

W. Theilheimer

Synthetic Methods
of Organic Chemistry

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Synthetic Methods of Organic Chemistry

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Preface to Volume 15

This is the final volume of the third series; it contains a cumulative alphabetical index to Volumes 11-15 and, in the body of the text, all reaction titles of these volumes. This arrangement again reduces a five-volume search to a search through a single volume. Most of the references in this volume concern papers published between 1958 and 1960.

I wish to acknowledge with gratitude the help and advice I have had from Dr. John T. Plati, Dr. Bernhard Prijs, and Dr. Peter Bamberg. Thanks are due again to Dr. J. A. Aeschlimann, Vice President of Hoffmann-La Roche, Inc., for liberally providing me with library and office facilities.

Nutley, New Jersey, U.S.A., May 1961.

W. Th.

Vorwort zu Band 15

Als letzter Band der dritten Serie enthält der vorliegende Band ein Generalregister für die Bände 11—15 und, im Text, alle Titel dieser Bände. Diese Anordnung reduziert wieder ein fünfmaliges Aufsuchen einer Methode auf ein einmaliges Nachschlagen. Die meisten Literaturzitate im vorliegenden Band betreffen Arbeiten aus den Jahren 1958—1960.

Nutley, New Jersey, USA, im Mai 1961.

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 664) 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 664) 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.

1. 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 ($\downarrow\downarrow$), rearrangement ($\curvearrowright$), exchange ($\updownarrow$), and elimination ($\uparrow\uparrow$). 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 656

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 659.

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

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 656.

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 Tafel der Reihenfolge der Hilfsstoffe befindet sich auf Seite 659.

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
1961

Peptide chemistry has advanced to such a stage that large protein-like molecules have become accessible. The rapid progress from the synthesis of oxytocin to that of a 23-unit peptide with the full activity of natural ACTH¹ and the determination of the amino acid sequence of still larger molecules opens the way to the synthesis of complex key materials of living organisms. Two new methods of forming the peptide bond without racemization have been published in a single paper². Simple peptide syntheses with active esters in glacial acetic acid³ and, under mild conditions, with phosgene and dimethylformamide⁴ have been reported. A recently published smooth method uses isoxazolium salts as reactants and enolesters as intermediates⁵. Formylation has been recommended for the protection of the amino groups, especially since the formyl group can be later removed by oxidation with hydrogen peroxide⁶. A mild procedure in aqueous medium for the well known phthalimido blocking of the amino groups has been published⁷. Temporary conversion of the thioether function of methionine into the sulfoxide has been useful in the synthesis of methionine containing peptides⁸.

Among noteworthy recent achievements may also be mentioned the total synthesis of steroidal sapogenins and certain steroidal alkaloids⁹, of griseofulvin independently by two groups¹⁰, of chlorophyll¹¹, and of coenzyme A, a complex nucleoside diphosphate¹².

¹ K. Hofmann et al., *Am. Soc.* **83**, 487 (1961).

² G. Losse and H. Heddlge, *A.* **636**, 144 (1960).

³ F. Weygand and W. Steglich, *B.* **93**, 2983 (1960).

⁴ M. Zaoral and Z. Arnold, *Tetrah. Let.* **1960**, No. 14, 9.

⁵ R. B. Woodward, R. A. Olofson, and H. Mayer, *Am. Soc.* **83**, 1007, 1010 (1961).

⁶ G. Losse and W. Zönnchen, *Ang. Ch.* **72**, 385 (1960); *A.* **636**, 140 (1960).

⁷ G. H. L. Nefkens, G. I. Tesser, and R. J. F. Nivard, *R.* **79**, 683 (1960).

⁸ B. Iselin, *Helv.* **44**, 61 (1961).

⁹ Y. Mazur, N. Danieli, and F. Sondheimer, *Am. Soc.* **82**, 5889 (1960).

¹⁰ A. Brossi et al., *Helv.* **43**, 2071 (1960); A. C. Day, J. Nabney, and A. I. Scott, *Proc. Chem. Soc.* **1960**, 284.

¹¹ R. B. Woodward et al., *Am. Soc.* **82**, 3800 (1960).

¹² J. G. Moffatt and H. G. Khorana, *Am. Soc.* **83**, 663 (1961).

