ORGANIC SYNTHESES

VOLUME 66

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NOTICE

With Volume 62, the Editors of *Organic Syntheses* began a new presentation and distribution policy to shorten the time between submission and appearance of an accepted procedure. The soft-cover edition of this volume is produced by a rapid and inexpensive process, and is sent at no charge to members of the Organic Divisions of the American and French Chemical Societies, The Perkin Division of the Royal Society of Chemistry, and The Society of Synthetic Organic Chemistry, Japan. The soft-cover edition is intended as the personal copy of the owner and is not for library use. A hardcover edition is published by John Wiley and Sons, Inc. in the traditional format, and differs in content primarily in the inclusion of an index. The hardcover edition is intended primarily for library collections and is available for purchase through the publisher. Annual volumes 60–64 will be included in a new five-year version of the collective volumes of *Organic Syntheses* which will appear as *Collective Volume Seven* in the traditional hardcover format, after the appearance of annual volume 64. It will be available for purchase from the publishers. The Editors hope that the new *Collective Volume* series, appearing twice as frequently as the previous decennial volumes, will provide a permanent and timely edition of the procedures for personal and institutional libraries. The Editors welcome comments and suggestions from users concerning the new editions.

NOMENCLATURE

Both common and systematic names of compounds are used throughout this volume, depending on which the Editor-in-Chief felt was more appropriate. The *Chemical Abstracts* indexing name for each title compound, if it differs from the title name, is given as a subtitle. Systematic *Chemical Abstracts* nomenclature, used in both the 9th and 10th Collective Indexes for the title compound and a selection of other compounds mentioned in the procedure, is provided in an appendix at the end of each preparation. Registry numbers, which are useful in computer searching and identification, are also provided in these appendixes. Whenever two names are concurrently in use and one name is the correct *Chemical Abstracts* name, that name is preferred.

SUBMISSION OF PREPARATIONS

Organic Syntheses welcomes and encourages submission of experimental procedures which lead to compounds of wide interest or which illustrate important new developments in methodology. The Editorial Board will consider proposals in outline format as shown below, and will request full experimental details for those proposals which are of sufficient interest. Submissions which are longer than three steps from commercial sources or from existing *Organic Syntheses* procedures will be accepted only in unusual circumstances.

Organic Syntheses Proposal Format

1. Authors
2. Literature reference (enclose preprint if available)
3. Proposed sequence
4. Best current alternative(s)
5. a. Proposed scale, final product
   b. Overall yield
   c. Method of isolation and purification
   d. Purity of product (%)
   e. How determined
6. Any unusual apparatus or experimental technique

7. Any hazards
8. Source of starting material
9. Utility of method or usefulness of product

Submit to: Dr. Jeremiah P. Freeman, Secretary
Department of Chemistry
University of Notre Dame
Notre Dame, IN 46556

Proposals will be evaluated in outline form and again after submission of full experimental details and discussion. A procedure that has been accepted by The Editorial Board will not be published until the procedure has been satisfactorally reproduced and accepted for publication by an Editor. A form that details the preparation of a complete procedure (Notice to Submitters) can be obtained from the Secretary.

Additions, corrections, and improvements to the preparations previously published are welcomed; these should be directed to the Secretary. However, checking of such improvements will only be undertaken when new methodology is involved. Substantially improved procedures have been included in the Collective Volumes in place of a previously published procedure.

PREFACE

This volume contains 28 preparations that illustrate many of the most active areas of synthetic organic chemistry. It starts with a procedure for the preparation of **1-METHYL-1-(TRIMETHYLSILYL)ALLENE** and the use of this interesting reagent for **[3+2] ANNULATION.** These procedures are followed by another organosilicon procedure, for the preparation of the useful reagent **(1-OXO-2-PROPENYL)-TRIMETHYLSILANE.**

Claisen rearrangement of a propargyl alcohol is illustrated by the synthesis of the allenic ester **ETHYL 3,4-DECADIENOATE,** which is isomerized by treatment with alumina to form the α,β,γ,δ-unsaturated ester **ETHYL (E,Z)-2,4-DECADIENOATE.** Büchi's useful method for the formation of γ,δ-unsaturated aldehydes, Claisen rearrangement of (E)-allyloxyacrylic acids, is illustrated in the preparation of **3-PHENYL-4-PENTENAL.**

The aprotic Michael addition reaction is demonstrated in an imaginative fashion in the reaction of the dienolate of 3-methyl-2-cyclohexen-1-one with methyl crotonate to give the methyl ester of **1,3-DIMETHYL-5-OXOBICYCLO-[2.2.2]OCTANE-2-CARBOXYLIC ACID.** From enolates we turn to homoenolates in the **COPPER-CATALYZED CONJUGATE ADDITION OF A ZINC HOMOENOLATE.** The latter procedure, in which silicon, zinc, and copper all play major roles, vividly demonstrates the importance of metals in modern organic synthesis.

