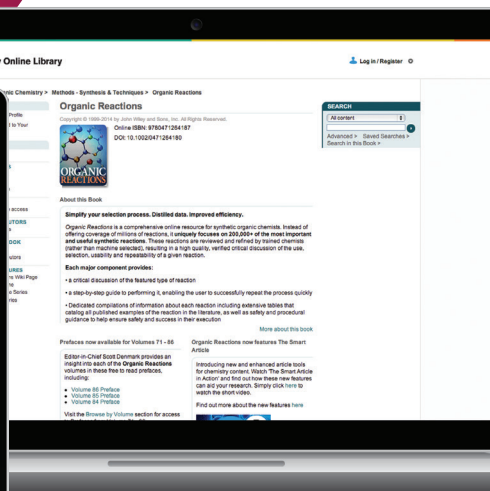
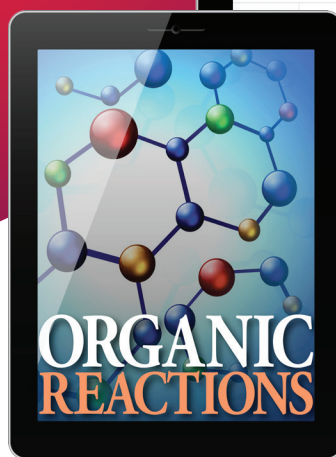


# 有機反応についての 最良の知識を凝縮した オンライン情報源

## Organic Reactions

Online ISBN: 978-0-471-26418-7

DOI: 10.1002/0471264180



世界的化学者  
による権威  
ある総説を  
収録

主要な有機  
反応タイプの  
概要と反応  
例が分かる

構造・反応  
検索を含む  
高い機能性

### Organic Reactions とは

- \* *Organic Reactions* は、1942年に創刊され現在まで刊行が続く伝統ある書籍シリーズです。2015年8月現在、86巻・約270章を出版済みです。
- \* 各章は「光延反応」「ヒドロホルミル化反応」「鉄触媒によるクロスカップリング反応」「ワッカー酸化」といった重要性・有用性の高い反応タイプに焦点を当てた総説として、反応機構・立体化学・適用範囲と限界・副反応・合成への応用・他の手法との比較・実験法などを分かりやすく記述します。
- \* 例えば[4+3]型付加環化反応にどのようなバリエーションがあるかといったように、特定の反応タイプの全体像を理解した上で、目的に合った反応を見つけることができます。
- \* 各章の執筆者にはArthur C. Cope, E. J. Corey, Carl Djerassi, 向山光昭、野依良治ら世界的な有機化学者が名前を連ね、ハンドピックで選んだ20万以上の反応例とともに権威ある解説を提供します。
- \* 詳しい情報はウェブでもご覧いただけます。 [www.wileyonlinelibrary.com/db/or](http://www.wileyonlinelibrary.com/db/or)

### オンライン版を選ぶ理由

- \* Organic Reactionsオンライン版は、冊子体と同じすぐれた内容を、ご契約機関のネットワーク内から24時間いつでも、同時アクセス無制限でご利用いただけます。
- \* 全文検索に加えて、cycloaddition(付加環化反応)のような反応タイプから関連する章を抽出したり、構造式・反応式を描画してそれが含まれる章を検索するなど、冊子体にはないパワフルな検索機能で必要な章をピンポイントで見つけることができます。

**期間限定!**  
冊子体からのお乗り  
かえキャンペーン

ご契約方法は ①一回払い(買い切り)と ②年間契約 のどちらかをお選びいただけます。価格はお客様の機関の規模によって決まります。

現在冊子体を継続でご購入中のお客様(または最近までご購入いただいたお客様)が2016年3月31日までにオンライン版を一回払いでご契約の場合、通常価格の40%引きとさせていただきます。

WILEY-VCH

お問い合わせは最寄りの洋書店または  
ワイリー・ジャパン(書籍営業)  
TEL (03) 3830-1232 E-MAIL [marketing@wiley.co.jp](mailto:marketing@wiley.co.jp)

WILEY

## 章を閲覧する

各章はabstract(抄録)から始まり、対象とする反応タイプ(この例では「ネバー転位」)を簡潔に記述します。Jump to...のドロップメニューを使うと、読みたいセクションにジャンプできます。本文は印刷・保存に便利なPDFでも提供されます。

Standard Article

### The Neber Rearrangement

William F. Berkowitz

Published Online: 31 OCT 2012  
DOI: 10.1002/0471264180.or078.02  
Copyright © 2004 by Organic Reactions, Inc.  
Published by John Wiley & Sons, Inc.

