

ORGANIC SYNTHESES

AN ANNUAL PUBLICATION OF SATISFACTORY
METHODS FOR THE PREPARATION
OF ORGANIC CHEMICALS

VOLUME 64

1986

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ANDREW S. KENDE, *Editor-in-Chief*

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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 Division of the American Chemical Society. The soft cover edition is intended as the personal copy of the owner and is not for library use. A hard cover edition is published by John Wiley & Sons, Inc. in the traditional format, and differs in content primarily in the inclusion of an index. The hard cover 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 hard cover 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 adopted. For example, both diethyl ether and ethyl ether are normally used. Since ethyl ether is the established *Chemical Abstracts* name for the 8th Collective Index, it has been used in this volume. The 9th Collective Index name is 1,1'-oxybisethane, which the Editors consider too cumbersome.

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 that are of sufficient interest. Submissions that 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 or 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

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, again after submission of full experimental details and discussion, and, finally by checking experimental procedures. A form that details the preparation of a complete procedure (Notice to Submitters) may 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 be undertaken only when new methodology is involved. Substantially improved procedures have been included in the Collective Volumes in place of previously published procedures.

PREFACE

This annual volume presents 32 checked and edited procedures which the editors believe represent current research activity that would be useful to many synthetic chemists in diverse areas of organic chemistry. Unlike the emphasis on chiral synthesis in the previous volume, Volume 64 does not offer a principal unifying theme in its selection of procedures. Rather, the methods in Volume 64 in large measure parallel the chronological order in which approved contributions to *Organic Syntheses* became available for publication subsequent to checking. Nevertheless, the character of Volume 64 is heavily flavored by an emphasis on transformations of alkenes and alkynes, α -oxygenations of ketones, and the synthesis of diverse Michael acceptors.

The mild synthesis of acetylenes is described in the **CONVERSION OF METHYL KETONES INTO TERMINAL ALKYNES**, and the partial reduction of acetylenes is delineated in the preparations of **ETHYL ISOCROTONATE** and the **STEREOSPECIFIC REDUCTION OF PROPARGYL ALCOHOLS**. Related chemistry, accompanied by skeletal rearrangement, is seen in the formation of **2-ALKENYL CARBINOLS FROM 2-HALO KETONES**, and dichloroacetylene is involved in the **DICHLOROVINYLLATION OF AN ENOLATE**. A modification of the stereoselective Normant **ADDITION OF AN ETHYLCOPPER COMPLEX TO 1-OCTYNE** further illustrates the role of acetylenes in modern organic synthesis.

Alkene synthesis is represented by the convenient preparation given for **CYCLOBUTENE** and by the Horner-Emmons type intermediate **DIETHYL [(2-TETRAHYDROPYRANYLOXY)METHYL]PHOSPHONATE**. Highly electrophilic alkenes that could serve as Michael acceptors are in turn represented by the preparation of **DI-tert-BUTYL METHYLENEMALONATE** as well as of **PHENYL VINYL SULFONE AND SULFOXIDE**. A chiral Michael acceptor which effectively controls enantioselective conjugate addition of organometallic reagents is featured as **(S)-(+)-2-(p-TOLUENESULFINYL)-2-CYCLOPENTENONE: PRECURSOR FOR ENANTIOSELECTIVE SYNTHESIS OF 3-SUBSTITUTED CYCLOPENTANONES**. The selective reduction of olefinic compounds is exemplified by **SELECTIVE HYDROBORATION OF A 1,3,7-TRIENE: HOMOGERRANIOL** and by chemoselective reduction of the carboxyl group of an unsaturated ester acid in the synthesis of **ETHYL**

4-HYDROXYCROTONATE. Useful oxidative transformations of alkenes are found in the STEREOCONTROLLED IODOLACTONIZATION OF ACYCLIC OLEFINIC ACIDS and by the versatile OZONOLYTIC CLEAVAGE OF CYCLOHEXENE TO TERMINALLY DIFFERENTIATED PRODUCTS.

