SERVING THE SCIENTIFIC COMMUNITY FOR OVER 30 YEARS

Aldrichimica ACTA

VOL. 33, NO. 1 • 2000

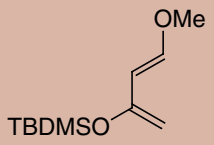
The Chemical Vapor Deposition of Metal Nitride Films Using Modern Metalorganic Precursors

Synthetic Applications of Indium Trichloride Catalyzed Reactions

Purpald®: A Reagent That Turns Aldehydes Purple!

New Products

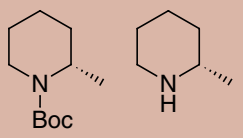
The *tert*-butyldimethylsilyl analog of Danishefsky's diene is now available. It has been used to prepare a variety of bicyclic enones and 2,3-dihydro-4*H*-pyran-4-ones.[1-3]



(1) Uchida, H. et al. *Tetrahedron Lett*. **1999**, *40*, 113. (2) Pudukulathan, Z. et al. *J. Am. Chem. Soc*. **1998**, *120*, 11953. (3) Annunziata, R. et al. *J. Org. Chem*. **1992**, *57*, 3605.

51,536-1 ***trans*-3-(*tert*-Butyldimethylsilyloxy)-1-methoxy-1,3-butadiene**, 95%

Building blocks for *trans*-2-methyl-6-substituted piperidines via deprotonation with *sec*-butyllithium followed by reaction with an electrophile.[1-3]



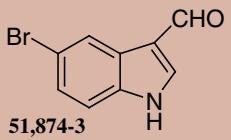
52,288-0 **52,290-2**

(1) Chackalamannil, S. et al. *J. Am. Chem. Soc*. **1996**, *118*, 9812. (2) Beak, P.; Lee, W. K. *J. Org. Chem*. **1993**, *58*, 1109. (3) Idem *ibid*. **1990**, *55*, 2578.

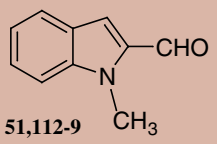
52,288-0 **(*S*)-(+)-*N*-(*tert*-Butoxycarbonyl)-2-methylpiperidine**, 98%

52,290-2 **(*S*)-(+)-2-Methylpiperidine**, 97%

Precursors for a wide variety of substituted indoles.[1-3]

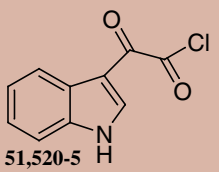


51,874-3



51,112-9

(1) Battaglia, S. et al. *Eur. J. Med. Chem*. **1999**, *34*, 93. (2) Joseph, B. et al. *J. Heterocycl. Chem*. **1997**, *34*, 525. (3) Le Borgne, M. et al. *Bioorg. Med. Chem. Lett*. **1999**, *9*, 333.



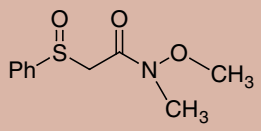
51,520-5

51,874-3 **5-Bromoindole-3-carboxaldehyde**, 98%

51,112-9 **1-Methylindole-2-carboxaldehyde**, 97%

51,520-5 **3-Indoleglyoxylyl chloride**, 98%

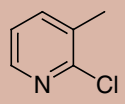
α,β-Unsaturated *N*-methoxy-*N*-methylamides are prepared from this reagent through deprotonation with sodium hydride, reaction with an alkyl halide, and in situ heating.



Beney, C. et al. *Tetrahedron Lett*. **1998**, *39*, 5779.

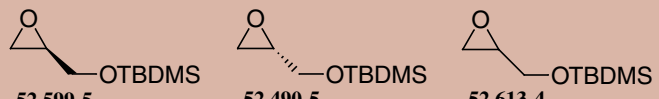
51,139-0 ***N*-Methoxy-*N*-methyl-2-(phenylsulfinyl)acetamide**, 96%

2-Substituted picolines have been prepared from this compound. Examples include (2-pyridyl)indoles and endothelin receptors.[1,2]



(1) Amat, M. et al. *J. Org. Chem*. **1997**, *62*, 3158. (2) Kourounakis, A. et al. *Biorg. Med. Chem. Lett*. **1997**, *7*, 2223.

