NAME REACTIONS AND REAGENTS IN ORGANIC SYNTHESIS Second Edition

This page Intentionally Left Blank

NAME REACTIONS AND REAGENTS IN ORGANIC SYNTHESIS

This page Intentionally Left Blank

NAME REACTIONS AND REAGENTS IN ORGANIC SYNTHESIS Second Edition

Bradford P. Mundy

Prof. of Chemistry, Emeritus Colby College Waterville, ME

Michael G. Ellerd

Maxim Technologies Bozeman, MT

Frank G. Favaloro, Jr. Helicon Therapeutics Farmingdale, NY



A JOHN WILEY & SONS, INC., PUBLICATION

Copyright © 2005 by John Wiley & Sons, Inc. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey. Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400, fax 978-646-8600, or on the web at <u>www.copyright.com</u>. Requests to the publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030. (201) 748-6008, fax (201) 748-6008.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herin may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our products and services contact our Customer Care Department within the U.S. at 877-762-2974, outside the U.S. at 317-572-3993 or fax 317-572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print, however, may not be available in electronic format.

Library of Congress Cataloging-in-Publication Data is available. ISBN 0-471-22854-0

Printed in the United States of America

10987654321

Preface

It has been a long haul. The start for this revision came almost the same way that the original edition started. For the first edition it was Mike Ellerd, then an undergraduate at Montana State, who organized my crude Name Reaction handouts so well that others encouraged the conversion into a book. At Colby College, Frank Favaloro did the same thing, making "study sheets" and adding to the list of Name Reactions. He graduated in 1996 and I started reformatting and expanding. With encouragement from Darla Henderson, this became a project. By then Frank had finished graduate school and was enthusiastic about participating. I had also retired from formal teaching and found much more time for creative work. The three of us started to work in earnest!

This edition differs substantially from the first by the inclusion of many modern Name Reactions instead of sticking exclusively with the old, tried and true. There are many reactions not covered; indeed, we ultimately eliminated those that had little contemporary use. We generally applied a "rule of thumb" that a newer name had to be cited by multiple authors. Therefore there are some relatively new protocols that have not stood the test of time; however the breadth of recent use warranted inclusion. As for reagents, we have focused on both Name Reagents and those whose acronyms are often used in place of the actual name. We have noted the common use of these forms in current literature.

First and foremost, this is a book to be used. Feel free to write in the text ... use any available blank space to add your own notes. Transform this into **your** book of Name Reactions! It is intended to serve as a starting point. Within a two page format for reactions and one page for reagents, the reader will find a basic, generalized definition / formula, a mechanism that conveys a possible course from starting material to product, notes which describe a few of the major highlights of the reaction or which points the reader to related reactions (by name or similarity) and recent examples of use. We have tried to convey the current mechanistic thinking with special care to show intermediate steps, point out proton exchanges, and sometimes suggest transition states, but without going through kinetics, isotope effects, etc.

Wherever appropriate, we have included references to selected secondary sources. They contain more detailed discussions on the topics introduced in this book. In all cases, we recommend use of the primary literature. The examples in the following pages are but a small taste of the detail, variation, scope and experimental detail available. Our choices reflect our personal interests; there is no "better or worse" implied! We tried to use current examples from journals that seem to be most commonly accessible, both in paper form and electronically, to student and professional alike. When recent references were difficult to come by, we made use of the abstracts and reaction-search engine of *SciFinder* (American Chemical Society). In these cases, we supplied a number [AN year: XXXX] that will allow ready access to the abstract. To the authors of the works we have chosen to describe, we hold the most sincere gratitude and we hope we have faithfully represented your work.

Colby College Waterville, ME Feb 1, 2005

ACKNOWLEDGMENTS

As always, completion of a project requires more than just the work of the authors. Without the consideration, support and patience of spouses: Margaret (Brad), Mary (Mike) and Michelle (Frank), this probably could not have been completed.

Special thanks goes to the chemistry community for their endless development of new methods for creating C-C and C-heteroatom bonds. It has been an enlightening experience to chronicle the explosion of new "named" reactions and protocols. We have not lost view of the obvious new participation of the world chemical community.

Each of us can thank mentors and special people that have given us encouragement:

Brad:

I still owe much to my formal mentors:

Richard F. Smith who first provided the excitement of chemistry, A.Paul Krapcho, graduate mentor and friend, and the late Henry Rapoport, postdoctoral advisor.

