# Carbon-Carbon Bond Formation by Selective Coupling of Alkylthioallylcopper Reagent with Allylic Halides

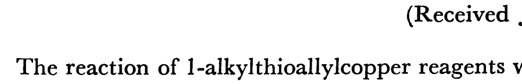
Koichiro Oshima, Hisashi Yamamoto, and Hitosi Nozaki
*Department of Industrial Chemistry, Kyoto University, Yoshida, Kyoto 606*

(Received January 30, 1975)

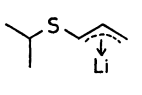
The reaction of 1-alkylthioallylcopper reagents with allylic halides affords the $S_N2'$ type substitution product in excellent yield. The more synthetically useful reagent, 1,3-bis(methylthio)allylcopper reagent behaves in the same fashion. Attempts to hydrolyze the vinyl sulfide moiety to an aldehyde unit is successful only in the latter case. Yomogi alcohol is synthesized stereospecifically in the light of these results.

The remarkable regio- and stereospecificity of simple organocopper derivatives, *e.g.*, CuR or $LiCuR_2$, where R=alkyl, vinyl, or aryl, to form carbon-carbon bond with organic halides[2)] raises the question whether the specific reactivity of more stable carbanionic intermediates could be enhanced by copper(I) ion.[3)] The answer to the question is of particular interest for the 1-alkylthioallyl anions since the reaction of these systems has substantial synthetic utility. Moreover, the recent development of effective methods for converting allylic sulfides to 1-alkylthioallyllithium species[4)] has made 1-alkylthioallylcopper(I) derivatives readily available for synthetic studies.

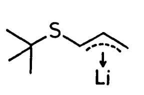
1-Alkylthioallyl anion is synthetically equivalent to either the 1-oxopropyl anion ($-COCH_2CH_3$) or 3-oxopropyl anion ($-CH_2CH_2CHO$). It was already known that aryl- or alkylthioallyllithium undergoes reaction with organic halides to introduce an alkyl group specifically on the carbon α to the alkylthio group and not γ to the sulfur atom.[4)] In this study we have synthesized alkylthioallylcopper(I) derivatives and have examined their behavior as potential synthon of 3-oxopropyl anion. We have also examined 1,3-bis(methylthio)allylcopper(I) as a synthon of 3-oxopropenyl anion (-CH=CHCHO).



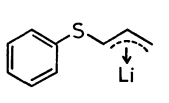
A solution of 1-alkylthioallyllithium **1**—**3** in ether or tetrahydrofuran was prepared from the corresponding allyl sulfide and *sec*-butyllithium at −25 °C for 30 min. Treatment of the ethereal solution of organolithium derivative **1** or **2** with slightly excess cuprous iodide (CuI) at −78 °C for 15 min furnished a gray to white suspension which by analogy with the previous work[5)] probably due to the polymeric organocopper derivatives **4** and **5**, respectively.



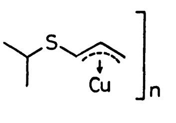
1



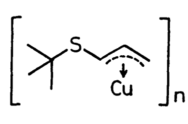
2



3



4



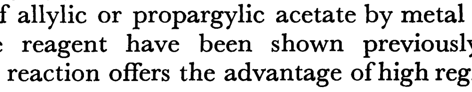
5

These suspensions were stable at −78 °C for 1 hr but decomposed gradually at −25 °C to form a black precipitate.[6)] Although the similar complex could be formed in tetrahydrofuran, the resulting complex was found to decompose much faster. Thus, alkylthioallylcopper derivatives should be prepared in ether at −78 °C in a period of 15—30 min. It is noteworthy, however, that similar treatment of **3** with CuI failed to produce analogous monoalkylcopper derivatives but only a black tar.

