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Collective Volume 7

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ORGANIC SYNTHESSES

PREFACE

Beginning a new tradition for *Organic Syntheses*, collective volumes will be compiled every 5 years instead of the previous 10. Thus Collective Volume VII contains procedures previously published in annual volumes 60–64 (1981–1985) but revised and updated in the light of experience and advances since their first appearance. This new format reflects in part the increased pace of research in organic chemistry and our belief that *Organic Syntheses* should be publishing the most up-to-date and significant procedures for the use of our readership. The Editor is grateful to the submitters for their cooperation in reviewing and updating their procedures. In a few instances the Editor has revised the original title so that each procedure has a title compound.

Through the efforts of Assistant Editor Theodora Greene the nomenclature, presentation of spectroscopic data, and other variable elements of style have been standardized during the preparation of recent annual volumes. She reexamined those volumes published before her association with the enterprise to ensure as much conformity as possible in this compendium.

In accord with past practice, extensive hazard warnings have been included. In addition we are now soliciting from submitters any information needed for special disposal problems. The Board of Editors is discouraging the use of potentially hazardous solvents such as benzene and hexamethylphosphoric triamide (HMPA) by asking submitters to replace them with others. In the particular case of HMPA procedures involving that solvent have been rechecked with a replacement. One of those (p. 326) appears in this volume.

In some instances changes have been made in the experimental procedure reflecting experience since their publication. In the case of the reduction of α -amino acids to amino alcohols, a version employing lithium aluminum hydride has been added to the original version, which used borane–dimethyl sulfide. The conversion of cycloheptanone to azocinone has been improved by extending the reaction time, which removes small amounts of the oxime that had contaminated the desired lactam. In the case of the preparation of the homochiral Wieland–Miescher ketone, some reactions in the procedure described by the original submitters have been included. Because of an unusual combination of circumstances, these submitters had not had the opportunity to review the checker's version of their procedure which appeared in Volume 63.

Following the practice of Collective Volume VI, the table of contents has been arranged alphabetically by title compound (not by the name of the method). Since this listing is probably the least used, this ordering, while often not keeping related procedures adjacent to each other, is likely to have the least effect on users. The concordance listing introduced in Collective Volume VI, which relates the title to the annual volume in which it first appears, is retained in the contents section. If one has a literature citation to an annual volume, the concordance index at the end of the volume allows the reader to find the latest version.

In this volume the Editor has returned to the earlier practice of multiple indices. Where names of title compounds, isolated intermediates, and uncommon reagents appear, they are accompanied by *Chemical Abstracts* registry numbers. In the titles in the text, the *Chemical Abstracts* name, which is usually different, is given below the main title name in brackets. The practice introduced in recent annual volumes, of following each

procedure with an appendix of *Chemical Abstracts* registry numbers and names has been dropped in this collective volume to save space, but, as indicated above, this information is retained in the indices.

The editors of *Organic Syntheses* welcome corrections, suggestions, and procedures being submitted for consideration by the Board of Editors. Prospective submitters should consult the section entitled "Submission of Preparations" at the front of one of the latest annual volumes for guidance. Correspondence should be addressed to the current Secretary of the Board of Editors of *Organic Syntheses*, Dr. Jeremiah P. Freeman, Department of Chemistry, University of Notre Dame, Notre Dame, IN 46556.

The Editor is grateful to the submitters, checkers, and editors of annual volumes 60-64 who made this collective volume possible. He is indebted to previous editors Richard E. Benson, Robert M. Coates, and the late William E. Sheppard for the useful Style Guide for *Organic Syntheses*, and to Theodora Greene, whose careful attention to the detail of this guide and whose skill in the use of *Chemical Abstracts* provides us with accurate nomenclature, registry numbers, and conformity of style. The major burden of this work as well as the preparation of the annual volumes in recent years has fallen to my secretary, Mrs. Myra Martin, whose diligence and passion for thoroughness has left these volumes as error-free as is humanly possible.

