CHCl$_3$/EtOAc; (E) 3/2 CHCl$_3$/EtOAc; (F) 98.5/1.0/0.5 CHCl$_3$/CH$_3$OH/Et$_3$N. One column volume equals 1.5 min; data are given in the order trans/cis isomers (see Chart II), solvent system, and retention time in minutes: **32a/32b**, D, 2.9/2.5; **33a/33b**, E, 9.7/9.1; **34a/34b**, E, 6.1/4.1; **35**, E, 3.3; **35**, F, 1.7; **37a/37b**, F, 3.4/2.3; **38a/38b**, F, 6.1/2.9; **39a**[28]/**39b**,[29] F, 10.8/2.8; **40a**[30]/**40b**,[30] F, 9.3/2.5.

Registry No. 8, 148-53-8; 9, 86-51-1; 10, 79618-90-9; 11 (isomer 1), 79618-91-0; 11 (isomer 2), 79618-92-1; 12 (isomer 1), 79618-93-2; 12 (isomer 2), 79618-94-3; 13 (isomer 1), 79618-95-4; 13 (isomer 2), 79618-96-5; 14 (isomer 1), 79618-97-6; 14 (isomer 2), 79618-98-7; 15, 79618-99-8; 16, 79619-00-4; 17, 79619-01-5; 18, 79619-02-6; 19a, 74974-54-2; 19b, 51076-95-0; 19c, 1445-45-0; 19d, 78-39-7; 19e, 40070-40-4; 19f, 18871-66-4; 21a (isomer 1), 79619-03-7; 21a (isomer 2), 79619-04-8; 21b (isomer 1), 79619-05-9; 21b (isomer 2), 79619-06-0; 21c, 79619-07-1; 21d, 79619-08-2; 21e (isomer 1), 79619-09-3; 21e (isomer 2), 79619-10-6; 21f, 79619-11-7; 22, 79631-85-9; 23, 79619-12-8; 24, 79619-13-9; 25, 79619-14-0; 26, 79619-15-1; 27, 79619-16-2; 28, 79619-17-3; 29, 79619-18-4; 30, 79619-19-5; 32a, 79619-20-8; 32b, 79646-97-2; 33a, 79619-21-9; 33b, 79646-98-3; 34a, 79619-22-0; 34b, 79646-99-4; 35, 79631-86-0; 36a, 79631-88-2; 36b, 79703-00-7; 37a, 79619-23-1; 37b, 79647-00-0; 38a, 79619-24-2; 38b, 79647-01-1; ethyl hydrogen malonate, 1071-46-1; ethyl cyanoacetate, 105-56-6; lithium *tert*-butyl malonate, 73859-00-4.

Stereochemistry of Transition-Metal-Catalyzed Cross-Coupling Reactions[1]

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The stereochemical results of transition-metal-catalyzed cross-coupling of methyllithium with chiral (+)-(S)-(4-methylcyclohexylidene)bromomethane (1) are reported. The use of bis(triphenylphosphine) dichlorocobalt(II), iron(III) tris(dibenzoylmethide), and dichloro[1,2-bis(diphenylphosphino)ethane]nickel(II) yielded chiral 1-methyl-4-ethylidineeycyclohexane (2) with 89%, 96%, and 96% retention of configuration, respectively. By contrast, the use of silver bromide yielded totally racemic product.

The coupling reaction of organolithium and Grignard reagents with organic halides, by using *stoichiometric* amounts of either Cu(I), Cu(II),[2] Ag(I),[3] or a variety of transition metals,[4] is an attractive means of forming carbon-carbon σ-bonds. The observation by Tamura and Kochi[3] that the coupling reaction can be promoted by using *catalytic* amounts of complexed forms of Ag, copper, and iron indicated this reaction to have potential practicality as a synthetic tool. Almost simultaneously, Kumada[5] and Corriu[6] showed the synthetic applicability by demonstrating that a catalytic amount of a nickel–phosphine complex caused the efficient *cross-coupling* of Grignard reagents with aryl and vinyl halides. The scope and limitation of this reaction has been reported by Kumada,[7] who also demonstrated that the reaction is stereospecific when isomeric vinyl halides are coupled with phenyl- and methylmagnesium bromide.[8] Moreover, asymmetric inductions have been observed during the reactions of Grignard reagents with organic halides in the presence of a nickel catalyst containing a chiral ligand.[9] The Kumada[7]