Attempted preparation of lithium di(alkylthioallyl)cuprate derivatives failed. After addition of a half equiv of CuI to the lithium derivative **1** a black precipitate formed, the behavior of which was quite similar to that of **1**. From the previous observation,[6b)] it would appear that the tendency of metal cuprate species to undergo specific reaction is retarded by the presence of carbon ligand which could form reasonably stable anion.

$$R_2Cu^- \rightleftharpoons RCu + R^-$$

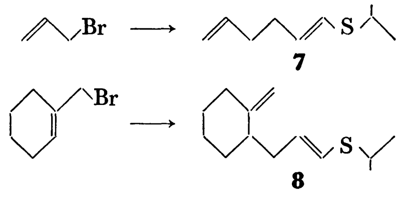
The reaction of 2-cyclohexylideneethyl bromide (1.0 equiv) with isopropylthioallylcopper (2.0 equiv) in ether at −78 °C for 4 hr produced the substitution product **6** in 92% yield;>96% pure by glpc and NMR assay.



6

The reaction appears to be a pure $S_N2'$ type displacement of bromine by isopropylthioallyl group. In addition this ambident anion undergoes alkylation exclusively γ to sulfur atom in high yield: thus, the alkylthioallylcopper reagent did behave as a synthon of 3-oxopropyl anion. Although the $S_N2'$ type displacement of allylic or propargylic acetate by metal dialkylcuprate reagent have been shown previously,[7)] the present reaction offers the advantage of high regio selectivity to a unique degree.

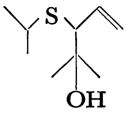
In a similar experiment, allyl bromide and 1-cyclohexenylmethyl bromide gave the sulfides **7** and **8** in 88% and 87% yields, respectively.



7
8

Further study is required before the stereochemical and mechanistic details of these reactions can be undestood. However, we could assume the involvement of a radical type intermediate for this reaction on the basis of the following results. Treatment of benzyl bromide with the copper complex **4** at −78 °C for 2 hr produced bibenzyl in a moderate yield. Similarly benzhydryl chloride gave 1,1,2,2-tetraphenylethane as a major product. These observations are possibly indicative of the presence of benzyl radical or benzhydryl radical in the course of the reaction, since both of which are known to be dimerized easily to form the isolated coupling products.8)

Alkylthioallylcopper also reacts with substances other than allylic halides. The isopropylthio complex **4** reacts with acetone in ether at −78 °C to yield **9** as a major product. Thus, the behavior of carbonyl compounds toward the copper derivative **4** contrasts sharply with that of allylic halides as those appearing above.

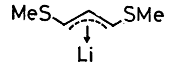


**9**

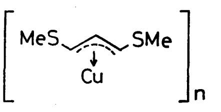
Finally, we examine the possibility of Michael reactions including the addition of **4** or **5** to mesityl oxide. In no case, however, did the presence of excess copper(I) derivatives in the reaction mixture have any substantial effect on the rate or product distribution of the Michael reaction.

The experimental procedure generally used for hydrolysis of vinyl sulfides with mercuric chloride9) was applied to the product **6** without any success. Only minimal conversion to the corresponding aldehyde was observed, and the major products constitute a complex mixture, possibly as a result of acid-catalyzed cyclization followed by rearrangements. The relative difficulties associated with δ,ε-unsaturated aldehyde synthesis led us to explore the following route starting from 1,3-bis(methylthio)propene.

1,3-Bis(methylthio)allyllithium (**10**) was readily prepared by metallation of 1,3-bis(methylthio)propene with *sec*-butyllithium in ether at −25 °C, a procedure superior to previous methods10) for our present purpose in that **10** is formed in high yield in the absence of secondary amine. Although a solution of the lithio derivative **10** was reported to be purple, a pale yellow solution was obtained in the absence of diisopropylamine. Treatment of this solution with CuI at −78 °C and stirring for 15 min produced the corresponding copper derivative **11** which behaved similarly as isopropylthioallylcopper in the following reaction with allylic halides.