Book Title: Organic Reactions

Additional Information (Show All)  
How to Cite | Author Information | Publication History

Abstract

**Abstract**

An early investigation of the Beckmann rearrangement led Neber to discover that the mechanism of formation of 2*H*-azirines. Neber's subsequent papers described in detail the full range of reactions associated with the reaction, including  $\alpha$ -amino ketones formed by acidic hydrolysis of oximes promoted rearrangement of oxime O-derivatives, commonly O-sulfonates, representing the corresponding reaction of *N,N,N*-trimethylhydrazonium iodides, the "modified Neber rearrangement".

**Acknowledgments**

The author wishes to thank the staffs of Columbia University (NY) Chemistry Library, the Rosenthal and Mina Rees Libraries of Queens College, the Graduate School of the City University of New York, and the Medical Library of Memorial Sloan Kettering Institute for Cancer

SEARCH: All content, Advanced > Saved Searches > Search in this Book > Chemistry Structure Search >

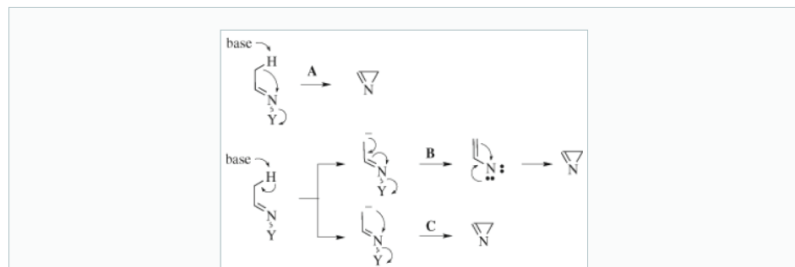
ARTICLE TOOLS: Save to My Profile, Export Citation for this Article, E-mail Link to this Article, Compound Browser On Off, Term Highlighter On Off, Share, Get PDF (1078K)

Jump to...  
Top of page  
Acknowledgments  
Introduction  
Mechanism and Stereochemistry  
Scope and Limitations  
Applications to Synthesis  
Comparison with other Methods  
Experimental Conditions  
Experimental Procedures  
Tabular Survey

### Mechanism and Stereochemistry

Neither the mechanism of the Neber rearrangement, nor whether a single mechanism operates for all substrates under all conditions, is firmly established. In this section, evidence for mechanisms that have been proposed will be presented and evaluated.

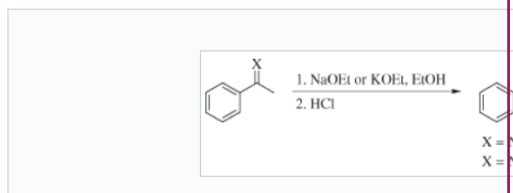
With respect to the mechanism for 2*H*-azirine formation, the three options that have been frequently discussed<sup>7, 8, 13, 17, 20-26</sup> are shown in Scheme 2.



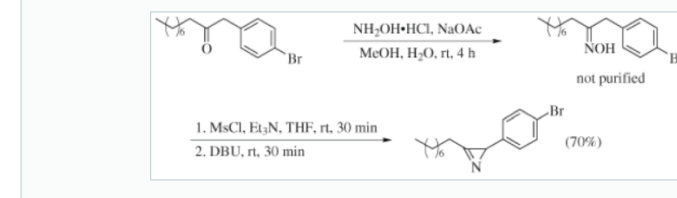
### Scope and Limitations

#### General Considerations

Whereas both oxime<sup>8</sup> and hydrazone<sup>42</sup> derivatives of aldehydes give nitriles when treated with a base, the majority of suitably activated ketoximes and the corresponding *N,N,N*-trimethylhydrazonium salts will undergo Neber rearrangements, provided that an  $\alpha$ -hydrogen is available. As noted in the preceding section, the success of the reaction is not dependent upon the configuration of the oxime derivative, and isomeric mixtures or single isomers of unknown configurations are often employed. Activated amidoximes also react to form 3-amino-2*H*-azirines or their hydrolysis products. Some failed attempts to induce Neber reactions are discussed in the Limitations and Side-Products section. Although *O*-tosyl oximes and hydrazone<sup>42</sup> derivatives are the derivatives most frequently employed, many other oxime derivatives are also suitable substrates. As expected, other sulfonates including benzenesulfonates,<sup>43-45</sup> 2,4,6-trimethyl-*s*-butylsulfonates,<sup>46</sup> and *O*-trichloroacetates<sup>53, 54</sup> are known. Although few direct comparisons are available (Eq. 7),<sup>55</sup> lead to the conclusion that the choice of leaving group has no predictable effect on the yield of  $\alpha$ -amino ketal.



