 \xrightarrow{RHgCl} R\text{–}CH_3 \qquad (1)$$

Bergbreiter and Whitesides have reported that the reaction of primary and secondary alkylmercurials, iodo(tri-*n*-bu-

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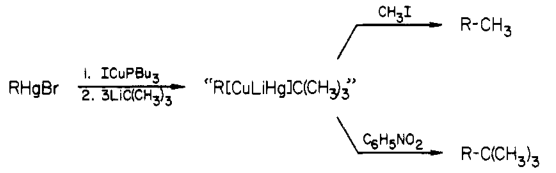
Table I. Methylation of Phenylmercuric Chloride[a]

entry	methylcopper reagent	added reagents	reaction procedure[b]	quenching agent	% yield of toluene[c]
1	$LiCuMe_2$	...	A	O_2	45
2		...	B		48
3		$PdCl_2$[d]			57
4		$NiCl_2$[d]			60
5		$FeCl_2$[d]			59
6	CuMe	...			6
7	Li_2CuMe_3	...	A		60
8		...	B		66
9	$LiCuMe_2$	...		MeI	34
10		...	A		55
11		...		MeI, O_2	76
12	Li_2CuMe_3	...		MeI, O_2	92
13		...			65[e]
14	$LiCuMe_2 \cdot SMe_2$	SMe_2	A	O_2	52
15		SMe_2	B		51
16		SMe_2	A	MeI, O_2	81
17	$Li_2CuMe_3 \cdot SMe_2$	SMe_2			92
18	$LiCuMe_2 \cdot PBu_3$	...	B	O_2	68
19	$LiCuMe_2 \cdot$HMPA	...			53
20	LiCu(CN)Me	...			31
21	LiCu(SPh)Me[f]	...			11
22	$LiCu(C{\equiv}CCMe_2OMe)Me$[f]	...			18
23	LiCu(O-*t*-Bu)Me[f]	...	A	MeI, O_2	28

[a] Reactions were carried out by adding 0.5 mmol of 1 to 2.5 mmol of methylcopper reagent dissolved in 10 mL of diethyl ether unless otherwise noted, followed by quenching with methyl iodide and/or oxygen and finally aqueous ammonium chloride. [b] Procedure A: reaction maintained at −78 °C for 1 h, warmed to 0 °C for 1 h, and then quenched. B: −78 °C for 1 h before quenching. [c] Yields were determined by gas chromatography using an internal standard. [d] 0.025–0.05 mmol. [e] 1.0 mmol of Li_2CuMe_3. [f] Reaction run in THF solvent.

tylphosphine)copper(I), and *tert*-butyllithium gives an intermediate of unknown composition that may either be alkylated with methyl iodide or oxidatively coupled with nitrobenzene (eq 2).[8] It was concluded that the inter-



(2)

mediate is a ternary ate complex containing all three metals and not a simple organocuprate reagent, since conjugate addition to mesityl oxide could not be effected. Unfortunately, arylmercurials could not be cross-coupled with alkyl halides. Alkenylmercurials were not examined. With the recent report that organomercurials undergo a number of radical anion chain reactions[9] and the propensity of organocopper reagents to undergo similar reactions,[10] we decided to reinvestigate the reactions of organomercurials and organocopper reagents as a potentially valuable new way to alkylate organomercurials. At this time we wish to report that this reaction is quite general in scope, gives fair to excellent yields of cross-coupled products, and takes advantage of the ability of both copper and mercury organometallics to accommodate a variety of organic functionality.

Results and Discussion

Alkylation of Arylmercurials. While arylmercurials could not be alkylated by alkyl halides with use of Whitesides' procedure,[8] we have obtained our best yields of cross-coupled products by using these organomercurials. Initially, we chose the reaction of phenylmercuric chloride (1) and methylcopper reagents as a model system on which to study the effect on the yield of toluene of each of the following reaction variables: oxidizing agents, solvent, temperature, transition-metal salts, methylcopper stoichiometry, methyl iodide addition, ligands, and the use of heterocuprate reagents. The results are summarized in Table I.

The oxidation of organocopper–organic halide cross-coupling reactions prior to hydrolysis has been shown to significantly increase the yield of cross-coupled product.[11,12] The effect of different oxidizing agents was therefore examined on the reaction of 1 and lithium dimethylcuprate (2) (5 equiv). Compound 1 was added to 2 at −78 °C and maintained at that temperature for 1 h, before warming to 0 °C (1 h) and either flushing with pure oxygen or adding excess nitrobenzene. Both oxidation procedures gave essentially the same result, a 45% yield of toluene and small amounts of biphenyl (<5%). All subsequent work was carried out by using oxygen due to its convenience.

Both diethyl ether and tetrahydrofuran (THF) have been examined as possible solvents for these cross-coupling reactions. The reaction of 1 and 2 (5 equiv) was carried out at −78 °C for 1 h in ether and THF and quenched with oxygen and aqueous ammonium chloride. Yields of 48% and 43%, respectively, were obtained. Since little difference was observed, all subsequent methylcopper reactions with 1 were run in ether, except the heterocuprate reactions where literature procedures employing THF were utilized. However, it was observed in later work that *n*-butyl- and vinylcopper reactions generally give higher yields in THF.

The temperature range in which these reactions can be run is limited by the stability of the organocopper reagent

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employed. Methylcopper reagents appear stable even at room temperature, while vinylcopper species are unstable above 0 °C. *n*-Butylcopper reactions were best run at −78 °C. With **2**, essentially identical results were obtained from reactions run either at −78 °C for 1 h and then quenched (48% yield) or at −78 °C for 1 h followed by warming to 0 °C for 1 h and then quenching (45%) (entries 1 and 2, Table I).

