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Synthetic Methods of Organic Chemistry

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Synthetic Methods of Organic Chemistry

Synthetische Methoden
der Organischen Chemie

Jahrbuch mit deutschem Registerschlüssel

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Preface

This is the second volume of the seventh series. New references to material in the preceding series have, however, been included in the text. The index is cumulative for volumes 31 and 32, and also contains additional and revised entries to previous volumes. The Formula Index of Functional Combinations has been expanded to include pertinent items from all previous volumes as well as nomenclature which had been discontinued in the later volumes. Most of the references in this volume are to papers published between 1975 and 1977.

I again wish to thank my collaborators listed on the title page for their valuable advice and assistance, and other members of Hoffmann-La Roche, Inc., Nutley, for their kind cooperation.

Nutley, New Jersey, U.S.A., May 1978 W. Th.

From the Prefaces to the Preceding Volumes

New methods for the synthesis of organic compounds and improvements of known methods are being recorded continuously in this series.

Reactions are classified on a simple though purely formal basis by symbols, which can be arranged systematically. Thus searches can be performed without knowledge of the current trivial or author names (e.g., "Oxidation" and "Friedel-Crafts reaction").

Users accustomed to the common notations will find these in the subject index. By consulting this index, use of the classification system may be avoided. It is thought that the volumes should be kept close at hand. The books should provide a quick survey, and obviate the immediate need for an elaborate library search. Syntheses are therefore recorded in the 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

reference under the related simpler compounds. General terms, such as synthesis, replacement, heterocyclics, may also be brought to the attention of the reader.

A table that indicates the sequence of the reagents (see vol. 31, p. 596) may help the reader to locate reactions in the body of the text. This table also contains such frequently used reagents as NaOH and HCl, not included in the subject index.

A brief review, *Trends in Synthetic Organic Chemistry*, stresses highlights of general interest and calls 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. In order to carry out a particular synthesis it is therefore advisable 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 575) make it possible to keep abstracts of previous volumes up-to-date.

Syntheses that are divided into their various steps and 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).

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 as follows: H, O, N, Hal (Halogen), S, and Rem (the remaining elements). C is always placed last.

The "principle of the latest position" is used whenever possible.

The methods of obtaining a particular chemical bond are subdivided according to types of formation. Four types are distinguished: addition (⇓), rearrangement (↶), exchange (↓↑), and elimination (↑). The last part of the symbol refers to the bonds which are destroyed in the reaction or to a characteristic element 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 572.

2. Reagents

A further subdivision, not included in the reaction symbols, is made on the basis of the reagents characteristic of the reaction. A table indicating the sequence of the reagents may be found on page 596 of vol. 31.

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. Der erste Teil des Reaktions-Formelzeichens besteht somit aus den Symbolen der an der entstehenden Bindung beteiligten Elemente, z. B. HN bei einer Bindung zwischen Wasserstoff und Stickstoff. Die Reihenfolge der Elemente ist wie folgt: H, O, N, Hal (Halogen), S, Rem (Übrige Elemente). C steht an letzter Stelle.

Das *«Princip der letzten Stelle»* ist nach Möglichkeit immer angewandt worden.

Die Methoden zur Herstellung einer bestimmten Bindung werden nach deren Bildungsweise eingeteilt. Es werden 4 Fälle unterschieden: Aufnahme (⇓), Umlagerung (↶), Austausch (↓↑) und Abgabe (⇑).

Der letzte Teil des Reaktionszeichens gibt die Bindung an, die gelöst wird, oder ein charakteristisches Element, das eliminiert 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 Übersicht: siehe Seite 572.

2. Hilfsstoffe

Eine weitere Unterteilung, die im Reaktionszeichen nicht mehr zum Ausdruck kommt, wird nach den für die Reaktion charakteristischen Hilfsstoffen vorgenommen. Eine Tabelle der Reihenfolge der Hilfsstoffe befindet sich in Band 31 auf Seite 596.

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.

High-Coverage Searches

A search through Synthetic Methods provides a selection of key references from the journal literature. For greater coverage, as for bibliographies, a supplementary search through the following publications is suggested.