### Experimental Procedures



#### 2-(4-Bromophenyl)-3-octyl-2*H*-azirine (Preparation of a 2*H*-Azirine from an *O*-Methanesulfonyl Oxime)<sup>47</sup>

Methanol (20 mL) and water (1 mL) were added to a mixture of 1-(4-bromophenyl)decan-2-one (0.631 g, 2.03 mmol), hydroxylamine hydrochloride (0.212 g, 3.05 mmol), and sodium acetate (0.250 g, 3.05 mmol) contained in a round-bottom flask. After stirring the mixture at rt for 4 h, the solvent was removed under vacuum. The reaction mixture was partitioned between MTBE and, sequentially, water, saturated aq NaHCO<sub>3</sub>, and brine. The combined organic extract was dried (Na<sub>2</sub>SO<sub>4</sub>). Concentration provided crude 1-(4-bromophenyl)decan-2-one oxime (0.635 g), which was used directly in the next reaction.

To a solution of the crude oxime (0.635 g) in THF (35 mL) was added triethylamine (296 mg, 2.93 mmol) and methanesulfonyl chloride (332 mg, 2.93 mmol) sequentially at rt. The solution became cloudy after the addition of the methanesulfonyl chloride. After 30 min, DBU (890 mg, 5.86 mmol) was added over 1 min. After 30 min, the reaction mixture was passed through a pad of silica gel, washing with MTBE. The eluate was concentrated under vacuum and the residue was chromatographed to give 3-(4-bromophenyl)-2-(1-octyl)-2*H*-azirine (437 mg, 1.42 mmol, 70% yield from the ketone) as a colorless oil. TLC R<sub>f</sub> 0.69 (petroleum ether/MTBE 4:1); IR (film) 2927, 2855, 1765, 1487, 830 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  0.88 (t, *J* = 6.8 Hz, 3H), 1.25–1.31 (m, 8H), 1.38–1.42 (m, 2H), 1.72–1.76 (m, 2H), 2.80 (t, *J* = 7.2 Hz, 2H), 2.82 (s, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H); <sup>13</sup>C NMR (100 MHz, solvent not given)  $\delta$  14.2, 22.8, 24.5, 27.1, 29.2, 29.3, 29.4, 31.9, 33.0, 120.5, 127.2, 131.4, 140.9, 167.5; HRMS (*m/z*): calcd for C<sub>16</sub>H<sub>22</sub>NBr, 307.0936; found, 307.0943.

各セクションでは、その章が扱う反応タイプの機構・立体化学・適用範囲と限界・副反応・合成への応用・他の手法との比較・実験法などが豊富な反応例とともに論じられます。参考文献を参照することもできます。

## 各章が取り上げる化合物が一目で分かる

各章のAbstractページ(タブで切り替え)では、その章の中で取り上げられる化合物を **Featured Compounds** として一覧できます。**View compound in article** をクリックすると、本文中の該当箇所にジャンプします。

### Abstract

An early investigation of the Beckmann rearrangement led Neber to discover that treatment of *O*-sulfonyl ketoximes with base led to the formation of 2*H*-azirines. Neber's subsequent papers described in detail the full panoply of reactions, intermediates, and byproducts associated with the reaction, including  $\alpha$ -amino ketones formed by acidic hydrolysis of the azirines. This chapter is devoted to the base-promoted rearrangement of oxime *O*-derivatives, commonly *O*-sulfonates, representing the original "Neber" rearrangement, and the corresponding reaction of *N,N,N*-trimethylhydrazonium iodides, the "modified Neber" rearrangement, discovered by Smith.