51,894-8 **2-Chloro-3-methylpyridine**, 97%



52,599-5 **52,490-5** **52,613-4**

A variety of nucleophiles have been used to open the oxirane ring of these compounds. Examples include lithium acetylides[1,2] and lithium dithianes.[3]

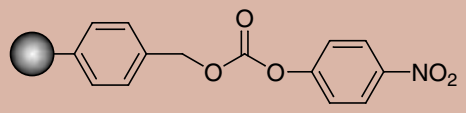
(1) Arista, L. et al. *Heterocycles* **1998**, *48*, 1325. (2) Maguire, R. J. et al. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2853. (3) Smith, A. B., III; Boldi, A. M. *J. Am. Chem. Soc*. **1997**, *119*, 6925.

52,599-5 ***tert*-Butyldimethylsilyl (*R*)-(+)-glycidyl ether**, 98%

52,490-5 ***tert*-Butyldimethylsilyl (*S*)-(–)-glycidyl ether**, 98%

52,613-4 ***tert*-Butyldimethylsilyl glycidyl ether**, 98%

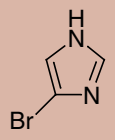
This carbonate resin is used to bind amines or amino acids as urethanes. Dipeptides and hydantoins have been prepared from these polymer-bound urethanes.[1-3]



(1) Dixit, D. M.; Leznoff, C. C. *J. Chem. Soc., Chem. Commun*. **1977**, 798. (2) Dressman, B. A. et al. *Tetrahedron Lett*. **1996**, *37*, 937. (3) Gouilleux, L. et al. *ibid*. **1996**, *37*, 7031.

51,529-9 **4-Nitrophenyl carbonate, polymer-bound on Wang Resin**

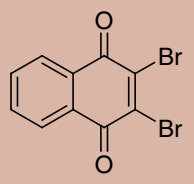
Starting material for the preparation of 4-substituted imidazoles.[1,2]



(1) Lange, J. H. M. et al. *Tetrahedron* **1995**, *51*, 13447. (2) Singh, B. et al. *J. Med. Chem*. **1992**, *35*, 4858.

47,869-5 **4-Bromo-1*H*-imidazole**, 97%

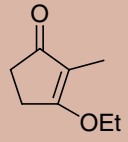
Naphthoquinones are prepared from this compound via palladium-catalyzed coupling reactions with tributylstannyl-heteroaromatics or by nucleophilic displacement of one or both bromides.[1,2]



(1) Yoshida, S. et al. *Chem. Lett*. **1996**, 139. (2) Falling, S. N.; Rapoport, H. *J. Org. Chem*. **1980**, *45*, 1260.

52,342-9 **2,3-Dibromo-1,4-naphthoquinone**, 97%

Precursor for 3-substituted-2-methyl-2-cyclopenten-1-ones.[1,2]



(1) Cossy, J. et al. *Tetrahedron Lett*. **1997**, *38*, 4069. (2) Junga, H.; Blechert, S. *ibid*. **1993**, *34*, 3731.

51,440-3 **3-Ethoxy-2-methyl-2-cyclopenten-1-one**, 97%

Aldrichimica ACTA

VOL. 33, NO. 1 • 2000

Aldrich Chemical Co., Inc.
1001 West Saint Paul Ave.
Milwaukee, WI 53233 USA

To Place Orders

Telephone	800-558-9160 (USA)
	or 414-273-3850
FAX	800-962-9591 (USA)
	or 414-273-4979
Mail	P.O. Box 2060
	Milwaukee, WI 53201 USA

General Correspondence

William J. Seitz, Sharbil J. Firsan, or Jennifer L. Botic
P.O. Box 355, Milwaukee, WI 53201 USA