Chemical Reactions Documentation Service[1]
(with its monthly Journal of Synthetic Methods) which also includes abstracts from patents and provides the data coded on magnetic tape and punched cards as additional retrieval tools. All the abstracts in Synthetic Methods have been coded according to the same system, and the respective tapes or punched cards are also available from Derwent Publications. 'One-line' interactive access will be provided as well.

Science Citation Index[2]
for which Synthetic Methods serves as a source of starting references.

Chemical Abstract Service[3]

References may not be included in Synthetic Methods

1) to reactions which are routinely performed by well known procedures,
2) to subjects which can be easily located in handbooks and indexes of abstract journals, such as the ring system of heterocyclics or the metal in case of organometallic compounds, and
3) to inadequately described procedures, especially where yields are not indicated.

References to less accessible publications such as those in the Russian or Japanese language are, as a rule, only included if the method in question is not described elsewhere.

[1] Derwent Publications Ltd., 128 Theobalds Road, London WCIX 8RP, England.
[2] Institute for Scientific Information, Philadelphia, Pa., USA.
[3] Chemical Abstracts Service, Columbus, Ohio, USA.

Trends in Synthetic Organic Chemistry 1978

Compounds with a variety of functional groups can be synthesized from arsine oxides by metalation and reaction with electrophiles[1], subsequent reduction and replacement of the arsenic group by nucleophiles[2]. Benzothiazoles have been used as versatile carbonyl equivalents, which react under very mild conditions[3]; one or two C-branches can be attached stereoselectively[4] and annelation of fused and spiro rings has been described[5].

Acetylene derivatives can be conveniently reduced to *cis*-olefins with magnesium hydride and cuprous iodide or cuprous *tert*-butoxide[6].

A direct selective deamination of aliphatic as well as ar. prim. amines with hydroxylamine-O-sulfonic acid has been published[7]. Using sodium methylmercaptide, aliphatic nitro groups have been replaced by hydrogen[8]. A remarkable reduction of aromatic nitrogenous functional groups, particularly nitro groups, to aniline derivatives in liquid paraffin has been reported[9]. Prim. aliphatic amino groups can be replaced by hydrogen[10] and a variety of functional groups, such as halogen[11], acoxy or thiocyano groups[12], via pyridinium salts.

Oxo compounds can easily be reduced to alcohols with inexpensive sodium dithionite[13]. An efficient regio- and stereo-specific preparation

1 Synth. Meth. *32*, 811.
2 T. Kauffman, R. Joussen, and A. Woltermann, Ang. Ch. *89*, 759 (1977).
3 E. J. Corey and D. L. Boger, Tetrah. Let. *1978*, 5.
4 Ibid. *1978*, 9.
5 Ibid. *1978*, 13.
6 E. C. Ashby, J. J. Lin, and A. B. Goel, J. Org. Chem. *43*, 757 (1978).
7 G. A. Doldouras and J. Kollonitsch, Am. Soc. *100*, 341 (1978).
8 N. Kornblum, S. C. Carlson, and R. G. Smith, Am. Soc. *100*, 289 (1978).
9 L. B. Din, J. M. Lindley and O. Meth-Cohn, Synthesis *1978*, 23.
10 Synth. Meth. *32*, 61.
11 N. F. Eweiss et al., Synthesis *1977*, 634.
12 U. Gruntz et al., Chem. Commun. *1977*, 701; *1978*, 133.
13 J. G. de Vries, T. J. van Bergen, and R. M. Kellog, Synthesis *1977*, 246.

of homoallylic alcohols by oxetane ring opening with diethylaluminum N-methylanilide has been reported[14].

Efficient 2-phase dehydrogenation, e.g. of hydrazo to azo compounds, have been performed with phenoxyl radicals generated in situ by oxidation of phenols[15].

α,β-Ethylene-aldehydes and -esters have been obtained directly from enolethers through reaction with singlet oxygen[16] and nitriles have been prepared directly from prim. nitro compounds with phosphorus trichloride in pyridine[17].