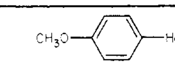
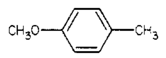
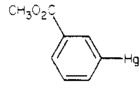
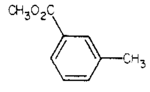
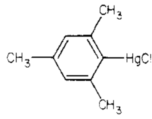
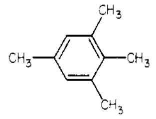
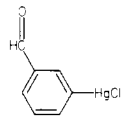
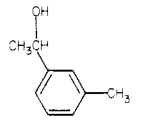
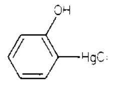
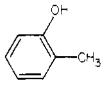
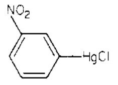
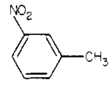
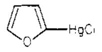
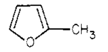
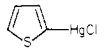
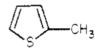
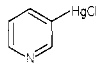
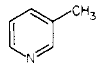
In a further effort to increase the yield of cross-coupled product, the effect of several transition-metal salts was investigated. It has been shown that iron(II) chloride and nickel(II) bromide catalyze the coupling of **2** with iodobenzene.[12] We, therefore, added 5–10% of iron(II) chloride, nickel(II) chloride, and palladium(II) chloride to the reaction of **1** and **2**. While the yield of toluene increased after oxidation from 48% in the absence of salts to 57–60% in their presence (entries 3–5), the salts produced no substantial increase in yield without oxidation.

Ashby has reported that by using appropriate ratios of methyl lithium and copper(I) iodide, organocuprates of the composition $LiCu_2(CH_3)_3$ and $Li_2Cu(CH_3)_3$ may be prepared.[13] The reactivity of these reagents has been studied, and $Li_2Cu(CH_3)_3$ has been found to be superior to **2** in coupling reactions with organic halides.[14,15] We have also examined the effect of a variety of different methylcopper reagents on the yield of cross-coupling product from **1** (entries 6–8). Methylcopper proved totally ineffective (6%), but $Li_2Cu(CH_3)_3$ (**3**) gave increased yields (60–68%) and appears to be the reagent of choice.

Corey and Posner[16] and Whitesides et al.[12] have reported that in the coupling reactions between an alkyl halide RX and an organocuprate reagent R'_2CuLi, addition of R′X often substantially increases the yield of cross-coupled product. It has been postulated that this is due to metal–halogen exchange. We have observed the same effect in the methylation of **1** (entries 9–12). Reacting **1** and **3** (5 equiv) for 1 h at −78 °C, warming to 0 °C for 1 h, adding excess methyl iodide and stirring for 30 min, flushing with oxygen, and finally quenching with aqueous ammonium chloride solution, we were able to obtain a 92% yield of toluene. Decreasing the amount of **3** from 5 to 2 equiv resulted in only a 65% yield. The addition of the corresponding alkyl iodide has not always improved the yield, however. In some instances to be discussed later, addition of alkyl halides lowered the yield of cross-coupling product.

While an excellent yield of cross-coupled product can be obtained by using a large excess of the methylcopper reagent, we have examined several methods by which we hoped to be able to employ smaller amounts of methyl lithium. Ligands often have a profound effect on organocopper reactions. House has recommended the use of organocopper reagents generated in the presence of excess dimethyl sulfide.[17] We have examined the effect of this ligand on the methylation of **1** (entries 14–17, Table I). Dimethyl sulfide does appear to slightly increase the yield of toluene in some cases. However, in later studies to be described, it has also proved detrimental. No clear conclusions can be drawn at this time as to the advantages or disadvantages of this ligand. Trialkylphosphines have also been employed as ligands in organocopper reactions.[12] While the dimethylcuprate reagent derived from iodo(tri-*n*-butylphosphine)copper(I) and 2 equiv of methyl lithium gave an improved yield of toluene (68%) (entry 18), this procedure is not very attractive due to the difficulties presented by the phosphine upon workup. Hexamethylphosphoramide (HMPA) proved less effective (53%) (entry 19).

Table II. Methylation of Arylmercurials[a]

entry	arylmercurial	product	% yield[b]
1			65
2			82
3			75
4			86
5			7
6			0
7			30
8			19
9			0

[a] For reaction conditions see entry 12, Table I. [b] Yields were determined by gas chromatography using an internal standard.

On occasions heterocuprate reagents have been employed to make more effective use of the organic groups attached to copper. Unfortunately, none of the mixed organocuprate reagents investigated by us, lithium methylcyanocuprate (31%), lithium methyl(thiophenoxy)cuprate (11%), lithium methyl(3-methyl-3-methoxy-1-butynyl)cuprate (18%), or lithium methyl-*tert*-butoxycuprate (28%) gave yields as high as **2** (entries 20–23, Table I).

With use of the optimum conditions for **1** as determined above, the scope of the methylation of arylmercurials was examined on a variety of other arylmercuric chlorides (eq 3). The results are summarized in Table II. Arylmercurials bearing electron-donating and -withdrawing groups gave good yields (entries 1 and 2), as did sterically demanding mesitylmercuric chloride (entry 3). The aldehyde group present in *m*-chloromercuribenzaldehyde proved too reactive, however, and only the product of methyl addition to the aldehyde could be obtained, even when the temperature was maintained at −78 °C throughout. *o*-Chloromercuriphenol gave only a very low yield of *o*-cresol, and (*m*-nitrophenyl)mercuric chloride, not surprisingly, failed to give any cross-coupling product. As noted earlier, nitroaromatics readily oxidize organocopper reagents. To our disappointment, 2-chloromercurifuran and 2-chloromercurithiophene gave only low yields. It is not obvious why this should be so. Finally, no 3-

$$ArHgCl + 5Li_2CuMe_3 \xrightarrow{Xs\ MeI} \xrightarrow{O_2} \xrightarrow{NH_4Cl} Ar{-}CH_3 \quad (3)$$

