Theilheimer's

Synthetic Methods

of Organic Chemistry

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	1975	Second Edition
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Vol. 16	1962	
Vol. 17	1963	
Vol. 18	1964	
Vol. 19	1965	
Vol. 20	1966	with Reaction Titles Vol. 16–20 and Cumulative Index
Vol. 21	1967	
Vol. 22	1968	
Vol. 23	1969	
Vol. 24	1970	
Vol. 25	1971	with Reaction Titles Vol. 21–25 and Cumulative Index
Vol. 26	1972	
Vol. 27	1973	
Vol. 28	1974	
Vol. 29	1975	
Vol. 30	1976	with Reaction Titles Vol. 26–30 and Cumulative Index
Vol. 31	1977	
Vol. 32	1978	
Vol. 33	1979	
Vol. 34	1980	
Vol. 35	1981	with Reaction Titles Vol. 31–35 and Cumulative Index
Vol. 36	1982	
Vol. 37	1983	
Vol. 38	1984	
Vol. 39	1985	
Vol. 40	1986	with Reaction Titles Vol. 36–40 and Cumulative Index
Vol. 41	1987	

Preface

This is the second volume of the ninth series of *Theilheimer's Synthetic Methods of Organic Chemistry*. References are taken from papers published in 1986 and the early part of 1987, being a selection of the data preliminarily reported in the monthly *Journal of Synthetic Methods* (Derwent Publications Limited, London).

As is true for the second volume of each 5-yearly series, the Subject Index is cumulative for the first two volumes, so that references to abstracts in both Volume 41 and 42 can be located quickly. In addition, the Formula Index of Functional Groups, which follows the Subject Index and is a support for the latter, has been updated to include new functions appearing in this volume.

Abstracts and supplementary data are arranged in these yearbooks according to the specially devised Systematic Classification, details of which are included in these introductory pages

As chemistry has diversified, so too has the technology required to present chemical reactions to the reader in a compact, readily digestible format. The indexing methods for this series of yearbooks are constantly reviewed and updated, and in endeavouring to keep up with the times I am indebted to my colleagues at Derwent for their expertise. I would also like to express my gratitude to Dr. Theilheimer for his continued support.

Derwent Publications Ltd., London   A.F. Finch
May 1988

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 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 580) 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

1. Reaction Symbols

As summarized in the Systematic Survey (p. XVIII), reactions are classified firstly according to the bond formed in the synthesis, secondly according to the reaction type, and thirdly according to the bond broken or the element eliminated. This classification is summarized in the reaction symbol, e.g.

$$OC \Uparrow N$$

|		
↗	↑	↖
Bond formed	Reaction type	Bond broken or element eliminated
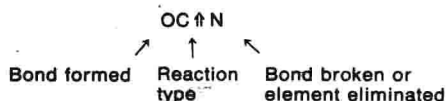
The first part of the symbol refers to the chemical bond formed during the reaction, expressed as a combination of the symbols for the two elements bonded together, e.g. HN, NC, CC. The order of the elements is as follows:

H, O, N, Hal (Halogen), S, Rem (Remaining elements), and C.

Thus, for the formation of a hydrogen-nitrogen bond, the notation is HN, not NH.

If two or more bonds are formed in a reaction, the 'principle of the latest position' applies. Thus, for the reduction

$$RCH{=}O \ + \ H_2 \rightarrow \underset{H}{R\overset{|}{C}H}{-}OH$$
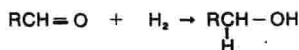
in which both hydrogen-oxygen and hydrogen-carbon bonds are formed, the symbol is HC $\Downarrow$ OC and not HO $\Downarrow$ OC.

