

W. Theilheimer

Synthetic Methods
of Organic Chemistry

17

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Yearbook

Synthetische Methoden der Organischen Chemie

Jahrbuch

Vol. 17

Mit deutschem Register-Schlüssel



BASEL (Switzerland)

S. KARGER

NEW YORK

Preface to Volume 17

Most of the references in this volume concern papers published between 1960 and 1962. The index includes volumes 16 and 17, the first two of the fourth series. It also contains additional or revised entries to former volumes.

I again wish to acknowledge with gratitude the help and advice I have had from Dr. John T. Plati, Dr. Bernhard Prijs, and Mr. Peter Schneider. I also want to thank Dr. William R. Sullivan, Director of Research Services, for his kind cooperation in matters concerning Hoffmann-La Roche Inc., Nutley, N. J., as headquarters of this enterprise, and Mrs. Carole Majdanski for skilled secretarial help.

Nutley, New Jersey, U.S.A., May 1963.

W. Th.

Vorwort zu Band 17

Die meisten Literaturzitate in diesem Band betreffen Arbeiten aus den Jahren 1960—1962. Das Register umfaßt die Bände 16 und 17, die ersten der vierten Serie, und enthält auch zusätzliche oder revidierte Schlagworte zu früheren Bänden.

Nutley, New Jersey, USA, im Mai 1963.

W. Th.

From the Prefaces to the Preceding Volumes

New methods for the synthesis of organic compounds, improvements of known methods, and also old proved methods scattered in periodicals, are being recorded continuously in this book series.

An attempt has been made to develop the system of Weygand (Organic Preparations, Interscience Publishers, Inc., New York, 1945), and to group the reactions on a simple, although purely formal, basis. This has led to the invention of reaction symbols that can be classified systematically so that the methods can be

treated without knowledge of the current trivial and author names (e.g., "Oxidation" and "Friedel-Crafts reaction").

Readers accustomed to the common notations will find these in the subject index. In many cases, particularly in searching for complex reactions, use of the classification system may be avoided by consulting the subject index. It is thought that the volumes should be kept close at hand. They should provide a quick survey, and obviate the immediate need for an elaborate library search. Syntheses are therefore recorded in the subject index by starting materials and end products, along with the systematic arrangement for the methods. This makes possible a sub-classification within the reaction symbols by reagents, a further methodical criterion. Complex compounds are indexed with cross references under the related simpler compounds. General terms, such as synthesis, replacement, heterocyclics, may also be brought to the special attention of the reader.

Starting with Volume 5, a table that indicates the sequence of the reagents has been included. It may help the reader to locate reactions in the body of the text, particularly within large chapters. This table also contains such frequently used reagents as NaOH and HCl, which are not included in the alphabetical index.

Volume 8 and subsequent volumes contain a brief review, *Trends in Synthetic Organic Chemistry*, stressing some highlights of general interest and calling attention to developments too recent to be included in the body of the text.

The abstracts are limited to the information needed for an appraisal of the applicability of a desired synthesis. This includes the number and nature of the reaction steps, the yield, and the important literature in question. In order to carry out a particular synthesis it is therefore still necessary to have recourse to the original papers or, at least, to an abstract journal. In order to avoid repetition, selections are made on the basis of most detailed description and best yields, whenever the same method is used in similar cases. Continuations of papers already included will not be abstracted, unless they contain essentially new information. They may, however, be quoted at the place corresponding to the abstracted papers. These supplementary references (see page 502) make it possible to keep abstracts of previous volumes up-to-date.

Furthermore, to avoid a "jungle" of references, the following limitations have been decided on: Papers are not included, if their content does not fit the subject matter of "Synthetic Methods" and if they can be found easily in the indexes of the abstract journals. Less accessible and readable papers, such as the Russian

or Japanese ones, are only abstracted, as a rule, if the method in question is described nowhere else. Since publications dealing with organic chemistry are increasing from year to year, some unintentional omissions may occur as well. Therefore, the editor will be grateful if important methods not yet mentioned are brought to his attention.