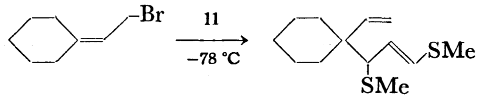


10



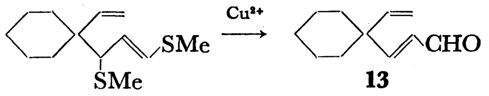
11

Thus, 2-cyclohexylideneethyl bromide was treated with the copper reagent **11** at −78 °C to furnish the expected $S_N2'$ type substitution product **12** in almost quantitative yield.



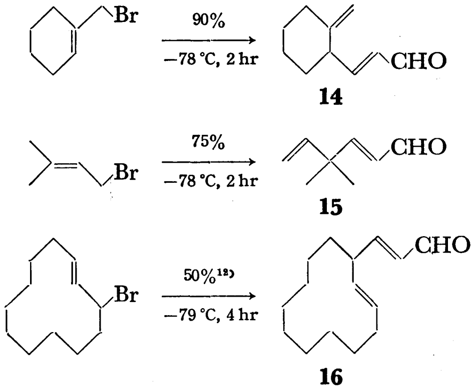
**12**

Previously, the hydrolysis of 1,3-bis(methylthio)propene derivatives to α,β-unsaturated carbonyl compounds has been effected by mercury(II) ion.10) Seeking a milder hydrolysis procedure, we investigated the use of cupric ion in ethanol11) and found that this ion afforded very high yields of pure aldehydes. The process is devoid of the cationic cyclization of **11** as well as other side reactions.



**13**

The δ,ε-unsaturated aldehyde **13** was obtained in 92% over-all yield from the cyclohexylideneethyl bromide. Similarly, the reaction of 1,3-bis(methylthio)allylcopper with several allylic halides in ether as solvent, followed by cupric ion catalyzed hydrolysis, led to efficient cross coupling as indicated below.



The observed regio- and stereoselectivity of our new reaction portends its broad synthetic application in the field of natural product chemistry. As an example, Yomogi alcohol, (*E*)-2,5,5-trimethyl-3,6-heptadien-2-ol (**17**),13) was prepared regio- and stereoselectively when the aldehyde **15** was subjected to the following two-step sequence.

**18** **17**

The aldehyde **15** was converted to the corresponding carboxylic ester **18** stereospecifically in good yield by manganese dioxide-cyanide ion method.14) The homogeneity of the ester **18** was indicated by tlc and glpc analysis. In addition, the NMR and infrared spectra of **18** were entirely analogous to those of the corresponding ethyl ester.13) The ester so obtained was alkylated by the treatment of excess methyllithium13) at −25 °C for 30 min to yield Yomogi alcohol (**17**) in 75% yield. The NMR, infrared, and mass spectra of **17** were identical with those of the natural alcohol **17**.13)

The authors acknowledge with pleasure the financial support by the Grant-in-aid administered by the Ministry of Education, Japanese Government. We are also grateful to Dr. Y. Kato, Teijin Limited, for the exact mass spectral data.

## Experimental

IR spectra were determined on a Shimadzu IR-27-G spectrometer, mass spectra on a Hitachi RMU-6L mass spectrometer, glpc analyses on a Yanagimoto GCG-550F, and NMR spectra on a JEOL-C-60-H or Varian EM-360 spectrometer; chemical shifts are given in $\delta$ with TMS as the internal standard. Analyses were carried out by Mrs. K. Fujimoto at Prof. Kawanisi's Laboratory and by the staffs at the Elemental Analyses Center of Kyoto University. High resolution mass spectra were taken on a JMS-D100 mass spectrometer operating at 75 eV. All experiments were carried out under an atmosphere of dry nitrogen, preparative thin layer chromatography (plc) on silica gel PF-254 (Merck) plates with hexane or benzene as a developing solvent, and preparative column chromatography on silica gel WAKO-gel C-100 (Wako).