Nucleophilic substitution, e.g. the preparation of thiocyanates from lipophilic alcohols, can be facilitated by substrate hydrophilation via ammonioethanesulfonic acid esters (betylates)[18]. Mercaptans can be easily prepared from alcohols with inversion of configuration via thiolic esters prepared with thioacetic acid in the presence of 2-fluoropyridinium salts[19]. C-Sulfenylation of β-dicarbonyl compounds with mercaptans by air oxidation in the presence of tetraethylammonium fluoride has been reported[20]. Activated thiolic and selenolic esters can be prepared at room temperature from carboxylic acids and aryl thiocyanates or selenocyanates in the presence of tri-*n*-butylphosphine[21]. Phenylselenolactones have been obtained under very mild conditions from unsaturated acids and benzeneselenyl chloride[22].

Vinyl chloroformate can be used for the protection of hydroxyl and amino groups[23] as well as for N-dealkylation[24]. Sec. alcohol groups have been conveniently tritylated with triphenylcarbonium perchlorate in the presence of 2,4,6-tri-*tert*-butylpyridine as acid acceptor[25]. Wet silica gel has been recommended as a convenient reagent for deacetalization[26]. p-Nitrobenzyl carboxyl-protective groups can be rapidly re-

14 Y. Kitagawa et al., Am. Soc. *99*, 3864 (1977).
15 K. Dimroth and W. Tüncher, Synthesis *1977*, 339.
16 G. Rousseau, P. Le Perchec, and J. M. Conia, Synthesis *1978*, 67.
17 P. A. Wehrli and B. Schaer, J. Org. Chem. *42*, 3956 (1977).
18 J. F. King et al., Am. Soc. *100*, 1637 (1978).
19 K. Hojo, H. Yoshino, and T. Mukaiyama, Chem. Lett. *1977*, 133; cf. ibid. *1977*, 437.
20 J. H. Clark and J. M. Miller, Can. J. Chem. *56*, 141 (1978).
21 P. S. Grieco, Y. Yokoyama, and E. Williams, J. Org. Chem. *43*, 1283 (1978).
22 K. C. Nicolaou and Z. Lysenko, Am. Soc. *99*, 3185 (1977); cf. D. L. J. Clive and G. Chittattu, Chem. Commun. *1977*, 484.
23 R. A. Olofson et al., Tetrah. Let. *1977*, 1563, 1571, 1575.
24 Synth. Meth. *23*, 479s*32*.
25 Y. V. Wozney and N. K. Kochetkov, Carbohyd. Res. *54*, 300 (1977).
26 F. Huet et al., Synthesis *1978*, 63.

moved with sodium sulfide, even in highly sensitive azetidinone antibiotics[27].

An oxidative nucleophilic C-alkylation of ar. nitro compounds has been reported[28].

Amines have been metalated as hindered acylamines whereby dipole-stabilized carbanions are formed[29]. The Δ^2-oxazolin-2-yl group can activate aromatic substitution through regiospecific o-metalation[30]. α-Subst. ketones have been obtained by a regiospecific reductive alkylation of α,β-ethyleneazomethines. This regiospecificity is different from and complements that of previous methods[31]. Syntheses via metalation of cyclic boronic acid esters have been described, e.g. an efficient regiospecific general synthesis of α-(phenylthio)ketones[32].

A novel Michael addition with B → C-alkyl migration has been reported[33]. Ketones with acid-labile functional groups can be synthesized from aldehydes via new α-siloxyphosphonates[34].