Syntheses that are split into their various steps, which are recorded in different places, can be followed with the help of the notations *startg. m. f.* (starting material for the preparation of . . .) and *prepn. s.* (preparation, see).

Aus den Vorworten zu den vorhergehenden Bänden

In dieser Buchreihe sollen neue Methoden zur Synthese organischer Verbindungen, Verbesserungen bekannter und auch bewährte ältere Methoden, die sich in den in Fachzeitschriften veröffentlichten Originalarbeiten verstreut vorfinden, laufend registriert werden.

Aufbauend auf der Weygandschen Systematik wurde versucht, alle Reaktionen an Hand weniger einfacher, wenn auch rein formaler Richtlinien zu ordnen. Dies führte zur Ausarbeitung von Reaktions-Formelzeichen, die sich im Gegensatz zu den bisherigen Trivial- bzw. Autorennamen, wie Oxydation, Friedel-Crafts-Synthese, systematisch anordnen lassen. Man kann so die Methoden, ohne ihre Namen zu kennen, mittels des Formelzeichens auffinden.

Benutzer, die an die alten Bezeichnungen gewöhnt sind, finden diese im alphabetischen Register, das in vielen Fällen den Gebrauch der Systematik entbehrlich machen und besonders zum Aufsuchen komplizierter Reaktionen mit Vorteil benutzt werden dürfte. Da die Sammlung für die Handbibliothek am Arbeitsplatz im Laboratorium gedacht ist, soll sie eine rasche Orientierung gestatten, ohne daß fürs erste die Literatur der Instituts- oder Werkbibliothek herangezogen werden muß. Neben der systematischen Registrierung der Methoden werden deshalb im alphabetischen Register auch Synthesen durch ihre Ausgangs- und Endprodukte registriert. Dies ermöglicht es, im Text, innerhalb der Reaktionszeichen, nach einem weiteren methodischen Kriterium, nämlich den Hilfsstoffen, einzuteilen. Neuartig ist ferner die Registrierung der komplizierten Verbindungen. Auf Sammelbegriffe wie Aufbau, Austausch, Heterocyclen sei noch besonders hingewiesen.

Von Band 5 an ist eine Tabelle aufgenommen worden, die die Reihenfolge der Hilfsstoffe angibt. Sie dürfte zum Aufsuchen von Reaktionen im Text, besonders in großen Kapiteln, nützlich sein. Sie enthält auch häufig gebrauchte Hilfsstoffe wie NaOH und HCl, die im alphabetischen Register nicht aufgeführt sind.

Band 8 und die folgenden Bände enthalten einen kurzen Überblick, «Trends in Synthetic Organic Chemistry», der einige der wichtigsten Fortschritte allgemeinen Interesses aufzeigt und auf neue Arbeiten hinweist, die nicht mehr in den Hauptteil des Bandes aufgenommen werden konnten.

Die Referate beschränken sich auf das zur Beurteilung der Zweckmäßigkeit einer Synthese Notwendige, wie Zahl und Art der Reaktionsstufen, die Ausbeute, wichtige, die Methode betreffende Literatur usw. Vor Ausführung einer bestimmten Synthese ist es deshalb erforderlich, das chemische Zentralblatt oder ein anderes Referatenblatt und, wenn möglich, auch die Originalarbeit zu Rate zu ziehen. Zur Vermeidung von Wiederholungen wurden bei der Anwendung einer Methode in ähnlichen Fällen diejenigen ausgewählt, die am ausführlichsten beschrieben sind und die besten Ausbeuten geben. Fortsetzungen bereits aufgenommener Arbeiten, die nichts wesentlich Neues bringen, werden nicht mehr referiert, evtl. aber an der Stelle der aufgenommenen Arbeit zitiert. Diese Ergänzungszitate (siehe Seite 502) ermöglichen es, Referate aus früheren Bänden auf den neuesten Stand zu bringen.