Customer & Technical Services

Customer Inquiries	800-558-9160
Technical Service	800-231-8327
Sigma-Aldrich Fine Chemicals	800-336-9719
Custom Synthesis	800-336-9719
Flavors & Fragrances	800-227-4563
International	414-273-3850
24-Hour Emergency	414-273-3850
Web Site	http://www.sigma-aldrich.com
E-Mail	aldrich@sial.com

To request your **FREE** subscription to the *Aldrichimica Acta*,

please call: **800-558-9160** (USA)

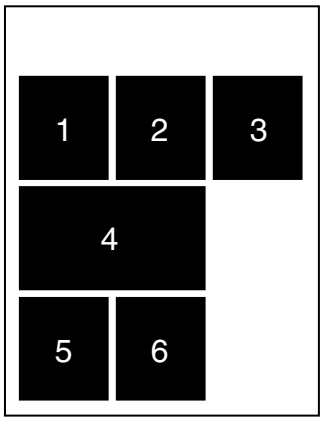
or write: **Attn: Mailroom**
Aldrich Chemical Co., Inc.
P.O. Box 355
Milwaukee, WI 53201-9358

International customers, please contact your local Sigma-Aldrich office.

The *Aldrichimica Acta* is also available on the Internet at **http://www.sigma-aldrich.com**.

For worldwide mailing/contact information, please see the inside back cover.

About Our Cover

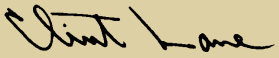


Our first cover of 2000 is a montage of various art works that have graced some of our past publications. The top three and number 6 are part of the extensive personal art collection of Dr. Alfred Bader, founder of Aldrich Chemical Co. and formerly the *Acta's* "Chemist Collector". These are *The Farm Scale* by John Whalley [no. 1], *King David* by Govaert Flinck [no. 2], *Trompe L'oeil* [no. 3], and *Lady in Black* [no. 6].

The other two are *The Dreamer* by Pierre Auguste Renoir [no. 4] and *The Column* by Hubert Robert [no. 5]. Both of these paintings are in the permanent collection of the Saint Louis Art Museum, Saint Louis, MO.

A reproduction (11x14 in.) of each of these six paintings is available for only a nominal $4.00 shipping-and-handling charge. Request your own copy by calling **800-558-9160** (USA) or your local Sigma-Aldrich office, e-mailing us at **aldrich@sial.com**, or visiting our Web site at **www.sigma-aldrich.com**.

"Please Bother Us."



Clint Lane, President

Dear Fellow Chemists:

It is a great pleasure for me to again provide a contribution to our *Aldrichimica Acta*, this time as President of Aldrich. During the years 1973–1977, I contributed nine reviews to this publication. Now, 23 years later, I am back on these pages. Much has changed over the years, but we never stopped publishing what we here at Aldrich simply call "the ACTA".

Year 2000 was viewed as a perfect time to roll out a new look for our classic. However, we have not deleted any of the features that you have come to expect. Art on the cover (reprints available), excellent and timely reviews, lab notes, featured new products, etc. are all here for you to enjoy. Our goal is to continue to be *Chemists Helping Chemists* as we move into the new millennium. We know you will continue to find new ideas and information to help you in your research efforts.

Thank you for staying with us over all these years. This is the first issue in the year 2000. We are up to Volume 33 (33 years) and still counting. As always, "Please Bother Us" with comments or contributions.

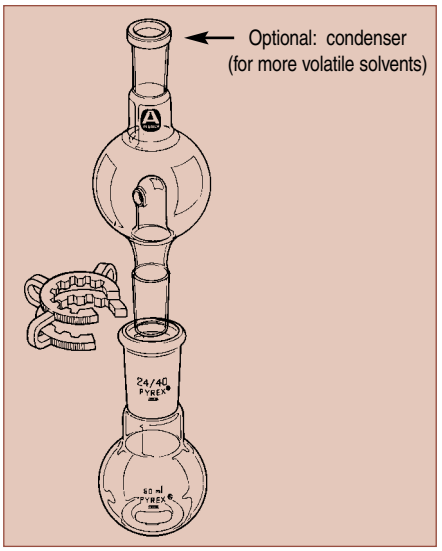
Do you have a compound that you wish Aldrich could list, and that would help you in your research by saving you time and money? If so, please send us your suggestion; we will be delighted to give it careful consideration. You can contact us in any one of the ways shown on this page or on the inside back cover.