*Preparation of Allyl Alkyl Sulfides.* A mixture of alkyl mercaptane (0.27 mol), sodium ethoxide (20 g, 0.30 mol), and ethanol (200 ml) was heated at reflux and treated with a solution of allyl bromide (37 g, 0.30 mol) in ethanol (20 ml) dropwise over 30 min. The mixture was heated at reflux for 1 hr, and allowed to cool to room temperature. The reaction was quenched by the addition of water and the separated organic layer was dried. Fractional distillation through a 20 cm Vigreux column afforded NMR-pure allyl sulfides in 60—80% yield.

Allyl isopropyl sulfide: bp 127—128 °C (760 mmHg); IR (neat) 1640, 1250, 1230, 990, 910 $\mathrm{cm}^{-1}$; NMR ($\mathrm{CCl_4}$) $\delta$ 1.20 (d, $J=7$, 6H), 2.82 (dq, $J=7$, 1H), 3.12 (d, $J=8$, 2H), 4.85—5.27 (m, 2H), 5.45—6.10 (m, 1H); mass *m/e* (%) 116 (38), 74 (80), 59 (35), 43 (42), 41 (100).

Allyl *tert*-butyl sulfide: bp 60 °C (43 mmHg); NMR ($\mathrm{CCl_4}$) $\delta$ 1.29 (s, 9H), 3.0—3.3 (m, 2H), 4.8—6.3 (m, 3H); mass *m/e*: 130 ($\mathrm{M}^+$).

*Generation of Isopropylthioallylcopper **4** and* tert-*Butylthioallylcopper **5**.* Allyl isopropyl sulfide or allyl *tert*-butyl siulfide (2.0 mmol) was dissolved in dry ether (15 ml). The solution was cooled to −78 °C and treated with *s*-butyllithium in pentane (2.0 ml of 1.02 M solution). After stirring for 30 min at −26 °C, the resulting organge or pale yellow solution was recooled to −78 °C. Solid cuprous iodide (2.4 mmol) was added. A white precipitate formed immediately and the mixture was stirred at the same temperature for 15 min before subsequent treatments described below.

*Reaction of **4** with Cyclohexylideneethyl Bromide.* A solution of cyclohexylideneethyl bromide (1.9 g, 10 mmol) in either (10 ml) was added at −78 °C to a solution of **4** prepared from allyl isopropyl sulfide (2.4 g, 20 mmol), ether (70 ml), *s*-butyllithium (20 ml of 1.02 M solution in pentane), and cuprous iodide (5.0 g, 26 mmol). The mixture was kept at −78 °C for 4 hr. The resulting black mixture was filtered through a pad of Celite 545 and the filter cake was washed with ether. The filtrate and washings were combined, washed with water, dried, and freed of the solvent. The residual liquid was separated through a column chromatography on silica gel (100 g) with hexane-benzene as an eluant. The less polar fraction (tlc $R_f$ 0.50 (hexane)) provided the sulfide **6** (2.1 g, 92% yield): bp 145 °C (bath temp., 3 mmHg); IR (neat) 1640, 1242, 945, 912 $\mathrm{cm}^{-1}$; NMR ($\mathrm{CCl_4}$) $\delta$ 1.25 (d, $J=7$, 6H), 1.40 (bs, 10H), 2.03 (d, $J=7$, 2H), 3.00 (dq, $J=7$, 1H), 4.96 (dd, $J=2$ and 17, 1H), 5.09 (dd, $J=2$ and 12, 1H), 5.60 (dt, $J=7$ and 15, 1H), 5.70 (dd, $J=12$ and 17, 1H), 6.02 (d, $J=15$, 1H); mass *m/e* (%) 224 (5), 181 (16), 116 (20), 115 (100), 73 (70); Anal. Found: C, 75.2; H, 11.0. Calcd for $\mathrm{C_{14}H_{24}S}$: C, 74.9; H, 10.8. The more polar fraction (tlc $R_f$ 0.15 (hexane)) afforded the dimer of allyl isopropyl sulfide (0.48 g, *m/e* 230 ($\mathrm{M}^+$)) which was not identified completely.