Um ferner das Material nicht zu sehr auf Kosten der Übersichtlichkeit anschwellen zu lassen, werden Veröffentlichungen, die nicht ganz in den Rahmen der «Synth. Meth.» passen und die in den Sachregistern der Referatenblätter leicht aufgefunden werden können, nicht aufgenommen. Arbeiten aus schwerer zugänglichen und lesbaren Zeitschriften, wie z. B. den russischen und japanischen, werden im allgemeinen nur dann referiert, wenn die betreffende Methode sonst nirgends beschrieben ist. Da die Zahl der Veröffentlichungen auf dem Gebiete der organischen Chemie von Jahr zu Jahr zunimmt, unterbleibt die Aufnahme von Arbeiten manchmal auch unabsichtlich. Wir wären deshalb dankbar, wenn wir auf wichtige Methoden aufmerksam gemacht würden, die in unserer Sammlung noch nicht enthalten sind.

Synthesen, die in ihre Stufen zerlegt und an verschiedenen Stellen eingeordnet sind, können mit Hilfe der Vermerke *startg. m. f.* (Ausgangsmaterial für die Darstellung von ...) und *prepn. s.* (Darstellung siehe) zusammengesetzt werden.

Method of Classification

The following directions serve to explain the system of Classification.

I. Reaction Symbols.

The first part of the symbol refers to the chemical bonds formed during the reaction. These bonds appear in the reaction symbols as the symbols for the two elements that have been linked together (e.g., the bond between hydrogen and nitrogen, as HN). The order of the elements is the same as in *Chemisches Zentralblatt*: H, O, N, Hal (Halogen), S, and the remaining elements (Rem). C is always placed last.

The "principle of the latest position" determines the order of the element symbols, and is used whenever possible.

The methods of obtaining a particular chemical bond are subdivided according to types of formation. Four types are distinguished: addition ($\downarrow$), rearrangement ($\cap$), exchange ($\updownarrow$), and elimination ($\uparrow$). The last part of the symbol refers to the bonds which are destroyed in the reaction or to a characteristic element of that part of the molecule which is eliminated.

The following simplifying stipulations facilitate the use of the reaction symbols: (1) The chemical bond is rigidly classified according to the structure formula without taking the reaction mechanism into consideration. (2) Double or triple bonds are treated as being equivalent to two or three single bonds, respectively. (3) Generally speaking, only stable organic compounds are taken into consideration. Intermediary compounds, such as Grignard compounds and sodiomalonic esters, and inorganic reactants, such as nitric acid, are therefore not expressed in the reaction symbols.

Examples:

see Volume II, page viii

Systematic Survey

see page 488

2. Reagents.

A further subdivision, not included in the reaction symbols, is made on the basis of the reagents characteristic of the reaction. The order usually follows that of the periodic system. Reagents made up of several components are arranged according to the element significant for the reaction (e.g., KMnO_4 under Mn, NaClO under Cl). When a constituent of the reagent goes into the products of the reaction, the remainder of the reagent, which acts as a carrier of this constituent, is the criterion for the classification; for example, phosphorus is the carrier in a chlorination with PCl_5 and sodium in a nitrosation with NaNO_2 . A table indicating the sequence of the reagents may be found on page 492.

3. The material between the listings of the reagents is arranged with the simple examples first and the more complicated ones following.

4. When changes in more than one chemical bond occur during a reaction, as, for example, in the formation of a new ring, or if the reaction can be carried out in different ways, these reactions are introduced in several places when necessary. The main entry in such cases is placed usually according to the "principle of the latest position"; the other entries are cross-referenced back to it.

Systematik

Für die Reihenfolge der Methoden gelten folgende Richtlinien:

1. Reaktionszeichen.

Die Einteilung erfolgt zuerst nach den Bindungen, die bei einer Reaktion entstehen. Diese erscheinen im Reaktions-Formelzeichen in Gestalt ihrer beiden Elementsymbole, z. B. die Bindung zwischen Wasserstoff und Stickstoff als HN. Die Reihenfolge der Elemente ist die gleiche wie im Chemischen Zentralblatt: H, O, N, Hal (Halogen), S, Rem (Übrige Elemente). C steht an letzter Stelle.

Das «Prinzip der letzten Stelle» bestimmt die Reihenfolge der Elementsymbole und ist auch sonst nach Möglichkeit immer angewandt worden.

