Theilheimer's Synthetic Methods of Organic Chemistry

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Preface

This is the first of the biannual volumes of *Theilheimer* for 1998, containing abstracts of new synthetic methods and supplementary data from papers published in the scientific literature during the first nine months of 1997.

For browsing purposes, these are displayed according to the Systemic Classification (symbol notation) so that reactions of the same type and associated data appear together. For example, all deprotections appear in the early sections (under HO↓↑, HN↓↑, HS↓↑); reduction of oxo compds., imines and carbon-carbon multiple bonds under the HC⇓ sections; C-defunctionalization under the HC↓↑ sections; oxy-functionalization under the OC sections; aminations, nitrations, peptide coupling etc. under the NC sections; halogenation under the HalC sections; sulfurations, under the SC sections; selenation, stannations, phosphonylations, etc. under the RemC sections; syntheses involving C-C bond formation in the latter half of the book under the CC sections; and data on resolutions (Res) at the end. A list of reaction symbols and references thereto is given in the Systematic Survey (p. XXI).

The displayed data are supported by the customary in-depth Subject Index, and access to supplementary data can be made in the usual manner via the Supplementary References Index, e.g. the reader interested in updates to asym. dihydroxylation (Synth. Meth. *47*, 114), will note from p. 295 that additional references can be found on p. 40, and 242 of this volume.

As usual, the volume contains a 'Reviews' section (p. 239), covering reviews published up to and including February 1998, and a 'Trends' section (p. XI) incorporating key developments in synthetic chemistry up to and including March 1998. These latter references will appear as abstracts in the next volume.

I would like to express my gratitude to Dr. Theilheimer for his encouragement in the preparation of these yearbooks, and to my colleagues at Derwent Information Ltd., London, whose *Journal of Synthetic Methods* provides data for inclusion in these volumes. A special thank you goes to my wife and to Rabeya Das and Kath Ince of Derwent for processing the information and overseeing the electronic processing by which these volumes are published.

April 1998 *A.F. Finch*, Editor

Advice to the User

General Remarks

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.

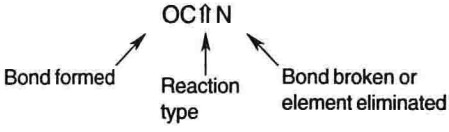
A brief review, *Trends and Developments in Synthetic Organic Chemistry*, stresses highlights of general interest and calls attention to key methods too recent to be included in the body of the text.

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 289) 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 such as *startg. m. f.* (starting material for the preparation of ...).

Method of Classification

Reaction Symbols. As summarized in the Systematic Survey (p XXI), 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.



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:

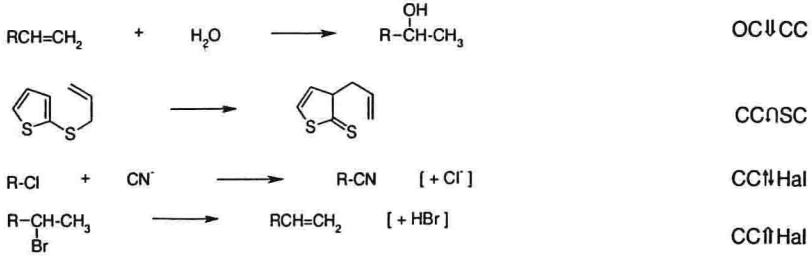
H, O, N, Hal (Halogen), S, Rem (Remaining elements), and C.

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

in which both hydrogen-oxygen and hydrogen-carbon bonds are formed, the symbol is HC⇓OC and not HO⇓OC.

The second part of the symbol refers to the reaction type. Four types are distinguished: addition (⇓), rearrangement (∩), exchange (⇅), and elimination (⇑), e.g.



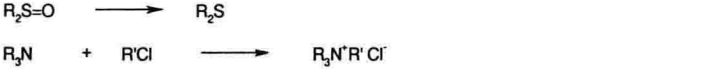
Monomolecular reactions are either rearrangements (∩), where the molecular weight of the starting material and product are the same, or eliminations (⇑), where an organic or inorganic fragment is lost; bimolecular and multicomponent reactions are either additions (⇓), such as intermolecular

Diels-Alder reactions, Michael addition and 1,4-addition of organometallics, 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.

For addition, 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. 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 incorporate the special symbols El (electron pair), Het (heteropolar bond), Rad (radical), Res (resolutions), and Oth (other reaction types), e.g.



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.