The White deamination has been used successfully for the preparation of alcohols from amines¹³. Compounds with an aldehyde group at a quaternary carbon atom can be easily prepared from active halides and enamines¹⁴. A new class of β -alkoxyaldehydes with no α -H-atom is accessible by rearrangement of m-dioxanes¹⁵. Allylic alcohol groups can be converted into keto groups by Oppenauer oxidation without affecting other hydroxyl groups¹⁶. Under appropriate conditions, a sec. hydroxyl group can be directly esterified with retention of prim. hydroxyl groups¹⁷. High yields of acids can be obtained from trichloromethyl compounds under mild conditions when ferric chloride is used as catalyst¹⁸. Salts can be used in the reaction with α -diazoketones to produce α -subst. ketones if the respective free acids are not available or decompose the diazoketones. Excellent yields of α -ketothiocyanates have been obtained in this manner¹⁹.

Various O-functions can be easily replaced by chlorine with α,α -dichloromethyl ether and zinc chloride²⁰. Alkyl halides can be prepared from acids with red mercuric oxide more conveniently than through silver salts²¹. Mercaptopurines have been converted to chloropurines with chlorine in the presence of excess hydrogen chloride²².

Enzymatic hydrolysis is selective and can be applied to alkali- or acid-sensitive compounds²³. Certain hydroxyl groups in steroids can thus be deacylated smoothly and preferentially. Conditions have been found for a direct 4-alkylation of Δ^4 -3-ketosteroids making it a successful preparative method²⁴. 3-Oxo- Δ^1 -5 β -steroids have been made easily accessible through 1,11 α -oxidosteroids²⁵.

O-Methyl blocking groups, used e.g. in carbohydrate chemistry, can be readily removed at low temp. with boron chloride²⁶. The

¹³ Synth. Meth. 15, 269.

¹⁴ Synth. Meth. 15, 616.

¹⁵ C. S. Rondstvedt, Jr., and G. J. Mantell, Am. Soc. 82, 6419 (1960).

¹⁶ K. Heusler et al., Helv. 44, 179 (1961).

¹⁷ L. Almirante and G. Tosolini, J. Org. Chem. 26, 177 (1961).

¹⁸ M. E. Hill, J. Org. Chem. 25, 1115 (1960).

¹⁹ E. Fahr, A. 638, 1 (1960).

²⁰ Synth. Meth. 15, 438-440.

²¹ S. J. Cristol and W. C. Firth, Jr., J. Org. Chem. 26, 280 (1961).

²² R. K. Robins, J. Org. Chem. 26, 447 (1961).

²³ S. Noguchi, K. Morita, and M. Nishikawa, Chem. Pharm. Bull. 8, 563 (1960).

²⁴ Synth. Meth. 15, 627.

²⁵ J. Kalvoda et al., Helv. 44, 186 (1961).

²⁶ A. B. Foster, Soc. 1960, 2587.

reductive fission of cyclic trithiocarbonates provides a useful method for the preparation of dithiols²⁷.

High yields of diacylamines can be easily obtained from imino-chlorides and acids by Mumm-Hesse rearrangement²⁸. Certain aromatic amines can be conveniently oxidized to nitroso and nitro compounds with hydrogen peroxide²⁹. A facile synthesis of amidinium salts has been reported³⁰.

The reaction of phosphine with aliphatic aldehydes is a useful method of C-P bond formation³¹. Dialkyl phosphites are smoothly converted to pyrophosphates with nitrosyl chloride³². 2-Cyanoethyl phosphate has been introduced as a phosphorylating agent in the nucleotide field. The cyanoethyl group can be removed under mild alkaline conditions, which do not affect the essential part of the nucleotide³³.

Photolysis of aromatic iodo compounds may become a valuable tool in organic synthesis, because aryl radicals can be effectively generated at low temp. by this method³⁴.

A simultaneous reaction of isonitriles with two, three, or even more reactants gives complex molecules in generally high yield³⁵. Formaldehyde is particularly suited for such multi-component reactions and has also been used in 3-carbon condensations³⁶, which yield products not otherwise accessible.

The intermediate dehydration in the Barbier-Wieland degradation is facilitated if phenylmagnesium halide is replaced by the p-dimethylaminophenyl or anisyl analog³⁷.

The development of the chemistry of boranes continues with outstanding results: It has produced a convenient route to the less stable, terminally unsaturated compounds from the more stable, highly substituted ethylene derivatives³⁸, a facile procedure for the asymmetric synthesis of alcohols of high optical purity³⁹, and a

²⁷ Synth. Meth. 15, 487.

²⁸ F. Cramer and K. Baer, B. 93, 1231 (1960).

²⁹ R. R. Holmes and R. P. Bayer, Am. Soc. 82, 3454 (1960).

³⁰ E. C. Taylor and W. A. Ehrhart, Am. Soc. 82, 3138 (1960).