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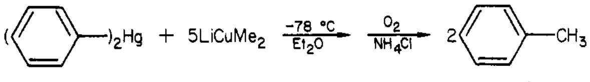
Table III. Alkylation of Phenylmercuric Chloride[a]

entry	organocuprate reagent	solvent	reaction procedure[b]	product	% yield[c]
1	$LiCu(n\text{-}C_4H_9)_2$	Et_2O	B	$n\text{-}C_4H_9C_6H_5$	18
2		THF			42
3					21[d]
4	$LiCu(n\text{-}C_4H_9)_2\cdot SMe_2$	Et_2O			30
5			A		19
6		THF	B		37
7					11[d]
8	$Li_2Cu(n\text{-}C_4H_9)_3$				40
9					15[d]
10	$Li_2Cu(n\text{-}C_4H_9)_3\cdot SMe_2$				13[d]
11			A		18
12	$LiCu(s\text{-}C_4H_9)_2$		B	$s\text{-}C_4H_9C_6H_5$	35
13	$LiCu(s\text{-}C_4H_9)_2\cdot SMe_2$				25
14	$Li_2Cu(s\text{-}C_4H_9)_3$				30
15	$Li_2Cu(s\text{-}C_4H_9)_3\cdot SMe_2$		A		24
16		Et_2O			12
17	$Li_2Cu(s\text{-}C_4H_9)_3\cdot PBu_3$	THF			25
18	$LiCu(CH{=}CH_2)_2$		B	$H_2C{=}CHC_6H_5$	5
19		Et_2O			28
20	$LiCu(CH{=}CH_2)_2\cdot SMe_2$				52
21	$Li_2Cu(CH{=}CH_2)_3$	THF			14
22			A		54
23	$Li_2Cu(CH{=}CH_2)_3\cdot SMe_2$				59
24			B		10
25		Et_2O			51
26			A		56

[a] Reactions were carried out by adding 0.5 mmol of 1 to 2.5 mmol of organocopper reagent dissolved in 10 mL of solvent. All reactions were quenched with oxygen and finally aqueous ammonium chloride. [b] Procedure A: reaction maintained at -78 °C for 1 h, warmed to 0 °C for 1 h, and then quenched B: -78 °C for 1 h before quenching. [c] Yields were determined by gas chromatography using an internal standard. [d] Reaction was quenched with excess *n*-butyl iodide prior to oxygen.

methylpyridine was observed from the reaction of **3** and 3-chloromercuripyridine. It is not clear if this is simply due to methylation of the anticipated product by methyl iodide or a failure of the organomercurial to react.

It is worth noting that diphenylmercury also reacts with **2** to give toluene in modest yield (based on both phenyl groups) (eq 4). Presumably under our optimal conditions, much higher yields could be obtained if so desired.

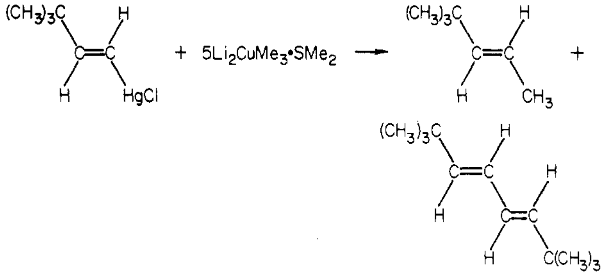


(4)

40%

The scope of the reaction with **1** has also been examined by using several other organocuprate reagents (Table III). Organocopper reagents derived from *n*-butyllithium give greatly reduced yields of cross-coupled product no matter what stoichiometry, solvent, or reaction procedure was used. As a solvent, THF appears to give better results than ether (compare entries 1 and 2 and 4 and 6). Maintaining the reaction at -78 °C (procedure B) also seems to promote better cross-coupling (entries 4 and 5). The stoichiometry of the organocopper reagent or its complexation with dimethyl sulfide seemed to have little effect (entries 2, 6, and 8). Quite surprising was the observation that quenching with *n*-butyl iodide sharply reduced the yield of *n*-butylbenzene, contrary to what was observed in the cross-coupling of **1** and methylcopper compounds. *sec*-Butylcopper reagents gave still lower yields of cross-coupled product. Again, the reagent itself does not seem terribly important. Best results are observed in THF at low temperatures. Using vinylcopper reagents, one can obtain significantly better yields than with either of the butylcopper reagents. Contrary to previous results, ether gives better yields than THF and warming the reaction up to 0 °C prior to quenching (procedure A) is also generally beneficial. Unfortunately, from these reactions no clear picture emerges as to exactly what procedure is preferrable. One must examine each system individually.

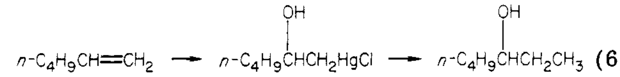
Alkylation of Alkenylmercurials. Alkenylmercurials can also be alkylated by using these cross-coupling reactions (Table IV). Yields of 44–66% have been obtained. In the reaction of *trans*-1-hexenylmercuric chloride and methylcopper reagents, quenching with methyl iodide lowered the yield of methyl olefin, quite the opposite from what is observed with arylmercurials. Especially noteworthy is the fact that *n*-butyl and vinyl groups can be introduced in good yield. In the methylation of (*trans*-3,3-dimethyl-1-butenyl)mercuric chloride, substantial amounts of the corresponding symmetrical diene were also observed (eq 5). The stereospecificity of the cross-coupling



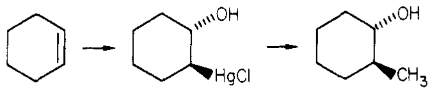
(5)

reaction has been examined on both *cis*- and *trans*-1-hexenylmercuric chloride (entries 1 and 9). Each alkenylmercurial was observed to give 99% retention of configuration upon methylation, as determined by comparison of gas chromatographic retention times of authentic samples of *cis*- and *trans*-2-heptene.

