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Preface to Volume 12

Most of the references in the present volume concern papers published between 1955 and 1957. The index includes volumes 11 and 12, the first two of the third series. It also contains a few additional or revised entries to former volumes.

I want to thank Dr. John T. Plati once more for having checked the manuscript and Dr. Bernhard Prijs for his thorough proof-reading. I also greatly appreciate the valuable advice they have given me. 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 1958.

W. Th.

Vorwort zu Band 12

Die meisten Literaturzitate im vorliegenden Band betreffen Arbeiten aus den Jahren 1955—1957. Das Register umfaßt die Bände 11 und 12, die ersten der dritten Serie, und enthält einige zusätzliche oder revidierte Schlagworte zu früheren Bänden.

Nutley, New Jersey, USA, im Mai 1958.

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 539) 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 ihren 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 Re-

aktionszeichen, 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.

Beginnend mit Band 5 ist eine Tafel 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 so 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 539) ermöglichen es, Referate aus früheren Bänden auf den neuesten Stand zu bringen.

Um ferner das Material nicht zu sehr auf Kosten der Übersicht 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 (Ψ), rearrangement (∇), exchange ($\dagger\dagger$), 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 531

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 535.

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 ($\leftrightarrow$) 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 531.

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 535.

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

1958

Modern tools and techniques make possible the elucidation of intricate reaction mechanisms and the isolation of hitherto elusive intermediates. Although the extensive research on reaction mechanisms is usually beyond the scope of this compilation, some attention must be devoted to this subject when intermediates or their stabilized derivatives are used as starting materials for new reactions. Interesting examples of this kind, recently published, are a diene synthesis with the thermally unstable intermediate of a reversible Claisen rearrangement¹, the preparation of tetrazenes via diazo-like intermediates², the synthesis of isocyclics through an iron carbonyl complex³, the use of trialkyloxonium ions, which react like unstable free alkyl cations⁴, and reactions with radicals, e.g. substitution reactions⁵.

A number of general rules concerning stereochemistry has been suggested by Henbest and coll. in a series of papers⁶ dealing mostly with steroid derivatives. A detailed account of the total synthesis of reserpine, another of the brilliant stereospecific syntheses of Woodward and coll. has now been published⁷. Partially substituted sugars not readily available may be prepared by selectively blocking their equatorial hydroxyl groups⁸. A new convenient selective hydrolysis of sterically hindered esters also has been suggested as a diagnostic tool for differentiating axial from the less hindered equatorial carboxyls⁹. Stereoisomeric *cis*-glycols can be prepared by Woodward hydroxylation¹⁰ and osmium tetroxide hydroxylation¹¹ respectively¹².

Interesting reactions in the complex nucleotide field have been pub-

¹ Synth. Meth. 12, 729.

² W. R. McBride and H. W. Kruse, Am. Soc. 79, 572, 6568 (1957).

³ H. W. Sternberg, R. Markey, and I. Wender, Am. Soc. 80, 1009 (1958).

⁴ H. Meerwein et al., B. 89, 2060 (1956).

⁵ M. S. Kharasch, G. Sosnovsky, and A. Fono, Am. Soc. 80, 756 (1958); J. Org. Chem. 23, 324/5 (1958).

⁶ H. B. Henbest et al., Soc. 1957, 1958, 1965, 1974.

⁷ R. B. Woodward et al., Tetrahedron 2, 1 (1958).

⁸ Synth. Meth. 12, 159.

⁹ E. Wenkert and B. G. Jackson, Am. Soc. 80, 217 (1958).

¹⁰ Synth. Meth. 12, 201; J. Org. Chem. 23, 618 (1958).

¹¹ Synth. Meth. 2, 177/8.