³¹ S. A. Buckler and V. P. Wystrach, Am. Soc. 83, 168 (1961).

³² J. Michalski and A. Zwierak, Chem. & Ind. 1960, 376.

³³ G. M. Tener, Am. Soc. 83, 159 (1961).

³⁴ W. Wolf and N. Kharasch, J. Org. Chem. 26, 283 (1961).

³⁵ Synth. Meth. 15, 523.

³⁶ H. Hellmann and D. Dietrich, A. 632, 73 (1960).

³⁷ M. Fetizon, M. Golfier, and A. Rassat, C. r. 252, 139 (1961).

³⁸ Synth. Meth. 15, 550.

³⁹ H. C. Brown and G. Zweifel, Am. Soc. 83, 486 (1961).

new general coupling reaction⁴⁰. Bis-(3-methyl-2-butyl)borane has been used for stereospecific and preferential hydration of C-C double bonds⁴¹. It exhibits remarkable selectivity permitting reductions otherwise not feasible⁴². The bonding of boron, more or less directly, to other hetero atoms, e.g. nitrogen and phosphorus, in carbon compounds⁴³ opens the road to a great variety of new materials. A development closely related and in many respects parallel to that of the boron compounds is that of organic aluminum compounds, to which an entire volume of Liebig's *Annalen der Chemie* (629) has been devoted. Silicon compounds have recently been used as intermediates in the preparation of N-acyl derivatives, certain N-heterocyclics, and other N-containing compounds⁴⁴. A growing number of publications on still other organo-metallic compounds, e.g. aromatic metal complexes⁴⁵, creates a steady transition from inorganic to organic chemistry, two areas formerly clearly set apart.

It has been found that Friedel-Crafts type catalysts, e.g. aluminum chloride, catalyze also diene syntheses⁴⁶. Unusual cyclic conjugated trienes and their cyclophane dimers can be obtained by a 1,6-Hofmann degradation across e.g., a furan or thiophene ring⁴⁷. Facile syntheses of aziridines through nitroso chlorides⁴⁸ and of aziridinium salts with diazomethane⁴⁹ have been described. A practical synthesis of certain azetidines has been reported⁵⁰. A modified Michael addition has been used for the synthesis of pyrroles and other N-heterocyclics⁵¹. α -Polyfluoroketones undergo a number of characteristic reactions and form amazingly stable cyclic compounds⁵². 4-Aminoquinazolines and other compounds with a condensed 4-aminopyrimidine ring can be prepared from

⁴⁰ H. C. Brown and C. H. Snyder, *Am. Soc.* **83**, 1001, 1002 (1961).

⁴¹ H. C. Brown and G. Zweifel, *Am. Soc.* **82**, 3222, 3223 (1960); **83**, 1241 (1961); F. Sondheimer and M. Nussim, *J. Org. Chem.* **26**, 630 (1961).

⁴² H. C. Brown and D. B. Bigley, *Am. Soc.* **83**, 486 (1961).

⁴³ M. F. Hawthorne, *Am. Soc.* **83**, 367 (1961).

⁴⁴ L. Birkofer, P. Richter, and A. Ritter, *B.* **93**, 2804, 2810 (1960); *Ang. Ch.* **73**, 143 (1961).

⁴⁵ E. O. Fischer and K. Plesske, *B.* **92**, 2841 (1959); *B.* **94**, 93 (1961).

⁴⁶ P. Yates and P. Eaton, *Am. Soc.* **82**, 4436 (1960); G. I. Fray and R. Robinson, *Am. Soc.* **83**, 249 (1961).

⁴⁷ H. E. Winberg et al., *Am. Soc.* **82**, 1428 (1960).

⁴⁸ G. L. Closs and S. J. Brois, *Am. Soc.* **82**, 6068 (1960).

⁴⁹ N. J. Leonard and K. Jann, *Am. Soc.* **82**, 6418 (1960).

⁵⁰ W. R. Vaughan et al., *J. Org. Chem.* **26**, 138 (1961).

⁵¹ J. B. Hendrickson and R. Rees, *Am. Soc.* **83**, 1250 (1961).

⁵² H. F. Simmons and D. W. Wiley, *Am. Soc.* **82**, 2288 (1960).

o-aminonitriles⁵³. A convenient method for the preparation of 2-subst. benzothiazole and benzoxazole rings has been found⁵⁴. Two methods have been reported for the preparation of the unusually stable perinaphthenium cation⁵⁵. The yohimbine skeleton can be obtained from 3-acetylindole by a simple procedure⁵⁶. A novel rearrangement of 5-nitroso-6-aminopyrimidines yields cyano-s-triazines⁵⁷.