Three complementary procedures for the α -hydroxylation of ketones are offered for the synthetic chemist. They include the formation of α -HYDROXY KETONES FROM THE OXIDATION OF ENOL SILYL ETHERS WITH *m*-CHLOROPERBENZOIC ACID, the HYDROXYLATION OF ENOLATES WITH OXODIPEROXYMOLYBDENUM-(PYRIDINE)(HEXAMETHYLPHOSPHORIC TRIAMIDE) and the procedure by way of an α -hydroxyacetal intermediate, the α -HYDROXYLATION OF A KETONE USING *o*-IODOSYLBENZOIC ACID. This volume also teaches how to delete a hydroxyl group in DEOXYGENATION OF SECONDARY ALCOHOLS, of particular value in carbohydrate chemistry.

Condensation reactions, in many ways the mainstay of organic synthesis, are suitably represented in this volume. Examples include the CONDENSATION OF DIMETHYL 1,3-ACETONEDICARBOXYLATE WITH 1,2-DICARBONYL COMPOUNDS, the Vilsmeier-type synthesis of METHYL DIFORMYLACETATE, the use of Gold's reagent in β -DIMETHYLAMINOMETHYLENATION, the classical FORMYL TRANSFER TO GRIGNARD REAGENTS, and the regioselective STORK-DANHEISER KINETIC ALKYLATION PROCEDURE.

Small-ring heterocycles are involved in the synthesis of α -AMINO ACETALS and the CONVERSION OF EPOXIDES TO β -HYDROXY ISOCYANIDES. Heterocyclic synthesis is specifically featured in the preparation of 2,2':6',2''-TERPYRIDINE and of 1,3-DIMETHYLMIMIDAZOLE-2-THIONE. A general method is offered for ELECTROPHILIC N-AMINATION OF IMIDE SODIUM SALTS WITH *o*-DIPHENYLPHOSPHINYLDIHYDROXYLAMINE, and a pyrolytic reaction is exemplified in TOSYLHYDRAZONE SALT PYROLYSES: PHENYLDIAZOMETHANES. Finally, two syntheses of fluorinated reagents are offered at the end of this volume. They describe preparations of the highly reactive TRIFLUOROACETYL TRIFLATE and of the organic-soluble salt TRIS(DIMETHYLAMINO)SULFONIUM DIFLUOROTRIMETHYLSILICATE.

Diagrams of chiral molecules were drawn with geometric and topographic stereodescriptors according to a recently proposed convention (H. Maehr, *J. Chem. Educ.* 1985, 62, 114).

We hope that these 32 syntheses will provide stimulating and useful

reading and are indeed representative of the research interests of the organic synthesis community. In this context, the Board of Editors welcomes both the submission of preparations for future volumes and suggestions for change that will enhance the usefulness of *Organic Syntheses*. Submitters are kindly asked to examine the instructions appearing before the Preface in this volume that describe the type of preparation we wish to receive and also the information to be included in each contribution. A Notice to the Submitters for preparing manuscripts is available from the Secretary to the Board, and submitters are requested to follow its instructions.

We wish to especially acknowledge Professor Jeremiah P. Freeman, current Secretary to the Board, who has carried on the voluminous correspondence with the submitters and the checkers behind the scenes and who provided valuable guidance to the Editor-in-Chief. Dr. Freeman and his secretary, Mrs. Myra Martin, also assembled the Cumulative Author and Subject Indices, incorporating the indexing for Volume 64 done by Mrs. Roberta Ferron. We are indebted to Dr. Theodora W. Greene for providing the *Chemical Abstracts* names and registry numbers given in the appendix following each procedure as well as for her assistance in editing all the procedures. The structures and several of the tables of this volume were drawn with consummate skill by Dr. H. Maehr and his associates. We are also grateful to Professor Carl R. Johnson, currently Treasurer of *Organic Syntheses, Inc.*, for overseeing the publication of the soft cover version of Volume 64.