Scheme I. Kumada Mechanism for Nickel-Catalyzed Cross-Coupling
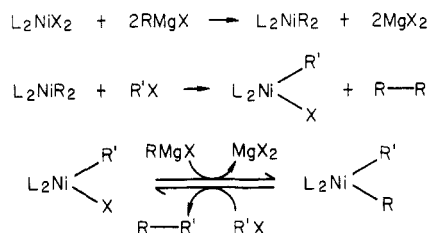
mechanism for the nickel-catalyzed cross-coupling reaction is shown in Scheme I. Kochi and Morrell[10] have suggested that step 2 in the Kumada mechanism is rate determining and involves an electron transfer from nickel to R′X′ to give an intimately associated radical–anion pair. Felkin[11] and Corriu[12] have proposed a mechanism which involves the oxidative addition of Grignard reagents to a Ni(0) intermediate.

The use of ferric chloride for the coupling of Grignard reagents with alkyl halides has been known for some time.[4] Kochi and co-workers[3,13] have carried out a detailed investigation of this reaction. Complexes of β-diketones with Fe(III) were shown to be very effective catalysts for the conversion. Moreover, their use in the coupling of *cis*- and *trans*-vinyl halides with Grignard reagents resulted in coupled products of retained configuration.[13] They have

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proposed an Fe(I) species which is isoelectronic with Co(II) as the catalytically active intermediate.[13]

The effect of catalytic amounts of cobalt(II) chloride on the cross-coupling of Grignard reagents with organic halides has been reviewed.[14] The cobalt-catalyzed reactions are mechanistically very similar to the corresponding reactions catalyzed by iron(III). In both cases radicals are postulated as being formed during the reaction, and cross-coupled products are formed when Grignard reagents react with vinyl halides.[15] The stereochemistry of the coupling has not been determined.

The silver-catalyzed reactions of alkenyl Grignard reagents with alkyl halides and of alkyl Grignard reagents with alkenyl halides yield exclusively the cross-coupled product.[3] Although *cis*-1-propenylmagnesium reacts with methyl bromide to give exclusively *cis*-2-butene, the silver-catalyzed reaction of methylmagnesium bromide with *cis*-1-bromopropene gives a mixture consisting of 70% *cis*- and 30% *trans*-2-butene. This result, coupled with the observation[16] that *cis*- and *trans*-propenylsilver are configurationally stable, indicates that radical intermediates are involved in the latter reaction.

It is the purpose of this paper to evaluate the stereochemistry of the cross-coupling reaction of chiral (+)-(*S*)-(4-methylcyclohexylidene)bromomethane and methyllithium by using nickel(II), iron(III), cobalt(II), and silver(I) as catalysts.

Results

The synthesis and the establishment of the absolute configurations of optically pure (+)-(*S*)-(4-methylcyclohexylidene)bromomethane (**1**) and (4-methylcyclohexylidene)ethane (**2**) has previously been reported.[17,18] Thus, the stereochemistry of the reaction of **1** with methyllithium can be evaluated.

(+)-(*S*)-**1**   (+)-(*S*)-**2**
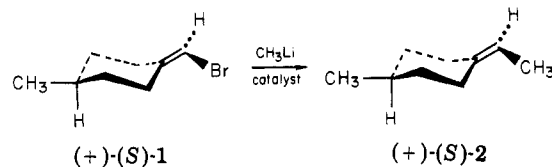
Reaction of an excess of methyllithium with racemic **1** in diethyl ether at room temperature for 24 h resulted in the formation of only a trace of **2** and the recovery of most of the starting material. Therefore, in the absence of catalyst, methyllithium does not react in significant yield with the vinyl bromide used in the present study.

Four metal catalysts were chosen for study of the stereochemistry of the cross-coupling of methyllithium with chiral **1**. Two of these catalysts, dichloro[1,2-bis(diphenylphosphino)ethane]nickel(II)[19] and tris(dibenzoylmethiodo)iron(III),[13] were chosen because they have been reported to catalyze the cross-coupling of Grignard reagents with *cis*- and *trans*-vinyl halides with complete retention of configuration. Cross-coupling catalyzed by silver(I) salts is believed to involve free radicals;[15] use of