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_5 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:

Derwent Reaction Service[1]. Designed for both current awareness and retrospective retrieval. Its monthly publication, the *Derwent Journal of Synthetic Methods*, covers the journal and patent literature, and provides 3,000 abstracts of recently published papers annually.

On-line REACCS and keyword access is available to over 80,000 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. This is particularly useful for accessing papers quoting details of a particular method which has been included in these volumes from a preliminary communication.

Chemical Abstracts 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 abstracts 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 Chinese or Japanese language are usually only included if the method in question is not described elsewhere.

[1] Derwent Information Ltd., 14 Great Queen Street, London WC2B 5DF, England.

[2] Institute for Scientific Information, Philadelphia, Pa., USA.

[3] Chemical Abstracts Service, Columbus, Ohio, USA.

Trends and Developments in Synthetic Organic Chemistry 1998

In designing a route to complex molecules, functional group compatibility often becomes a central issue at each stage in the synthesis. Where reduction or oxidation is involved, a wide range of reaction conditions, reagants and general strategies may be available to target one specific group in the presence of another potentially reactive function, as in the chemoselective reduction of ketones in the presence of aldehydes. In Lewis acid-catalyzed conversions, however, **functional group differentiation** is less developed and, until recently, few attempts had been made to reverse traditional reactivity patterns. Now, through bidentate carbonyl group coordination with an aluminum aroxide, aldol-type condensation and Sakurai-type coupling of ketones or aldehydes can be undertaken in the presence of acetals (which are considerably more reactive under Lewis acid catalysis with the more familiar Me_3SiOTf or $TiCl_4$)[1]. More remarkably, the bulky aluminum tris(2,6-diphenylphenoxide) directs preferential γ-deprotonation of enals in the presence of satd. aldehydes[2], while ytterbium triflate[3] and polymer-based scandium bis(triflate)[4] preferentially activate aldimines in the presence of aldehydes. More remarkable still is the concept of 'parallel differentiated recognition', as evident in aldol-type condensation involving a four-component mixture of a ketone, an acetal, a silyl enolether and an O-silyl O-alkyl ketene acetal: the weak Lewis acid, bis(pentafluorophenyl)tin dibromide, directs the silyl enolether to react preferentially with the acetal, while the ketene acetal reacts with the ketone![5]

Contracting two or more steps of a multi-step synthesis into one or lesser steps without isolation of intermediate(s) can be advantageous in terms of cost and manipulation. Hence the emergence of *in situ*-methodologies[6]. What promises even more is the combining of two distinct catalytic processes in one pot by the agency of different catalysts - with control of stereochemistry at each site! This is illustrated by the simultaneous asym. hydrogenation of both the enamide unsaturation and the keto group of an enamidoketone in the presence of a rhodium(I) complex (for reduction of the former function) and $RuBr_2$((S)-BINAP) (for the keto reduction)[7]. Differential palladium-catalyzed Heck and Suzuki coupling of an iodoaryldiazonium salt can also be effected in one pot, the regioselectivity being determined by the order of

addition of the alkene and boronic acid[8]. The coupling of reactions in tandem, domino or serial fashion is a further synthetic ploy to 'cut corners', the latter being represented by a novel total steroid synthesis involving a radical cascade tetracyclization[9]. A recent 3-component domino tricyclization is also notable in that five new bonds and four new chiral centres are created in one step[10], while the classical Ugi condensation has been upgraded to a 5-component condensation in the presence of CO_2 (CS_2 or COS), thereby providing α-(carb-alkoxyamino)carboxylic acid amides (or thio analogs) in one step from inexpensive substrates[11].