Die Methoden zur Herstellung einer bestimmten Bindung werden nach ihrer Bildungsweise eingeteilt. Es werden 4 Fälle unterschieden: Aufnahme ($\downarrow$), Umlagerung ($\curvearrowright$), Austausch ($\updownarrow$) und Abgabe ($\uparrow$).

Der letzte Teil des Reaktionszeichens gibt die Bindung an, die

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gelöst wird, oder ein charakteristisches Element desjenigen Molekülteils, der abgespalten wird.

Die Bildung des Reaktionszeichens wird durch folgende vereinfachende Annahmen erleichtert:

1. Die Bindungen für die Registrierung ergeben sich rein formal aus den Strukturformeln, ohne daß auf Reaktionsmechanismen Rücksicht genommen wird.

2. Doppel- und Dreifachbindungen werden 2 bzw. 3 Einfachbindungen gleichgesetzt.

3. Es werden in der Regel nur stabile organische Verbindungen berücksichtigt. Zwischenprodukte, wie z. B. Grignard-Verbindungen, Na-Malonester und anorganische Reaktionspartner, wie z. B. Salpetersäure, werden deshalb nicht zur Bildung des Reaktionszeichens herangezogen.

Beispiele

siehe Band 2, Seite VI.

Systematische Uebersicht

siehe Seite 488.

2. Hilfsstoffe.

Eine weitere Unterteilung, die im Reaktionszeichen nicht mehr zum Ausdruck kommt, wird nach den für die Reaktion charakteristischen Hilfsstoffen vorgenommen. Ihre Reihenfolge richtet sich im wesentlichen nach dem periodischen System. Hilfsstoffe, die sich aus mehreren Bestandteilen zusammensetzen, werden nach demjenigen eingeteilt, der für die Reaktion verantwortlich ist, z. B. steht KMnO_4 bei Mn, NaClO bei Cl. Geht ein Bestandteil des Hilfsstoffs in das Reaktionsprodukt ein, dann ist der Rest als Träger dieses Bestandteils für die Einordnung maßgebend; das ist z. B. bei einer Chlorierung mit PCl_5 Phosphor, bei einer Nitrosierung mit NaNO_2 Natrium. Eine Tabelle der Reihenfolge der Hilfsstoffe befindet sich auf Seite 492.

3. Innerhalb dieser Unterteilung sind die einzelnen Referate von einfachen zu komplizierten Beispielen fortschreitend angeordnet.

4. Treten bei einer Reaktion Veränderungen an mehreren Bindungen ein, wie z. B. bei Ringschlüssen, oder kann sie auf verschiedene Art durchgeführt werden, dann wird sie, falls notwendig, an mehreren Stellen eingeordnet. Das Hauptzitat steht in diesen Fällen in der Regel an der letzten Stelle; an den übrigen Stellen befinden sich Hinweise auf dieses.

Trends

in Synthetic Organic Chemistry

1963

Photochemical reactions have gained much attention and have been applied with remarkable results. Thus, irradiation causes the rearrangement of the 6-membered rings A and B of 3-oxo-4,5-oxidosteroids to an azulene ring system in high yield¹. The santonin rearrangement is a similar profound molecular change induced by irradiation². Another interesting photochemical reaction is the addition of two fragments of acetylacetone to a carbon-carbon double bond³. Photocyclomerization may yield cyclobutane derivatives not otherwise accessible⁴.

A novel hydrogenation technique has been introduced, in which both catalyst and hydrogen are prepared in situ⁵. These investigations have also yielded highly active carbon-supported catalysts. Preferential reduction of diaryl ketones can be achieved by using lithium N-dihydropyridylaluminum hydride⁶. Base-sensitive oxo compounds can be reduced to hydroxy compounds by a 3-step sequence through diazo compounds⁷. Enamines can be hydrogenolyzed to alkenes with lithium aluminum hydride and aluminum chloride⁸.

Certain non-reactive chlorides can be dehydrochlorinated with sodium 1-butyl-2-cyclohexoxide without the use of an autoclave⁹. A simple and selective demethylation of o-methoxyphenols has been found¹⁰.