*Reaction of **4** with 1-Cyclohexenylmethyl Bromide.* A solution of **4** prepared from allyl isopropyl sulfide (0.23 g, 2.0 mmol) was treated with 1-cyclohexenylmethyl bromide (0.18 g, 1.0 mmol) at −78 °C and stirred at −78 °C for additional 4 hr. The orange liquid obtained on extractive work-up was submitted to preparative tlc on silica gel with hexane as an eluant. The band at $R_f$ 0.4—0.6 provided the sulfide **8** (0.18 g, 87% yield) as a colorless liquid: bp 130 °C (bath temp., 3 mmHg); IR (neat) 1645, 1240, 945, 905, 890 $\mathrm{cm}^{-1}$; NMR ($\mathrm{CCl_4}$) $\delta$ 1.25 (d, $J=7$, 6H), 2.95 (dq, $J=7$, 1H), 4.58 (bd, $J=7$, 2H), 5.63 (dt, $J=7$ and 15, 1H), 5.90 (d, $J=15$, 1H); mass *m/e* (%) 210 (24), 167 (92), 134 (44), 116 (76), 115 (100). Found: C, 73.9; H, 10.4%. Calcd for $\mathrm{C_{13}H_{22}S}$: C, 74.2; H, 10.5%.

*Reaction of **4** with Allyl Bromide.* A solution of **4** prepared from allyl isopropyl sulfide (0.23 g, 2.0 mmol) was treated with allyl bromide (86 μl, 1.0 mmol) at −78 °C. The resulting solution was kept at −78 °C for 4 hr, and the color of the solution was turned black at the end of the period. Tetralin (100 μl, 97 mg) was injected and the entire mixture was filtered through a pad of Celite 545 and washed with ether. The filtrate was washed with dilute hydrochloric acid, water, and dried. The resulting organic phase was submitted directly to glpc to obtain the yield of the sulfide **7** using tetralin as the internal standard: 88% yield. The analytical sample was prepared by preparative tlc and bulb to bulb distillation: bp 110 °C (bath temp., 45 mmHg); IR (neat) 1640, 1240, 990, 940, 910 $\mathrm{cm}^{-1}$; NMR ($\mathrm{CCl_4}$) $\delta$ 1.30 (d, $J=7$, 6H), 2.02—2.38 (m, 4H), 2.98 (dq, $J=7$, 1H), 4.75—5.16 (m, 2H), 5.40—6.05 (m, 3H); mass *m/e* (%) 156 (8), 115 (51), 113 (18), 84 (14), 73 (100); Found: C, 69.2; H, 10.2%. Calcd for $\mathrm{C_9H_{16}S}$: C, 69.2; H, 10.3%.

*Reaction of **4** with Benzyl Bromide.* Benzyl bromide (0.17 g, 1.0 mmol) was treated with the complex **4** (2.0 mmol) in ether (13 ml) at −78 °C for 2 hr. The preparative tlc separation of the crude reaction mixture gave bibenzyl (71 mg, 78% yield) as the major product; it was identical in all respects with an authentic sample.

*Reaction of **4** with Benzhydryl Chloride.* Benzhydryl chloride (0.20 g, 1.0 mmol) was treated with the complex **4** (2.0 mmol) in ether (10 ml) at −78 °C for 2 hr. After the concentration of the dried extracts *in vacuo*, a white solid was obtained. Recrystallization from benzene-hexane (1: 1) gave pure 1,1,2,2-tetraphenylethane (0.12 g, 70%) as colorless crystals; the product was identical in all respects with an authentic sample.