Alkylation of Alkylmercurials. Unlike our earlier work on the rhodium-promoted alkylation of organomercurials, using organocopper reactions we are able to effect the alkylation of alkylmercurials. Some examples are included in Table V. Primary alkylmercurials react to give fair yields of alkylated product, while secondary alkylmercurials give significantly lower yields. The ability to alkylate organomercurials prepared via oxymercuration of alkenes provides a novel method for the overall hydroxyalkylation of olefins (eq 6). Unfortunately, β-hydroxymercurials derived from internal olefins give only very low yields upon organocopper cross-coupling. When the reaction is carried out at −78 °C, retention of the organomercurial stereochemistry is observed (eq 7). We were unable to observe any methylation product from the reaction of (*trans*-2-methoxycyclohexyl)mercuric chloride. Whitesides obtained similar results using his approach.[8]



$$n\text{-}C_4H_9CH{=}CH_2 \rightarrow n\text{-}C_4H_9\overset{OH}{C}HCH_2HgCl \rightarrow n\text{-}C_4H_9\overset{OH}{C}HCH_2CH_3 \quad (6)$$



(7)

95:5 trans/cis

Mechanism. The mechanism of these cross-coupling reactions seems best represented by Scheme I, the important feature of which is the formation of a mixed diorganocopper intermediate LiCuRR′ which can either oxidatively or thermally cross-couple to give the observed products. The following observations are consistent with this mechanism. Upon adding phenylmercuric chloride to a clear colorless solution of $LiCuMe_2$ in ether, one observes the immediate formation of a heavy yellow precipitate presumed to be insoluble methylcopper. Within 15–30 min, the precipitate disappears, presumably due to lithium methylphenylcopper formation. Addition of phenylmercuric chloride to a suspension of methylcopper followed by oxidation gives only small amounts of toluene. However, treatment of methylcopper with either diphenylmercury or methylphenylmercury (prepared in situ from phenylmercuric chloride and methyl lithium) followed by oxidation afforded toluene in good yield. These observations support initial formation of a diorganomercury intermediate which eventually transfers its original organic group to copper to form a mixed diorganocopper species which would be expected to cross-couple as indicated. The high stereospecificity (>99%) of the alkenylmercurial methylation reactions (Table IV, entries 1 and 9) seems to rule out any sort of radical anion chain mechanism for this cross-coupling. It should also be pointed out that our intermediates behave significantly different from the ternary complexes of lithium, copper, and mercury described by Bergbreiter and Whitesides.[8] Their intermediate fails to undergo conjugate addition to mesityl oxide while ours adds readily to 2-cyclohexenone (eq 8). They also report that arylmercurials do not cross-couple with alkyl halides under their conditions, while we observe a significant increase in the yield of alkylbenzene upon addition of the corresponding alkyl iodide to our arylmercurial reactions. While the exact nature of either species is unknown, all observations in our own work are consistent with the formation of "simple" organocopper species and their subsequent thermal or oxidative cross-coupling.

Scheme I

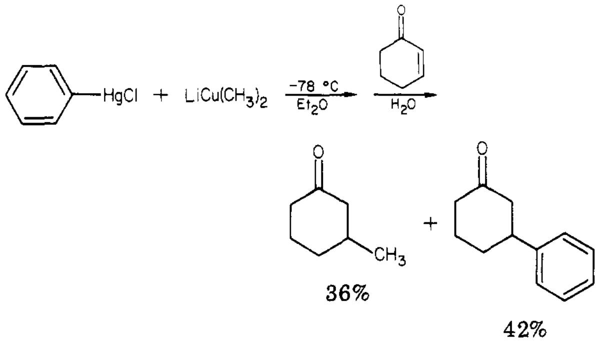
$$RHgCl + LiCuR'_2 \rightarrow RHgR' + CuR' + LiCl$$

$$RHgR' + CuR' + LiCl \rightarrow LiCuRR' + R'HgCl$$

$$RHgR' + LiCuR'_2 \rightarrow LiCuRR' + HgR'_2$$

$$LiCuRR' \xrightarrow{O_2} R\text{–}R'$$

$$LiCuRR' + R'I \rightarrow R\text{–}R'$$



(8)

Conclusions. A general method for carbon–carbon bond formation between organomercurials and organocopper reagents has been discovered. Optimal conditions for the cross-coupling of a variety of aryl-, alkenyl-, and alkylmercurials with primary and secondary alkyl- and alkenylcuprate reagents have been examined. Lithium diorganocuprates and dilithium triorganocuprates give the best results with yields tending to decrease in the order methyl > vinyl > primary alkyl > secondary alkyl. With organomercurials, yields tend to decrease as follows: aryl > vinyl > primary alkyl > secondary alkyl. However, substantial deviations from this ordering have been observed as one varies reaction conditions. These reactions appear to proceed via mercury–copper transmetalation to generate a mixed diorganocopper species which then thermally or oxidatively eliminates the cross-coupled product. Consistent with this picture is the fact that an organic group originally attached to mercury can be readily added in a conjugate fashion to α,β-unsaturated ketones, a reaction typical of an organocopper species.

Experimental Section

Equipment. The infrared and NMR spectra were recorded on a Beckman IR-4250 infrared spectrometer and either a Varian Associates HA-100 or Hitachi Perkin-Elmer R-20B NMR spectrometer, respectively. Mass spectra were obtained on an AEI MS-902 high-resolution mass spectrometer, while the GC–mass spectra were recorded on a Finnegan 4023 GC-MS data system. A Varian 3700 gas chromatograph was used for all gas chromatographic analyses. Most analyses were performed by using a 6 ft × $^1/_8$ in 5% SE-30 column, while isomer distributions were determined by using a 30-m SE-30 capillary column from J. W. Scientific. All GLC yields were determined by addition of a hydrocarbon internal standard and use of appropriate correction factors determined from authentic samples.