JEREMIAH P. FREEMAN

Notre Dame, Indiana
January 1990

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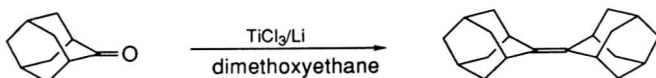
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REDUCTIVE COUPLING OF CARBONYLS TO ALKENES: ADAMANTYLIDENEADAMANTANE

(Tricyclo[3.3.1.1^{3,7}]decane, tricyclo[3.3.1.1^{3,7}]decylidene-)



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1. Procedure

A 2-L, three-necked flask is thoroughly flamed while being flushed with argon and is then fitted with three rubber septa. Anhydrous titanium trichloride (63.16 g, 0.409 mol) (Notes 1 and 2) is added to the weighed flask in an argon-filled glove bag. The flask is reweighed, and one of the rubber septa is replaced with a dry (12 hr at 120°C) reflux condenser through which a stream of argon is flowing (Note 3). The flask is fitted with a mechanical stirrer equipped with a glass shaft and Teflon paddle (Note 4). Into the flask is syringed 600 mL of 1,2-dimethoxyethane (Note 5), and the remaining rubber septum is exchanged for a glass stopper. Lithium (8.52 g, 1.23 mol) (Note 6) is etched to brilliance in methanol, quickly washed in petroleum ether (Note 7), and cut into small pieces directly into the stirred suspension. The mixture is heated at reflux for 1 hr by an oil bath that is then removed (Note 8). Immediately after the solvent has ceased to reflux, 2-adamantanone (15.36 g, 0.102 mol) (Note 1) is added in one portion, and the mixture is heated at reflux for 18 hr.

Stirring is maintained as the mixture is allowed to cool to room temperature, and 600 mL of petroleum ether (Note 7) is added in 100-mL portions at 5-min intervals (Note 9). The stirrer is disconnected from its motor, and the solution is poured into a sintered-glass funnel containing 50 g of Florisil (approximately 7 cm in depth) (Note 1). The black material remaining in the reaction vessel is washed with eight 50-mL portions of petroleum ether, which are poured into the same pad of Florisil (Notes 10 and 11). The filter pad is then washed with 400 mL of petroleum ether. Removal of the solvent from the combined filtrates by means of a rotary evaporator followed by high vacuum (0.05 mm) gives 12–13 g of a white crystalline solid. This crude product is dissolved in 3.5 L of hot methanol (Note 1), and the volume is reduced to 2 L by boiling. The solution is allowed to slowly cool to room temperature. The colorless needles are vacuum filtered through sintered glass (medium frit) and washed with 50 mL of ice-cold methanol. The crystals are dried under vacuum (0.05 mm Hg) to give 10.3–10.4 g (75–76%) of adamantylideneadamantane, mp 184–186°C; ¹H NMR (CDCl₃) δ: 1.5–2.1 (br m, 24 H) 2.7–3.1 (br m, 4 H). Concentration of the mother liquor to 350 mL and crystallization as described above yields an additional 1.2–1.5 g (9–11%) of product, mp 182–184°C (Note 12).

2. Notes

1. The following reagents were used as supplied: titanium trichloride from Alfa Products, Morton Thiokol, Inc.; 2-adamantanone from Aldrich Chemical Company, Inc.; methanol from MCB, Inc.; and acetone from Mallinckrodt, Inc.
2. Because of its sensitivity toward oxygen and water, anhydrous titanium trichloride should always be handled under an inert atmosphere. The submitters report that titanium trichloride in bottles that have been opened and resealed undergoes a slow deterioration that causes erratic results in the coupling reaction. This decomposition is frequently detectable by the evolution of white fumes from the titanium trichloride during transfer. If a number of small-scale reactions are to be performed, the use of a Schlenk tube is advisable to extend the useful life of the titanium trichloride.
3. Substitution of nitrogen for argon does not significantly decrease the yield.
4. The coupling reaction may be adversely affected if metallic stirrers are employed. The bore of the stirrer should be water-cooled. Lubricants such as mineral oil are to be avoided since they complicate product isolation.
5. The 1,2-dimethoxyethane was obtained from Aldrich Chemical Company, Inc., and was allowed to stand over molecular sieves (type 4A in $\frac{1}{16}$ -in. pellet form from Union Carbide Corporation) for several days. Final purification was accomplished by heating at reflux over potassium in a nitrogen atmosphere for at least 10 hr, followed by distillation from potassium. The solvent was used on the same day that it was distilled to minimize the formation of peroxides.
6. Lithium wire (3.2-mm diam, 0.02% sodium) was obtained from Alfa Products, Morton Thiokol, Inc., and was washed in petroleum ether before weighing.
7. Petroleum ether (bp 35–65°C) was obtained from Fisher Scientific Company and was distilled from potassium permanganate.
8. The color of the reaction mixture at this point varies from gray-green to gray-black. The success of the reaction seems to be independent of the color.
9. Addition of petroleum ether causes a viscous black precipitate to cling to the walls of the flask, leaving a milky-white solution that can be conveniently poured into the filter.
10. The black residue, which consists of inorganic salts, titanium, and unreacted lithium, is retained in the reaction vessel, where it is washed with petroleum ether while the mass is manually stirred with the paddle. No problem has been encountered in exposing the black material to the air during the washing procedure.
11. The black residue is destroyed in the following manner. The stirrer motor is reattached, and the flask is flushed with argon. The flask is cooled in an ice-water bath before adding 300 mL of petroleum ether and 300 mL of acetone. As the mixture is vigorously stirred, ca. 10 mL of methanol is added from a dropping funnel. After reaction has begun (an induction period of up to 0.5 hr may occur before gas evolution becomes noticeable), an additional 590 mL of methanol is added dropwise over a 6–10-hr period. Stirring is continued at 0°C until pieces