β-Carotene and other sym. carotenoids have been efficiently prepared by oxidation of P-ylids with hydrogen peroxide[35].

cis-2-Ethoxyvinyllithium is a conveniently prepared and relatively stable nucleophilic acetaldehyde equivalent. It has been used for the synthesis of α,β-ethylenealdehydes. An analogous synthesis of 2,4-dienals from oxo compounds with addition of 4-C-atoms has also been reported[36]. By the use of a phase transfer technique, reactive aliphatic aldehydes can be successfully condensed in the presence of a strong base[37]. Quinone methid ketals have been employed as intermediates in a sequence which is equivalent to nucleophilic aromatic substitution[38]. A virtually completely asym. synthesis of (S)-(+)-atrolactic acid has been achieved via 1,3-oxathiane derivatives[39]. A rapid peptide syn-

[27] S. R. Lammert et al., J. Org. Chem. *43*, 1243 (1978).
[28] F. Kienzle, Helv. *61*, 449 (1978).
[29] R. von Schlecker, D. Seebach, and W. Lubosch, Helv. *61*, 512 (1978).
[30] A. I. Meyers and R. A. Gabel, Tetrah. Let. *1978*, 227; cf. ibid. *1978*, 223.
[31] P. A. Wender and M. A. Eissenstat, Am. Soc. *100*, 292 (1978).
[32] D. S. Matteson and K. Arne, Am. Soc. *100*, 1325 (1978).
[33] A. Pelter and L. Hughes, Chem. Commun. *1977*, 913.
[34] T. Hata et al., Tetrah. Let. *1978*, 363.
[35] Synth. Meth. *28*, 863s32.
[36] R. H. Wollenberg, K. F. Albizati, and R. Peries, Am. Soc. *99*, 7365 (1977); Tetrah. Let. *1978*, 717.
[37] J. M. McIntosh and H. Khalil, J. Org. Chem. *42*, 2123 (1977).
[38] D. J. Hart, P. A. Cain, and D. A. Evans, Am. Soc. *100*, 1548 (1978).
[39] E. L. Eliel, J. K. Koskimies, and B. Lohri, Am. Soc. *100*, 1614 (1978).

thesis in a 2-phase liquid medium with 1-ethyl-3(3-dimethylaminopropyl)carbodiimide has been reported[40].

C-Acylation with a polymer-bound ester in the presence of polymer-based tritylllithium has been demonstrated as example of efficient multi-polymer reactions[41]. A novel degradation of peptides from the carboxyl end through the acid azide is performed on a controlled-pore glass support[42].

The readily available and thermally stable phenyl vinyl sulfoxide has been used successfully as an acetylene equivalent in diene syntheses[43].

Alkoxycyclopropane ring rearrangements have been used in the synthesis of several terpenes[44]. Steroids can be obtained by a cobalt-catalyzed stereospecific triple ring closure of enediynes[45]. Practical routes for large-scale preparation of Cinchona alkaloids and their analogs, including the preparation of quinine and quinidine by a highly stereospecific autoxidation, have been found[46].

An efficient oxidative ring expansion of enecyclics has been discovered[47]. An interesting ring expansion of polyaminolactams has been reported and appropriately named "zip reaction" because the amino groups can be compared to the teeth of a zipper[48]. A reductive variant of the Japp-Klingemann cleavage has been applied to the ring opening of highly functionalized cyclic ketones[49].

New "dry media" reagents have been introduced: Ferric chloride adsorbed on silica gel, an easily controllable multipurpose reagent, has been used for high yield selective dehydration of alcohols[50] and basic silica gel for the conversion of aliphatic nitro into oxo compounds (modified Nef reaction)[51]. Barium manganate has been recommended as an oxidant for alcohols; high yields of oxo compounds, e.g. o-dial-

[40] S. Nozaki, A. Kimura, and I. Muramatsu, Chem. Lett. *1977*, 1057.
[41] B. J. Cohen, M. A. Kraus, and A. Patchornik, Am. Soc. *99*, 4165 (1977).
[42] G. M. Loudon and M. E. Parham, Tetrah. Let. *1978*, 437.
[43] L. A. Paquette et al., Am. Soc. *100*, 1597 (1978).
[44] E. Wenkert, D. A. Berges, and N. F. Golob, Am. Soc. *100*, 1263, 1267 (1978).
[45] R. L. Funk and K. P. C. Vollhardt, Am. Soc. *99*, 5483 (1977).
[46] M. R. Uskokovic et al., Am. Soc. *100*, 571–589 (1978).
[47] Synth. Meth. *32*, 123.
[48] U. Kramer et al., Ang. Ch. *89*, 899 (1977); *90*, 210 (1978).
[49] A. P. Kozikowski and W. C. Floyd, Tetrah. Let. *1978*, 19.
[50] E. Keinan and Y. Mazur, J. Org. Chem. *43*, 1020 (1978).
[51] E. Keinan and Y. Mazur, Am. Soc. *99*, 3861 (1977); J. L. Hogg, T. E. Goodwin, and D. W. Nave, Org. Prep. Proced. Int. *10*, 9 (1978).