Reagents. All chemicals were used directly as obtained commercially unless otherwise indicated. THF and diethyl ether were distilled from calcium hydride under nitrogen. Copper(I) iodide was obtained from Alfa and purified by a literature procedure.[18] Methyllithium, *sec*-butyllithium, *n*-butyllithium, and *tert*-butyllithium were obtained from Alfa, while vinyllithium was purchased from Org-Met. Methyllithium was titrated by the method of Watson and Eastham,[19] while all other alkyllithium reagents were titrated with 2,5-dimethoxybenzyl alcohol.[20] Dimethyl sulfide was obtained from Aldrich and methyl iodide from Eastman.

Phenylmercuric chloride and diphenylmercury were obtained from Aldrich. *p*-Anisylmercuric chloride,[21] (*m*-(carbomethoxy)-phenyl)mercuric chloride,[22] (*m*-nitrophenyl)mercuric chloride,[22] 2-chloromercurithiophene,[23] 2-chloromercurifuran,[5] 3-chloromercuripyridine,[24] (*o*-hydroxyphenyl)mercuric chloride,[25] 3-

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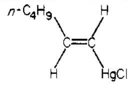
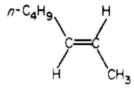
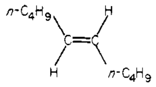
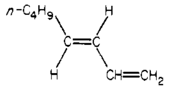
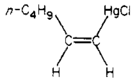
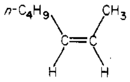
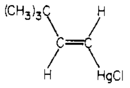
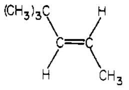
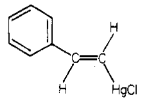
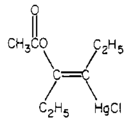
Table IV. Alkylation of Alkenylmercurials[a]

entry	alkenylmercurial	organocopper reagent	solvent	reaction procedure[b]	product	% yield[c]
1		$LiCuMe_2 \cdot SMe_2$	Et_2O	A		57, 20[d]
2		Li_2CuMe_3				34
3			THF			41
4		$Li_2CuMe_3 \cdot SMe_2$	Et_2O			56, 26[d]
5				B		44, 35[d]
6			THF	A		36[e]
7		$LiCu(n\text{-}C_4H_9)_2 \cdot SMe_2$		B		44
8		$Li_2Cu(CH{=}CH_2)_3 \cdot SMe_2$	Et_2O	A		66
9		$LiCuMe_2 \cdot SMe_2$				62
10						32[f]
11				B		45
12		$Li_2CuMe_3 \cdot SMe_2$		A		27[g]
13		$LiCuMe_2$		B		51
14		$LiCuMe_2 \cdot SMe_2$		A		59
15		$Li_2CuMe_3 \cdot SMe_2$				0

[a] Reactions were carried out by adding 0.5 mmol of organomercurial to 2.5 mmol of organocopper reagent dissolved in 10 mL of solvent, followed by quenching with oxygen and finally aqueous ammonium chloride. [b] Procedure A: reaction maintained at -78 °C for 1 h, warmed to 0 °C for 1 h, and then quenched. B: -78 °C for 1 h before quenching. [c] Yields were determined by gas chromatography using an internal standard. [d] Reaction quenched with excess methyl iodide prior to oxygen. [e] 26% yield of *trans,trans*-5,7-dodecadiene also present. [f] 55% yield of *trans,trans*-2,2,7,7-tetramethylocta-diene also present. [g] 62% yield of *trans,trans*-2,2,7,7-tetramethyloctadiene also present.

chloromercuribenzaldehyde,[22] and mesitylmercuric chloride[22] were all prepared according to literature procedures.

The majority of the alkenylmercurials were prepared by published hydroboration–mercuration procedures.[26,27] (*E*)-3-Acetoxy-4-chloromercuri-3-hexene was prepared according to a literature procedure.[28]

(*Z*)-1-Hexenylmercuric chloride was prepared from the corresponding organolithium compound which was obtained as follows. To 20 mmol of dicyclohexylborane[26] in 20 mL of THF was added at 0 °C 16 mmol of 1-iodo-1-hexyne. The solution was stirred at 0 °C for 1.5 h, and 5 mL of glacial acetic acid was added. The reaction was then stirred at room temperature for 5 h, diluted with ether, washed with water and dilute HCl, and dried over anhydrous sodium sulfate. Removal of the solvent in vacuo and distillation afforded 2.05 g (61%) of (*Z*)-1-iodo-1-hexene: bp 87–88 °C (45 torr); ^1H NMR ($CDCl_3$) δ 1.02 (3 H, t, J = 6 Hz, CH_3), 1.2–2.0 (4 H, m, CH_2CH_2), 2.0–2.5 (2 H, m, ${=}CCH_2$), 6.1–6.45 (2 H, m, $CH{=}CH$); IR (max) (thin film) 3060, 2950, 2920, 2845, 1605, 1270 cm^{-1}; high-resolution mass spectrum calcd for $C_6H_{11}I$ m/e 209.9905, found m/e 209.9898. (*Z*)-1-Iodo-1-hexene (6.0 mmol) was converted to the corresponding alkenyllithium compound upon treatment with 2 equiv of *tert*-butyllithium according to the procedure of Corey and Beames.[29] The solution of organolithium compound was decanted away from precipitated lithium iodide via canula into a −78 °C solution of mercuric chloride (6.26 mmol) in THF. The lithium iodide was washed once with −78 °C pentane, and this solution was also added to the THF solution which was then allowed to warm to room temperature and filtered through Celite. The solvent was removed in vacuo and the residue taken up in methylene chloride which was then washed with water and brine and dried over anhydrous sodium sulfate. Removal of the solvent and distillation (bp 110 °C (0.05 torr), Kugelrohr) afforded 1.50 g (78%) of (*Z*)-1-hexenylmercuric chloride: ^1H NMR ($CDCl_3$) δ 0.8–1.1 (3 H, m, CH_3), 1.15–2.0 (4 H, m, CH_2CH_2), 2.05–2.45 (2 H, m, $={CCH_2}$), 5.95 (1 H, d, J = 9 Hz, CHHgCl), 6.4–6.8 (1 H, m, $={CH}$). Anal. Calcd for $C_6H_{11}ClHg$: C, 22.58; H, 3.47. Found: C, 22.41; H, 3.53.