In asym. catalysis with chiral transition metal complexes, enhancement of enantioselectivity by ligand manipulation has met with limited success, being subject rather more to chance than design. A more expedient practice is to generate more active variants of traditional ligands *in situ* by incorporating inexpensive additives or simply by adjusting the relative amount of metal and ligand. Thus, in asym. catalytic protonation of silyl enol ethers with $PdCl_2$[(R)-BINAP] (using water as proton source), enantioselectivity is increased simply by the addition of a sec. amine[12]. More remarkably, while enantiopure $RuCl_2$(tol-BINAP)$(dmf)_n$ is ineffective in catalytic hydrogenation of simple enones, the combination of the racemic complex with a relatively inexpensive chiral 1,2-diamine effects a quantitative conversion to the allyl alcohol in 95% e.e![13] It is also notable that the relative proportion of Ti(OPr-*i*)$_4$ and (S)-BINOL critically determines the enantioselectivity of dialkylzinc addition to aldehydes (a monochiral species derived from Ti((S)-BINOL)$_2$ and excess of Ti(OPr-*i*)$_4$ being optimum)[14]. In the titanium(IV)-catalyzed carbonyl-ene reaction, a further element enters into the equation: the self-association of 'smart' catalysts formed from Ti(IV) and two *different* chiral diol ligands: the resulting 1:1:1 complex exhibits significantly higher enantioselectivity than the 1:2 complexes formed from Ti(IV) and either of the chiral diols[15]. High levels of enantioselectivity can also be achieved inexpensively under asym. autoinduction, as in Lewis acid-catalyzed Diels-Alder reaction in the presence of Et_2AlCl and a chiral biphenanthrol[16]. Here, enantioselectivity increases as the reaction proceeds through generation of a more active catalyst formed by interaction of the product with Al-biphenthrolate (an effect which is further enhanced by the addition of an achiral carbonyl compd.).

With the advent of Noyori's asym. hydrogenation (*43*, 51), the axially asymmetric binaphthol motif assumed centre stage in the development of novel and highly effective chiral auxiliaries for a variety of disparate transformations. More recently, chiral bis(Δ^2-oxazolines)[17] and relatively uncomplex di(phosphines)[18] have materialized in a variety of guises, and

the emergence of Trost's chiral 1,2-bis[2'-(diphenylphosphino)benzamido]-cyclohexane introduced a further structural motif - **the 1,2-diaminocyclohexane residue** - for ligand design[19]. In one adaptation, it serves as a highly effective chiral platform for the generation of Lewis acidic transition metal complexes, a chromium(III) Schiff base variant being notably of value in asym. hetero-Diels-Alder syntheses[20]. The corresponding titanium(IV) equivalent is even more remarkable, being the first complex of this type to be isolated and characterized[21]. As in previous years, chiral 2-oxazolidones[22] and sultams[23] are well represented as stoichiometric auxiliaries, and a particular reference might be given to the lithium/(–)-sparteine combination[24] which is particularly effective in asym. deprotonation of urethan-protected amines[25] and in asym. carbolithiation[26].

While reviews and essential developments in combinatorial chemistry are covered in these volumes, the subject matter of this key subdivision of organic synthesis is, unfortunately, not readily amenable to systematic analysis in the customary *Theilheimer* manner[27]. Developments in non-combinatorial **polymer-based syntheses**, however, are handled in depth, as evident from the Subject Index entries under 'Polymer-based ...' and 'Polymer supports'. Some recent additions to the 'polymer pool' include polymer-based radical cross-coupling[28], Mannich[29] and Suzuki-type[30] reactions, [3+2]-cycloaddition[31], nucleophilic displacement of polymer-based arene-sulfonates[32], and multipolymer-based asym. dihydroxylation[33]. A number of new polymer-based reagents have also been designed for ease of separation, such as supported-variants of lithium naphthalenide[34], a dioxirane[35], and 1,5,7-triazabicyclo[4.4.0]dec-5-ene[36] as a readily removable base. Developments have also been made in liquid-phase syntheses with *soluble* polymer supports, which can be readily precipitated after reaction. Thus, the classical 2-azetidinone synthesis (*7*, 836) can now be conducted with polyethylene glycol-based imines[37], which also feature in the α-alkylation of α-(alkylideneamino)carboxylic acid esters in the presence of a polyethylene glycol as phase transfer catalyst[38]. For clean-up purposes, a novel polymer-based sec. borane has also evolved for the purification ('fishing out') of 2-aminoalcohols[39], and in aqueous chemistry a new polymeric rhodium complex is available for the regioselective hydroformylation of styrenes and higher olefins[40]. However, for the classical palladium-catalyzed arylation of acetylenes in the presence of CuI and base (*27*, 851), as well as syntheses via palladium π-allyl complexes, a water-soluble poly(N-isopropyl)acrylamide-based palladium phosphine complex is preferred for coupling in pure water or mixed aqueous solvents[41].