Further illustration of the utility of metals is provided in the next six procedures, involving copper, palladium, zinc, tin, silicon, and iron. This section of the volume begins with use of Pd(II) in the catalytic dimerization of methyl acrylate to **DIMETHYL (E)-2-HEXENEDIOATE,** which reacts with a "higher-order" cuprate (Lipshutz reagent) to provide **2-CARBOMETHOXY-3-VINYLCYCLOPENTANONE.** Following are procedures for the **PALLADIUM-CATALYZED SYNTHESIS OF CONJUGATED DIENES** and the **SYNTHESIS OF BIARYLS VIA PALLADIUM-CATALYZED CROSS COUPLING** of an arylzinc reagent with an aryl bromide. The former procedure is illustrated by the preparation of **(5Z,7E)-5,7-HEXADECADIENE** and the latter by the formation of **2-METHYL-4′-NITROBIPHENYL.** The next preparation, **VINYL RADICAL CYCLIZATION VIA ADDITION OF TIN RADICALS TO TRIPLE BONDS,** provides an example of the interesting

radical cyclization chemistry that has recently been developed in Gilbert Stork's laboratory. Another organosilicon procedure follows, **CYCLOPENTANONES FROM CARBOXYLIC ACIDS VIA INTRAMOLECULAR ACYLATION OF ALKYLSILANES: 2-METHYL-2-VINYLCYCLOPENTANONE.** In addition to demonstrating the "alkyl Friedel–Crafts acylation," the latter procedure also provides an example of the α-alkylation of the lithium dienolate resulting from deprotonation of an α,β-unsaturated ester. The (cyclopentadienyl)(dicarbonyl)iron complex of ethyl vinyl ether is used as a vinyl cation synthon in the preparation of **trans-3-METHYL-2-VINYLCYCLOHEXANONE.** This interesting procedure also illustrates the electrophilic capture of the enolate resulting from the conjugate addition of a cuprate reagent to an enone.

A novel annulation process is demonstrated in Ley's **PREPARATION OF tert-BUTYL ACETOTHIOACETATE** and its use in the synthesis of **3-ACETYL-4-HYDROXY-5,5-DIMETHYLFURAN-2(5H)-ONE.** Following are procedures for the preparation of ketones and aldehydes from carboxylic acids, which are demonstrated with the copper-catalyzed reaction of a Grignard reagent with an acyl chloride in the preparation of **METHYL 6-OXODECANOATE** and the reduction of an acyl chloride with lithium (tri-tert-butoxy)aluminum hydride, giving **6-OXODECANAL.**

The acetylene "zipper reaction" is illustrated by the conversion of **2-DECYN-1-OL** to **9-DECYN-1-OL** by the use of a mixture of potassium tert-butoxide and lithiated 1,3-diaminopropane. The next procedure involves the unusual reagent **[I,I-BIS(TRIFLUOROACETOXY)]-IODOBENZENE** in the formation of **CYCLOBUTYLAMINE HYDROCHLORIDE FROM CYCLOBUTANECARBOXAMIDE,** a version of the Hofmann rearrangement that proceeds under mildly acidic conditions. The **INVERSE ELECTRON DEMAND DIELS-ALDER REACTION OF AN ELECTRON-DEFICIENT HETEROCYCLIC AZADIENE** is illustrated by the preparation of **TRIETHYL 1,2,4-TRIAZINE-3,5,6-TRICARBOXYLATE.**