n-Hexylmercuric chloride and *n*-butylmercuric chloride were prepared from the corresponding alkenes via hydroboration–mercuration.[30] 1-Chloromercuri-2-hexanol,[31] *trans*-2-chloromercuricyclohexanol,[31] and (*trans*-2-methoxycyclohexyl)mercuric chloride[32] were prepared by solvomercuration of 1-hexene and

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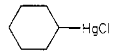
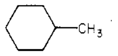
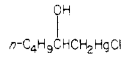
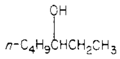
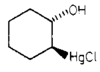
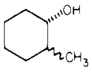
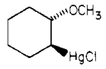
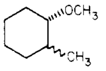
Table V. Alkylation of Alkylmercurials[a]

entry	alkylmercurial	organocopper reagent	reaction procedure[b]	alkyl iodide quench	product	% yield[c]
1	n-C_4H_9HgCl	$Li_2Cu(CH=CH_2)_3$	A	–	n-$C_4H_9CH=CH_2$	17
2			B	–		5
3		$Li_2Cu(CH=CH_2)_3 \cdot SMe_2$	A	–		28
4			B	–		7
5	n-$C_6H_{13}HgCl$	Li_2CuMe_3	A	+	n-C_7H_{16}	62
6		$LiCu(n\text{-}C_4H_9)_2$		–	n-$C_{10}H_{22}$	5
7		$Li_2Cu(n\text{-}C_4H_9)_3$	B	–		49
8				+		57
9		Li_2CuMe_3	A	+		39
10		$Li_2CuMe_3 \cdot SMe_2$		+		36
11	 $n\text{-}C_4H_9\overset{OH}{C}HCH_2HgCl$	Li_2CuMe_3	B	+	 $n\text{-}C_4H_9\overset{OH}{C}HCH_2CH_3$	51, 10[d]
12		$Li_2CuMe_3 \cdot SMe_2$	A	–		4
13				+		4
14			B	+		33
15		Li_2CuMe_3		+		4
16		$Li_2CuMe_3 \cdot SMe_2$		+	95:5 trans/cis	27
17			A	–		8
18				+	43:57 trans/cis	31
19		Li_2CuMe_3	B	+		0
20		$Li_2CuMe_3 \cdot SMe_2$	A	+		0

[a] Reactions were carried out by adding 0.5 mmol of organomercurial to 2.5 mmol of organocopper reagent dissolved in 10 mL of ether. Some reactions were quenched with an alkyl iodide corresponding to the organocopper reagent and then with oxygen and aqueous ammonium chloride. [b] Procedure A: reaction maintained at −78 °C for 1 h, warmed to 0 °C for 1 h, and then quenched. B: −78 °C for 1 h before quenching. [c] Yields were determined by gas chromatography using an internal standard. [d] THF used as the solvent.

cyclohexene, respectively, and subsequent treatment with aqueous sodium chloride.

Preparation of Authentic Samples of Reaction Products. Toluene, iodobenzene, styrene, *n*-butylbenzene, *sec*-butylbenzene, *p*-methylanisole, 2-methylfuran, 1,2,3,5-tetramethylbenzene, *m*-tolualdehyde, 1-(3-methylphenyl)ethanol, *o*-cresol, β-picoline, 2-methylthiophene, 1-phenyl-1-propene, *cis*- and *trans*-2-heptene, 4,4-dimethyl-2-pentene, 1,3-octadiene, *trans*-5-decene, 1-hexene, 3-heptanol, and *cis*- and *trans*-2-methylcyclohexanol were all obtained from commercial sources. Methyl 3-methylbenzoate was synthesized via the Grignard reagent of *m*-bromotoluene and carbon dioxide and subsequent acid-catalyzed esterification in refluxing methanol. *trans*-2-Methylcyclohexanol was synthesized via hydroboration–oxidation of 1-methylcyclohexene.[33] Identity of the reaction products was confirmed in each case by comparison of GLC retention times with those of authentic samples and by gas chromatography–mass spectral analysis.

Preparation of Organocopper Reagents. Lithium dimethylcuprate was prepared by the following procedure. Copper(I) iodide (480 mg, 2.5 mmol) was placed in a round-bottom flask with a gas inlet tube and septum inlet. Diethyl ether (7.0 mL) was added and the suspension cooled to 0 °C. To this solution was added 3.15 mL (5.0 mmol) of methyllithium in diethyl ether. The clear solution was stirred for 15 min at 0 °C. The dimethyl sulfide complex was prepared similarly except that copper(I) iodide was first dissolved in 1.0 mL of dimethyl sulfide before addition of ether. Dilithium trimethylcuprate was prepared similarly except that 3 equiv of methyllithium was employed.

Lithium divinylcuprate was prepared as follows. Copper(I) iodide (480 mg, 2.5 mmol) was placed in a round-bottom flask as described above and dissolved in 1.0 mL of dimethyl sulfide. Diethyl ether (8.0 mL) was added, and the solution was cooled to −78 °C whereupon 2.15 mL (5.0 mmol) of vinyllithium in THF was added. The dark red solution was then stirred for 30 min at −78 °C. Dilithium trivinylcuprate was prepared by an analogous procedure.