Inorganic supports (SiO_2, Al_2O_3...), zeolites, and solid acids were a feature

of the *Trends* section of the last volume, and applications are no less evident six months on. Perhaps one might single out their role as supports for microwave enhancement of chemical reactions in the absence of solvent[42]. Layered hydrotalcites (Al/Mg type) have also been developed as regenerable solid bases, e.g. for heterogeneous epoxidation of olefins with H_2O_2/benzonitrile[43] and for Meerwein-Pondorf-Verley reduction[44]. Heterogeneous and readily removable, silica-supported polysiloxane-palladium complexes also merit consideration as useful alternatives to conventional homogeneous palladium catalysts in, for example, Heck arylation (*53*, 425), syntheses via palladium π-allyl complexes (*52*, 273s*53*), and Friedel-Crafts monoalkylation with olefins in supercritical CO_2[45].

Developments in brief:

Baylis-Hillman reaction: an in-depth review with particular reference to Morita's original work with triphenylphosphine[46]; note the same conversion can be achieved with thioethers[47].

Pauson-Khand reaction: with $Co_2(CO)_8$ in *catalytic* amount in supercritical CO_2[48]; with the cobalt cluster complex, $Co_4(CO)_{12}$, in catalytic amount[49]; with *in situ*-generated $Co_2(CO)_8$[50]; a titanocene variant with bis(trichloromethyl) carbonate as a crystalline carbon monoxide equivalent[51]; with allenes[52]; an asym. variant[53]; and rate enhancement with added prim. amine[54].

Aldol condensation: $TiCl_4$-mediated aldol condensation at the *more* encumbered α-site of unsym. ketones[55]; $TiCl_4$-mediated regio- and stereospecific cross-aldol condensation of two different ketones or aldehydes[56]; asym. aldol-type condensation with trichlorosilyl enol ethers in the presence of a chiral Lewis *base*[57]; catalytic asym. condensation with a silylated dienolate induced by a chiral copper(II) fluoride complex[58]; asym. synthesis of β-hydroxycarboxylic acids based on aldol condensation of a camphor-derived α-siloxyketone[59]; and aldol-type condensation in water or aq. micelles with a catalytic amount of $InCl_3$ as Lewis acid[60].

Dearomatization by nucleophilic addition: by stereospecific intramolecular carbanion addition[61] and via thia-Sommelet rearrangement[62]; asym. nucleophilic addition to $Cr(CO)_3$-complexed phenolethers[63].

Enzymatic, peptide- and protein-catalysis: surfactant-mediated enzymatic peptide synthesis in *alcoholic* media with subtilisin[64], and α-chymotrypsin-catalyzed peptide synthesis with 'poor' amino acids as their carbamylmethyl esters[65]; lipase-catalyzed enzymatic desymmetrization of ketones by asym. hydrolysis of their enolesters[66]; a highly selective enzyme-like kinetic resolution of acylaminoalcohols catalyzed by an imidazole-

derivatized tripeptide[67]; and asym. reductive amination of α-keto acids within a pyridoxamine-functionalized protein cavity[68].

Ring closing metathesis: a review[69]; asym. conversion with a chiral Mo-carbene complex[70]; and metathesis in supercritical CO_2[71].

'Fluorous' reagents and chemistry as an aid to work-up: palladium-catalyzed cross-coupling of organozinc halides with a fluorous triarylphosphine as ligand in a fluorous 2-phase medium[72]; radical carbonylation with a fluorous organotin hydride in *catalytic* amount[73]; and solvent-less syntheses with fluorous allylstannanes based on a facile solid-phase chromatographic extraction procedure on fluorous reverse-phase silica gel[74].

Radical syntheses: deoxygenation of alcohols via xanthates with non-toxic phosphine-borane complexes[75] or di-*n*-butylphosphine oxide[76]; triethylamine-mediated radical ring closures of vinyl iodides via photo-induced electron transfer as a clean alternative to the standard tin hydride route[77]; oxidative ring closures of unsatd. malonic acid esters via single electron transfer with ferrocenium ion as an alternative to the traditional Mn(III)- or Ce(IV)-mediated procedures[78]; and γ-thiolactone ring closure via radical carbonylation[79].

Syntheses with samarium diiodide: generation of allyl- and benzyl-samarium(III) compds. in *tetrahydropyran*[80]; medium-ring closures under normal dilution[81]; *non-basic,* reductive [2.3]-Wittig rearrangement via 1,5-hydrogen atom transfer[82]; and syntheses with YbI_2 as an alternative to SmI_2[83].

Syntheses with titanium η^2-olefin complexes: elaboration of allenes via 5-alkylidenetitanacyclopent-2-enes[84]; asym. intramolecular variant[85]; and Δ^3-2-pyrrolones via carboxylation of 1,2-azatitanacyclopent-3-enes[86].