¹ *Synth. Meth.* 17, 786.

² D. H. R. Barton, J. E. D. Levisalles, and J. T. Pinhey, *Soc.* 1962, 3472; E. E. van Tamelen, K. Kirk, and G. Brieger, *Tetrah. Let.* 1962, 939.

³ *Synth. Meth.* 17, 751; s. a. *Can. J. Chem.* 41, 440 (1963).

⁴ G. O. Schenck et al., *B.* 95, 1409, 1642 (1962); *Bl. Soc. chim. Belg.* 71, No. 11/12 (devoted entirely to photochemistry), 781 (1962).

⁵ *Synth. Meth.* 17, 96.

⁶ *Synth. Meth.* 17, 58.

⁷ *Synth. Meth.* 17, 67.

⁸ J. W. Lewis and P. P. Lynch, *Proc. Chem. Soc.* 1963, 19.

⁹ *Synth. Meth.* 17, 953.

¹⁰ *Synth. Meth.* 17, 14.

Nickel peroxide, which is readily obtainable, has proved to be a useful oxidation agent¹¹. Permanganate oxidation is an effective general method for the conversion of aliphatic nitro into oxo compounds¹². α,β -Ethyleneketones as well as 1,4-naphthoquinones can be cheaply and safely epoxidized with hypochlorite¹³. A rapid direct preparation of peroxy acids in methanesulfonic acid has been published¹⁴. An efficient method for the oxidative removal of the methyl group in position 19 of steroids has been described¹⁵. The application of hydride transfer for carboxylations¹⁶ has been continued.

Difluoroamine is an efficient and direct deaminating agent for aliphatic and aromatic prim. amines and certain sec. amines¹⁷. A convenient mono- β -hydroxyethylation of amines has been reported¹⁸.

Amides can be easily prepared under mild conditions from acid chlorides with ammonium acetate¹⁹ and from oximes by a mild modification of the Beckmann rearrangement²⁰. Lactams can be prepared by this method from cyclic oximes. β - and γ -Lactams have been synthesized in a simple manner from aminomalonates²¹. α -Aminoacids can be converted into α -ketoacids and related compounds through 2-trifluoromethyl-5-oxazolones²².

An improved method for the preparation of nitriles and thiocyanates from halides with benzyltrimethylammonium salts²³ and a convenient preparation of both aliphatic and aromatic nitriles from aldehydes through N,N,N-trimethylhydrazonium salts have been reported²⁴. Nitriles can be easily converted into amidines with ammonium halides²⁵. Acylisocyanates can be conveniently prepared from amides with oxalyl chloride²⁶. A simple preparation of alkyl and aryl carbamates with N-carboxylsulfamic acid

¹¹ Synth. Meth. 17, 225.

¹² H. Shechter and F. T. Williams, Jr., J. Org. Chem. 27, 3699 (1962).

¹³ S. Marmor, J. Org. Chem. 28, 250 (1963).

¹⁴ Synth. Meth. 17, 145.

¹⁵ H. Ueberwasser et al., Helv. 46, 344 (1963).

¹⁶ H. Koch and J. Franken, B. 96, 213 (1963).

¹⁷ C. L. Bumgardner, K. J. Martin, and J. P. Freeman, Am. Soc. 85, 97 (1962).

¹⁸ F. H. Clarke, J. Org. Chem. 27, 3251 (1962).

¹⁹ P. A. Finan and G. A. Fothergill, Soc. 1962, 2824.

²⁰ J. Cymerman Craig and A. R. Naik, Am. Soc. 84, 3410 (1962).

²¹ Synth. Meth. 17, 869.

²² F. Weygand, W. Steglich, and H. Tanner, A. 658, 128 (1962).

²³ N. Sugimoto et al., Chem. Pharm. Bull. 10, 427 (1962).

²⁴ R. F. Smith and L. E. Walker, J. Org. Chem. 27, 4372 (1962).

²⁵ Synth. Meth. 17, 374.