The second part of the symbol refers to the reaction type. Four types are distinguished: addition ($\Downarrow$), rearrangement ($\cap$), exchange ($\Updownarrow$), and elimination ($\Uparrow$), e.g.

$$RCH{=}CH_2 \ +\ H_2O \rightarrow \underset{}{R\overset{OH}{\overset{|}{C}}H}{-}CH_3 \qquad\qquad OC \Downarrow CC$$

$$\text{(thiophene structure)} \rightarrow \text{(thiophene structure)} \qquad\qquad CC \cap SC$$

$$R-Cl \;+\; CN^- \to R-CN \;\; [+Cl^-] \hspace{3cm} \text{CC } \text{↓↑ Hal}$$
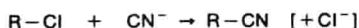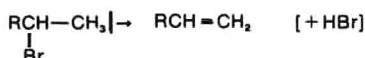
$$RCH-CH_3 | \to \; RCH=CH_2 \;\;\; [+HBr] \hspace{2.5cm} \text{CC ↑ Hal}$$
$$| $$
$$Br$$
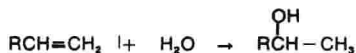
Monomolecular reactions are either rearrangements ($\cap$), where the molecular weight of the starting material and product are the same, or eliminations (↑), where an organic or inorganic fragment is lost; bimolecular and multicomponent reactions are either additions (↓), where the combined molecular weight of the starting materials is the same as that of the product,[1] or exchanges (↓↑), such as substitutions and condensations, where an organic or inorganic fragment is lost.

The last part of the symbol refers to the essential bond broken or, in the case of exchange reactions and eliminations, to a characteristic fragment which is lost. While the addition symbol is normally followed by the two elements denoting the bond broken, in the case of valency expansion, where no bonds are broken, the last part of the symbol indicates the atom at which the addition occurs, e.g.
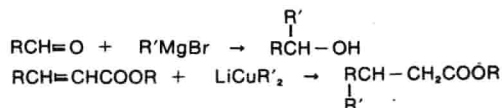
$$R_2S \to R_2SO \hspace{5cm} \text{OS ↓ S}$$
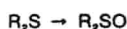
$$RONO \to RONO_2 \hspace{4.7cm} \text{ON ↓ N}$$

For additions, exchanges, and eliminations, the 'principle of the latest position' again applies if more than one bond is broken. However, for rearrangements, the most descriptive bond-breakage is used instead.[2] Thus, for the thio-Claisen rearrangement depicted above, the symbol is CC ∩ SC, and not CC ∩ CC.

Deoxygenations, quaternizations, stable radical formations, and certain rare reaction types are included as the last few methods in the yearbook. The reaction symbols for these incorporates the special symbols El (electron pair), Het (heteropolar bond), Rad (radical), Res (resolutions), and Oth (other reaction types), e.g.

$$R_2S=O \to R_2S: \hspace{4.7cm} \text{ElS ↑ O}$$
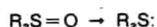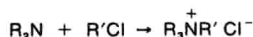
$$R_2N \;+\; R'Cl \to R_3\overset{+}{N}R'\,Cl^- \hspace{3.5cm} \text{Het ↓ N}$$

---

[1] Exceptions being additions of organometallics, e.g.

$$\overset{R'}{\underset{|}{}}$$
$$RCH=O \;+\; R'MgBr \;\to\; RCH-OH \hspace{3cm} \text{CC ↓ OC}$$
$$RCH=CHCOOR \;+\; LiCuR'_2 \;\to\; RCH-CH_2CO\dot{O}R \hspace{1.3cm} \text{CC ↓ CC}$$
$$| $$
$$R'$$

[2] Similarly, the formation of a peroxy function is classified under OO ↓ CC, instead of OC ↓ CC.

The following rules simplify the use of the reaction symbols:

1. The chemical bond is rigidly classified according to the structural 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. Only stable organic compounds are usually considered: intermediates such as Grignard compounds and sodiomalonic esters, and inorganic reactants, such as nitric acid, are therefore not expressed in the reaction symbols.

2. *Reagents*

A further subdivision, not included in the reaction symbols, is based on the reagents used. The sequence of the reagents 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 forms part of the product, 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_3 and sodium in a nitrosation with $NaNO_2$.

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]
designed for both current awareness and retrospective retrieval. Its monthly publication, the Journal of Synthetic Methods, covers the journal and patent literature, and provides 3,000 abstracts of recently published papers annually, together with 3,000 supplementary references.
On-line access is available to over 60,000 reactions, including the data in all the abstracts in Synthetic Methods.

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 if yields are not indicated.

