W. Theilheimer

Synthetic Methods of Organic Chemistry

Vol. 25 Yearbook 1971

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With Reaction Titles and Cumulative Index of Volumes 21–25

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Preface

This is the final volume of the fifth series. It contains a cumulative subject index and all reaction titles for Volumes 21–25, including recent supplementary references. This arrangement again reduces a five-volume search to a search through a single volume. Most of the references in this volume are to papers published between 1968 and 1970. To prevent an unwieldy expansion of this volume, repetitive parts have been held to a minimum. However, the omitted parts can be found in Vol. 24, and the respective page numbers are listed on the contents page of this volume. Supplementary references to preceding series will be included in Vol. 26.

I again wish to thank Dr. John T. Plati, Dr. Bernhard Prijs, Dr. S. Kasparek, and Dr. Helmut Mäcke for their valuable advice and assistance, Mrs. Helen Makus for her skilled secretarial help, and other members of Hoffmann-La Roche, Inc., Nutley, for their kind cooperation.

Nutley, New Jersey, U.S.A., May 1971. W. Th.

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 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 (⇓), 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 682.

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 490 of vol. 24.

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.

Trends in Synthetic Organic Chemistry 1971

The now well-known 5,6-dihydro-4H-1,3-oxazine intermediates[1] have been followed by 4,4-dimethyl-Δ^2-oxazolines for the synthesis of aldehydes, acids, and esters[2]. Metallo aldimines derived from isonitriles have been found to be new versatile intermediates for the synthesis of compounds with a variety of O-functional groups such as aldehydes, ketones, hydroxyketones, and α-ketoacids[3].

A new dehydration agent for alcohols, methyl(carboxysulfamoyl)-triethylammonium hydroxide inner salt, has been used for the introduction of double bonds into steroids. The mild conditions and selectivity of the reaction as well as the unexpected nature of some products make this method attractive[4].

The oxidation of the boranes in the Brown hydration has recently been performed under very mild conditions with oxygen instead of alkaline hydrogen peroxide[5]. Alcohols can be obtained in high yield by electroreduction. The same process gives aldehydes in the presence of absolute ethanol as proton source[6]. Another new and convenient method for the preparation of aldehydes is the reaction of bromides with Na-tetracarbonylferrate(-II)[7].

Ar. ketals and thioketals, ar. and aliphatic epoxides, and ar. aziridines can be rapidly and conveniently reduced by alkali metals in liq. ammonia[8].

9-Phenyl-9-hydroxyanthrone has been recommended for the protection of alcohols; the protective tritylone group can be removed by the base-catalyzed Wolff-Kishner reduction[9]. Optically active alcohols can

[1] Trends Vol. *24*, footnotes 44–46.
[2] A. I. Meyers and E. W. Collington, Am. Soc. *92*, 6644, 6646, 6676 (1970).
[3] H. M. Walborsky and G. E. Niznik, Am. Soc. *91*, 7778 (1969); *92*, 6675 (1970).
[4] P. Crabbé and C. León, J. Org. Chem. *35*, 2594 (1970).
[5] H. C. Brown, M. M. Midland, and G. W. Kabalka, Am. Soc. *93*, 1024 (1971).
[6] Synth. Meth. *25*, 57.
[7] M. P. Cooke, Am. Soc. *92*, 6080 (1970).
[8] E. M. Kaiser et al., J. Org. Chem. *36*, 330 (1971).
[9] W. E. Barnett and L. L. Needham, Chem. Commun. *1971*, 170.

be conveniently protected by the sym. 4-methoxytetrahydropyran-4-yl group which does not give unwanted diasteroisomers like the customary tetrahydro-2-pyranyl group[10]. A $NaBH_4$-iodine reagent easily converts alkoxy- to hydroxy-esters with retention of optical activity[11].