¹² R. B. Woodward and F. V. Brutcher, Jr., Am. Soc. 80, 209 (1958).

lished¹³. They include a convenient one step preparation of phosphoramidates, improved methods for the synthesis of unsym. pyrophosphates¹⁴, a simple and selective method for the preparation of triphosphates¹⁵, and a convenient synthesis of polyphosphates from unprotected nucleotides by the use of N-subst. phosphoramidic acids¹⁶.

In peptide chemistry, several N-carbalkoxy groups have been introduced as protective groups having advantages over the conventional carbobenzoxy group, e.g. carbocyclopentoxyl¹⁷ and carbo-*tert*-butoxyl¹⁸. Formyl has also been recommended as an N-protective group¹⁹ and used as part of a thiazolidine protective system in the synthesis of cysteinyl peptides²⁰. Brenner and coll. have more extensively described their aminoacyl insertion reaction and its application in peptide synthesis²¹. The first naturally occurring cyclic peptide has been synthesized by the activated ester method²².

Hydrogenolysis of oxo compounds and alcohols has been performed with lithium aluminum hydride/aluminum chloride²³. Also hydrogenolysis of nitriles is possible in certain cases²⁴ as shown by Leonard and coll. in one of their interesting papers on piperidine chemistry, or, generally, on cyclic *tert.* amines²⁵. The reduction of acid azides to *prim.* alcohols is part of a new technical chloramphenicol synthesis²⁶.

A modified Wurtz synthesis with tetraphenylethanedisodium has been described²⁷. A novel way of increasing carbon chains by one atom has been found whereby the new atom is inserted between two atoms of a double bond²⁸. Glaser coupling has been improved by substituting amines, particularly *tert*-butylamine, for ammonia²⁹. A synthesis of aliphatic compounds through unsym. conjugated diacetylene derivatives has been devised³⁰. New catalysts have been used for the alkylation of ar-

¹³ Synth. Meth. 12, 162.

¹⁴ Synth. Meth. 12, 371.

¹⁵ M. Smith and H. G. Khorana, Am. Soc. 80, 1141 (1958).

¹⁶ Synth. Meth. 12, 165.

¹⁷ F. C. McKay and N. F. Albertson, Am. Soc. 79, 4686 (1957).

¹⁸ G. W. Anderson and A. C. McGregor, Am. Soc. 79, 6180 (1957).

¹⁹ J. C. Sheehan and D.-D. H. Yang, Am. Soc. 80, 1154 (1958).

²⁰ J. C. Sheehan and D.-D. H. Yang, Am. Soc. 80, 1158 (1958); cf. Synth. Meth. 12, 458.

²¹ M. Brenner et al., Helv. 40, 1497, 1933 (1957).

²² R. Schwyzer and P. Sieber, Helv. 40, 624 (1957).

²³ B. R. Brown and A. M. S. White, Soc. 1957, 3755.

²⁴ N. J. Leonard and F. P. Hauck, Jr., Am. Soc. 79, 5279 (1957).

²⁵ Synth. Meth. 12, 176; Am. Soc. 80, 371 (1958).

²⁶ G. Ehrhart, W. Siedel, and H. Nahm, B. 90, 2088 (1957).

²⁷ Synth. Meth. 12, 840.

²⁸ W. von E. Doering and P. M. LaFlamme, Tetrahedron 2, 75 (1958).

²⁹ M. D. Cameron and G. E. Bennett, J. Org. Chem. 22, 557 (1957).

³⁰ W. Chodkiewicz et al., C. r. 245, 322 (1957).

omatics with olefins. Phosphoric acid-boron fluoride is very effective in the alkylation of arenes³¹. Phenols have been alkylated with cation exchange resins as catalysts³² and predominantly o-alkylation of phenols and ar. amines has been achieved with aluminum³³. Carbon chains can be extended by attaching a variety of cyclic compounds and subsequently opening the rings. In addition to thiophene derivatives³⁴ and cycloalkane-carboxylates³⁵, dihydroresorcinol³⁶ and recently 1-morpholino-1-cyclohexene³⁷ have been used for this purpose.