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

Trends in Synthetic Organic Chemistry 1988

The successful application of organoselenium chemistry to routine synthetic methodology stems largely from the availability of inexpensive selenylating agents and such methods as the classical selenoxide elimination (Synth. Meth. *29*, 912) for elaborating intermediates. Super-electrophilic phenylselenenyl triflate may add yet another dimension, as illustrated in an interesting Se-mediated Polonovski rearrangement via 1,1-selenoxyamines[1]. Oxyselenation[2] may also be initiated with the same electrophile, while a two-step variant via oxymercuration is reliant on a mercury-selenium exchange with benzoylsulfenyl phenyl selenide as electrophile[3].

No less notable are new syntheses based on organotellurium chemistry. A recent highlight is a simple route to stabilised organolithium compds. via tellurium-lithium exchange, which has also been adapted for halogen-lithium exchange in a one-pot process[4]. As an addition to organotellurium(II) electrophiles, phenyltellurinyl trifluoroacetate is advantageous in securing N-protected 2-aminotellurides from olefins[5], whereas phenyltellurenyl iodide has been applied to the α-functionalisation of enolates[6].

Among silicon-based methodologies, the Peterson olefination and syntheses with allylsilanes and their oxa-analogs (silyl enol ethers) are well established. To these one can now add a new concept: that expanding the coordination number at silicon to five may impart exceptional lability to both the hydrido- and organo-silicon bond[7]. Thus, sodium hydridobiscatecholatosilicates are more efficient reducing agents than neutral silicon hydrides[8], while C-allylation with pentacoordinate Si-allylsilicates has clear advantages in terms of

[1] R. Okazaki, Y. Itoh, Chem. Letters *1987*, 1575–8.
[2] S. Murata, T. Suzuki, Tetrahedron Letters *28*, 4297–8, 4415–6 (1987).
[3] T. Toru et al., Chem. Letters *1987*, 1827–30.
[4] T. Hiiro et al., Angew. Chem. Intern. Ed. *26*, 1187–8 (1987); reviews of organotellurium compds. in organic synthesis s. I.D. Sadekov et al., Russ. Chem. Rev. *56*, 343–54 (1987); H. Suzuki, Yuki Gosei Kagaku Kyokaishi *45*, 603–15 (1987).
[5] N.X. Hu et al., Chem. Letters *1987*, 1327–30.
[6] T. Hiiro et al., Synthesis *1987*, 1096–7.
[7] A. Boudin et al., Bull. Chem. Soc. Japan *61*, 101–6 (1988).
[8] M. Kira, K. Sato, H. Sakurai, Chem. Letters *1987*, 2243–6; asym. variant s. S. Kohra et al., Tetrahedron Letters *29*, 89–92 (1988).

regio- and chemo-selectivity over the conventional allylsilanes[9]. Noteworthy, also, is the novel difluorotrimethylsilicate, $[Me_3SiF_2]^-$, which undergoes cross-coupling with aryl halides in a new methylarene synthesis[10].

Perhaps no aspect of chemistry has developed faster in the last 2–3 years than radical ring closure[11], conventionally terminated by H-atom transfer from tri-n-butyltin hydride[12]. Novel variations on this theme include an indoline synthesis via radical arylation[13], a pyrrolizidine ring closure via allyl radicals[14], a ring expansion by 3 or 4 carbon atoms to yield macrocyclic ketones[15], and a ring expansion to macrolides through a consecutive intramolecular homolytic addition-β-scission of alkoxyl radicals[16]. In addition, the concept of "atom transfer cycloaddition" is exemplified for the first time in an intermolecular cyclopentane annelation via iodine atom transfer[17]; and, more recently, ring-fused chiral γ-lactones have been prepared via tin hydride-induced desulfurization through α-acoxy radicals[18]. Continuing this theme, Barton's radical methodology based on decarboxylation of acyl thiohydroxamates has been applied to N-heterocyclic ring closure via aminium radicals[19]; and, in the acyclic context, chiral acyl thiohydroxamates derived from tartaric acid smoothly decarboxylate to chiral radicals which add to unactivated olefins without loss of optical integrity[20]. Alternative methods of generating alkyl radicals, from both alkyl iodides[21] and acylcobalt complexes[22], have also been reported, as has an alkyl equivalent of the Heck reaction based on photolysis of an alkylcobalt(III) complex[23].

Syntheses via palladium π-allyl intermediates have developed with reductive variants, so that 1,2-addition to aldehydes is now possible

[9] A. Hosomi, S. Kohra, Y. Tominaga, J. Chem. Soc. Chem. Commun. *1987*, 1517–8.