²⁶ A. J. Speziale and L. R. Smith, J. Org. Chem. 27, 3742 (1962).

has been reported²⁷. An interesting phospholine oxide-catalyzed preparation of carbodiimides from isocyanates has been published²⁸. In situ preparation of intermediate carbodiimides, isocyanates, and isothiocyanates by metal ion-assisted elimination of mercaptans avoids the isolation of these difficult to handle compounds²⁹.

Efficient syntheses of N-monomethylated amino acids have been described³⁰. For the protection of amino groups in peptide syntheses, the 2-hydroxyarylidene system has the advantages of color and easy removal³¹. Carboxyl groups can be protected as phenylhydrazides and restored selectively without racemization by oxidation with manganese dioxide³². Protective groups containing coordinating parts that form stable metal chelates after hydrolysis can be removed in the presence of metal ions under remarkably mild conditions³³. Extensive literature is quoted in a review on the synthesis of biologically active peptides³⁴.

Nitrates have been prepared under mild conditions from chloroformates³⁵. Hydroxylamines can be obtained conveniently from oximes with diborane³⁶.

Unsym. sulfonium perchlorates can be efficiently prepared from sulfides and alcohols with perchloric acid. The non-nucleophilic nature of the perchlorate ion as compared to the halide ion makes the process irreversible and avoids alkyl interchange³⁷.

Catalytic reactions and condensations with alkoxides, alkyl compounds, hydrides, and amides of group I and II metals can be modified by using the boron ester complexes of the above reagents. In combination with solvent variations, this makes possible the establishment of highly selective reaction conditions³⁸. α -N-Pyridiniumdithioacetates have a remarkably high methylene activity, which allows aldol condensation even with a keto group³⁹. Tri-

²⁷ R. Graf, B. 96, 56 (1963).

²⁸ T. W. Campbell and J. J. Monagle, Am. Soc. 84, 1493, 3673 (1962).

²⁹ A. F. Ferris and B. A. Schutz, J. Org. Chem. 28, 71 (1963).

³⁰ P. Quitt, J. Hellerbach, and K. Vogler, Helv. 46, 327 (1963); H. Peter et al., Helv. 46, 577 (1963).

³¹ J. C. Sheehan and V. J. Grenda, Am. Soc. 84, 2417 (1962).

³² R. B. Kelly, J. Org. Chem. 28, 453 (1963).

³³ E. J. Corey and R. L. Dawson, Am. Soc. 84, 4899 (1962).

³⁴ J. Meienhofer, Chimia 12, 385 (1962).

³⁵ Synth. Meth. 17, 152.

³⁶ H. Feuer and B. F. Vincent, Jr., Am. Soc. 84, 3772 (1962).

³⁷ T. W. Milligan and B. C. Minor, J. Org. Chem. 28, 235 (1963).

³⁸ G. Hesse and M. Maurer, A. 658, 21 (1962).

³⁹ F. Kröhnke and K. Gelach, B. 95, 1108 (1962).

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phenylcarboxymethylphosphonium salts have also a high methylene activity. They react easily with diazonium salts of weak coupling ability⁴⁰. Various syntheses can be performed with mercaptals, which are metallated with remarkable ease⁴¹.

Syntheses by hydrogenolytic desulfuration of S-heterocyclics have found wide application. Long-chain hydroxycarboxylic acids and macrocyclic ketones have been prepared from thiophene derivatives⁴². The thianaphthene ring has also been used with this method⁴³. C-Labeled compounds have been prepared, and deuteriated compounds can be obtained by replacing the water in the hydrogenolysis step by D₂O⁴⁴.

H-Labeled olefins can be efficiently prepared by Wittig synthesis, which yields *trans*-olefins exclusively if performed with tricyclohexylphosphonium salts⁴⁵.

Improved cyclohydrations could be performed with cyclic acetals in place of the previously used imino derivatives of oxo compounds such as oximes or semicarbazones⁴⁶. A facile ring closure of suitably o-subst. benzonitriles to anthracene rings has been published⁴⁷. Cyclization of dinitriles with hydrogen halides affords an efficient isoquinoline ring synthesis⁴⁸.