Lithium di-*n*-butylcuprate–dimethyl sulfide was prepared by the following procedure. Copper(I) iodide (480 mg, 2.5 mmol) was placed in a round-bottom flask as described above and dissolved in 1.0 mL of dimethyl sulfide and 8.0 mL of THF. This solution was then cooled to −78 °C, and 2.12 mL (5.0 mmol) of *n*-butyl lithium in hexane was added. The resulting dark red solution was then stirred for 30 min at −78 °C before use. Dilithium tri-*n*-butylcuprate–dimethyl sulfide, lithium di-*sec*-butylcuprate, and dilithium tri-*sec*-butylcuprate were all prepared analogously.

Lithium methylcyanocuprate,[34] lithium dimethylcuprate–tri-*n*-butylphosphine,[12] lithium dimethylcuprate–HMPA,[35] lithium methyl(thiophenoxy)cuprate,[36] lithium methyl-*tert*-butoxycuprate,[36] and lithium methyl(3-methyl-3-methoxy-1-butynyl)cuprate[37] were all prepared according to literature procedures.

Methylation of Arylmercurials. Procedure A is representative of those used in the methylation of 1 (Table I). To a 10-mL solution of methylcopper reagent (2.5 mmol) in THF or diethyl ether was added 160 mg of solid phenylmercuric chloride (0.50 mmol) while back-flushing with nitrogen. The solution was stirred for 1 h at −78 °C followed by 1 h at 0 °C. The reaction was then quenched by adding 0.75 mL of methyl iodide by syringe and stirring 15–30 min at that temperature and/or flushing with pure oxygen after which saturated aqueous ammonium chloride and an appropriate hydrocarbon internal standard were added and the organic layer was analyzed by gas chromatography. In

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procedure B, the reaction mixture was never warmed to 0 °C. In procedure B with only methyl iodide as a quenching agent (entry 9), the reaction mixture was allowed to warm to room temperature before hydrolysis. Otherwise, all quenching and hydrolysis reactions were carried out at either −78 °C or 0 °C depending on the procedure employed. In certain reactions, 0.025–0.05 mmol of transition-metal reagents (5–10%) were added immediately after 1 or 1 mL of dimethyl sulfide was added prior to 1.

In the methylation of other arylmercurials summarized in Table II, dilithium trimethylcuprate (5 equiv) was employed and the reaction was carried out for 1 h at −78 °C and then 1 h at 0 °C, followed by methyl iodide and oxygen quenching and hydrolysis as described above.

The following preparation of *p*-methylanisole is illustrative of the procedure used to isolate the methylation products. To a solution of 10.5 mmol of dilithium trimethylcuprate in 40 mL of diethyl ether at −78 °C was added 1.03 g of *p*-anisylmercuric chloride (3.0 mmol). The reaction mixture was stirred for 1 h at −78 °C and then warmed to 0 °C for 1 h. Methyl iodide (5 g) was then slowly added by syringe, and the mixture was stirred for 10 min before flushing with oxygen. After hydrolysis with saturated aqueous ammonium chloride, the mixture was diluted with ether, washed with saturated aqueous ammonium chloride until the washes were colorless, and then dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator, and the residue (330 mg) was chromatographed on 40 g of silica gel by using 19:1 hexane/ethyl acetate affording 230 mg of *p*-methylanisole (63% yield). All spectra were identical with those of an authentic sample.

Alkylation of 1. The following procedure is representative of that used to study the alkylation of 1 (Table III). To a solution of 2.5 mmol of organocopper reagent in 10 mL of THF or ether was added 0.50 mmol of 1 while back-flushing with nitrogen. The reaction mixture was maintained at −78 °C for 1 h and then flushed with oxygen or warmed to 0 °C for 1 h and then oxidized. After hydrolysis and addition of an appropriate hydrocarbon internal standard, the reaction was analyzed by GLC analysis.

Alkylation of Alkenylmercurials. The following procedure for the reaction of di- and triorganocuprates with alkenylmercurials is representative of that used to obtain the results reported in Table IV. To a −78 °C solution of organocopper reagent (2.5 mmol) in THF or ether was added 0.5 mmol of alkenylmercurial. The reaction was stirred at −78 °C for 1 h, in some cases warmed to 0 °C for 1 h, and then quenched as described earlier by either methyl iodide and/or oxygen. After hydrolysis by saturated aqueous ammonium chloride, an appropriate hydrocarbon internal standard was added and the solution was analyzed by GLC analysis.

The stereochemical outcome of these reactions was ascertained by using the following procedure. *cis*- or *trans*-1-Hexenylmercuric chloride (0.96 g, 3.0 mmol) was added to a −78 °C solution containing 9.0 mmol of lithium dimethylcuprate–dimethyl sulfide in 20 mL of diethyl ether. The reaction was stirred at −78 °C for 1 h, warmed to 0 °C for 1 h, and then flushed with oxygen. The mixture was then hydrolyzed with saturated aqueous ammonium chloride and diluted with 50 mL of ether. The ether layer was washed with ammonium chloride solution until the washes were colorless, dried over anhydrous sodium sulfate, and carefully concentrated by fractional distillation to a volume of about 10 mL which was analyzed on a 30-m SE-30 capillary gas chromatography column. The *trans*-alkenylmercurial afforded 98.9% *trans*-2-heptene and 1.1% *cis*-2-heptene, while the *cis*-alkenylmercurial gave 99.0% *cis*-2-heptene and 1.0% *trans*-2-heptene. The exact stereochemical purity of the starting alkenylmercurials is unknown.