I thank my colleagues from Colby College, Dasan Thamattoor and Jeff Katz, for their help in reading parts of this manuscript. And, of course my former graduate and undergraduate students... two of the latter are now coauthors, who were the reason for my continued interest in the academic life. Special thanks goes to Prof.Tom Poon (Claremont McKenna, Pitzer, & Scripps Colleges) for a great two years as a Dreyfus Fellow with me at Colby. He taught me much, and worked closely with Frank Favaloro.

I would like to thank several Colby staff that made my working easier: Susan W. Cole of the Science Library could always be depended on to solve any library problem that developed in the absolutely great electronic resources of Colby College, and patiently put up with my many requests, piled up books and journals and general use of the library. The Colby College ITS staff was extremely good-natured and helpful for computer questions. Their help was greatly appreciated.

Mike:

My appreciation goes out to all of my professors at Montana State, who, years ago sparked my interest in chemistry, and to those who still today keep that interest very much alive.

Frank:

I would like to thank all of those who not only taught me organic chemistry, but also to be excited for the art it contains: Gordon W. Gribble, Tadashi Honda, Thomas Spencer, Peter Jacobi, David Lemal, Thomas Poon, Philip Previte and, most importantly, Brad Mundy. Thank you to the many friends and co-workers who provided support, advice and the occasional reference: Erin Pelkey, Janeta Popovici-Müller, Tara Kishbaugh, Jeanese Badenock, Alison Rinderspacher and Chaoyang Dai.

Of course a project with a publisher requires interaction. Darla Henderson, Amy Byers, Camille Carter and Dean Gonzalez were the people who kept the ball rolling and the project in focus.

Colby College Waterville, ME

Feb 1, 2005

CONTENTS

Acronyms and Abbreviations / viii Name Reactions / 1 Name Reagents and Acronyms / 714 Index / 872

ACRONYMS AND ABBREVIATIONS

Acronym	Name	
Ac	Acetyl	Me Contraction of the contractio
Acac	Acetylacetonate	Me Me
AcOH (HOAc)	Acetic acid	Ме -СООН
AIBN	2,2'-Azobisisobutyronitrile	Me NC−C−N≥N−C−CN Me Me
ACN	1,1'-Azobis-1-cyclohexanenitrile	$\sum_{N=N}^{CN NC}$
<u>9-BBN</u>	9-Borobicyclo[3.3.1]nonane	Н
<u>BINAP</u>	2,2'-Bis(Diphenylphosphino)-1,1'- binaphththyl	PP h ₂ .\PPh2
<u>BINOL</u>	1,1'-bi-2,2'-naphthol	он он
BITIP	Binol/Titanium isopropoxide	Ti(iPrO) ₄ / BINOL
<u>BMDA</u>	Bromomagnesium Diisopropylamide	$Me \xrightarrow[N]{Me} MgBr$ $Me \xrightarrow[Me]{Me} Me$
BMS	Borane Dimethylsulfide	BH ₃ -Me ₂ S

Acronyms and Ab	breviations	ix
<u>BMS</u>	Borane Dimethylsulfide	BH ₃ -Me ₂ S
Bn-	Benzyl	E CH2
Boc- (t-Boc)	t-Butoxycarbonylchloride	$\begin{cases} Me \\ \xi - C - O - C \\ H \\ O \\ Me \end{cases}$
BOM-	Benzyloxymethyl-	СН2-О-СН2-\$
Bs	Brosylate	
<u>Bu₃SnH</u>	tri-"butylstannane	ⁿ Bu) ₃ SnH
Bz	Benzoyl	
CAN	Ceric ammonium nitrate	$Ce(NH_4)_2(NO_3)_6$
CAS	Ceric ammonium sulfate	$Ce(NH_4)_4(SO_4)_4$
<u>Cbz-</u>	Carbobenzyloxy	$ \begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $
<u>CDI</u>	1,1'-Carbonyldiimidazole	
Cetyl	Hexadeca-	C ₁₆ H ₃₃ -
<u>cod</u>	Cyclooctadiene	$\bigcirc \bowtie$
ср	Cyclopentadienyl	Ô
ср*	Tetramethylcyclopentadienyl	Me Me Me Me Me
<u>CSA</u>	Camphorsulfonic Acid	HO ₃ S-H ₂ C
<u>DABCO</u> <u>TED</u>	1,4-Diazabicylo[2.2.2]octane, TED, triethylenediamine	