Stereospecific diazotization is used for the preparation of **(S)-2-CHLOROALKANOIC ACIDS OF HIGH ENANTIOMERIC PURITY FROM (S)-2-AMINO ACIDS.** The (S)-2-chloropropanoic acid produced in this process is reduced by lithium aluminum hydride to give (S)-2-chloropropan-1-ol, which is cyclized by base to give the optically active epoxide in **(R)-ALKYLOXIRANES OF HIGH ENANTIOMERIC PURITY FROM (S)-2-CHLOROALKANOIC ACIDS VIA (S)-2-CHLORO-1-ALKANOLS: (R)-METHYLOXIRANE.**

A version of the Grob fragmentation reaction is used to prepare an α,β-acetylenic ester in **UTILIZATION OF β-CHLORO ALKYLIDENE/ARYLIDENE MALONATES IN THE SYNTHESIS OF ETHYL CYCLOPROPYLPROPIOLATE.** Another uncommon process is illustrated in **OXIDATIVE CLEAVAGE OF AN AROMATIC RING: cis,cis-MONOMETHYL MUCONATE FROM 1,2-DIHYDROXYBENZENE.** A novel twist on the Beckmann rearrangement is demonstrated in **PREPARATION OF 2-PROPYL-1-AZACYCLOHEPTANE FROM CYCLOHEXANONE OXIME.** The next procedure is a preparation of **6-DIETHYLPHOSPHONOMETHYL-2,2-DIMETHYL-1,3-DIOXEN-4-ONE,** a useful reagent for the synthesis of acyl tetronic and tetramic acids. Following is a recipe for the preparation of the Davis oxidizing agent, **(±)-trans-2-(PHENYLSULFONYL)-3-PHENYLOXAZIRIDINE.** The procedure for the preparation of the important reagent **TRISAMMONIUM GERANYL DIPHOSPHATE** utilizes techniques not often used in organic chemistry laboratories, lyophyilization and ion exchange chromatography. The volume concludes with a preparation of **ETHYL α-(HYDROXYMETHYL)ACRYLATE,** a useful intermediate for the preparation of bis-electrophiles such as ethyl α-(bromomethyl)acrylate.

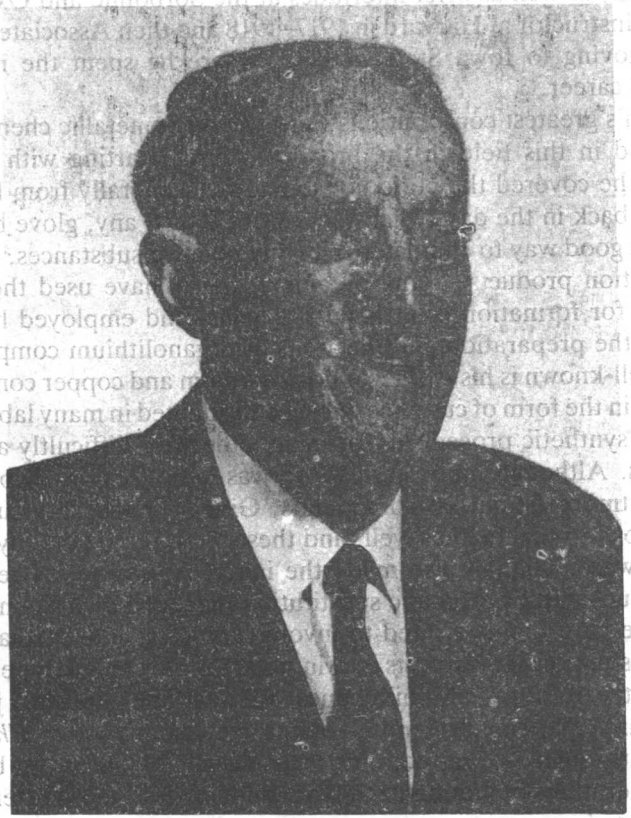
The Editors of *Organic Syntheses* welcome communications from the chemical community about important preparations or procedures that might be included in future volumes. These communications may take the form of an actual proposed submission (see the Organic Syntheses Proposal Format at the end of the paperback version of this volume) or suggestions about important reactions that the Board might solicit from some third party. Keep in mind that the philosophy of the publication is dual—to provide reliable procedures for the preparation of specific compounds and to demonstrate general procedures. If the purpose is to demonstrate a procedure, it is nevertheless important to select an application for which the demonstrated procedure is superior to other available methods for the specific product.