dehydes, have been obtained by this method[52]. 5,5-Dibromo-2,2-dimethyl-1,3-dioxane-4,6-dione is useful for the bromination of sensitive oxo compounds[53]. Dibromoborane-dimethyl sulfide is a new active yet stable monofunctional hydroborating agent[54].

The following references in Vol. 31 under Trends have been entered in this volume[55].

1/148; 3/500; 4/499; 6/78; 9/138; 10/230; 11/16; 12/895; 17/208; 18/179; 19/836; 21/520; 22/887; 23/811; 26/932; 27/454; 29/809; 30/824; 31/801; 34/995; 35/956; 36/61; 38/981; 39/353; 40/667; 41/324, 427, 453; 43/95; 46/52; 48/209; 49/757; 50/604.

[52] H. Firouzabadi, and E. Ghaderi, Tetrah. Let. *1978*, 839.
[53] R. Bloch, Synthesis *1978*, 140.
[54] H. C. Brown and N. Ravindran, Am. Soc. *99*, 7097 (1977).
[55] The first figure refers to the footnote in Trends, Vol. 31, the second figure to the entry number of this volume.

Formation of H—O Bond

Uptake ⇓

Addition to Carbon-Carbon Bonds HO⇓CC

Electrolysis ↯

Electrochemical reductive ring closure ○

s. *28*, 1; 2-methylenecyclopentanols from δ,ε-acetyleneketones s. Chem. Lett. *1976*, 1233

Rearrangement ∩

Hydrogen/Carbon Type HO∩HC

Without additional reagents *w.a.r.*

Oximes from aliphatic nitroso compds. CH(NO) → C : NOH

s. *12*, 4; also by allowing to stand briefly in pyridine s. G. R. Lenz, J. Org. Chem. *41*, 3532 (1976)

Pyridine C_5H_5N

s. *12*, 4 suppl. *32*

Oxygen/Carbon Type HO∩OC

Potassium tert-butoxide/pyridine *t-BuOK/C_5H_5N*

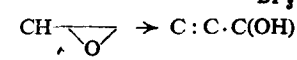
2-Ethylenealcohols from oxido compds.

CH → C(OH)C : C

with alc. KOH cf. *14*, 3; with K-*tert*-butoxide, preferably in pyridine s. Z. Rykowski and K. Burak, Rocz. Chem. *50*, 1709 (1976); C. A. *86*, 140258

Boron fluoride BF_3

β,γ-Ethylene-α-hydroxycarboxylic from glycidic acid esters



s. *32*, 127

Exchange ⇅

Remaining Elements ↑ HO⇅Rem

Without additional reagents *w.a.r.*

o-Hydroxyketones from 1-oxa-3-oxonia-2-boratanaphthalenes C

s. *32*, 898

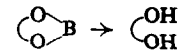
Boron fluoride BF_3

Cleavage of alkoxysilanes OSi⩽ → OH

with pyridinium trifluoroacetate s. *29*, 881; with BF_3-etherate s. A. H. Schmidt, U. Schirmer, and J.-M. Conia, B. *109*, 2588 (1976)

1,3-Propanediol $HO[CH_2]_3OH$

Protection of diols as cyclic phenylboronates



s. *20*, 12; s. a. J. E. McCormick and R. S. McElhinney, Soc. Perkin I *1976*, 2533