*Reaction of **4** with Acetone.* A solution of **4** prepared from allyl isopropyl sulfide (0.23 g, 2.0 mmol) was treated with acetone (1.0 ml) at −78 °C and kept there for 1 hr. The mixture was filtered through a pad of Celite 545 and washed through with ether. The filtrate was washed with dilute hydrochloric acid and water, dried, and concentrated *in vacuo*. The residual liquid (0.31 g) was submitted to glpc; $\alpha$-adduct/$\gamma$-adduct=20: 1 by comparison with an authentic sample.[15]

*Generation of 1,3-bis(Methylthio)allylcopper **11**.* *sec*-Butyllithium in pentane (1.02 M, 2.0 ml, 2.0 mmol) was added to a solution of 1,3-bis(methylthio)propene (2.0 mmol) in ether (15ml) with stirring under nitrogen at −78 °C and kept at −26 °C for 30 min. The resulting orange solution was recooled to −78 °C and treated with cuprous iodide (2.4 mmol) and stirred at that temperature for 15 min before subsequent treatments described below.

*Reaction of **11** with Cyclohexylideneethyl Bromide.* A solution of **11** derived from 0.27 g (2.0 mmol) of 1,3-bis(methylthio)propene was treated with cyclohexylideneethyl bromide (0.19 g, 1.0 mmol) at −78 °C. The color of the solution turned brown rapidly and black after stirring for additional 2 hr. The liquid (0.35 g) obtained on extractive work-up was treated with cupric chloride (0.44 g, 3.0 mmol) and cupric oxide (0.24 g, 3.0 mmol) in ethanol (20 ml) at 25 °C for 1 hr. The mixture was filtered through a pad of Celite 545 and the filter cake was washed with ether. The ethereal solutions were washed with dilute hydrochloric acid and water and concentrated *in vacuo*. The residual liquid was submitted to preparative tlc with benzene as an eluant. The band at $R_f$ 0.5—0.6 provided the aldehyde **13** (0.15 g, 92% yield) as a colorless liquid: bp 120 °C (bath temp., 18 mmHg); IR (neat) 1685, 1625, 1110, 980, 915, 850 cm$^{-1}$; NMR ($CCl_4$) $\delta$ 1.2—2.1 (m, 10H), 4.7—5.8 (m, 2H), 5.95 (dd, $J$=7 and 15, 1H), 6.6 (d, $J$=15, 1H), 9.45 (d, $J$=7, 1H); mass *m/e* (%) 164 (12), 135 (67), 121 (24), 107 (36), 81 (64), 79 (70), 67 (100); Mol wt. Found: 164.1170. Calcd for $C_{11}H_{16}O$: 164.1201.

*Reaction of **11** with 1-Cyclohexenylmethyl Bromide.* A solution of **11** derived from 1,3-bis(methylthio)propene (0.27 g, 2.0 mmol) was treated with 1-cyclohexenylmethyl bromide (0.18 g, 1.0 mmol) at −78 °C and kept there for 2 hr. After extractive work-up, a mixture of residual liquid, cupric chloride (0.40 g, 3.0 mmol), and cupric oxide (0.24 g, 3.0 mmol) in ethanol (20 ml) was stirred under nitrogen at 25 °C for 1 hr. The black suspension was filtered through a pad of Celite 545 and the filter cake was washed with ether. The ethereal solutions were washed with water, dried, and freed of the solvent. The remaining oil was submitted to preparative tlc on silica gel with benzene as an eluant. The band at $R_f$ 0.45—0.60 provided the aldehyde **14** (0.14 g, 90% yield) as a colorless liquid: bp 100 °C (bath temp., 18 mmHg); IR (neat) 1690, 1645, 1150, 1120, 980, 890 cm$^{-1}$; NMR ($CCl_4$) $\delta$ 4.5—4.65 (bd, 2H), 6.0 (dd, $J$=7 and 15, 1H), 6.8 (dd, $J$=8 and 15, 1H), 10.1 (d, $J$=7, 1H); mass *m/e* (%) 150 (21), 135 (33), 121 (62), 107 (65), 93 (39), 81 (94), 79 (100); Anal. Found: C, 79.8; H, 9.65%. Calcd for $C_{10}H_{14}O$: C, 80.0; H, 9.39%.