Directed ω-chlorinations[12] and remarkably selective (ω–1)-monochlorinations of C_6 and C_8 alcohols, ethers, and acids[13] have been reported. Cyanuric chloride has been recommended for the conversion of alcohols to chlorides. It does not require added base and does not cause isomerization[14]. The base induced *anti*-Markownikoff hydrobromination of terminal olefins[15] has been supplemented by the *anti*-Markownikoff prepn. of sec. bromides from internal olefins by reaction of intermediate B-*sec*-alkyl-9-borabicyclo[3.3.1]nonanes with bromine in the dark[16]. Ar. fluorides can be obtained by photolysis of diazonium fluoroborates or fluorophosphates in some cases with higher yields than those obtained by pyrolysis[17]. α-Halogenoketones can be conveniently dehalogenated under mild conditions with LiI and BF_3[18]. Oxo compounds have been regenerated from their oximes under mild conditions through reduction with tervalent titanium[19].

Benzyl 4,6-O-benzylidene-β-D-galactopyranoside has been preferentially benzoylated in the 3-position with N-benzoylimidazole[20]. Esterification can be performed smoothly in high yields with *tert*-butyl ethers[21].

Benzoyloxylation provides a simple, one-step method for the prepn. of oxygenated indoles[22]. Indoline derivatives have been used for a highly specific asym. synthesis of α-amino from α-keto acids. The indolines can be regenerated and used repeatedly[23].

Amino acids and peptides can be N-trifluoroacetylated under essentially neutral conditions with 1,1,1-trichloro-3,3,3-trifluoroacetone and

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[23] Synth. Meth. *25*, 233.

dimethyl sulfoxide[24]. N-Acyl derivatives of amino esters can be obtained directly from their easily accessible and stable hydrochlorides with orthoesters[25]. Glucosamine has been conveniently and selectively N-acylated with p-nitrophenyl esters[26]. Instead of the usual hydrazine, methylamine can be used for the removal of N-protective phthaloyl groups[27].

Exclusive alkylation of normally unfavored positions in (poly-N)-heterocyclics can be achieved by simply using an acyl group, such as acetyl or benzoyl, as N-blocking group[28]. Quaternary ammonium salts can be obtained directly from prim. and sec. amines under mild conditions in the presence of a suitable sterically hindered organic base such as 1,2,2,6,6-pentamethylpiperidine[29].

A facile thermal cleavage of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone gives *tert*-butylcyanoketene, a surprisingly stable yet very reactive ketene[30].

Acetyl hypobromite gives high yields of N-brominated amides and imides[31]. Isocyanates can be obtained at low temperature from aminosilanes or silazanes and phosgene[32], and subst. unsym. ureas from 2 different amines and CO in the presence of sulfur[33].

Unsym. disulfides have been obtained very easily and selectively from sulfenyl thiocarbonates, which are remarkably stable yet highly reactive[34]. Sym. and unsym. di- and tri-sulfides can also be efficiently prepared with thiophthalimides[35]. The latter give high yields of sulfenamides by reaction with amines[36].

A novel method for the preparation of mixed phosphoric acid diesters proceeds through pyridinium phosphate betaines[37].

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[36] K. Boustany, Chimia *24*, 396 (1970).
[37] T. Hata, Y. Mushika, and T. Mukaiyama, Tetrah. Let. *1970*, 3505.

An interesting and facile diaxial-diequatorial rearrangement with positional interchange of phenylthio and mesyl groups[38], and a new nucleophilic ar. N-N-rearrangement[39] have been reported.

Benzylic and allylic iodides may readily be coupled in excellent yields under mild conditions via air-induced iodine abstraction using triethylborane as reagent[40]. A mixture of $TiCl_4$ and pyridine in tetrahydrofuran or dioxane is an excellent condensing agent for Knoevenagel condensations at 0–25°[41]. 1-Alkenyl halides couple readily with Grignard reagents in the presence of iron[42]. An efficient one-step Grignard-type synthesis with lithium has been published[43]. Branched alcohols can be synthesized simply by a light-induced reaction of bromine with trialkylboranes in the presence of water[44]. Pd-compds. such as Pd-acetylacetonate catalyze the transfer of allylic groups. 3-(2,7-Octadien-1-yl)acetylacetone has thus been prepared from 2,7-octadien-1-yl acetate[45].

High yields of dicarbanions of β-ketoesters have been obtained in 2 stages via the monoanions, with NaH in the first and n-C_4H_9Li in the second stage. γ-Alkylated β-ketoesters can be obtained in this manner[46]. Reformatskii syntheses are reported to proceed best at room temperature, and in the case of base-sensitive carbonyl compounds in trimethyl borate-tetrahydrofuran as a mildly acidic medium[47]. The advantages of intramolecular sulfur elimination have been discussed and demonstrated for the preparation of vinylogous sec. amides and β-dicarbonyl compounds[48].