Alkylation of Alkylmercurials. The results summarized in Table V were obtained by using procedures essentially identical with those described above. The following preparation of 3-heptanol is representative of the isolation procedure used in helping to characterize the products of alkylation. To a solution of 12 mmol of dilithium trimethylcuprate in 50 mL of ether at −78 °C was added 1.35 g of 1-chloromercuri-2-hexanol (4.0 mmol). The solution was stirred for 1 h at −78 °C, warmed to 0 °C for 1 h, and quenched with 5.0 g methyl iodide for 10 min. After oxidation, the mixture was hydrolyzed with saturated ammonium chloride, diluted with ether, washed with ammonium chloride until the washes were colorless, and dried over anhydrous sodium sulfate. The ether was removed on a rotary evaporator, and the residue (300 mg) was chromatographed on 50 g of silica gel by using 4:1 hexane/ethyl acetate (R_f = 0.33) to afford 150 mg 3-heptanol (35% yield). All spectra were identical with those of an authentic sample.

The stereochemistry of substitution was determined as follows. To a solution of 2.5 mmol of dilithium trimethylcuprate–dimethyl sulfide in 10 mL of ether was added 165 mg of solid (*trans*-2-hydroxycyclohexyl)mercuric chloride (0.49 mmol) while back-flushing with nitrogen. After the solution was stirred for 1 h at −78 °C, an excess of methyl iodide was slowly added and the solution stirred 15 min before flushing with oxygen. After hydrolysis with saturated aqueous ammonium chloride, analysis by glass capillary gas chromatography indicated *trans*- and *cis*-2-methylcyclohexanol in a ratio of 95:5.

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Registry No. **1**, 100-56-1; **2**, 15681-48-8; **3**, 61278-42-0; CuMe, 1184-53-8; $\mathrm{LiCuMe_2{\cdot}SMe_2}$, 79135-31-2; $\mathrm{LiCuMe_2{\cdot}PBu_3}$, 61817-79-6; $\mathrm{LiCuMe_2{\cdot}HMPA}$, 79135-32-3; LiCu(CN)Me, 41753-78-0; LiCu(SPh)Me, 56831-21-1; $\mathrm{LiCu(C{\equiv}CCMe_2OMe)Me}$, 79135-33-4; LiCu(O-*t*-Bu)Me, 64387-16-2; $\mathrm{Li_2CuMe_3{\cdot}SMe_2}$, 79135-34-5; LiCu(*n*–Bu)$_2$, 24406-16-4; LiCu(*n*-Bu)$_2$·SMe$_2$, 79135-35-6; Li$_2$Cu(*n*-Bu)$_3$, 61288-01-5; Li$_2$Cu(*n*-Bu)$_3$·SMe$_2$, 79135-36-7; LiCu(*sec*-Bu)$_2$, 23402-73-5; LiCu(*sec*-Bu)$_2$·SMe$_2$, 79135-37-8; Li$_2$Cu(*sec*-Bu)$_3$, 61288-02-6; Li$_2$Cu(*sec*-Bu)$_3$·SMe$_2$, 79135-38-9; Li$_2$Cu(*sec*-Bu)$_3$·PBu$_3$, 79135-39-0; $\mathrm{LiCu(CH{=}CH_2)_2}$, 22903-99-7; $\mathrm{LiCu(CH{=}CH_2)_2{\cdot}sMe_2}$, 79135-40-3; $\mathrm{Li_2Cu(CH{=}CH_2)_3}$, 79135-41-4; $\mathrm{Li_2Cu(CH{=}CH_2)_3{\cdot}SMe_2}$, 79152-59-3; (4-(chloromercuri)anisole, 3009-79-8; methyl 3-(chloromercuri)benzoate, 20883-44-7; (chloromercuri)mesitylene, 20883-32-3; 3-(chloromercuri)benzaldehyde, 20883-40-3; 2-(chloromercuri)phenol, 90-03-9; 3-(chloromercuri)nitrobenzene, 2865-17-0; 2-(chloromercuri)furan, 5857-37-4; 2-(chloromercuri)thiophene, 5857-39-6; 3-(chloromercuri)pyridine, 5428-90-0; (*E*)-1-hexenylmercuric chloride, 50874-36-7; (*Z*)-1-hexenylmercuric chloride, 79134-72-8; (*E*)-3,3-dimethyl-1-butenylmercuric chloride, 36525-02-7; (*E*)-2-phenylethenylmercuric chloride, 36525-03-8; (*E*)-3-acetoxy-4-(chloromercuri)-3-hexene, 73902-30-4; *n*-BuHgCl, 543-63-5; *n*-$\mathrm{C_6H_{13}HgCl}$, 17774-09-3; *c*-$\mathrm{C_6H_{11}HgCl}$, 24371-94-6; 1-(2-hydroxyhexyl)mercurichloride, 39849-97-3; *trans*-2-(chloromercuri)cyclohexanol, 29581-85-9; (*trans*-2-methoxycyclohexyl)mercuric chloride, 5274-83-9; toluene, 108-88-3; *p*-methylanisole, 104-93-8; methyl 3-methylbenzoate, 99-36-5; 1,2,3,5-tetramethylbenzene, 527-53-7; 1-(1-hydroxyethyl)-3-methylbenzene, 7287-81-2; o-methylphenol, 95-48-7; 1-methyl-3-nitrobenzene, 99-08-1; 2-methylfuran, 534-22-5; 2-methylthiophene, 554-14-3; 3-methylpyridine, 108-99-6; butylbenzene, 104-51-8; *sec*-butylbenzene, 135-98-8; styrene, 100-42-5; *trans*-2-heptene, 14686-13-6; *trans*-5-decene, 7433-56-9; *trans*-1,3-octadiene, 39491-65-1; *cis*-2-heptene, 6443-92-1; 1-hexene, 592-41-6; heptane, 142-82-5; decane, 124-18-5; methylcyclohexane, 108-87-2; 3-heptanol, 589-82-2; *trans*-2-methylcyclohexanol, 7443-52-9; *cis*-2-methylcyclohexanol, 7443-70-1; *trans*-1-methoxy-2-methylcyclohexane, 21547-36-4; *cis*-1-methoxy-2-methylcyclohexane, 53273-15-7.