The acyllactone rearrangement⁴⁹ has been simplified by using exchange resins instead of mineral acids as catalysts⁵⁰. Extension of this type of rearrangement to acyllactams gives a variety of pyrrolidine and piperidine derivatives related to alkaloids⁵¹. For the preparation of Δ^1 -pyrrolines and Δ^1 -piperideines, a new method has been found⁵². Easy access to 1-oxa- and 1-aza-azulene derivatives from tropones has been accomplished⁵³.

Acetylene derivatives are useful starting materials for the preparation of heterocyclics, e. t. thiazoles and imidazoles⁵⁴. Dicyano-

⁴⁰ G. Märkl, Z. Naturf. 17b, 782 (1962).

⁴¹ A. Fröling and J. F. Arens, R. 81, 1009 (1962).

⁴² Synth. Meth. 11, 139; 13, 130; 17, p. 51.

⁴³ Synth. Meth. 17, 126; R. Royer et al., J. Org. Chem. 27, 3808 (1962).

⁴⁴ Synth. Meth. 17, 126.

⁴⁵ H. J. Bestmann, O. Kratzer, and H. Simon, B. 95, 2750 (1962).

⁴⁶ C. K. Bradsher and J. C. Parham, J. Org. Chem. 28, 83 (1963).

⁴⁷ W. W. Zajac, Jr., and R. H. Denk, J. Org. Chem. 27, 3716 (1962).

⁴⁸ F. Johnson and W. A. Nasutavicus, J. Org. Chem. 27, 3953 (1962).

⁴⁹ s. Synth. Meth. 13, 218; 16, 647.

⁵⁰ K.-H. Büchel and F. Korte, Z. Naturf. 17b, 628 (1962).

⁵¹ K.-H. Büchel and F. Korte, B. 95, 2453 (1962) and other papers of this series.

⁵² W. Koller and P. Schlack, B. 96, 93 (1963).

⁵³ T. Nozoe, T. Mukai, and T. Suzuki, Bull. Chem. Soc. Japan 36, 38 (1963).

⁵⁴ Y. Yura, Chem. Pharm. Bull. 10, 372, 376, 1087, 1094 (1962).

acetylene proved to be a highly reactive acetylenic dienophile⁵⁵. Also cis-azo compounds are powerful dienophiles⁵⁶. A diene synthesis of pyridines from oxazoles has been used for a simple synthesis of pyridoxine⁵⁷. Propynylureas are the starting material for a facile preparation of otherwise inaccessible 1,3-disubst. 2-imidazolones⁵⁸.

Prim. phosphines can be conveniently obtained from halides and phosphine in the presence of aluminum chloride⁵⁹ and organotin hydrides from the corresponding halides with dialkyl-aluminum hydrides⁶⁰.

A simple and efficient synthesis of dihalocarbenes from trihalogenomethylmercury compounds has been published⁶¹.

Dimethylformamide derivatives have found new applications. The complex with sulfur trioxide previously used for the formation of peptide bonds⁶² has now been used for carbon-carbon condensations as well⁶³. Dimethylchloroformiminium chloride, readily available by reaction of phosgene or thionyl chloride with dimethylformamide, is a highly reactive compound and a versatile reagent⁶⁴.

Increasing use of dimethylacetamide as a solvent has been noticed⁶⁵. Tetramethylenesulfone has been used successfully as a solvent for N-quaternizations. It has a high dielectric constant and does not involve side reactions such as appear with nitrobenzene and dimethylformamide⁶⁶.

Dimethyl sulfoxide allows both the Wolff-Kishner reduction and the Cope elimination to be run at room temp.⁶⁷. It has also been used with advantage as a solvent in the permethylation of polyalcohols⁶⁸. With sodium hydride it forms the highly reactive

⁵⁵ C. D. Weis, *J. Org. Chem.* 28, 74 (1963).

⁵⁶ R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *Tetrah. Let.* 1962, 615.

⁵⁷ *Synth. Meth.* 16, 789; E. E. Harris et al., *J. Org. Chem.* 27, 2705 (1962).

⁵⁸ P. J. Stoffel and A. J. Speziale, *J. Org. Chem.* 27, 3079 (1962).