*Reaction of **11** with 4-Bromo-2-methyl-2-butene.* A solution of **11** prepared from 1,3-bis(methylthio)propene (0.27 g, 2.0 mmol) was treated with 4-bromo-2-methyl-2-butene (0.15 g, 1.0 mmol) at −78 °C for 2 hr. Ethereal extracts were washed with water, dried, and concentrated. Powdered cupric chloride (0.40 g, 3.0 mmol) and cupric oxide (0.24 g, 3.0 mmol) were sequentially added to a solution of the remaining liquid (0.25 g) in ethanol (20 ml). The heterogeneous reaction mixture was stirred under nitrogen at 25 °C for 1 hr. Extractive workup furnished a liquid which was submitted to preparative tlc with benzene as an eluant. The band at $R_f$ 0.5—0.65 provided the aldehyde **15** (0.18 g, 72% yield) as a colorless liquid: IR (neat) 1690, 1160, 1110, 986, 920, 785 cm$^{-1}$; NMR ($CCl_4$) $\delta$ 1.25 (s, 6H), 4.95 (dd, $J$=2 and 20, 1H), 5.02 (dd, $J$=2 and 10, 1H), 5.80 (dd, $J$=10 and 20, 1H), 5.95 (dd, $J$=7 and 16, 1H), 6.7 (d, $J$=16, 1H), 9.5 (d, $J$=7, 1H); mass *m/e* (%) 124 (13), 109 (85), 81 (90), 79 (64), 67 (100); Mol wt. Found: 124.0843. Calcd for $C_8H_{12}O$: 124.0889.

*Reaction of **11** with 2-Cyclododecenyl Bromide.* A solution of **11** prepared from 1,3-bis(methylthio)propene (0.27 g, 2.0 mmol) was treated with 2-cyclododecenyl bromide (0.24 g, 1.0 mmol) at −78 °C. The color of the solution changed very slowly to brown and then the solution was maintained at −78 °C for 4 hr. The similar procedure afforded the aldehyde **16** (0.11 g, 50% yield) as a colorless liquid: bp 140 °C (bath temp., 0.1 mmHg); IR (neat) 1690, 1630, 1130, 975 cm$^{-1}$; NMR ($CCl_4$) $\delta$ 1.2—2.2 (m, 19H), 5.1—5.7 (m, 2H), 6.95 (ddd, $J$=16, 7, and 1.5, 1H), 7.65 (dd, $J$=7 and 16, 1H), 9.41 (d, $J$=8, 1H); mass *m/e* (%) 220 (25), 135 (17), 121 (28), 107 (50), 95 (70), 81 (100); Mol wt. Found: 220.1862. Calcd for $C_{15}H_{24}O$: 220.1830.

*Generation of Yomogi Alcohol from the Aldehyde **15**.* The aldehyde **15** (0.26 g, 2.1 mmol) was stirred with a mixture of sodium cyanide (0.40 g), acetic acid (0.16 g), and manganese dioxide[16] (5.0 g) in methanol (25 ml) for 12 hr at 25 °C. The remaining liquid on extractive work-up after filtration was subjected to preparative tlc with benzene as an eluant. The band at $R_f$ 0.6—0.8 provided the ester **18** (0.24 g, 76% yield) as a colorless liquid: IR (neat) 1725, 1655, 1190, 1165, 1010, 985 cm$^{-1}$; mass *m/e* (%) 154 (6), 139 (12), 125 (10), 123 (12), 111 (16), 95 (100), 79 (44), 67 (38); Found: C, 70.2; H, 9.23%. Calcd for $C_9H_{14}O_2$: C, 70.1; H, 9.15%.