Lab Notes

Aldrich Rotary Evaporator Antisplash Adapters as Solvent Traps in Recrystallizations

For practicing synthetic chemists, recrystallization of reaction intermediates is routine. For maximal product recovery, it is important to prepare a saturated solution of the compound. In many instances, this is difficult to judge, since excess solvent is sometimes needed to completely dissolve the solute, or since filtration subsequent to charcoal treatment is followed by washing of the residue with hot solvent. These steps result in dilution of the crystallizing solution, and, therefore, concentration of such a solution has to be performed. This is usually accomplished by simply heating the solution to evaporate some of the solvent. However, this leads to two problems: (a) how much solvent is actually left in the flask cannot be accurately estimated, and (b) solvent vapors are discharged into the hood and are not collected for recycling or disposal. We have devised a simple solution to these two problems that uses the Aldrich rotary evaporator antisplash adapter (without return holes, Cat. No. Z17,604-4 to Z20,329-7).

The rotary evaporator antisplash adapter doubles as a solvent trap for the recovery of the crystallization solvent. The compound is placed in a round-bottom flask, and heated while the solvent is gradually added until the compound



dissolves completely. The antisplash adapter is then attached to the flask and heating is continued. The solvent that evaporates at this stage condenses and collects in the antisplash adapter. A couple of modifications of this setup are possible. For larger-scale operations, the solutions can be magnetically stirred and heated. Also, for better recoveries of volatile solvents, a reflux condenser can be attached to the top of the antisplash adapter. After the solvent has collected in the adapter, the adapter is disconnected, and the solvent is removed and its volume measured. Besides effecting the desired concentration of the crystallization solution, this procedure allows one to calculate the amount of solvent left in the crystallization flask, and to recycle or properly dispose of the condensed solvent.

We routinely use this setup and find it very convenient. We hope that other researchers will find it equally helpful.

Mahesh K. Lakshman, Assistant Professor
Department of Chemistry
University of North Dakota
Grand Forks, ND 58202-9024
E-mail: mlakshman@mail.chem.und.nodak.edu

Please turn to page 12 for more Lab Notes.

Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes, Aldrichimica Acta). For submitting your idea, you will receive a complimentary, laminated periodic table poster (Cat. No. **Z15,000-2**). If we publish your lab note, you will also receive an Aldrich periodic table turbo mouse pad (Cat. No. **Z24,409-0**). It is Teflon®-coated, 8½ x 11 in., with a full-color periodic table on the front. We reserve the right to retain all entries for future consideration.

Teflon is a registered trademark of E.I. du Pont de Nemours & Co., Inc.

The Chemical Vapor Deposition of Metal Nitride Films Using Modern Metalorganic Precursors

Charles H. Winter
Department of Chemistry
Wayne State University
Detroit, MI 48202
E-mail: cwinter@sun.science.wayne.edu

Outline

1. Introduction
2. Discussion
   - 2.1. Binary Metal Nitride Films
     - 2.1.1. Deposition of Tantalum Nitride Films
     - 2.1.2. Synthesis of Tantalum Amide Complexes for Use as CVD Precursors
     - 2.1.3. Film Depositions Using Tantalum Amide Based Precursors
     - 2.1.4. Precursors and Film-Deposition Processes for Niobium Nitride Films
     - 2.1.5. Low-Temperature Film Depositions Using Tantalum Pentabromide
     - 2.1.6. Synthesis and Evaluation of Precursors Derived from Tantalum Pentachloride
   - 2.2. Ternary Nitride Films
3. Conclusions and Prospects
4. Acknowledgments
5. References and Notes