of lithium can no longer be seen (approximately 1 hr after the addition of the methanol has been completed).

12. The second crop is slightly impure, as shown by its NMR spectrum.

3. Discussion

Adamantylideneadamantane has been prepared by (1) photolysis of 2-adamantylketene dimer,² (2) reduction of 4*e*-chloroadamantylideneadamantane with sodium in liquid ammonia,³ (3) rearrangement of spiro[adamantane-2,4'-homoadamantan-5'-ol] with Lewis acids,^{4,5} (4) reduction of 2,2-dibromoadamantane with magnesium⁶ or zinc-copper couple,⁷ and (5) treatment of the azine of 2-adamantanone with hydrogen sulfide, followed by oxidation with lead tetraacetate and heating with triphenylphosphine.⁸

The present method is a modification of a previous procedure by the submitters.⁹ Handling of lithium in the air is less hazardous and more convenient than that of potassium, which was originally used. Higher yields were obtained when the higher-boiling solvent 1,2-dimethoxyethane was employed rather than tetrahydrofuran. Although the titanium trichloride-lithium system results in slightly lower yields for aliphatic ketones than the corresponding potassium method, the former is considerably more convenient for large-scale reactions. The lithium procedure is applicable to both aromatic and aliphatic aldehydes and ketones (Table I). Reductive coupling of unsymmetrical carbonyl compounds usually results in a mixture of geometric isomers.

Details of the titanium-induced dicarbonyl coupling reaction can be found in a full paper¹⁰ and in a review article.¹¹

TABLE I
REACTION OF KETONES AND ALDEHYDES WITH TITANIUM
TRICHLORIDE-LITHIUM IN 1,2-DIMETHOXYETHANE

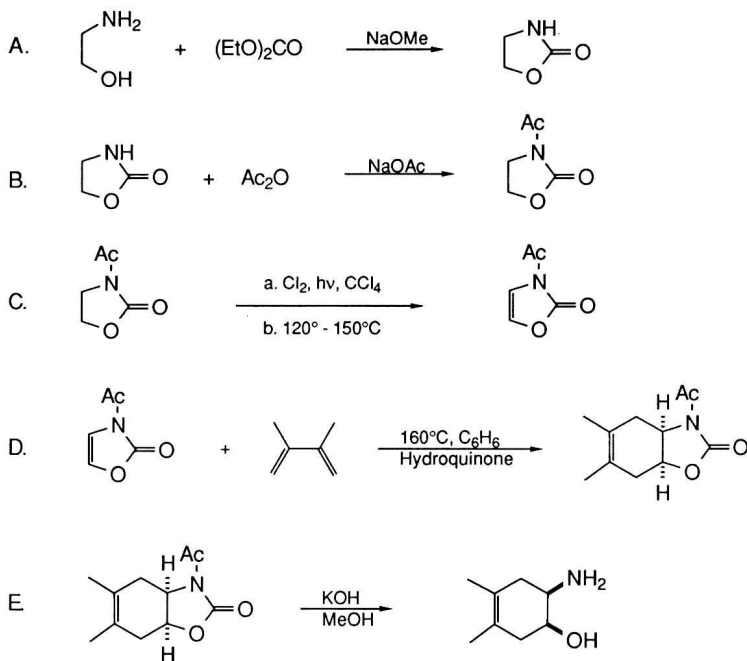
Carbonyl Compound	Yield of Alkene Product (%)
Acetophenone	94
Benzaldehyde	97
Benzophenone	96
Cholestanone	84
Cyclododecanone	90
Cycloheptanone	85
Cyclohexanone	81
Decanal	59
Hexanal	58 (28 : 72, <i>cis</i> : <i>trans</i>)