Table I. Stereochemistry of Cross-Coupling of Methyllithium with (+)-(*S*)-(4-Methylcyclohexylidene)bromomethane

catalyst[a]	[catalyst], M	% yield of **2**[b]	% optical purity of **2**[c]
NiCl₂(dpe)	4.74×10^{-3}	91 (30)	92
Fe(DBM)₃	4.2×10^{-3}	90 (49)	92
CoCl₂(Ph₃P)₂	3.8×10^{-3}	100 (61)	78
AgBr	2.66×10^{-2}	(41)	0

a Reactions with Ni, Co, and Ag catalysts were carried out in diethyl ether, and the reaction with Fe catalyst was run in THF. Reactions in the presence of Ni and Fe were carried out at 25 °C; reactions catalyzed by Co and Ag, were run at −75 °C. *b* Yields are based on hydrocarbon isolated before purification. The numbers in parentheses are yields of hydrocarbon after purification. *c* Rotations were corrected for the optical purity of the starting material. Unreacted bromide was recovered from the silver-catalyzed reaction with 88% retention of optical activity. For the cobalt-catalyzed reaction the bromide was recovered with 94% retention of optical purity.

silver bromide as the catalyst provided the opportunity to test this hypothesis and to directly observe the racemization of these radicals if formed. The stereochemistry of cross-coupling of organometallic reagents with vinyl halides catalyzed by cobalt(II) compounds has not been previously reported; bis(triphenylphosphine)dichlorocobalt(II) was chosen for the present study because of its ease of preparation and its structural similarity with highly effective nickel(II) catalysts.

Reaction mixtures were analyzed by NMR spectrometry and gas chromatography. Samples of (4-methylcyclohexylidene)ethane (**2**) obtained in the reaction were purified by column chromatography on silver nitrate–silicic acid and/or by bulb-to-bulb distillation prior to measurement of their rotations. In the case of catalysis by silver(I) and cobalt(II), where partial or complete racemization of the product was observed, unreacted **1** was recovered and purified by silver nitrate–silicic acid chromatography. The rotation of the bromide was then measured in order to determine whether the bromide was optically stable under the reaction conditions. The results of these experiments are summarized in Table I.

From these results it can be seen that the cross-coupling reactions catalyzed by nickel(II) and iron(III) proceed with very high (96%) degrees of retention of configuration. However, the cobalt(II)-catalyzed coupling reaction involves some loss of configuration, and the silver(I)-catalyzed reaction occurs with complete (>99%) racemization. Although the silver(I)-catalyzed coupling resulted in some racemization of the bromide under the reaction conditions, the loss of optical purity was small compared with the total racemization of the hydrocarbon product. The cross-coupling reaction with vinyl halide substrates fits two patterns: (1) a nonradical pathway in which product is formed with retention of double bond configuration via vinyl organometallic intermediates (e.g., nickel and iron) and (2) a mechanism in which vinyl radicals are formed prior to generation of vinyl organometallic intermediates, with consequent loss of double bond stereochemistry in the product (e.g., silver).

Methyllithium couples with chiral **1** in high yield and with very high retention of configuration when NiCl₂(dpe) or Fe(DMB)₃ are present in the reaction mixtures in catalytic amounts. The stereospecificity of these reactions can easily be accommodated by oxidative addition–reductive elimination mechanisms analogous to those postulated for similar reactions with Grignard reagents. However, alternate or additional pathways involving

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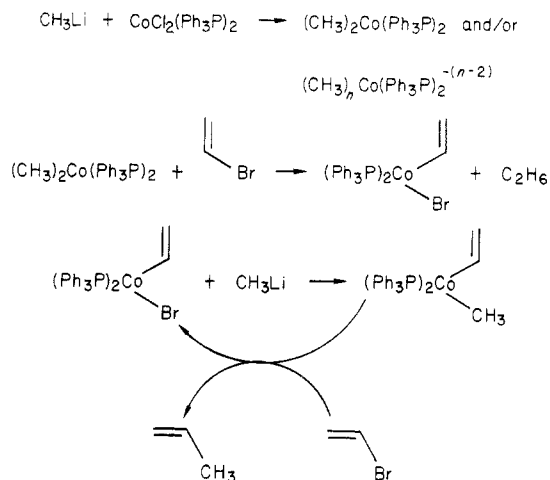
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Scheme II. Possible Mechanism for Co(II)-Catalyzed
Cross-Coupling of Methyllithium with Vinyl Halides

nickelate or ferrate intermediates are possible when organolithium reagents are used as reactants.