⁵⁹ *Synth. Meth.* 17, 713.

⁶⁰ *Synth. Meth.* 17, 50.

⁶¹ *Synth. Meth.* 17, 894.

⁶² *Synth. Meth.* 6, 432; 15, 350.

⁶³ *Synth. Meth.* 17, 836.

⁶⁴ *Synth. Meth.* 15, 184, 441; Zemlička, J. Smrt, and F. Šorm, *Tetrah. Let.* 1962, 397; W. Ziegenbein and K.-H. Hornung, *B.* 95, 2976 (1962).

⁶⁵ *Synth. Meth.* 17, 991; J. R. Campbell, *J. Org. Chem.* 27, 2207 (1962).

⁶⁶ C. K. Bradsher and J. C. Parham, *J. Org. Chem.* 28, 83 (1963).

⁶⁷ *Synth. Meth.* 17, 106.

⁶⁸ R. Kuhn and H. Trischmann, *B.* 96, 284 (1963).

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methyldisulfinyl carbanion, which allows improvement of various syntheses⁶⁶.

The following references in Vol. 16 under Trends have been entered in this volume⁷⁰.

1/892; 3/885; 4/864, 901; 5/893; 6/971; 7/971; 11/895; 12/889; 14/122; 15/444; 18/908; 19/827; 20/229; 21/129; 22/528; 24/477; 26/809; 27/187, 744; 28/741; 30/429; 32/970; 34/399; 35/850; 36/624; 37/853; 38/150; 39/155; 41/178; 42/766; 45/5; 45/5; 46/755; 47/774; 49/677; 50/907; 52/391; 54/28; 55/22, 83; 57/623; 59/473; 60/277, 278, 506.

⁶⁶ Synth. Meth. 17, 889, 895.

⁷⁰ The first figure refers to the footnote in Trends, Vol. 16, the second figure to the entry number in this volume.

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Formation of H—O Bond

Uptake

Addition to Oxygen and Carbon

HO↓OC

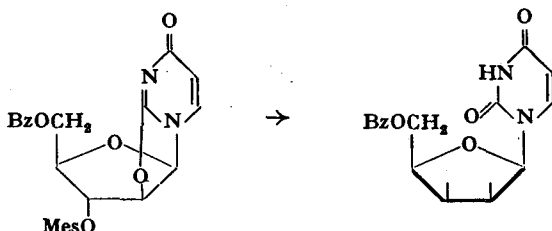
Without additional reagents

w.a.r.

Cyclonucleoside ring opening
with selective or partial O-demesylation

C

1.



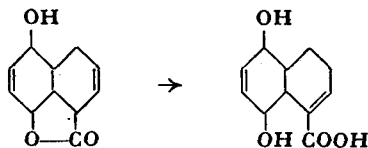
A mixture of 2,2'-anhydro-1-(5'-O-benzoyl-3'-O-mesyl- β -D-arabinofuranosyl)-uracil and water refluxed 4-5 hrs. $\rightarrow$ 1-(5'-O-benzoyl- β -D-lyxofuranosyl)uracil. Y: 83%.—This reaction is unusual from several viewpoints: it involves removal under mild conditions of a sec. mesyloxy group; this mesyloxy group is replaced with net inversion by a hydroxyl group in an acid medium; the reaction proceeds stereospecifically to a 2',3'-cis-configuration. F. e., also from the 3',5'-di-O-mesyl analog with partial O-demesylation, s. R. Fecher, J. F. Codington, and J. J. Fox, Am. Soc. 83, 1889 (1961).

Potassium hydroxide

KOH

Hydroxycarboxylic acids from lactones
with migration of a carbon-carbon double bond

2.



A mixture of *cis*-5,8-dihydroxy-1,4,5,8,9,10-hexahydronaphthoic acid 1 $\rightarrow$ 8-lactone, KOH, ethanol, and water refluxed 30 min. $\rightarrow$ *cis*-5,8-dihydroxy-3,4,5,8,9,10-hexahydronaphthoic acid. Y: 87%. L. Novák et al., Coll. 25, 2196 (1960).