[10] Y. Hatanaka, T. Hiyama, Tetrahedron Letters *29*, 97–8 (1988).

[11] Reviews s. M. Ramaiah, Tetrahedron *43*, 3541–76 (1987); G. Stork, Bull. Chem. Soc. Japan *61*, 149–54 (1988).

[12] Review of the reagent s. W.P. Neumann, Synthesis *1987*, 665–83.

[13] J.P. Dittami, H. Ramanathan, Tetrahedron Letters *29*, 45–8 (1988).

[14] D.C. Lathbury, P.J. Parsons, I. Pinto, J. Chem. Soc. Chem. Commun. *1988*, 81–3.

[15] P. Dowd, S.-C. Choi, J. Am. Chem. Soc. *109*, 6548–9 (1987).

[16] H. Suginome, S. Yamada, Chem. Letters *1988*, 245–8.

[17] D.P. Curran, M.-H. Chen, J. Am. Chem. Soc. *109*, 6558–60 (1987).

[18] J.P. Marino, E. Laborde, R.S. Paley, J. Am. Chem. Soc. *110*, 966–8 (1988).

[19] M. Newcomb, T.M. Deeb, J. Am. Chem. Soc. *109*, 3163–5 (1987); review s. D. Crich, Aldrichimica Acta *20*, 35–42 (1987).

[20] D.H.R. Barton et al., J. Chem. Soc. Chem. Commun. *1987*, 1790–2.

[21] F. Fontana, F. Minisci, E. Vismara, Tetrahedron Letters *28*, 6373–6 (1987).

[22] V.F. Patel, G. Pattenden, Tetrahedron Letters *29*, 707–10 (1988).

[23] B.P. Branchaud, M.S. Meier, Y. Choi, Tetrahedron Letters *29*, 167–70 (1988).

by virtue of a charge reversal of the intermediate complex[24]. In the same vein, vinylisocyclics are formed with valuable chemo-, stereo- and regio-selectivity via reductive ring closure using (tri-*n*-butyl-stannyl)diethylalane[25]. In a conventional nucleophilic displacement, precursor acoxy-2-ethylenes (or nitro-analogs) yield 1,3-dienes via palladium-catalyzed *in situ*-Wittig synthesis[26], while novel zwit-terionic palladium π-allyl intermediates may be generated from 2-subst. vinylcyclopropanes as the key step in dipolar [3 + 2]-annela-tion with heterocumulenes[27]. A palladium variant of Oppolzer's magnesium-ene reaction is complementary in that 1,2-divinylcyclo-pentanes may be formed from derivatives of 2-ene-1,4-diols[28]; bis-carbamates of the latter also cyclize via π-allyl intermediates to produce 4-vinyl-2-oxazolidones[29].

The chemistry of enyne ring closures has advanced rapidly. Thus, palladium-catalyzed isomerization to 1,2-dialkylidenecyclopentanes (Synth. Meth. *41*, 671) has now been extended to yield cyclohexane analogs by using an *in situ*-formed polymer-based nickel(0) cat-alyst[30]. A reductive method via hydridopalladation affords eniso-cyclics[31], which alternatively are obtainable, regio- and geo-specifi-cally, via hydrostannylation[32]; a recent review of the use of or-ganozirconium compounds also highlights enyne cyclization via intramolecular carbometalation[33]. The intermolecular Paulsen-Khand cyclopent-2-enone annelation, which is often limited by low yields, has been enhanced in the presence of suitably positioned directing ligands[34], and is clearly improved on a silica gel surface (as also, incidentally, is [4 + 2]-cycloaddition)[35].

In the field of asym. synthesis, the influence of chiral 2-aminoalco-hols is exemplified in asym. induction on dialkylzinc addition to aldehydes (Synth. Meth. *42*, 616); a variety of new ligands

[24] Y. Masuyama, N. Kinugawa, Y. Kurusu, J. Org. Chem. *52*, 3702–4 (1987); J. Chem. Soc. Chem. Commun. *1988*, 44–5; s.a. B.M. Trost, G.B. Tometzki, J. Org. Chem. *53*, 915–7 (1988).

[25] B.M. Trost, R. Walchli, J. Am. Chem. Soc. *109*, 3487–8 (1987).