1. Introduction

Metal nitrides of the formula $M_{1.0}N_{1.0}$ (M = Ti, Zr, Hf, V, Nb, Ta) possess a wide range of useful properties, including extreme hardness, good chemical resistance, desirable optical properties, and good electrical conductivity.[1] Application of a thin film of $M_{1.0}N_{1.0}$ to a substrate can confer these characteristics to the surface of the structure. Prominent uses of metal nitride coatings include wear-resistant tool coatings,[2] solar-control coatings for glass,[3] decorative coatings,[4] conductive coatings,[5] and barrier materials in microelectronics.[6,7]

The most urgent application of early transition-metal nitride films is as barrier materials between copper and silicon in microelectronics devices. Copper is replacing aluminum as the interconnection material in sub-0.50 µm ultralarge-scale integrated (ULSI) devices, due to its lower electrical resistivity and fewer electromigration problems.[7,8] However, copper readily diffuses into silicon dioxide layers and silicon substrates under the high temperatures encountered in device fabrication. The interaction of copper with silicon at deposition temperatures leads to the formation of copper silicides as well as copper-doped silicon, both of which degrade the properties of the copper–silicon interface. Therefore, a barrier between copper and silicon is required (**Figure 1**). This barrier must stop the diffusion of copper at deposition temperatures long enough to enable manufacturing of the device, must be unreactive toward both copper and silicon, and should exhibit good adhesion to both copper and silicon. Furthermore, the barrier should be extremely thin (≤10 nm in sub-0.25 µm features[8]) to allow a sufficient amount of copper metal to be placed in the features and to reduce the electrical resistivity of the interconnect structure. Finally, the resistivity of the barrier layer should be <1000 µΩ•cm to maintain excellent electrical conductivity between the copper and silicon features.

A strict requirement of the barrier material is that it must be applied with excellent conformal coverage in high-aspect-ratio features on the substrates (the aspect ratio of a feature is defined as the ratio of its depth to its width). Conformal coverage is the degree to which a film is deposited in shaped formations on the substrate. In excellent conformal coverage, the corners and bottoms of features are coated with the material equally as well as the flat portions of the substrate; in poor conformal coverage, the corners and bottoms of features may be poorly coated or not coated at all. The decreasing size of features and increasing aspect ratios in future generations of microelectronics devices imply that new deposition processes will have to be brought into production to meet the conformal

coverage requirements. Of the many film-forming processes that are available, only Chemical Vapor Deposition (CVD) can realistically deliver the conformal coverage that is needed in sub-0.25 µm devices. CVD involves the delivery of molecules to the growing film, as opposed to atoms and small groups of atoms that are involved in physical vapor deposition (PVD) techniques. Under optimum conditions, the molecules involved in CVD are able to adsorb/desorb on the growing film many times before decomposing and promoting film growth. Therefore, extremely uniform film growth can occur under CVD conditions and nearly perfect conformal coverage can ensue. In contrast, the atoms and small groups of atoms involved in PVD processes are highly reactive and adhere strongly to growing film surfaces. As a result, high-aspect-ratio features are poorly coated by PVD techniques, especially on the sides and corners.

This account describes recent advances that have occurred in the chemical vapor deposition of metal nitride films for

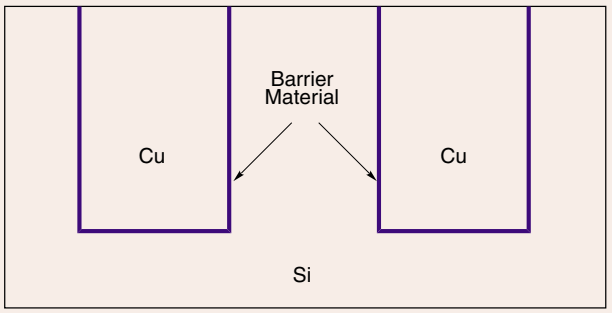


Figure 1. Schematic Representation of a Barrier Layer Between Cu and Si.