The ester **18** (0.15 g) was treated with methyllithium (5 ml of 1.5 M solution in ether) in ether at 0 °C and kept at 25 °C for an additional 1 hr. The reaction mixture was poured into ice-cold water and the product was extracted with ether repeatedly. The combined ethereal extracts were washed with water, dried, and freed of the solvent. The remaining oil was submitted to preparative tlc on silica gel with dichloromethane as an eluant to yield the desired Yomogi alcohol as a colorless liquid, identical in all respects with the authentic sample.

## References

1) A preliminary account of this work has appeared: K. Oshima, H. Yamamoto, and H. Nozaki, *J. Amer. Chem. Soc.*, **95**, 7926 (1973).

2) J. F. Normant, *Synthesis*, **2**, 63 (1972) and references cited therein.

3) E. J. Corey and M. Jautelat, *Tetrahedron Lett.*, **1968**, 5787; T. Mukaiyama, K. Narasaka, and M. Furusato, *J. Amer. Chem. Soc.*, **94**, 8641 (1972).

4) a) K. Oshima, H. Takahashi, H. Yamamoto, and H. Nozaki, *ibid.*, **95**, 2693 (1973); K. Oshima, H. Yamamoto, and H. Nozaki, *ibid.*, **95**, 4446 (1973); b) J. F. Bielmann and J. B. Ducep, *Tetrahedron Lett.*, 5629 (1968).

5) H. Gilman, R. G. Jones, and L. A. Woods, *J. Org. Chem.*, **17**, 1630 (1952); see also Ref. 2.

6) a) H. Gilman and J. M. Straley, *Rec. Trav. Chim. Pays-Bas.*, **55**, 821 (1936); b) H. O. House and W. F. Fischer, Jr., *J. Org. Chem.*, **34**, 3615 (1969).

7) Dimethylcopper and its homologs undergo the similar substitution reaction with allylic or propargylic acetate, although *n*-BuCu-LiI does not react. Allylic acetate: P. Rona, L. Tokes, J. Tremble, and P. Crabbe, *Chem. Commun.*, **1969**, 43; R. J. Anderson, C. A. Henrick, and J. B. Siddal, *J. Amer. Chem. Soc.*, **92**, 735 (1970); E. E. van Tamelen and J. P. McCormick, *ibid.*, **92**, 737 (1970); Propargyl acetate: P. Rona and P. Crabbe, *ibid.*, **90**, 4733 (1968); **91**, 3289 (1969).

8) K. Oshima, T. Shirafuji, H. Yamamoto, and H. Nozaki, This Bulletin, **46**, 1233 (1973).

9) E. J. Corey and J. I. Schulman, *J. Org. Chem.*, **35**, 777 (1970); K. Oshima, K. Shimoji, H. Takahashi, H. Yamamoto, and H. Nozaki, *J. Amer. Chem. Soc.*, **95**, 2694 (1973).

10) E. J. Corey, B. W. Erickson, and R. Noyori, *ibid.*, **93**, 1724 (1973).

11) H. Takahashi, K. Oshima, H. Yamamoto, and H. Nozaki, *ibid.*, **95**, 5803 (1973).

12) The low yield of this reaction was due to the low reactivity of the secondary halide.

13) W. Sucrow and W. Richter, *Chem. Ber.*, **103**, 3771 (1970); B. Willhalm and A. F. Thomas, *Chem. Commun.*, **1969**, 1380; H. Kwart and R. K. Miller, *J. Amer. Chem. Soc.*, **76**, 5403 (1954).

14) E. J. Corey, N. W. Gilman, and B. E. Ganem, *ibid.*, **90**, 5616 (1968).

15) Prepared from 1-isopropylthioallyllithium and acetone at 0 °C for 10 min.

16) Active manganes dioxide of E. Merck was used without further activation.