Carbon ↑ HO⇅C

Without additional reagents *w.a.r.*

β-Glycosides from acetobromosugars ←

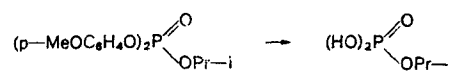
s. *32*, 164

Irradiation ≠

Removal of a photosensitive o-nitrobenzyl ester polymer support after peptide synthesis COOR → COOH

s. *30*, 5; liq. phase multi-step synthesis (cf. Synth. Meth. *21*, 426 suppl. *31*) on o-nitrobenzoylpolyethyleneglycol support s. F.-S. Tjoeng et al., Biochim. Biophys. Acta *490*, 489 (1977)

Phosphoric acid monoesters $P(O)(OR)(OH)_2$



An ethanolic soln. of dianisyl isopropyl phosphate irradiated ca. 5 hrs. in a quartz vessel with a 450 w. medium-pressure Hg-arc lamp → monoisopropyl phosphate. Y: 99%. F. e. s. R. A. Finnegan and J. A. Matson, Chem. Commun. *1975*, 928; cf. Synth. Meth. *28*, 900.

Potassium/biphenyl — $K/C_{12}H_{10}$

Regiospecific cleavage of alkyl aryl ethers — OR → OH

2. $n\text{-}C_{10}H_{21}O\text{-}C_6H_4\text{-}Ph \rightarrow n\text{-}C_{10}H_{21}OH\ [+\ C_6H_5\text{-}Ph]$

Metal specificity. p-Biphenylyl *n*-decyl ether treated 2 hrs. at room temp. with 5 moles potassium in tetrahydrofuran containing *biphenylyl as electron carrier* → *n*-decanol. Y: ca. 90%. F. e., also with Na and Li, formation of phenols particularly with Li, s. M. Itoh et al., Chem. Lett. *1976*, 271.

Sodium/alcohol — *NaOR*

Alcohols from monothiolcarbonic acid esters — OCOSR → OH

s. *32*, 520

Potassium tert-butoxide/water — *t-BuOK/H₂O*

Carboxylic acids from hindered esters — COOR → COOH

cf. *15*, 6 suppl. *31*; with 2 : 1 K-*tert*-butoxide-water, "anhydrous hydroxide", s. P. G. Gassman and W. N. Schenk, J. Org. Chem. *42*, 918 (1977)

Sodium hydrogen carbonate s. under MeI — *NaHCO₃*

Sodium nitrite — *NaNO₂*

Cleavage of phenolethers — ArOR → ArOH

with LiI cf. *25*, 7; of ethers with electron-withdrawing p-substituents by $NaNO_2$ in hexamethylphosphoramide s. T. Sakai et al., Chem. Lett. *1976*, 1203

Sodium n-propylmercaptide — *n-PrSNa*

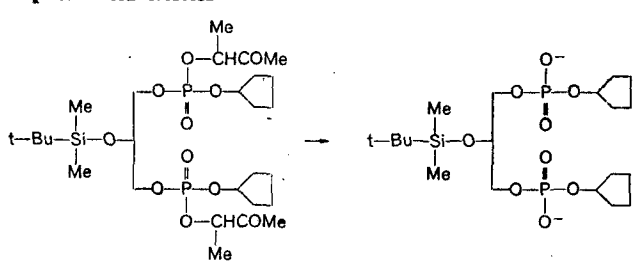
with EtSNa cf. *27*, 10; with Na-*n*-propylmercaptide s. F. T. Sher and G. A. Berchtold, J. Org. Chem. *42*, 2569 (1977)

Sodium chloride s. under $AlCl_3$ — *NaCl*

Triethylamine (s. a. under PhSH) — *Et_3N*

Mixed phosphoric acid diesters from phosphoric acid triesters — P·OR → P·OH

3.



A soln. of 2-(*tert*-butyldimethylsilyl)-1,3-bis(acetoinylcyclopentyl-phosphoryl)glycerol in water-acetonitrile containing triethylamine stirred 8 hrs. at 70° and overnight at 25° → bis(triethylammonium) 2-(tert-butyldimethylsilyl)-1,3-bis(cyclopentyl-phosphoryl(glycerol. Y: > 63%. Ramirez et al., Synthesis *1976*, 483; synthesis of phosphatides s. ibid. *1976*, 769.