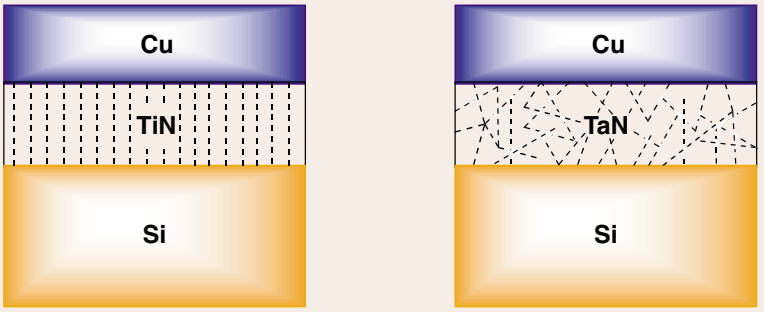


Figure 2. Schematic Representation of Grain Structures in TiN and TaN Films.

application as barrier materials in microelectronics devices. The focus is on new materials, chemical precursors, and chemical questions that address the many materials issues associated with chip manufacturing. Titanium nitride (TiN) is the leading barrier material used between silicon substrates and copper and has been the most studied.[9] Recently, new phases such as tantalum(III) nitride (TaN), amorphous tantalum silicon nitride (Ta–Si–N), and amorphous titanium silicon nitride (Ti–Si–N) have been suggested as barrier materials that are superior to TiN. The status of chemical vapor deposition routes to these materials is described. Additionally, the status of precursors to niobium(III) nitride (NbN) films is discussed, since NbN films should exhibit chemical and physical properties that are similar to those of TaN. Finally, mechanistic studies aimed at understanding the chemical intermediates that are involved in film depositions are presented.

2. Discussion

While many substances have been explored as possible barrier materials, titanium nitride (TiN) has been extensively investigated and is widely regarded as the leading candidate material for a barrier between copper and silicon.[7-9] However, the massive research effort that has been directed toward TiN has identified several shortcomings in its application as a barrier. TiN films are deposited with a characteristic columnar structure, in which the grain boundaries are parallel to each other and approximately perpendicular to the substrate (**Figure 2**). These grain boundaries create fast diffusion paths by which copper atoms can migrate to the silicon layer, leading to device failure.[10] This failure mechanism is particularly acute when thin barrier layers are used. Since future generations of microelectronics devices will require barrier layers that are ≤10 nm thick, new barrier materials will be required to solve the copper migration problem.

2.1. Binary Metal Nitride Films

In view of the potential problems associated with TiN, there has been a considerable research effort devoted to identifying barrier materials that are superior to TiN.[6,7] Recently, tantalum(III) nitride (TaN) films fabricated by PVD techniques were evaluated for their ability to act as a barrier between copper and silicon.[11] In general, TaN films deposited by PVD methods possess preferred (111) crystallographic orientation, exhibit close to 1:1 Ta:N stoichiometry, contain < 5% of elements other than tantalum and nitrogen, and have resistivities of < 600 μΩ•cm. Significantly, a 10-nm-thick TaN film was sufficient to stop diffusion of copper into the silicon substrate after annealing at 700 ºC for 30 min.[11] Moreover, a 25-nm-thick TaN film prevented copper diffusion into silicon after annealing at 800 ºC for 90 min. Based upon these annealing studies, it was claimed that TaN is the best barrier material yet identified for use between copper and silicon. The excellent barrier properties of TaN films were attributed to a disordered grain boundary structure that makes copper atom diffusion through the film inefficient, compared to other barrier materials with more ordered grain structures (**Figure 2**).

Another significant advance was the discovery that M–Si–N (M = Ti, Ta, W) films are excellent barrier materials.[12,13] The enhanced barrier properties of the ternary materials are due to their amorphous nature, which removes low-energy diffusion paths from the barrier. Barrier failure in these materials is associated with crystallization, which provides grain boundaries for rapid copper diffusion. Remarkably, the barrier structure Si/$Ta_{36}Si_{14}N_{50}$ (120 nm)/Cu (500 nm) is stable up to 900 ºC, at which temperature crystallization and concomitant barrier failure ensue.[12b] While many materials and manufacturing issues remain to be resolved, it is clear that TaN based barrier materials are among the best that have been identified to date. However, a detailed evaluation of TaN and Ta–Si–N barrier materials will require that these materials be deposited in high-aspect-ratio features on the substrate with excellent conformal coverage. The conformal coverage issue, in turn, requires a low-temperature CVD process for TaN films.