x		Acronyms and Abbreviations
<u>DAST</u>	Diethylamino)sulfur trifluoride	Et N -SF ₃ Et
DBN	1,5-Diazabicyclo[4.3.0]non-5-ene	
<u>DBU</u>	1,5-Diazabicyclo[5.4.0]undec-7-ene	
<u>DCC</u>	Dicyclohexylcarbodiimide	
<u>DDO</u>	2,3-Dichloro-5,6-dicyano-1,4- benzoquinone	
<u>DDO</u>	Dimethyldioxirane	$Me \xrightarrow{O}_{I}$
<u>DEAD</u>	Diethyl Azodicarboxylate	EtOOC-N=N-COOEt
DEIPS	Diethylisopropylsilyl	Et i-Pr-Si-Ş Et
DET	Dietkyl tartrate	OH EtOOC - CH-CH-COOEt HO in R-, S, and meso
<u>DIBAL</u> <u>DIBAL-H</u>	Disobutylaluminum hydride	$Me \qquad Me \qquad Me \qquad Me \qquad Me \qquad H$
DIEA DIPEA	Diisopropylethylamine <i>Hunig's base</i>	$Me \qquad Me \qquad$
<u>DIPT</u>	Diisopropyl tartrate	OH iPrOOC-CHCH-COOiPr HO in R-, S, and meso forms
<u>Diglyme</u>	Diethylene glycol dimethyl ether	MeO OMe

DMAP	4-(Dimethylamino)pyridine	
<u>DME</u>	1,2-Dimethoxyethane Glyme	MeO OMe
DMIPS	Dimethylisopropylsilyl	Me i-Pr-Si-\$ Me
DMF	Dimethylformamide	H-C, O
DMP	Dimethylpyrazole	Me Me
DMPU	N,N'-Dimethylpropyleneurea	Me. N. Me
DMS	Dimethylsulfide	Me ^{-S} Me
DMSO	Dimethylsulfoxide	Me-S-Me II O
DNP	2,4-dinitrophenyl	O ₂ N O ₂ N
dppe	1,2-Bis(diphenylphosphino)ethane (DIPHOS)	Ph-P $P-PhPh-Ph$ Ph
<u>dppp</u>	1,2-Bis(diphenylphosphino)propane	Ph-P $P-PhPh$ Ph Ph
ee	enantiomeric excess = % major enantiomer - % minor enantiomer	
Fmoc	9-Fluorenylmethoxycarbonyl	200

xii		Acronyms and Abbreviations
HCTU	2-(6-Chloro-1H-benzotriazole-1-yl)- 1,1,3,3-tetramethyluronium hexafluorophosphate	$(1) \qquad (1) $
HMPT HMPA	Hexamethylphosphoric triamide	Me M
НМТА	Hexamethylenetetramine	
НТІВ	Hydroxy(tosyloxy)-iodobenzene	OH O'S O'S
Im	Imidazoyl	
<u>Icp₂BH</u>	Diisopinocampheylborane	$Me Me Me B^2 H$
	Lead tetraacetate	$\begin{array}{c} OAc\\ AcO - Pb - OAc\\ OAc \end{array}$
<u>LTMP</u> <u>LiTMP</u>	Lithium 2,2,6,6- tetramethylpiperidide	Me Ne Me Me Li
<u>MAD</u>	Methylaluminum bis(2,6-di-t-butyl- 4-methylphenoxide)	Me 'Bu Bu' Me
МСРВА	m-Chlorperoxybenzoic acid	CI CO3H
MeCN	Acetonitrile	Me∼C≡N
<u>MEM-</u>	2-Methoxyethoxymethyl	MeO
Ms	Mesyl, Methanesulfonyl	S II S -Me S -Me S -Me O