Loudon's o-hydroxylation method^{37a} has been applied to the synthesis of 2-methoxyestrogens³⁸. Solid surfaces have been found to catalyze the decomposition of N'-sulfonylcarbohydrazides to aldehydes and consequently the McFadyen-Stevens aldehyde synthesis has been improved by addition of powdered glass³⁹. It may be a general phenomenon that solid surfaces catalyze reactions in which a gas is formed. The conversion of halides to oxo compounds with alkali salts of nitroparaffins⁴⁰ has been successfully applied to the preparation of α,β -ethyleneoxo compounds⁴¹. α,β -Ethyleneketones can also be prepared from α -diazoketones under mild conditions⁴². Pyrolysis of acetoacetic esters rather than hydrolysis has been recommended as ketone cleavage⁴³.

Alkylpropionic acids, the labile geometrical isomers of α,β -ethylene-carboxylic acids, and other α,β -unsatd. carboxylic acids can be conveniently made through 4-halogeno-5-pyrazolones⁴⁴. Complex and difficultly accessible derivatives of ketocarboxylic acids may be prepared through enollactones⁴⁵. A new route from ar. aldehydes to arylacetic acids has been found⁴⁶, which offers in certain cases, e.g. when a nitro

³¹ Y. M. Paushkin and M. V. Kurashev, *Izvest.* 1956, 1006; *C. A.* 51, 4973e; S. V. Zavgorodniĭ, L. S. Shvetsova, and B. S. Kromykh, *Ж* 26, 2180 (1956); *C. A.* 51, 4972c.

³² B. Loev and J. T. Massengale, *J. Org. Chem.* 22, 988 (1957).

³³ *Synth. Meth.* 12, 739; R. Stroh, W. Hahn et al., *Ang. Ch.* 69, 124, 699 (1957).

³⁴ *Synth. Meth.* 9, 146; 11, 139.

³⁵ *Synth. Meth.* 12, 860.

³⁶ *Synth. Meth.* 7, 202; K. J. Clark, *Soc.* 1957, 2202.

³⁷ S. Hünig, E. Lücke, and E. Benzing, *B.* 91, 129 (1958).

^{37a} *Synth. Meth.* 6, 162.

³⁸ J. Fishman, *Am. Soc.* 80, 1213 (1958).

³⁹ M. S. Newman and E. G. Caffisch, Jr., *Am. Soc.* 80, 862 (1958).

⁴⁰ *Synth. Meth.* 10, 201.

⁴¹ M. Montavon et al., *Helv.* 40, 1250 (1957).

⁴² V. Franzen, *A.* 602, 199 (1957).

⁴³ W. J. Bailey and J. J. Daly, Jr., *J. Org. Chem.* 22, 1189 (1957).

⁴⁴ L. A. Carpino, *Am. Soc.* 80, 599, 601 (1958).

⁴⁵ E. J. Cragoe, Jr., and A. M. Pietruszkiewicz, *J. Org. Chem.* 22, 1338 (1957).

⁴⁶ *Synth. Meth.* 12, 794.

group is involved, advantages over Erlenmeyer's azlactone synthesis. In the course of their investigations of allenic acids, Wotiz and coll. found a novel method for the preparation of highly branched unsatd. malonic acids⁴⁷. Cyanomethyl esters⁴⁸ have been used successfully for the preparation of N²-subst. hydrazides⁴⁹.

Hydrazine in the presence of nickel is a versatile reducing agent for nitrogen compounds⁵⁰. Amino- from nitro-indoles have been prepared recently in high yields⁵¹ with this reagent. It has been found that ammonium salts promote the Japp-Klingemann reaction⁵². Amidines can be prepared by rearrangement of hydrazones⁵³. Diazonium salts have been converted to sulfonylchlorides and sulfonic acids with sulfur dioxide⁵⁴.