2.1.1. Deposition of Tantalum Nitride Films

Reports of CVD processes to tantalum nitride phases have been limited in number. The common nitride phases of tantalum have stoichiometries of Ta_2N, TaN, and Ta_3N_5.[14] In CVD processes, there is an excess of the nitrogen source, and thus only the nitrogen-rich phases TaN and Ta_3N_5 are generally observed. A difficulty with the deposition of tantalum nitride films is that the reduction of Ta(V) to Ta(III) has a very negative potential.[15] As outlined above, TaN is the phase with the best barrier properties; Ta_3N_5 is an insulator with resistivities of > 10^6 μΩ•cm. Since volatile source compounds are only available in the Ta(V) oxidation state, Ta_3N_5 films are frequently obtained, and it is generally difficult to deposit TaN films at low temperatures. Traditional CVD routes to tantalum nitride phases have involved the CVD reactions of $TaCl_5$ with nitrogen sources at high

temperatures. In this way, TaN films have been deposited with a mixture of N_2 and H_2 at ≥ 900 °C (**eq 1**), while the use of ammonia affords Ta_3N_5 films at ≥ 900 °C (**eq 2**).[16,17] However, since semiconductor chip manufacturing has an upper temperature limit of about 400 °C, these two routes are not useful for the fabrication of microelectronics devices.

The CVD reaction of $Ti(NMe_2)_4$ or $Ti(NEt_2)_4$ with ammonia at 200–450 °C yields TiN films; this process has been developed into one of the leading routes to TiN films for barrier layer applications.[9] However, the analogous CVD process between $Ta(NMe_2)_5$ and ammonia at 200–400 °C yields Ta_3N_5 films instead (**eq 3**).[18]

2.1.2. Synthesis of Tantalum Amide Complexes for Use as CVD Precursors

Lower-temperature approaches to TaN films use dialkylamide-based complexes as single-source precursors. The complex $Ta(NMe_2)_5$ can be prepared in about 30% yield by treatment of $TaCl_5$ with lithium dimethylamide (5 equiv; **eq 4**).[19] $Ta(NMe_2)_5$ is an orange solid that can be sublimed at 90 °C/0.01 torr. While $Ti(NEt_2)_4$ and higher alkyl derivatives are stable up to at least 150 °C, the tantalum(V) analogs decompose at moderate temperatures to several products. The original synthesis of $Ta(NEt_2)_5$ by Bradley and Thomas demonstrated that $Ta(NEt_2)_5$ could be obtained as a pure orange liquid through treatment of $TaCl_5$ with lithium diethylamide.[19] $Ta(NEt_2)_5$ is thermally stable at ambient temperature. However, upon attempted distillation at 120 °C (0.1 torr), mixtures of $Ta(NEt_2)_4$, $Ta(NEt_2)_5$, and the imido complex $(Et_2N)_3Ta{=}NEt$ were obtained (**eq 4**). It was proposed that, upon heating, a diethylamino radical is eliminated from $Ta(NEt_2)_5$ to afford $Ta(NEt_2)_4$, which then reacts with the diethylamino radical to afford $(Et_2N)_3Ta{=}NEt$, diethylamine, and ethylene.