Acronyms and Abbr	eviations	X111
МТМ	Methylthiomethyl	s-Me
MVK	Methyl Vinyl Ketone	Me
<u>NBS</u>	N-Bromosuccinimide	
<u>NCS</u>	N-Chlorosuccinimide	
<u>NMM</u>	4-Methylmorpholine	$\left(\begin{array}{c} Me \\ I \\ O \end{array} \right)$
<u>NMO</u>	N-Methylmorpoline-N-oxide	
NMP	N-Methylpyrrolidone	
PCC	Pyridinium chlorochromate Corey's Reagent	$ \begin{array}{c} & 0 \\ & \parallel \\ \oplus \stackrel{N}{H} & O \\ H \end{array} $
PDC	Pyridinium dichromate	$\left(\begin{array}{c} \textcircled{\textcircled{0}}_{N} \\ \overset{H}{\overset{H}}{\overset{H}}{\overset{H}}{\overset{H}}{\overset{H}}}}}}}}}$
<u>Pd(dba)2</u>	Bis(dibenzylideneacetone)palladium (0)	
РМВ	p-Methoxybenzyl	EH2-OMe
PNB	para-Nitrobenzoyl	
<u>PPA</u>	Polyphosphoric Acid	Unspecified mixture with High concentration of P_2O_5
<u>PTT</u> (PTAB)	Phenyltrimethylammonium tribromide Phenyltrimethylammonium perbromide	$ \begin{array}{c} Me & \bigcirc \\ Ph - N - Me & Br_3 \\ Ne & Me \end{array} $

xiv		Acronyms and Abbreviations
<u>PPTS</u>	Pyridinium para-toluenesulfonate	$ \begin{array}{ c c } & Me \\ \hline \\ \hline \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $
<u>PTSA</u>	p-Toluenesulfonic acid; Tosic acid	Me SO ₃ H
Ρν	Pivaloyl	$ \begin{array}{c} O Me \\ $
Ру	Pyridine	
<u>RAMP</u>	(R)-1-Amino-2- Methoxymethylpyrrolidine	H-N-N H -H OCH3
<u>SAMP</u>	(S)-1-Amino-2- Methoxymethylpyrrolidine Ender's Reagent	H-N-N H OCH3
SEM	2-Trimethylsilylethoxy-methoxy	Me Me Me Si O Jos
<u>SMEAH</u>	Sodium Bis(2- methoxyethoxy)aluminum Hydride	$ \begin{array}{c} \bigoplus \\ \text{OCH}_2\text{CH}_2\text{OMe} \\ \text{Na} \\ \text{H} - \text{Al} - \text{OCH}_2\text{CH}_2\text{OMe} \\ \text{I} \\ \text{H} \end{array} $
<u>TBAF</u>	Tetrabutylammonium fluoride	$ \begin{array}{cccc} Bu & \ominus \\ Bu - N & Bu \\ I & Bu \\ Bu & Bu \end{array} $
TBDPS	tert-Butyldiphenylsilyl	Ph t-Bu-Si- Ph
<u>TBHP</u>	t-Butyl hydroperoxide	$Me \rightarrow O Me \rightarrow O Me$
TBS TBDMS	<i>tert</i> -Butyldimethylsilyl	Me t-Bu-Si-Ş Me
TEA	Triethylamine	$ \begin{array}{c} Et \\ Et - N \\ Et \\ Et \end{array} $
<u>TEBA</u> <u>TEBAC</u>	Benzyltriethylammonium chloride	$ \begin{array}{c} $
<u>TEMPO</u>	2,2,6,6-Tetramethylpiperidin-1-oxyl	
·	······································	

TES	Triethylsilyl	Et Et – Si – Š Et
Tf	Triflate	O S S O CF ₃
THF	Tetrahydrofuran	$\langle \rangle$
ТНР	Tetrahydropyranyl	₹ Co
TIPS	Triisopropylsilyl	i-Pr i-Pr-Si-\$ i-Pr'
TMEDA	N,N,N',N'- Tetramethylethylenediamine	Me ⁻ N N ⁻ Me I I Me Me
<u>TPAP</u>	Tetra-n-Propylammonium Perruthenate	Pr ₄ N ⁺ RuO ₄ ⁻
ТРР	Triphenyl phosphine	Ph Ph-P h Ph
TMS	Trimethylsilyl	Me Me-Si-Ş Me
TMSOTE	Trimethylsilyltrifluoro- methanesulfonate	TMS ^{-O} SO ₂ CF ₃
TPS	Triphenylsilyl	$ \begin{array}{c} Ph\\ Ph-Si-\xi\\ Ph' \end{array} $
Тп	Trityl	Ph Ph Ph
Ts- Tos-	Tosyl p-toluenesulfonyl	

xv

This page Intentionally Left Blank

•

NAME REACTIONS

In this section we provide a summary of Name Reactions. The format is slightly modified from our previous book, but maintains the essential features:

Reaction:

Summary reaction.