A short highly stereoselective juvenile hormone synthesis utilizes a new olefinic ketal Claisen reaction[49]. New total syntheses of prostaglandins include a number of interesting methods, such as the simplified synthesis of a key bicyclic intermediate, the protection of alcohol

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groups, and an improved stereospecific reduction of keto groups[50]. Peptide syntheses have been performed via in situ activation by oxidation of hydrazides or formation of enolesters[51]. An improved redoxidative peptide synthesis, which uses 2,2′-dipyridyl disulfide, is simple, gives high yield and optical purity, with few limitations regarding solvents and reaction conditions[52]. Pyrimidine and azapyrimidine nucleosides can be conveniently prepared under mild conditions with Friedel-Crafts catalysts[53]. 5′-Chlorinated or 5′-brominated ribonucleosides can simply be obtained by stirring the nucleoside with thionyl halide in hexamethylphosphoramide[54].

The Simmons-Smith cyclopropane ring synthesis does not require separate preparation of the zinc-copper compound. A mixture of Zn-dust and cuprous halide is even more effective[55]. Convenient procedures for the preparation of alkylcyclopropanes and *trans*-2-alkylcyclopropyl halides from 1-alkynes have been published[56]. Complex polyenic cycloadditions such as an *endo*[6+4]- with a simultaneous *exo*[4+2]-cycloaddition[57] as well as [8+2]-cycloadditions have been reported[58]. Photochemical 1,4-cycloaddition to a benzene ring has been achieved in comparatively good yield[59]. New S-aminosulfoxonium ylids can replace familiar sulfoxonium ylids[60] to form a 3-membered ring by methenylation[61]. A facile closure of the steroid D ring by intramolecular electrophilic attack on a 2-chloro-1-ene side chain has been found[62]. A short route to troponoids goes through the direct formation of 4-cycloheptenones from α,α'-dibromoketones and 1,3-dienes[63].

Convenient and unequivocal syntheses of heterocyclics can be achieved through 1,4-dianions, e.g. of hydrazones or oximes[64]. Un-

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saturated halides have been activated by adsorption for cyclization to acetylenebenzofurans[65]. A simple method for the 3-substitution of pyridine has been published[66]. Pteridines can be easily prepared by fusing the reaction products of 6-aminopyrimidines and diethyl azodicarboxylate with enamines[67]. Benz[d]isothia(IV)zol-3-one 1-oxides represent a remarkably acid- and alkali-stable new ring system[68]. The photocyclization of dienylboranes may open a new area of synthetic interest[69].

Hindered olefins can be obtained from certain heterocycles, such as 1,3-oxathiolan-5-ones, by 2-fold extrusion[70] and unsaturated as well as saturated 1,4-dicarbonyl compounds through fragmentation of cyclobutane rings[71].

A simple preparation of active MnO_2 with activated carbon has been reported[72]. The hazardous preparation of the $CrO_3 \cdot 2C_5H_5N$-complex, a choice reagent for the oxidation of alcohols to carbonyl compounds, can be avoided by its preparation *in situ* in methylene chloride[73]. Iron carbonyl has been used in a variety of reactions, old and new, such as ether cleavage[74], N-deoxygenation[75], and the synthesis of ketones[76]. A soluble iridium-phosphite catalyst gives exceptionally high proportions of axial alcohols from unhindered cyclohexanones[77]. An active cobalt oxide has been found to be an effective autoxidation catalyst, e.g. for the preparation of nitriles from prim. amines[78].

The following references in Vol. 24 under Trends have been entered in this volume[79].

1/104; 3/32; 5/42; 6/61; 8/49; 9/31; 10/46; 11/46; 12/54; 14/96; 15/99; 17/169; 19/9; 20/18; 21/330; 22/291; 23/255; 24/480; 25/348;

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[79] The first figure refers to the footnote in Trends, Vol. 24, the second figure to the entry number of this volume.