Kochi and Morrell[10] have cited evidence for formation of a nickelate species in the reaction of methyllithium with an arylmethylnickel(II)–diphosphine compound. Corey and Posner[20] have reported that methyllithium and nickel(II) iodide form a 3:1 reagent (presumably $(CH_3)_3Ni^-Li^+$) which reacts with vinyl halides with retention of configuration. Addition of methyllithium to ether solutions of ferric chloride,[21] ferrous iodide, or cobaltous iodide[20] results in the formation of similar complexes. The methyl ferrate and methyl cobaltate would couple stereospecifically with vinyl halides. It is likely that analogous complexes are produced as intermediates in the reaction of methyllithium with chiral 1 catalyzed by Fe(DBM)$_3$, NiCl$_2$(dpe), or CoCl$_2$(Ph$_3$P)$_2$.

If vinylnickel and vinyliron species are formed during the cross-coupling of methyllithium with chiral vinyl bromide, then these species must be configurationally stable under the reaction conditions in order to account for the observed stereospecificity. In addition, the oxidative addition and reductive elimination of the vinyl moiety must be stereospecific. These results are in agreement with those obtained for cross-coupling of Grignard reagents with cis- and trans-vinyl halides.

The moderate stereoselectivity observed for the cobalt-catalyzed reaction of methyllithium with chiral 1 is more difficult to rationalize. The stereochemistry of cross-coupling of Grignard reagents or alkyllithium reagents with vinyl halides has not been previously investigated. The reaction of dihalocobalt(II)–diphosphine complexes with Grignard reagents affords dialkylcobalt(II) compounds.[22] It is likely that such a compound is initially formed in the reaction of methyllithium with the optically active vinyl bromide catalyzed by CoCl$_2$(Ph$_3$P)$_2$. Further reaction of this compound with methyllithium to form a methyl cobaltate complex of the type previously described cannot be ruled out. Oxidative addition of the vinyl bromide to either of these intermediates, followed by reductive elimination, would also be a plausible mechanism for the catalysis (Scheme II).

This mechanism would account for the observed stereochemistry of the reaction if some racemization accompanied either or both the oxidative addition and reductive

elimination steps. The simultaneous operation of a stereospecific nonradical coupling mechanism and a nonstereoselective radical pathway cannot, of course, be ruled out.

Reaction of methyllithium with chiral (4-methylcyclohexylidene)bromomethane (1) gives racemic (4-methylcyclohexylidene)ethane (2) when silver bromide is used as the catalyst. This is the expected result for a process believed to involve radicals. Since the bromide does not racemize to an appreciable extent under the reaction conditions, it is likely that the racemization observed occurs during the cross-coupling.

Of the four catalytic reactions, cross-coupling in the presence of NiCl$_2$(dpe) and Fe(DMB)$_3$ produces product with the highest optical purity. Therefore, these are the catalysts of choice for use in the stereospecific syntheses of alkenes.

Experimental Section

All melting points are uncorrected. Infrared spectra were measured with a Perkin-Elmer Model 237 grating infrared spectrophotometer. NMR spectra were obtained by using a Varian A-60 spectrometer. Optical rotations were measured at the 546.1-nm mercury line with a Bendix-Ericsson Model 987 automatic polarimeter with a digital display attachment. The cell length was 0.4 dm. Error limits for rotations were calculated by multiplying the relative standard deviation by the specific rotation. The relative deviation was determined by dividing the standard deviation (0.002°) by the observed rotation.

GLC analyses were conducted by using a Bendix Chroma-Lab Series 2100 gas chromatograph with thermal-conductivity detectors. Analyses of (4-methylcyclohexylidene)bromomethane, (4-methylcyclohexylidene)ethane, (4-methylcyclohexylidene)-methane and reaction mixtures containing these compounds were made by using a 5 ft × $^1/_4$ in. copper column, packed with 20% Apiezon L on Chromasorb P.