[26] R. Tamura et al., J. Org. Chem. *52*, 4121–4 (1987).

[27] K. Yamamoto, T. Ishida, J. Tsuji, Chem. Letters *1987*, 1157–8.

[28] W. Oppolzer, J.-M. Gaudin, Helv. Chim. Acta *70*, 1477–81 (1987).

[29] T. Hayashi, A. Yamamoto, Y. Ito, Tetrahedron Letters *28*, 4837–40 (1987)

[30] B.M. Trost, J.M. Tour, J. Am. Chem. Soc. *109*, 5268–70 (1987).

[31] B.M. Trost, F. Rise, J. Am. Chem. Soc. *109*, 3161–3 (1987).

[32] K. Nozaki, K. Oshima, K. Utimoto, J. Am. Chem. Soc. *109*, 2547–9 (1987).

[33] E. Negishi, T. Takahashi, Synthesis *1988*, 1–18.

[34] M.E. Krafft, J. Am. Chem. Soc. *110*, 968–70 (1988).

[35] V.A. Smit et al., Izv. Akad. Nauk SSR Ser. Khim. *1987*, 2870–1; Tetrahedron Letters *29*, 175–8 (1988).

("chirands") of this type are now available[36], and may be prepared by asym. carbophilic addition to α-dibenzylaminoaldehydes, the diastereoselectivity being dependent on the choice of organometallic agent[37]. Numerous instances of stereochemical reversal ("switching") with added Group II halides have been noted. Thus, the sense of asym. induction on ketoacetal reduction with $LiAlH_4$ is completely reversed with added $MgBr_2$[38], which also "switches" the diastereoselectivity of allylophilic addition to chiral α-benzyloxyaldehydes[39]. LiBr may also exert dramatic effects, as in the asym. C-α-alkylation of a chiral glycine deriv. where the halide inhibits undesirable dianion formation[40]. Chiral camphorsulfonamide residues also have a remarkable influence on enantioselectivity[41], as evident in a nickel-catalyzed asym. [3+2]-cycloaddition with methylenecyclopropanes, affording chiral methylenecyclopentanes with up to 98% diastereoisomeric excess[42]. Chiral oxazaphospholan 2-oxides also exert a powerful asym. induction in, for example, asym. 1,4-addition[43], while chiral acetals feature in a novel asym. [4+4]-ene reaction[44]. The intramolecular variant of the latter mode of addition is rare by virtue of competing [4+2]-cycloaddition; however, 2,2'-bipyridyliron(0) clearly enhances the ene synthesis in a new stereospecific 3,4-divinyltetrahydropyran synthesis[45].

Asym. [4+2]-cycloaddition is reported with ca. 100% diastereoselectivity by using chiral menthol and lactol ester functions in the dienophile[46], while a captodative olefin substituted with a chiral 2-methoxymethylpyrrolidine residue undergoes a highly efficient asym. photo-diene synthesis with a substituted naphthalene[47].

[36] Recent references s. K. Soai, M. Nishi, Y. Ito, Chem. Letters *1987*, 2405–6; E.J. Corey, F.J. Hannon, Tetrahedron Letters *28*, 5233–6, 5237–40 (1987).

[37] M.T. Reetz, M.W. Drewes, A. Schmitz, Angew. Chem. Intern. Ed. *26*, 1141–3 (1987).

[38] Y. Tamura, H. Annoura, H. Fujioka, Tetrahedron Letters *28*, 5681–2 (1987); K. Hasegawa et al., ibid. *28*, 1671–2 (1987).

[39] D.R. Williams, F.D. Klingler, Tetrahedron Letters *28*, 869–72 (1987).

[40] R. Polt, D. Seebach, Helv. Chim. Acta *70*, 1930–6 (1987).

[41] Review of asym. synthesis with chiral camphor derivs. s. W. Oppolzer, Tetrahedron *43*, 1969–2004 (1987).

[42] P. Binger, B. Schäfer, Tetrahedron Letters *29*, 529–30 (1988); reviews of alkylidenecyclopropanes s. B. Halton, P.J. Stang, Acc. Chem. Res. *20*, 443–8 (1987); P. Binger, H.M. Buch, Topics Curr. Chem. *135*, 77–151 (1987).