The Editors of *Organic Syntheses* continue to benefit from the outstanding service of Professor Jeremiah P. Freeman, our Secretary, and Dr. Theodora W. Greene, our Assistant Editor.

The structures were prepared with the ChemDraw program.

CLAYTON H. HEATHCOCK

Berkeley, California
June, 1987



HENRY GILMAN
May 9, 1893–November 7, 1986

Henry Gilman was one of the dominant figures in American organic chemistry of the 20th century. A man of exceptional will and foresight who made prodigious and seminal contributions to chemistry, at the time of his death he was 93 and the oldest living member of the Advisory Editorial Board of *Organic Syntheses*. He joined the Editorial Board in 1924 and was Editor-in-Chief in 1926.

Gilman was born in Boston on May 9, 1893 and graduated *summa cum laude* from Harvard in 1915, working for part of his undergraduate period in close association with Roger Adams, who was then instructor. Gilman obtained his A.M. and Ph.D. at Harvard with E. P. Kohler in

1917 and 1918, respectively, and also spent some time at Zurich with Staudinger, as well as brief interludes at the Sorbonne and Oxford. Gilman was instructor at Harvard in 1917–1918 and then Associate at Illinois before moving to Iowa State in 1919, where he spent the rest of his academic career.

Gilman's greatest contributions were to organometallic chemistry and he worked in this field in the broadest sense. Starting with Grignard reagents, he covered the periodic table rather generally from lithium to uranium, back in the days when there were few, if any, glove boxes and almost no good way to characterize highly reactive substances, except by their reaction products. Many organic chemists have used the Gilman color test for formation of Grignard reagents and employed his procedures for the preparation and reactions of organolithium compounds.

Less well-known is his early work on cadmium and copper compounds; the latter, in the form of cuprates, have been adapted in many laboratories for use in synthetic procedures for many otherwise difficultly accessible substances. Although much early work was done by F. S. Kipping and F. C. Whitmore on silicon compounds, Gilman made very substantial contributions to this field as well, and these were recognized by the first Kipping award. Gilman also made the initial discoveries of rearrangements in nucleophilic aromatic substitution reactions by lithium amides, which were later demonstrated to involve arynes as intermediates. Another of his important interests was in heterocyclic chemistry, especially the chemistry of furans and thiophenes. All in all, he published just over 1000 research papers. The multivolume treatise, *Organic Chemistry*, which ran through several editions, starting in 1938, was the bible for several generations of graduate students studying for their written or oral examinations.

Gilman epitomized the work ethic in organic research. Not only did he work hard himself, he expected at least as much from his students. With quite a reputation as a laboratory slave driver, he turned out a coterie of very well-trained and highly successful students, while at the same time gaining their respect and affection.

Besides the Kipping Award, Gilman received many honors; among them were membership in the National Academy of Sciences, foreign member of the Royal Society, the Midwest Award and the Priestly Medal of the American Chemical Society.

That half of his papers were published after he lost almost all of his sight as the result of a detached retina and glaucoma in 1947 is quite a tribute to his will and tenacity, both of which were greatly reinforced by the substantial efforts of Ruth, his charming wife of 57 years, who literally

acted as his eyes for almost forty years of their life together. Henry Gilman died on November 7, 1986 and his wife just shortly thereafter on January 28, 1987. His many contributions to Iowa State University are fittingly memorialized by a chemistry building, Gilman Hall, by a Gilman Graduate Fellowship Fund, and by annual Gilman Lectures.

JOHN D. ROBERTS

September 11, 1987

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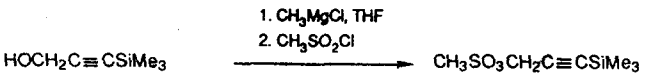
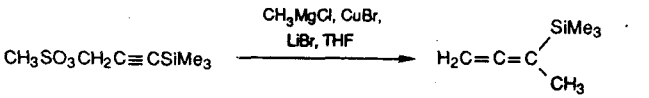
A GENERAL METHOD FOR THE SYNTHESIS OF ALLENYLSILANES: 1-METHYL-1-(TRIMETHYLSILYL)ALLENE

(Silane, trimethyl(1-methyl-1,2-propadienyl)-)





Submitted by Rick L. Danheiser, Yeun-Min Tsai, and David M. Fink.[1]
Checked by Marianne Marsi and Bruce E. Smart.