Chiral (4-Methylcyclohexylidene)ethane (2). To a solution of chiral (4-methylcyclohexylidene)bromomethane [1:[18] 3.0 mmol; $[\alpha]^{25}_{Hg}$ +54.5° (c 1.0, absolute ethanol; 87% optically pure)] in 10 mL of THF at –75 °C was added a solution (6 mL, 3.0 mmol) of 0.5 M sec-butyllithium in hexane. The mixture was allowed to stir at –75 °C for 2 h after complete addition. Cuprous iodide (0.6 g, 3.1 mmol) was then added, and the mixture was allowed to reach –35 °C and to stir for 45 min. During this time a dark black suspension was formed. HMPA (2.5 mL, freshly distilled from 13X molecular sieves) and 1.4 g of triethyl phosphite were added, and the mixture was allowed to stir at –35 °C for 5 min. Methyl iodide (0.4 g, 2.7 mmol) was then added. After being stirred at –35 °C for an additional 15 min, the mixture was allowed to warm to room temperature and to stir for 12 h. The reaction was quenched with water and the ether layer separated. The ether extracts were washed three times with water. It was found that triethyl phosphite could be completely removed by washing the extracts several times with dilute silver nitrate solution. The extracts were then washed with saturated sodium chloride and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure gave 0.25 g (76%) of a liquid. This liquid was chromatographed on 25 g of 25% silver nitrate–silicic acid, eluting first with 400 mL of pentane and then with 100 mL of 5% ether–hexane. The alkene was obtained in the ether fraction and after removal of the solvent was further purified by bulb-to-bulb distillation [25 °C (2 torr)] to give 50 mg (15%) of (4-methylcyclohexylidene)ethane:[23] $[\alpha]^{25}_{Hg}$ +14.7 ± 2.9° (c 0.16, CHCl$_3$; 83% optically pure) (lit.[23] $[\alpha]^{25}_{Hg}$ +17.6°); NMR (CCl$_4$) δ 5.0 (q, 1 H), 0.7–2.8 (complex m, 15 H); IR (NaCl plate) 2940, 1640, 1380, 815 cm^{-1}.

Reaction of (+)-(S)-(4-Methylcyclohexylidene)bromomethane (1) with Methyllithium in the Presence of NiCl$_2$-(dpe). To a mixture of 0.5 g (2.63 mmol) of bromide,[18] ($[\alpha]^{25}_{Hg}$

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+28.1° (*c* 1.3, absolute ethanol; 45% optically pure)) and 25 mg (0.047 mmol) of dichloro[1,2-bis(diphenylphosphino)ethane]nickel(II)[23] in 10 mL of ether at room temperature was added a solution (2 mL, 3 mmol) of 1.5 M methyllithium in ether. Upon addition of methyllithium the orange nickel complex completely dissolved, and a clear yellow solution was formed. The solution was stirred for 2.5 h and hydrolyzed with water. The ether layer was washed with 10% hydrochloric acid and saturated sodium chloride solutions and dried over anhydrous magnesium sulfate. Removal of solvent gave 0.3 g (91%) of a liquid which was shown by NMR and GLC analyses to consist almost entirely of (4-methylcyclohexylidene)ethane (2). Purification of the liquid by bulb-to-bulb distillation [25 °C (2 torr)] afforded 0.1 g (33%) of the alkene, $[\alpha]^{25}_{Hg}$ +7.14 ± 0.4° (*c* 1.2, CHCl$_3$; 40.3% optically pure, with a corrected optical purity of 92%). The IR and NMR spectra of the alkene were identical with those of authentic (4-methylcyclohexylidene)ethane.

Reaction of (+)-(*S*)-(4-Methylcyclohexylidene)bromoethane (1) with Methyllithium in the Presence of Fe(DBM)$_3$. To a mixture of 0.5 g (2.63 mmol) of bromide[18] ($[\alpha]^{25}_{Hg}$ +26.4° (*c* 1.2, absolute ethanol; 42% optically pure)) and 30 mg (0.042 mmol) of iron(III)[24] tris(dibenzoylmethide) in 10 mL of THF at room temperature was added dropwise a solution (2 mL, 3 mmol) of 1.5 M methyllithium in ether. The initial red solution became dark green and, finally, dark brown during the addition. After the mixture was stirred for 2 h at room temperature, the reaction was quenched with water. The ether layer was washed with dilute hydrochloric acid and saturated sodium chloride and dried over anhydrous magnesium sulfate. Removal of solvent under reduced pressure gave 0.3 g (91%) of liquid which was shown by GLC and NMR analyses to consist predominantly of (4-methylcyclohexylidene)ethane. Purification by bulb-to-bulb distillation [25 °C (2 torr)] afforded 0.15 g (43%) of the alkene, $[\alpha]^{25}_{Hg}$ +6.89 ± 0.4° (*c* 1.3, CHCl$_3$; 39% optically pure, with a corrected optical purity of 92%). The IR and NMR spectra of the compound were identical with those of an authentic sample.