The ring of certain cyclohexadienones can be easily opened by irradiation with ultraviolet light⁵⁸. A smooth base-catalyzed cleavage of certain pyrimidine ring has been discovered⁵⁹.

It has been noted that calcium boron hydride possesses an amazing stereospecificity in the reduction of ketones⁶⁰. The lower trialkyl phosphites are excellent reducing agents for ozonides⁶¹. Dehydrogenations have been performed with triphenylmethyl perchlorate⁶². Inorganic sulfates in the presence of sulfur or compounds with a lower valence state of sulfur have been recommended for oxidations, particularly of methyl to carboxyl groups⁶³. Also for oxidations and as substitute for peroxymonosulfuric acid a mixture of KHSO_5 , KHSO_4 , and K_2SO_4 has been recommended⁶⁴. Potassium methyl diazotate is a convenient substitute for diazo-methane⁶⁵ and azine monoxides are easily accessible and stable generators of diazo compounds in general⁶⁶.

An increasing application of N-methylpyrrolidone as a reaction medium has been noticed, e.g. in the Rosenmund-v. Braun nitrile synthesis⁶⁷, the halogenation of acetylene derivatives⁶⁸, and the synthesis of ethynylcarbinols⁶⁹. Pyridine is an excellent solvent for lithium aluminum hydride reactions⁶⁹.

⁵³ E. C. Taylor, R. J. Knopf, and A. L. Borrer, *Am. Soc.* 82, 3152 (1960).

⁵⁴ G. L. Jenkins, A. M. Knevel, and C. S. Davis, *J. Org. Chem.* 26, 274 (1961).

⁵⁵ *Synth. Meth.* 15, 698, 700.

⁵⁶ D. R. Liljegren and K. T. Potts, *Proc. Chem. Soc.* 1960, 340.

⁵⁷ E. C. Taylor, C. W. Jefford, and C. C. Cheng, *Am. Soc.* 83, 1261 (1961).

⁵⁸ *Synth. Meth.* 15, 584.

⁵⁹ E. C. Taylor et al., *Am. Soc.* 82, 6058 (1960).

⁶⁰ *Synth. Meth.* 15, 35.

⁶¹ *Synth. Meth.* 15, 168.

⁶² *Synth. Meth.* 15, 698; A. Schönberg and G. Schutz, *B.* 93, 1466 (1960).

⁶³ W. G. Toland, *Am. Soc.* 82, 1911 (1960).

⁶⁴ R. J. Kennedy and A. M. Stock, *J. Org. Chem.* 25, 1901 (1960).

⁶⁵ G. L. Closs and S. J. Brois, *Am. Soc.* 82, 6068 (1960).

⁶⁶ L. Horner, W. Kirmse, and H. Fernekesa, *B.* 94, 279 (1961).

⁶⁷ *Synth. Meth.* 15, 633.

⁶⁸ *Synth. Meth.* 4, 494; suppl. 15, p. 341.

⁶⁹ P. T. Lansbury, *Am. Soc.* 83, 429 (1961).

Solvent saponification has been used to remove water formed during reaction, e.g. with ethyl propionate as the solvent⁷⁰.

Mild reaction conditions have been attained by moving the reactant at high speed through the reactor, e.g. in cyclodehydrogenation⁷¹.

The following references in Vol. 14 under Trends have been entered in this volume⁷²:

3/69; 5/504; 7/496; 8/139-40; 9/696; 10/456, 500; 11/507; 12/132, 503; 13/295, 502; 14/294; 15/492; 16/505; 17/491; 18/92; 20/640; 21/276; 22/91; 23/555; 26/344; 27/123; 28/107; 29/70; 30/632; 31/8; 32/441; 33/190; 34/164; 36/346; 37/387; 38/398; 39/660; 40/442; 41/343; 42/303; 43/122; 44/17; 46/466; 47/479; 48/471; 49/105; 50/57; 51/83; 53/434; 54/611; 55/547; 56/85; 57/585; 58/275; 59/410; 60/331; 61/397; 62/61; 64/419; 65/663; 67/604; 68/297; 71/356; 72/51; 75/137; 77/121; 78/516, 521; 79/622; 80/447; 81/536; 82/630.

⁷⁰ S. L. Shapiro, K. Geiger, and L. Friedman, *J. Org. Chem.* 25, 1860 (1960).

⁷¹ L. A. Errede and J. P. Cassidy, *Am. Soc.* 82, 3653 (1960).

⁷² The first figure refers to the footnote in Trends, Vol. 14, the second figure to the entry number in this volume.

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