26/136; 27/390; 28/404; 29/385; 30/387; 31/439; 32/424; 33/266; 34/466; 35/281; 36/278; 38/88; 39/190; 40/91; 41/591; 42/605; 43/483; 45/612; 46/151; 47/633; 48/166; 50/603; 51/112, 198; 52/195; 53/588; 54/105; 55/270; 56/685; 57/684; 58/600; 59/335; 61/238; 62/110; 63/422; 64/400; 65/637.

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4-Hydroxyphenyltropenium salts from quinocycloheptatrienes ←
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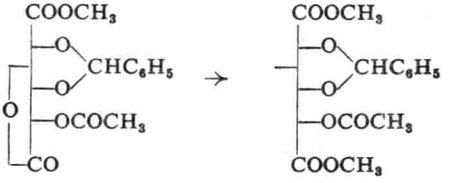
Sodium acetate CH_3COONa

Hydroxycarboxylic acid esters from lactones with retention of carbalkoxyl
Preferential methanolysis ←
s. *25*, 1

Triethylamine $(C_2H_5)_3N$

1.



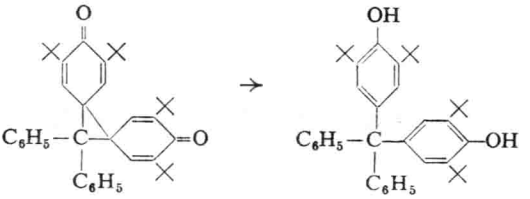
A mixture of 2,4-O-benzylidene-5-O-acetyl-D-glucaro-6,3-lactone 1-methyl ester, dry methanol, dry triethylamine or Na-acetate, and acetic acid stirred 2–4 hrs. at room temp. → dimethyl 2,4-O-benzylidene-5-O-acetyl-D-glucarate. Y: 73%. F. e. s. I. Matsunage and Z. Tamura, Chem. Pharm. Bull. *17*, 1383 (1969).

Sodium tetrahydridoborate $NaBH_4$

Quinolalcohols from quinonealdehydes ←
s. *21*, 65

Benzopinacol ←
Reduction of quinonoids ←

2.



Startg. bispirodienone derivative and an equimolar amount of benzopinacol heated 3 min. in dimethylformamide → bisphenol derivative. Y: 97%. F. e. s. H. D. Becker, J. Org. Chem. *34*, 2472 (1969).

Anion exchanger ←
Hydroxycarboxylic acids from lactones C
Carbohydrate derivatives s. *21*, 2

Ascorbic acid ←
Quinols from quinones ←
Selective reduction – Flavonoids *s. 21*, 3

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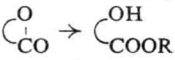
Hydroxycarboxylic acid esters from lactones 
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Addition to Carbon HO⇓CC

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Oxygen /Oxygen Type HO∩OO

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γ-Hydroxy-α,β-ethyleneketones from ethyleneperoxides C
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Oxygen/Carbon Type HO∩OC

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Quinols from cyclic 2-en-1,4-diones ↚
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2-Ethylenealcohols from oxido compounds  CH → C(OH)C : C
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Ethylenephenols by opening of O-heterocycles C
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Boron fluoride *BF_3*

2-Ethylenealcohols from oxido compounds ↚
with methyl group migration s. *23*, 4

Trifluoroacetic acid *CF_3COOH*

2-Ethylenealcohols from oxido compounds CH → C(OH)C : C
16-Methylenesteroids s. *21*, 6

Hydrogen chloride *HCl*

Ethylenealcohols by opening of O-heterocycles C
s. *21*, 7

Phenols from O-heterocyclics ☼
s. *25*, 534

Hydrogen bromide/acetic acid *HBr/CH_3COOH*

2-Ethylenealcohols from oxido compounds CH → C(OH)C : C
s. *22*, 153

Carbon/Carbon Type HO∩CC

Boron fluoride *BF_3*

2-Ethylenealcohols from oxido compounds ↚
with methyl group migration s. *23*, 4

Exchange ⇅

Nitrogen ↑ HO⇅N

Without additional reagents *w.a.r.*

1,2-Bromohydrins from 1,2-bromohydrin nitronates ↚
s. *22*, 555

Cation exchanger ↚

Alcohols from nitric acid esters ONO_2 → OH
s. *22*, 3

Formic acid *HCOOH*

s. *23*, 5