Reaction of (+)-(*S*)-(4-Methylcyclohexylidene)bromoethane (1) with Methyllithium in the Presence of CoCl$_2$-(Ph$_3$P)$_2$. To a mixture of 0.5 g (2.63 mmol) of bromide[18] ($[\alpha]^{25}_{Hg}$ +27.25° (*c* 1.4, absolute ethanol; 43% optically pure)) and 25 mg (0.038 mmol) of bis(triphenylphosphine)dichlorocobalt(II)[25] in 5 mL of THF at −75 °C was added a solution (2 mL, 3 mmol) of 1.5 M methyllithium in ether. The mixture was stirred at −75 °C for 30 min and then allowed to warm to room temperature. The resulting dark viscous mixture was allowed to stir for 2 h at

room temperature. The reaction was then quenched with water and the organic layer separated. The combined ether extracts were washed successively with water, 10% hydrochloric acid, and saturated sodium chloride. The extracts were dried over anhydrous magnesium sulfate, and the solvent was removed to give 0.4 g (100%) of a liquid which was purified by bulb-to-bulb distillation [25 °C (2 torr)]: 0.2 g (61%); $[\alpha]^{25}_{Hg}$ +6.0 ± 0.99° (*c* 0.5, CHCl$_3$; 34% optically pure). The corrected optical purity of the alkene was 79%. The compound was shoown by GLC and NMR analyses to be (4-methylcyclohexylidene)ethane (2).

In a separate experiment, an excess of bromide was allowed to react with methyllithium and the cobalt complex. A solution (0.5 mL, 0.75 mmol) of methyllithium in ether was added to a mixture of 0.5 g (2.63 mmol) of bromide ($[\alpha]^{25}_{Hg}$ +54.25° (*c* 1.0, absolute ethanol; 87% optically pure) and 25 mg (0.038 mmol) of cobalt complex in 10 mL of THF at −75 °C. After being stirred for 30 min at −75 °C, the mixture was allowed to warm to room temperature and to stir for 2 h. After the workup 0.4 g of liquid was obtained which was chromatographed on 25 g of 25% silver nitrate–silicic acid. Elution with 400 mL of pentane and removal of the solvent gave 0.2 g (40% recovery) of bromide, $[\alpha]^{25}_{Hg}$ +50.81 ± 0.5° (*c* 3.1, absolute ethanol; 82% optically pure). The bromide retained 94% of its original optical activity.

Reaction of (+)-(*S*)-(4-Methylcyclohexylidene)bromoethane (2) with Methyllithium in the Presence of Silver Bromide. To a mixture of 0.75 g (3.9 mmol) of bromide[18] ($[\alpha]^{25}_{Hg}$ +26.4° (*c* 1.2, absolute ethanol; 42% optically pure)) and 50 mg (0.027 mmol) of silver bromide in 10 mL of ether at −75 °C was added a solution (2 mL, 3 mmol) of 1.5 M methyllithium in ether. After being stirred at −75 °C for 5 min, the mixture was allowed to warm slowly to room temperature. This resulted in the formation of a black precipitate. The mixture was stirred at room temperature for 15 h and then hydrolyzed with water. The ether extracts were washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The solvent was removed to give 0.5 g of liquid which was chromatographed on 20 g of 25% silver nitrate–silicic acid. The bromide was recovered by elution with 400 mL of pentane. The alkene was then obtained by elution with 50 mL of anhydrous ether. From the pentane fraction was obtained 0.4 g (53%) of bromide which was further purified by bulb-to-bulb distillation (pot temperature 50–60 °C (2 torr); $[\alpha]^{25}_{Hg}$ +23.2° (*c* 2.9, absolute ethanol; 37% optically pure). The bromide retained 88% of its initial optical purity. The ether fraction afforded 0.15 g (41% based on methyllithium) of (4-methylcyclohexylidene)ethane which was distilled [25 °C (2 torr)] and was found to be completely racemic.

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Chemistry of Organic Chloramines. Formation of Arenesulfonamides by Derivatization of Organic Chloramines with Sodium Arenesulfinates[1]

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Organic chloramines react rapidly with sodium benzenesulfinate or sodium toluenesulfinate to form arenesulfonamides. Derivatization was carried out by three different methods, one involving derivatization of pure chloramines and two involving derivatization of the chloramines generated in situ by reaction of the amine with sodium hypochlorite. Seventeen arenesulfonamides whose amine precursors included primary and secondary aliphatic amines, aromatic amines, and amino acids were synthesized in poor to excellent yields depending on the method used. Effects of structure, stability, and water solubility of the chloramine precursors are discussed. Benzenesulfonyl chloride can be isolated from the reaction of 10^{-4} M *N*-chloropiperidine with sodium benzenesulfinate. Competing hydrolysis of the sulfonyl chloride accounts for low yields of sulfonamide for dilute solutions of chloramine.

Although haloamines are recognized byproducts of the chlorination of natural water systems, none have been

specifically identified because there is currently no suitable method for their isolation and identification.[2] As a class,