Proposed Mechanism:

Currently accepted mechanisms. We have tried to be complete in showing steps, intermediates and the necessary curly arrow notations.

Notes:

Additional comments and references from key sources.

Examples:

Current examples if possible.

When a term is underlined, (for example, <u>Aldol Condensation</u>) it means that the concept can be found under an independent heading in the book.

General Bibliography:

B. P. Mundy, M. G. Ellerd, *Name Reactions and Reagents in Organic Synthesis*, John Wiley and sons, Inc., New York, 1988;

M. B. Smith, J. March in *March's Advanced Organic Chemistry*, 5th ed., John Wiley and Sons, Inc., New York, 2001;

T. Laue, A. Plagens, *Named Organic Reactions*, John Wiley and Sons, Inc., New York, 1998; V. K. Ahluwalia, R. K. Parashar, *Organic Reaction Mechanisms*, Alpha Science International Ltd., Pangbourne, U.K., 2002;

J. J. Li, Name Reactions, Springer, Berlin, 2002;

Comprehensive Organic Synthesis, B. M. Trost, editor-in-chief, Pergamon Press, Oxford, 1991; M. B. East, D. J. Ager, Desk Reference for Organic Chemists, Krieger Publishing Company, Malabar, FL, 1995;

M. Orchin, F. Kaplan, R. S. Macomber, R. M. Wilson, H. Zimmer, *The Vocabulary of Organic Chemistry*, John Wiley and Sons, Inc., New York, 1980;

A. Hassner, C. Stumer, Organic Syntheses Based on Name Reactions and Unnamed Reactions, Pergamon, Oxford, 1994;

The Merck Index, Merck & CO., Inc., Whitehouse Station, N. J. (now in the 13^{th} Edition) Each edition has an updated list of Named Reactions.

See also: http://themerckindex.cambridgesoft.com/TheMerckIndex/NameReactions/TOC.asp

Other URL's to Name Reaction Websites: <u>www.monomerchem.com/display4.html</u> <u>www.chempensoftware.com/organicreactions.htm</u> <u>www.organic-chemistry.org/namedreactions/</u> <u>http://orgchem.chem.uconn.edu/namereact/named.html</u>

Some references are provided with a SciFinder (American Chemical Society) number so that one can access the abstract if needed.

OEt

Acetoacetic Ester Synthesis

The Reaction:



Proposed Mechanism:





The methylene protons are the most acidic by influence from both carbonyls.

X can be Cl, Br, I, OTs, etc.





Alkylation can be done a second time (with a different R) if desired.

Ester hydrolysis/saponification, then with heat, the β -keto acid decarboxylates to give an enol.



keto-enol tautomerism

Notes:

Acetoacetic Ester can be prepared by the condensation of ethyl acetate, called the *Acetoacetic Ester Condensation Reaction*, a *Claisen Condensation*:



See M. B. Smith, J. March in *March's Advanced Organic Chemistry*, 5th ed., John Wiley and Sons, Inc., New York, 2001, p 549; and C. R. Hauser, B. E. Hudson, Jr., *Organic Reactions* 1, 9

Weiler Modification: By using very strong bases, a dianion can be formed that will preferentially alkylate at the methyl group:



S. N. Huckin, L. Weiler Journal of the American Chemical Society 1974, 96, 1082



Name Reaction

Examples:



C. S. Marvel, F. D. Hager, Organic Syntheses 1941, 1, 248



K. A. Parker, L. Resnick, Journal of Organic Chemistry 1995, 60, 5726





K. Mori, Tetrahedron 1974, 30, 4223



W. L. Meyer, M. J. Brannon, C. da G. Burgos, T. E. Goodwin, R. W. Howard, Journal of Organic Chemistry 1985, 50, 438

Acyloin Condensation

The Reaction:



Proposed Mechanism:

An electron adds to the

LUMO of the ester.





Alkoxide leaves to give a 1,2 dione that further reacts with electrons in solution.



Notes:

M. B. Smith, J. March in *March's Advanced Organic Chemistry*, 5th ed., John Wiley and Sons, Inc., New York, 2001, p 1562; T. Laue, A. Plagens, *Named Organic Reactions*, John Wiley and Sons, Inc., New York, 1998, pp. 1-3; S. M. McElvain, *Organic Reactions*, 4, 4; J. P. Schaefer, J. J. Bloomfield, *Organic Reactions*, 4, 15; J. J. Bloomsfield, J. M. Owsley, J. M. Nelke, *Organic Reactions* 23, 2

The *Rühlmann modification (Bouveault-Blanc Condensation or Rühlmann Reaction)* traps the dienolate as a TMS derivative. This protocol generally results in improved yields.