ANDREW S. KENDE

Rochester, New York
August 1985

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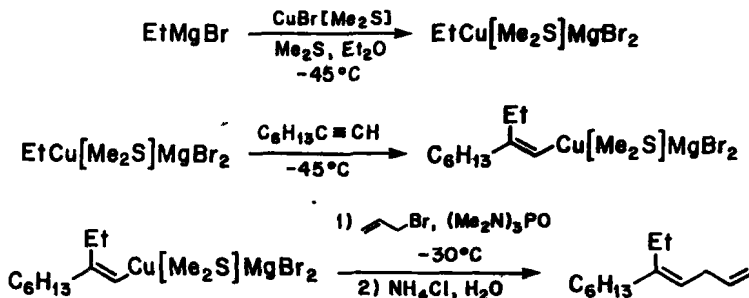
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ADDITION OF AN ETHYL COPPER COMPLEX TO 1-OCTYNE:

(E)-5-ETHYL-1,4-UNDECADIENE

(1,4-Undecadiene, 5-ethyl-, (E)-)



Submitted by Ramnath S. Iyer and Paul Helquist.¹

Checked by Brian H. Johnston and Andrew S. Kende.

1. Procedure

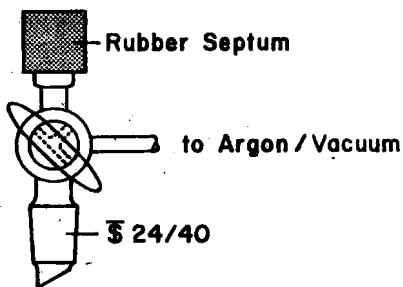
Caution! This experiment should be performed in an efficient fume hood because of the unpleasant odor of dimethyl sulfide.

A dry, 1-L, one-necked, round-bottomed flask is equipped with a Teflon-coated magnetic stirring bar and a three-way stopcock bearing a rubber septum (Note 1), and the flask is charged with 25.2 g (0.123 mol) of the dimethyl sulfide complex of cuprous bromide (Note 2). An argon or nitrogen (Note 3) atmosphere is established in the flask by repeated cycles of evacuation with an oil pump and refilling with the inert gas. Through use of a syringe or cannula, 150 mL of diethyl ether (Note 4) and 120 mL of dimethyl sulfide

(Note 4) are added. After the mixture is stirred for a few minutes at 25°C, the resulting clear and colorless solution is cooled to -15°C (Notes 5,6). A 2.73 M solution (45.0 mL, 0.123 mol) of ethylmagnesium bromide in ether (Note 7) is added dropwise with a syringe or cannula over a period of 10 min. The suspension of yellow-orange solid is stirred at -45°C for 2 hr, and 1-octyne (16.0 mL, 0.109 mol; Note 4) is added with a syringe or cannula over a period of 2 min. After the solution is stirred at -45°C for 2 hr, it is cooled to -78°C (Note 5) and maintained at this temperature during the successive additions of hexamethylphosphoric triamide (40 mL, 0.229 mol; Note 4) (*Caution: Hexamethylphosphoric triamide is a potent carcinogen. Avoid inhalation of vapor, ingestion of the liquid, and contact with skin.*) and allyl bromide (11.4 mL, 0.131 mol; Note 4). The mixture is immediately warmed to -30°C and stirred at -30°C for 12 hr; it is warmed to 0°C and quenched by the addition of 30 mL of a saturated, aqueous solution of ammonium chloride adjusted to pH 8 with ammonium hydroxide. The mixture is stirred at 25°C in the air for 1.5 hr (Note 8) and is then shaken in a separatory funnel with a mixture of additional diethyl ether (50 mL) and water (50 mL). The dark blue aqueous layer is drawn off and the organic layer is washed with additional 50-mL portions of the ammonium chloride solution (pH 8) until the washings are colorless. The organic layer is washed separately with water (50 mL) and saturated aqueous sodium chloride solution (50 mL), dried over anhydrous magnesium sulfate, filtered and concentrated by rotary evaporation at 25°C (25 min). The residue consists of 17.6 g of yellow oil which is purified by distillation under reduced pressure through a 15-cm Vigreux column to give 16.6 g (85%) of (E)-5-ethyl-1,4-undecadiene as a clear, colorless liquid, bp 56°C (0.70 mm; Note 9).