1. Procedure

A 500-mL, three-necked, round-bottomed flask is equipped with a magnetic stirring bar, rubber septum, low temperature thermometer, and a 250-mL pressure-equalizing dropping funnel fitted with a nitrogen inlet adapter (Note 1). The flask is charged with 30.0 g (0.234 mol) of 3-trimethylsilyl-2-propyn-1-ol (Note 2) and 230 mL of dry tetrahydrofuran (Note 3), and then cooled with an ice bath while 84 mL of a 2.8 M solution of methylmagnesium chloride in tetrahydrofuran (Note 4) is added at such a rate that the internal temperature does not rise above 10°C. Approximately 1.5 hr is required for the addition, after which time the gray solution is stirred at 0°C for 30 min, and then cooled below -70°C with a dry ice-acetone bath. Methanesulfonyl chloride (26.8 g, 0.234 mol) (Note 5) is added over 10 min via syringe, and after 30 min the cold bath is removed and the pale yellow reaction mixture is allowed to warm to room temperature over 2 hr.

A 2-L, three-necked, round-bottomed flask equipped with a vacuum adapter and two glass stoppers (Note 1) is charged with 21.4 g (0.246 mol) of anhydrous lithium bromide and 35.3 g (0.246 mol) of anhydrous cuprous bromide (Note 6). The reaction vessel is evacuated and the contents are briefly heated with a Bunsen burner flame. After 30 min the vacuum is replaced by nitrogen and the apparatus is equipped with a mechanical stirrer and two rubber septa. Dry tetrahydrofuran (260 mL) (Note 3) is added, and the resulting green solution containing a small amount of undissolved solid is cooled with an ice bath while 84 mL of a 2.8 M solution of methylmagnesium chloride in tetrahydrofuran (Note 4) is added rapidly via syringe over 1-2 min. After 20 min of further stirring at 0°C, the reaction mixture appears as a viscous yellow-green suspension. The solution of the mesylate derivative of 3-trimethylsilyl-2-propyn-1-ol prepared above is now transferred via cannula over 45 min to the reaction mixture, which is cooled below -70°C with a dry ice-acetone bath. After 30 min, the cold bath is removed and the green reaction mixture is stirred at room temperature for 2 hr. The blue-gray mixture is then poured into a 2-L Erlenmeyer flask containing a magnetically stirred mixture of 400 mL of pentane, 200 mL of water, and 400 mL of saturated ammonium chloride solution. The organic phase is separated and washed successively with two 200-mL portions of saturated ammonium chloride solution, ten 1-L portions of water (Note 7), and 100 mL of saturated sodium chloride solution. The organic phase is dried over anhydrous sodium sulfate, and the drying agent is removed by filtration. The solvent is removed from the filtrate by atmospheric distillation through a 10-cm Vigreux column. The residual liquid is carefully distilled through a 12-cm column packed with glass helices to give 21.3-22.2 g, (72-75%) of 1-methyl-1-(trimethylsilyl)-allene as a colorless liquid, bp 111°C (Notes 8-11).

2. Notes

1. The apparatus is flame-dried at 20 mm pressure and then maintained under an atmosphere of nitrogen during the course of the reaction.

2. 3-Trimethylsilyl-2-propyn-1-ol was obtained from Petrarch Systems, Inc. and used as received. Alternatively, it can be prepared by the silylation of 2-propyn-1-ol.[2]

3. Tetrahydrofuran was distilled from sodium benzophenone ketyl immediately before use.

4. Methylmagnesium chloride in tetrahydrofuran was purchased from Aldrich Chemical Company, Inc.

5. Methanesulfonyl chloride was obtained from the Aldrich Chemical Company, Inc. and purified by distillation from phosphorus pentoxide before use.

6. Lithium bromide, obtained from Aldrich Chemical Company, Inc., and cuprous bromide, supplied by Fluka Chemical Corporation, were dried at 120°C (0.02 mm) for 8 hr before use. The checkers obtained lower yields (54-58%) with cuprous bromide that was supplied by other commercial sources.

7. This procedure conveniently removes tetrahydrofuran from the organic phase.

8. The submitters report bp 112-113°C and state that an additional 2.2 g (7%) of product, bp 54-56°C (90 mm), can be obtained by combining the distillation forerun with the pot residue and redistilling the mixture at reduced pressure.