Diorganozinc addition: asym. Ti(IV)-promoted addition of dialkylzincs to *ketones* in the presence of a chiral 2-aminoalcohol[87]; asym. 1,4-addition and 1,4-addition-aldol condensation with BINOL-based phosphoromono-amidites[88].

Palladium catalysis: syntheses with amphiphilic bis(π-allylpalladium) species in a catalytic cycle[89]; regiospecific allylation of soft nucleophiles with added LiI[90]; C-allylation *with allyl alcohols* via *in situ*-activation as diallyl oxalates[91]; enhancement of catalytic lifetime with thermally stable, recyclable, inexpensive macrocyclic tetraphospholes as ligand[92]; further developments in Buchwald's catalytic N-arylation[93]; C-α-arylation of ketones[94]; synthesis of oxaspirocyclics and fused pyrans via Bäckvall-type intramolecular 1,4-dialkoxylation[95]; and Heck arylation with inexpensive ar. chlorides using Pd(II) salts and added tetraphenylphosphonium halide in

the presence of N,N-dimethylglycine[96].

Rhodium catalysis: catalytic oxidative amination of olefins[97]; 1,4-addition of arylstannanes[98]; asym. addition of CH-acidic compds. to aldehydes with chiral rhodium ferrocenylphosphine complexes[99]; and regiospecific C-α-allylation with a phosphite-modified Wilkinson catalyst[100].

Carbohydrate chemistry: review of transition metal-functionalization at the anomeric position[101]; review of enzymatic and whole-cell glycosidation[102]; and formation of glycosides from thioglycosides via glycosyl triflates[103] and glycosyl(fluoro)sulfonium salts[104].

Activation of hydrocarbons: reviews of activation by metal complexation[105]; electrochemical oxidation of remote isopropyl groups[106]; and asym. carbene insertion into unactivated carbon-hydrogen bonds[107].

Catalytic oxidation with molecular oxygen: transition metal-catalyzed oxidative cleavage of α-hydroxyketones with $VO(OEt)Cl_2$[108]; perruthenate-catalyzed oxidation of alcohols to oxo compds.[109]; oxidation of allyl alcohols to enals with homogeneous and supported palladium cluster complexes[110]; asym. epoxidation with a chiral Ru(II)-Δ^2-oxazoline complex and isobutanal[111]; regiospecific oxyamination with a polyaniline-supported Co(II) salen complex[112]; and co-catalytic S-oxidation with $Bi(NO_3)_3/BiBr_3$ [without a transition metal catalyst or an aldehyde!][113]; **biomimetic catalytic oxidation with molecular oxygen:** alkane hydroxylation with a mononuclear iron carboxylate supported on a modified silica surface[114]; and oxidation of allylic and benzylic alcohols with a copper-complexed tripeptide mimicking the active site of an a galactose oxidase[115].

Rhenium catalysis: improved Horner-type olefination with $ReOCl_3(PPh_3)_2$[116]; improved oxorhenium-catalyzed epoxidation with bis(trimethylsilyl) peroxide as reoxidant under anhydrous conditions[117]; with added base for acid-sensitive olefins[118]; and a review of rhenium(VII) oxo and imido complexes[119].

Finally, in the wake of co-catalysis, dual catalysis, sequential catalysis, and related catalytic strategies comes another variant: *consecutive* catalysis with the *same* catalyst, as illustrated by hydroacylation of olefins with aldehydes generated *in situ* from prim. alcohols[120]. Here, a rhodium phosphine complex (in the presence of a 2-aminopyridine to activate the aldehyde as aldimine) not only serves to oxidize the alcohol to aldehyde (with excess of the olefin as H-acceptor), it also catalyzes simultaneously the subsequent hydroacylation. Well, it's O.K. with inexpensive olefins!

[1] T. Ooi et al., Tetrahedron Lett. *38*, 7403-6 (1997).

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[3] S. Kobayashi, S. Nagayama, J. Am. Chem. Soc. *119*, 10049-53 (1997).

[4] S. Kobayashi, S. Nagayama, Synlett *1997*, 653-4.

[5] J.-X. Chen, J. Otera, Angew. Chem. Int. Ed. Engl. *37*, 91-3 (1998); differentiation between ketones and aldehydes s. Tetrahedron Lett. *39*, 1767-70 (1998).

[6] Examples s. *51*, 415; *52*, 411; *53*, 481.

[7] T. Doi et al., J. Org. Chem. *63*, 428-9 (1998).

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