2. Notes

1. The stopcock is constructed as shown below so that a source of inert gas and vacuum may be attached to the horizontal tubulation and liquid reagents and solutions may be transferred into the reaction flask with a syringe needle or cannula inserted through a rubber septum placed over the end of the vertical tubulation. In order to avoid air leaks through the septum into the reaction flask when reagents are not being added, the stopcock is normally turned to close off the vertical tubulation, but to leave the flask open to the argon source.



2. This complex is prepared from cuprous bromide and dimethyl sulfide according to the procedure of House.² The complex must be pure white. Slightly impure samples will produce pinkish solutions which are unsatisfactory for this procedure. Normally, the complex is dark red when it is first prepared, but the required state of purity can be achieved by two or three recrystallizations under a nitrogen atmosphere as described by House.² We have found, however, that if the initially-formed complex has a distinctly green appearance, it cannot be purified satisfactorily. Others have also been concerned about this matter of purification.³

3. The checkers found that the yields were diminished if the reaction was run under prepurified nitrogen, but did obtain the reported yields using argon. The submitters, however, have never experienced difficulty using the prepurified nitrogen available in their laboratory.

4. Commercially-obtained materials were purified before use as described below. Diethyl ether was distilled from a dark blue or dark purple solution of sodium benzophenone radical anion or dianion under nitrogen. This solution was obtained by dissolving 10 g of benzophenone in 1 L of commercial anhydrous ether, adding 10 g of freshly pressed sodium wire, and heating the mixture at reflux under nitrogen until the characteristic blue or purple color developed. Dimethyl sulfide (Aldrich Chemical Company, Inc.), 1-octyne (Chemical Samples Company or Albany International Chemicals), and allyl bromide (Columbia Organics) were distilled under nitrogen at atmospheric pressure. Hexamethylphosphoric triamide (Aldrich Chemical Company, Inc.) was distilled at aspirator pressure from calcium hydride.

5. Constant temperatures were maintained by using dry ice-acetone (-78°C) or dry ice-acetone-carbon tetrachloride baths (-25° to -45°C ; the temperature tends toward the upper part of this range as the amount of acetone used is decreased) or more conveniently through the use of an acetone bath equipped with a Neslab CryoCool Model CC-100F low temperature unit, a Cole-Parmer Versa-Therm Model 2158 temperature controller, and a 500-W immersible heating coil. The temperature of the alkenylcopper solution must not be allowed to exceed -15°C ; above this temperature rapid coupling to give a diene occurs.

6. When the solution of the cuprous bromide complex is cooled, a portion of the reagent may precipitate, but this behavior does not affect the overall results of the experiment.

7. The ethylmagnesium bromide solution was obtained from Alfa Products, Morton Thiokol, Inc. and was titrated before use by the method of Watson and Eastham.⁴

8. Stirring the mixture in the air simplifies the workup procedure because cuprous complexes are oxidized to cupric compounds that are highly soluble in water or the aqueous ammonia workup medium of this experiment.

9. The spectral characteristics of the final product are as follows: IR (neat) cm^{-1} : 3080, 2960, 2915, 2800, 1660, 1640, 1465, 1175, 940, and 910; ^1H NMR (80 MHz, CDCl_3) δ : 5.50-6.05 (m, 1 H, alkenyl C-H), 4.70-5.20 (m, 3 H, other alkenyl C-H's), 2.63 (t, 2 H, $J = 6.5$, $\text{C}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$), 0.78-2.13 (several overlapping m, 18 H, other saturated C-H's); mass spectrum (70 eV) m/e (relative intensity) 181.1 ($M + 1$, 1.3), 180.1 (M , 9.2).

3. Discussion

The procedure that is described above provides an approach to trisubstituted alkenes, compounds that are very common among natural products and which serve as key intermediates in the synthesis of other types of compounds.⁵ The methods that have been developed for the preparation of trisubstituted alkenes are far too numerous to discuss to any significant extent here, but they have been the subject of previous review articles.⁶ Very briefly, however, a large portion of the available methods may be divided among the following categories:⁷ (1) elimination or cleavage reactions of organic halides and other compounds bearing leaving groups; (2) carbonyl condensation reactions of phosphonium ylides and other carbanionic or at least nucleophilic organic intermediates; (3) cleavage or rearrangements of other systems; (4) substitution reactions of alkenyl halides and related compounds;