[43] D.H. Hua et al., J. Am. Chem. Soc. *109*, 5026–9 (1987).

[44] J.M. Takacs, L.G. Anderson, P.W. Newsome, J. Am. Chem. Soc. *109*, 2542–4 (1987).

[45] J.M. Takacs et al., Tetrahedron Letters *28*, 5627–30 (1987).

[46] H. Hartmann et al., Angew. Chem. Intern. Ed. *26*, 1143–5 (1987); M. Yamauchi, T. Watanabe, J. Chem. Soc. Chem. Commun. *1988*, 27–8.

[47] D. Döpp, M. Pies, J. Chem. Soc. Chem. Commun. *1987*, 1734–5; review of photoaddition to arenes s. J.J. McCullough, Chem. Rev. *87*, 811–60 (1987).

Asym. heterodiene synthesis has also been exploited with both chiral reagents and educts. Thus, new organoaluminium reagents based on chiral triarylsilylated binaphthols feature in an improved asym.   · dihydro-4-pyrone synthesis[48]; and a new carbacephem synthesis involves asym. heterodiene synthesis with a chiral Δ^1-azetine generated *in situ* from a 4-acoxy-2-azetidinone[49]. A new asym. synthesis of α-aryl-α-aminoacids is also based on chiral 2-azetidinones[50], whereas the element of asymmetry in the Ugi reaction is introduced with a carbohydrate template[51].

The correct sequencing of common transforms, such as cycloaddition, 1,4-addition, sigmatropic rearrangement, and retro-synthetic pathways, can provide ingenious routes to both simple and complex ring systems. A new vinylindole synthesis is exemplary in that it "lines up" a 1,3-dipolar cycloaddition, hetero-Cope rearrangement, and retro-Michael addition without isolation of intermediates[52]; a one-step conversion of a bridged tetrahydropyridine to a cyclohexene analog is achieved by retrodiene elimination of an imine with instantaneous trapping of the formed diene by [4+2]-cycloaddition[53]. Isolated, polysubstituted cyclohexenes, on the other hand, are formed in a one-pot sequence which combines [4+2]-cycloaddition with allylboration[54].

In asym. homogeneous hydrogenation, chiral ruthenium(II) phosphine complexes are on a par with enzymes in reducing functionalized ketones with ca. 100% enantioselectivity[55]; and the catalyst may also be employed in a highly efficient kinetic resolution of racemic allyl alcohols[56]. Chiral rhodium aminoferrocenylphosphine[57] and chiral titanocene complexes[58] are effective for asym. hydrogenation of olefins, while a novel nitrosylrhenium Lewis acid binds methyl ketones in such a manner to direct hydride attack

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with the highest recorded enantioselectivity for simple ketone reduction[59].

Very recently, the chemistry of iodine(III) compds. has been in the limelight. Thus, [hydroxy(mesyloxy)iodo]benzene efficiently converts carbonyl compds. to their α-mesyloxy derivs. under mild conditions[60], while an oxygenated allyl(phenyl)iodine(III) species is implicated in a novel aromatic allylation, the driving force of which is the liberation of iodobenzene[61]. Nucleophilic displacement of the latter also features in the syntheses of acetylene derivs. from acetyleneiodonium salts[62].

For the peptide chemist, a review of solid phase peptide synthesis traces the historical development of the Merrifield approach[63], though unfortunately it pre-dates the report of a novel resin with cobalt(III)-linked spacer groups which are simply removed under mild conditions with 2-mercaptoethanol[64]. Enzyme-catalyzed peptide syntheses have also been extended with the discovery that organic media so reduce the conventional L-specificity of simple proteases that D-aminoacids may now be incorporated under these conditions[65]. Media effects are indeed profound on enzymatic procedures[66], and may combine with other techniques, such as ultrasonication[67], to provide another dimension to this rapidly expanding field.

Lastly, brief mention of three highlights: the generation of functionalized organocopper(II) reagents by chemoselective insertion of Cu(0) into the carbon-halogen bond[68]; novel syntheses with lithiated imidoylsilanes[69]; and the intriguing observation that acetylene groups can be "bent" by cobalt complexation to secure the correct geometry for ring closure[70].