The use of aluminum halides, particularly aluminum iodide, has been found to be advantageous in replacement reactions to form halides⁵⁵. Perchloryl fluoride, an interesting reagent recently introduced, furnishes e.g. a new functional group, perchloryl, as a substituent on ar. rings⁵⁶. Hitherto unavailable ar. compounds can be prepared by using bromine as an *o,p*-directing blocking group⁵⁷.

Benzene derivatives not otherwise obtainable, e.g. nitrobenzene derivatives that cannot be made by nitration, may be synthesized from pyrylium salts⁵⁸. A convenient synthesis of 5-carboxy-2-cyclohexenones has been published⁵⁹. 2-Pyridones have been prepared through enol-betaines⁶⁰. Nitriles have been used as starting materials for the synthesis of heterocyclics⁶¹. Fischer indole syntheses have been performed thermally without the use of a catalyst⁶². Diethoxymethyl acetate has been recommended for the ring closure of 4,5-diaminopyrimidines to purines⁶³. Taylor and coll. have found another new approach to pteridine syn-

⁴⁷ J. H. Wotiz and H. E. Merrill, Am. Soc. 80, 866 (1958).

⁴⁸ s. Synth. Meth. 10, 299.

⁴⁹ T. Rinderspacher and B. Prijs, Helv. 41, 22 (1958).

⁵⁰ A. Furst and R. E. Moore, Am. Soc. 79, 5492 (1957); Synth. Meth. 12, 31.

⁵¹ Z. J. Vejdělek, Coll. Czech. Chem. Commun. 22, 1852 (1957).

⁵² D. Shapiro, H. Segal, and H. M. Flowers, Am. Soc. 80, 1194 (1958).

⁵³ Synth. Meth. 12, 405.

⁵⁴ Synth. Meth. 12, 671.

⁵⁵ J. Broome, B. R. Brown, and G. H. R. Summers, Soc. 1957, 2071.

⁵⁶ Chem. Eng. News 36, No. 8, 52 (1958).

⁵⁷ A. H. Blatt, N. Gross, and E. W. Tristram, J. Org. Chem. 22, 1588 (1957).

⁵⁸ K. Dimroth, G. Neubauer et al., B. 90, 1634, 1668 (1957).

⁵⁹ Synth. Meth. 12, 793.

⁶⁰ Synth. Meth. 12, 733.

⁶¹ E. J. Tillmanns and J. J. Ritter, J. Org. Chem. 22, 839 (1957).

⁶² J. T. Fitzpatrick and R. D. Hiser, J. Org. Chem. 22, 1703 (1957).

⁶³ J. A. Montgomery and C. Temple, Jr., Am. Soc. 79, 5238 (1957); 80, 409 (1958).

thesis⁶⁴ through pyrazolo[b]pyrazines followed by reductive ring opening⁶⁵. 8-Thiapurines have been synthesized from 4-amino-5-nitrosopyrimidines and thiourea by a novel reaction⁶⁶.

The Wagner synthesis of silanes with olefins in the presence of platinum catalysts has been the subject of several papers⁶⁷. Brown and coll., continuing their work on organoboron compounds, have found diborane in particular to be a useful and convenient synthetic tool. With it, they converted olefins to *prim.* alcohols⁶⁸ and used it also as selective reducing agent⁶⁹. Boric acid esters have been found to promote water-forming reactions⁷⁰, and hydraulic binders, e.g. Portland cement, have served the same purpose⁷¹. A convenient preparation of phosphinic and arsenic acids from phosphine and arsine oxides respectively is a result of investigations carried out by Horner and coll. on organophosphorus compounds⁷².

The greatly increased use of triethylamine as a reagent can be seen from the large number of entries under this heading in the index⁷³. It has been found to be particularly useful for the preparation of esters from active halides⁷⁴. Highly branched aliphatic tert. amines, strong bases which can hardly be alkylated, have been recommended as excellent proton acceptors for N-alkylation and dehydrohalogenation reactions⁷⁵. Dimethyl sulfoxide as a solvent can be used in place of dimethylformamide⁷⁶ and is sometimes superior. Recently, it has been discovered that as a reagent it easily converts halides to oxo compounds⁷⁷. Very active nickel catalysts of the Langenbeck type containing magnesium oxide have been described⁷⁸. Rhodium on alumina has been recommended as dehydrogenation agent⁷⁹.