This reaction is better than either the <u>Dieckmann</u> or <u>Thorpe-Zeigler</u> reactions for preparing large rings.

Examples:



N. L. Allinger, Organic Syntheses 1963, 4, 840



E. Butkus, A. Ilinskasa, S. Stoniusa, R. Rozenbergasa, M. urbanováb, V. Setnikac, P. Bouc, K. Volkac, *Tetrahedron: Asymmetry* **2002**, <u>13</u>, 633



J. A. Marshall, J. C. Peterson, L. Lebioda, Journal of the American Chemical Society 1984, <u>106</u>, 6006



G. Mehta, R. Vidya, Journal of Organic Chemistry 2001, 66, 6913



M. J. Meyers, J. Sun, K. E. Carlson, B. S. Katzenellenbogen, J. A. Katzenellenbogen, *Journal of Medicinal Chemistry* **1999**, <u>42</u>, 2456



A. N. Blanchard, D. J. Burnell, Tetrahedron Letters 2001, 42, 4779

Acyloin Rearrangement

The Reaction:



Proposed Mechanism:

In acid:



In base:



Examples:



P. A. Bates, E. J. Ditzel, M. P. Hartshorn, H. T. Ing, K. E. Richards, W. T. Robinson, Tetrahedron Letters 1981, 22, 2325



T. Sate, T. Nagata, K. Maeda, S. Ohtsuka, Tetrahedron Letters 1994, 35, 5027

Name Reaction



a mixture of acyl esters

M. Rentzea, E. Hecker, Tetrahedron Letters 1982, 23, 1785



J. Liu, L. N. Mander, A. C. Willis, Tetrahedron 1998, 54, 11637

Adamantane Rearrangement (Schleyer Adamantization)

The Reaction:



Proposed Mechanism:

P. von R. Schleyer, P. Grubmeller, W. F. Maier, O. Vostrowsky, Tetrahedron Letters 1980, 21, 921

M. Farcasiu, E. W. Hagaman, E. Wenkert, P. von R. Schleyer Tetrahedron Letters 1981, 22, 1501

E. M. Engler, M. Farcasiu, A. Sevin, J. M. Cense, P. V. R. Schleyer, *Journal of the American Chemical Society* 1973, <u>95</u>, 5769

M. A. McKervey, Tetrahedron 1980, 36, 971 provides a useful review:

This reaction consists of a series of deprotonations, protonations, hydride transfers and <u>Wagner-Meerwein rearrangements</u>. There are postulated to be 2897 possible routes between starting material and product! A few of the steps have been tested experimentally; most of the data are computational. The following structural features seem to be supported:



Notes:

Tricyclic molecules having 10 carbon atoms are converted to adamantane with Lewis acids. Additional carbon atoms become alkyl appendages:



M. A. McKervey, Tetrahedron 1980, 36, 971

Name Reaction

Examples:



H. W. Whitlock, Jr., M. W. Siefken, Journal of the American Chemical Society 1968, 90, 4929

Verification of the first steps:



P. A. Krasutsky, I. R. Likhotvorik, A. L. Litvyn, A. G. Yurchenko, D. Van Engen Tetrahedron Letters 1990, <u>31</u>, 3973

Aldehyde Syntheses

Arens-van Dorp Cinnamaldehyde Synthesis



Bodroux-Chichibabin Aldehyde Synthesis



Bouveault Aldehyde Synthesis



DMSO-based Oxidations

Albright-Goldman Oxidation / Albright-Goldman Reagent





also for ketones

Swern Oxidation

$$R \stackrel{OH}{\underset{H}{\longleftarrow}} H \xrightarrow{\text{Oxalyl chloride, DMSO}} R \stackrel{O}{\underset{CH_2Cl_2}{\longleftarrow}} R \stackrel{O}{\underset{R}{\longleftarrow}} H$$

also for ketones

Dess-Martin Oxidation



also for ketones

Duff Reaction



Étard Reaction



Fukuyama Reduction



M. Kimura, M. Seki, Tetrahedron Letters 2004, 45, 3219