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SYNTHESIS AND DIELS-ALDER REACTIONS OF 3-ACETYL-2(3H)-OXAZOLONE: 6-AMINO-3,4-DIMETHYL-*cis*-3-CYCLOHEXEN-1-OL

[2(3H)-Oxazolone, 3-acetyl- and 3-cyclohexen-1-ol, 6-amino-3,4-dimethyl-, *cis*-]



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1. Procedure

A. *2-Oxazolidinone*. A 2-L, three-necked flask equipped with a thermometer, magnetic stirring bar, and a Vigreux column fitted with a distillation head is charged with 305 g (5.0 mol) of freshly distilled 2-aminoethanol, 730 g (6.2 mol) of diethyl carbonate, and 2.5 g (0.05 mol) of sodium methoxide (Note 1). The mixture is stirred

and the flask is heated in an oil bath maintained at 125–130°C. Ethanol begins to distill off when the internal temperature reaches 95–100°C. After heating for about 8 hr, the internal temperature reaches 125°C and ethanol ceases to distill (Note 2). The reaction mixture is allowed to cool to 60–70°C and is poured into 1 L of cold chloroform (Note 3). The resulting solution is chilled thoroughly in an ice–water bath and the precipitated product is recovered by filtration. The filtrate is concentrated to 250 mL and chilled to give a second crop. The combined crops are dried in a vacuum oven at 50°C to give 320–339 g (74–78%) of white crystals, mp 86–88°C [lit.² mp 87–89°C] (Note 4).

B. *3-Acetyl-2-oxazolidinone*. A 3-L, one-necked flask equipped with a reflux condenser and a magnetic stirring bar is charged with 326 g (3.75 mol) of 2-oxazolidinone, 94 g (1.15 mol) of anhydrous sodium acetate, and 1.6 L of acetic anhydride. The stirred solution is refluxed for 3 hr and the acetic anhydride is then removed by distillation at 15–20 mm. The residue is extracted with three 875-mL portions of boiling toluene (Note 5), and the hot toluene extractions are filtered, combined, and concentrated to a total volume of 675 mL. Diethyl ether (675 mL) is added with stirring to the toluene solution and the mixture is chilled in an ice–water bath. The precipitate is removed by filtration and washed with 250 mL of diethyl ether to give 328–403 g (68–83%) of colorless to very light tan crystals, mp 65–67°C [lit.² mp 69–70°C] (Note 6). A second crop of 63–24 g (13–5%), mp 65–68°C, is obtained by concentrating the filtrate to 275 mL and chilling it in an ice–water bath.

C. *3-Acetyl 4- and 5-chloro-2-oxazolidinone*. A 3-L, four-necked flask is equipped with a reflux condenser topped with a gas discharge tube, thermometer, fritted-glass inlet tube extending to the bottom of the flask, and a glass sleeve for accepting an ultraviolet (UV) lamp (Note 7). The reaction vessel is charged with 258 g (2.0 mol) of 3-acetyl-2-oxazolidinone, 2 L of carbon tetrachloride, and several boiling chips. The mixture is heated to gentle reflux, the light source is turned on, and 155 g (2.18 mol) of chlorine gas (Note 8) is introduced at such a rate that no chlorine escapes from the condenser (Note 9). After the addition is complete, heating is discontinued and nitrogen is bubbled through the reaction mixture to remove the dissolved hydrogen chloride. The solvent is then removed on a rotary evaporator to give a yellow oil, which consists of a mixture of 3-acetyl 4- and 5-chloro-2-oxazolidinones³ and is used in Step D without further purification.

D. *3-Acetyl-2(3H)-oxazolone*. The crude mixture of 3-acetyl 4- and 5-chloro-2-oxazolidinone from Step C is placed in a 2-L, three-necked flask equipped with a thermometer, sealed mechanical stirrer, and gas discharge tube. The material is heated to 120°C with stirring, and the temperature is then slowly increased to 150°C and held there until the evolution of gas ceases (Note 10). The cooled, black reaction mixture is distilled at 20 mm. The fractions boiling up to 150°C are collected and redistilled through a 50-cm × 3-cm Vigreux column fitted with a variable take-off head. There is obtained 140–172 g (55–68%) of product, bp 108–112°C (24 mm), which solidifies, mp 35–37°C (Note 11).

E. *4-Acetyl-7,8-dimethyl-2-oxa-4-azabicyclo[4.3.0]non-7-en-3-one*. A solution of 63.5 g (0.5 mol) of 3-acetyl-2(3H)-oxazolone, 27.5 g (0.33 mol) of 2,3-dimethylbu-