Volume 37 of Organic Syntheses contains examples of the use of a

⁶⁴ cf. Synth. Meth. 11, 575.

⁶⁵ E. C. Taylor, J. W. Barton, and T. S. Osdene, Am. Soc. 80, 421 (1958).

⁶⁶ G. M. Timmis, Soc. 1958, 804.

⁶⁷ Synth. Meth. 12, 699, 700; mostly with fluoroolefins s. P. Tarrant et al., Am. Soc. 79, 6536 (1957).

⁶⁸ H. C. Brown and B. C. Subba Rao, J. Org. Chem. 22, 1137 (1957).

⁶⁹ H. C. Brown and B. C. Subba Rao, J. Org. Chem. 22, 1135 (1957).

⁷⁰ J. Kollonitsch and J. Vita, Nature 178, 1307 (1956).

⁷¹ M. Lepage and J. Elian, C. r. 242, 1989 (1956).

⁷² L. Horner, H. Hoffmann, and H. G. Wippel, B. 91, 64 (1958); s. a. B. 91, 45, 50.

⁷³ s. a. J. D. Reinheimer et al., J. Org. Chem. 22, 1743 (1957); R. L. Bixler and C. Niemann, J. Org. Chem. 23, 575 (1958).

⁷⁴ Synth. Meth. 12, 286.

⁷⁵ S. Hünig and M. Kiessel, B. 91, 380 (1958).

⁷⁶ N. Kornblum and J. W. Powers, J. Org. Chem. 22, 455 (1957).

⁷⁷ N. Kornblum et al., Am. Soc. 79, 6562 (1957).

⁷⁸ Synth. Meth. 12, 94.

⁷⁹ Synth. Meth. 12, 881.

continuous reactor, which can have a number of advantages over the batch process commonly used in the laboratory⁸⁰.

The following references in Vol. 11 under Trends have been entered in this volume⁸¹:

5/99; 6/85; 9/321; 11/323; 14/49, 521; 15/43; 16/666; 17/135; 18/365; 19/109; 22/893; 23/878; 24/697; 26/330; 28/238; 30/235; 32/305; 35/42; 36/125; 37/549; 38/596; 39/612; 40/619; 41/615; 42/269; 43/581; 44/270, 272, 273; 45/859; 46/836; 49/713; 53/465; 55/920; 56/817; 57/537; 58/834; 59/494; 60/284; 61/433, 457; 62/189; 63/910; 65/962; 66/335; 67/184; 68/237; 69/493.

⁸⁰ C. F. H. Allen, W. J. Humphlett, and J. R. Byers, Jr., *Org. Synth.* 37, 2, 66 (1957).

⁸¹ The first figure refers to the footnote in Trends, Vol. 11, the second figure to the entry number in this volume.

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Preface to Volume 12

Most of the references in the present volume concern papers published between 1955 and 1957. The index includes volumes 11 and 12, the first two of the third series. It also contains a few additional or revised entries to former volumes.

I want to thank Dr. John T. Plati once more for having checked the manuscript and Dr. Bernhard Prijs for his thorough proof-reading. I also greatly appreciate the valuable advice they have given me. 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 1958.

W. Th.

Vorwort zu Band 12

Die meisten Literaturzitate im vorliegenden Band betreffen Arbeiten aus den Jahren 1955—1957. Das Register umfaßt die Bände 11 und 12, die ersten der dritten Serie, und enthält einige zusätzliche oder revidierte Schlagworte zu früheren Bänden.

Nutley, New Jersey, USA, im Mai 1958.

W. Th.