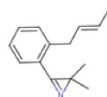
### Keywords:

Beckmann Rearrangement; Ketoximes; 2*H*-Azirines;  $\alpha$ -amino ketones; Neber Rearrangement

[View Full Article \(HTML\)](#)

### Featured Compounds

VIEW [1 - 250](#) | [251 - 500](#) | [501 - 750](#) | [751 - 861](#)



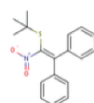
### Compound Information

Molecular Weight: 199.2915

Molecular Formula: C<sub>14</sub>H<sub>17</sub>N

InChIKey: IVOUFLRYERFMTA-SNAWJCMRSA-N

[View compound in article](#) | [Full details](#) | [Search for this compound](#)



### Compound Information

Molecular Weight: 313.414

Molecular Formula: C<sub>18</sub>H<sub>19</sub>NO<sub>2</sub>S

InChIKey: ZBGVUFUNOUPEBTQ-UHFFFAOYSA-N

[View compound in article](#) | [Full details](#) | [Search for this compound](#)

## 読みたい章を一覧から見つける

*Organic Reactions* に収録された各章は、章の表題順(Articles by Title)または冊子体の巻号順(Browse by Volume)に並べた中から選んで読むことができます。さらに、反応タイプを一覧の中から選んで、それに該当する反応とそれらを含む章を抽出することもできます。(下図)

トップページのメニューでReaction Typeをクリックして、表示された一覧から反応タイプを選びます。この例では"Diels-Alder"を選ぶと、それに関する3つの章がヒットします。

### Organic Reactions

Copyright © 1999-2014 by John Wiley and Sons, Inc. All Rights Reserved.

Online ISBN: 9780471264187

DOI: 10.1002/0471264180

SELECT A REACTION KEYWORD:

A B C D E F G H I J K L M N O P Q R S T U V W X Y Z 0-9

Diazotization  
Dieckmann condensation  
Diels-Alder  
Diels-Alder cycloaddition  
Diels-Alder cycloaddition; H  
Diels-Alder/Passerini  
Dihydroxylation  
Dihydroxylation of cis 1,2-di  
Dihydroxylation of trans 1,2  
Dimerization

VIEW 1 - 3

There are 13 matching reaction results from 3 articles

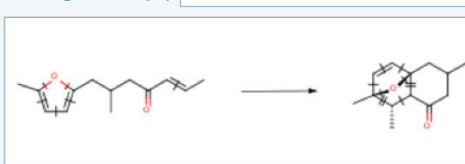
#### The Retro-Diels-Alder Reaction Part I. C—C Dienophiles Organic Reactions

Bruce Rickborn

Published Online : 15 APR 2004, DOI: 10.1002/0471264180.or052.01

[Abstract](#) | [Full Article \(HTML\)](#) | [Enhanced Article \(HTML\)](#) | [PDF\(4683K\)](#)  
[References](#)

Matching reaction (11)



Yield: 83 Temp: -65°C

[View reactions in article](#)

[View reaction details](#)

[Search for this reaction](#)

## 構造式・反応式による検索

*Organic Reactions* では、全文検索ができるだけでなく、構造式・反応式を描画またはアップロードして、それを含む章を検索することもできます。

構造式による検索は、メニューの Structure Search から実行します。Java アプレットを使えば、簡単なマウス操作で構造式を描けます。予め作っておいた構造式をアップロードすることも可能で、CDX, SMILES, MolFile, SDFFile, InChi など広く用いられるフォーマットに対応しています。

The screenshot shows the 'Organic Reactions' website interface. On the left is a 'BOOK MENU' with sections for 'FIND ARTICLES', 'GET ACCESS', 'FOR CONTRIBUTORS', 'ABOUT THIS BOOK', and 'SPECIAL FEATURES'. The 'FIND ARTICLES' section has 'Structure Search' highlighted. The main content area has a 'Name/Identifier' and 'Draw/Upload' button. Below is a drawing tool with a menu (File, Edit, View, Insert, Atom, Bond, Structure, Calculations, Services, Help) and a toolbar. A search box is in the top right corner.

構造式に矢印を追加することで、反応式を描いて検索に用いることができます。触媒・溶媒・温度などの条件を追加して、検索結果を絞り込むこともできます。

The screenshot shows the drawing tool interface with a chemical structure of a piperidine ring attached to a sulfonamide group. A blue arrow is drawn over the structure, indicating a reaction. The 'Atom' menu item is highlighted in the top toolbar. The bottom status bar shows 'Reaction Substructure'.

### Reaction Properties

Reaction Keyword, Catalyst, Solvent, Temperature, Yield

Reaction Keyword:

Catalyst Name:

Solvent Name:

Temperature (°C):   ?

Yield (%):