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Systematic Survey Vols 41 and 42

Reaction symbol	41	42
NC∩HC	136	144
NC∩OC	136	145
NC∩NN	137	145
NC∩NC	137	
NC∩SC	137	
NC∩CC	138	146
NC↓↑H	139	147
NC↓↑O	143	151
NC↓↑N	158	165
NC↓↑Hal	163	168
NC↓↑S	168	176
NC↓↑Rem	171	178
NC↓↑C	174	181
NC↑H	178	184
NC↑O	179	185
NC↑N	184	190
NC↑Hal		192
NC↑S	186	192
NC↑Rem	187	193
NC↑C	188	193
HalS↓↑Hal	190	196
HalS↓↑S	190	
HalS↓↑Rem		196
HalRem⇓ORem		197
HalRem⇓Rem		197
HalRem↓↑H		198
HalRem↓↑O		198
HalRem↓↑C		198
HalC⇓OC	190	198
HalC⇓NC		199
HalC⇓CC	191	199
HalC∩OC		202
HalC∩NHal		202
HalC↓↑H	194	203
HalC↓↑O	199	208
HalC↓↑N	203	213
HalC↓↑Hal	203	213
HalC↓↑S	205	215
HalC↓↑Rem	205	215
HalC↓↑C	206	216
HalC↑Rem		217
SS↓↑H	207	218
SS↓↑N	207	
SS↓↑Hal	207	
SS↓↑S	208	218
SS↑H	208	

Reaction symbol	41	42
SRem⇓Rem	208	
SRem↓↑H	208	
SRem↓↑O	209	
SRem↓↑N	209	
SRem↓↑Hal	209	
SRem↓↑S		219
SRem↓↑Rem		219
SRem↓↑C		219
SC⇓OC	209	219
SC⇓NC	210	
SC⇓SC	211	220
SC⇓CC	211	221
SC∩HC		222
SC∩OC		222
SC∩CC	213	222
SC↓↑H	214	222
SC↓↑O	215	223
SC↓↑N	217	227
SC↓↑Hal	219	228
SC↓↑S	224	231
SC↓↑Rem	225	233
SC↓↑C	226	236
SC↑H		237
SC↑O	229	237
SC↑N		238
SC↑Hal	230	
SC↑Rem		238
SC↑C	230	239
RemRem↓↑Hal		239
RemRem↓↑C	231	239
RemC⇓ORem	231	
RemC⇓OC	231	240
RemC⇓NC	232	
RemC⇓HalC		240
RemC⇓C	232	241
RemC⇓CC	232	241
RemC∩ORem		243
RemC∩OC		244
RemC∩SRem	236	
RemC∩CC		244
RemC↓↑H	237	245
RemC↓↑O	238	246
RemC↓↑N	240	247
RemC↓↑Hal	241	248
RemC↓↑S	243	253
RemC↓↑Rem	244	253
RemC↓↑C	245	254
RemC↑O		256
RemC↑N		256

Reaction symbol	41	42
RemC↑Hal	247	
RemC↑Rem		256
CC⇓HC	247	257
CC⇓OC	248	257
CC⇓NC	258	271
CC⇓SC	261	274
CC⇓CC	261	274
CC∩HO	281	299
CC∩HN	282	
CC∩HC	283	299
CC∩ON	286	
CC∩ORem	286	
CC∩OC	286	302
CC∩NN		305
CC∩NS	290	
CC∩NC	290	305
CC∩HalC	292	307
CC∩SC	292	307
CC∩RemC	293	307
CC∩CC	293	308
CC↓↑H	295	312
CC↓↑O	299	315
CC↓↑N	314	333
CC↓↑Hal	319	339
CC↓↑S	349	368
CC↓↑Rem	352	373
CC↓↑C	379	399
CC↑H	385	404
CC↑O	389	406
CC↑N	395	412
CC↑Hal	396	414
CC↑S	403	421
CC↑Rem	405	423
CC↑C	410	427
ElN↑O	416	431
ElN↑C	416	
ElS↑O	417	432
ElS↑C	418	
ElRem↑O	418	432
ElRem↑Hal	419	
ElC↑O	419	
RadN↑El		433
Het⇓O	419	
Het⇓N	419	433
Het⇓S	419	
Het⇓Rem		433
Het↓↑		434
Res	420	434