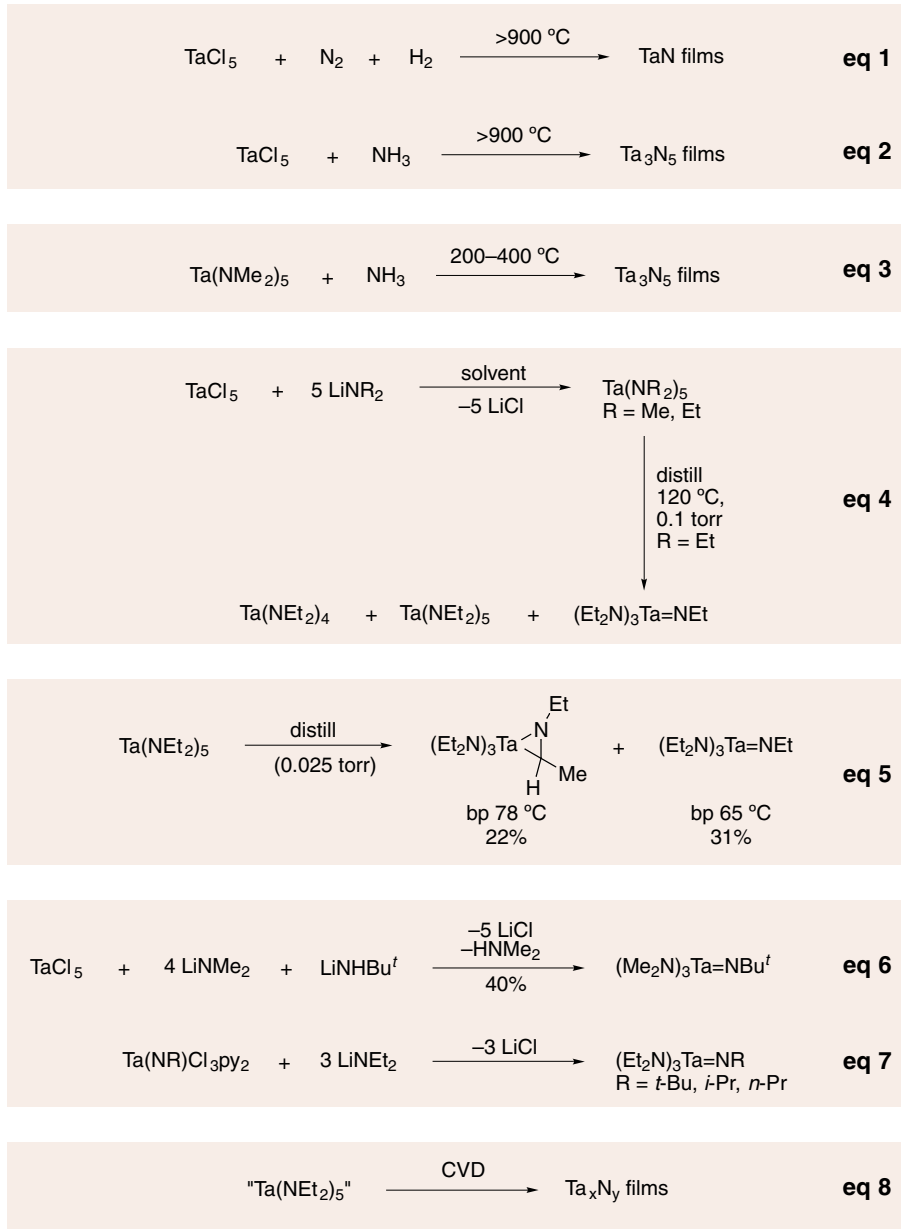
A later study by Sugiyama and coworkers found that distillation of $Ta(NEt_2)_5$ afforded a pale yellow liquid from which $Ta(EtNCHCH_3)(NEt_2)_3$ (bp 78 °C/0.025 torr, 22% yield) and $(Et_2N)_3Ta{=}NEt$ (bp 65 °C/0.025 torr, 31% yield) were isolated as pure materials by fractional distillation (**eq 5**).[20] The imino complex $Ta(EtNCHCH_3)(NEt_2)_3$ was stable below 100 °C, but decomposed to $(Et_2N)_3Ta{=}NEt$ above about 120 °C. Because Sugiyama found no evidence for $Ta(NEt_2)_4$ formation during the synthetic work, the prior claim for the existence of this complex[19a] cannot be regarded as conclusive.[21,22]

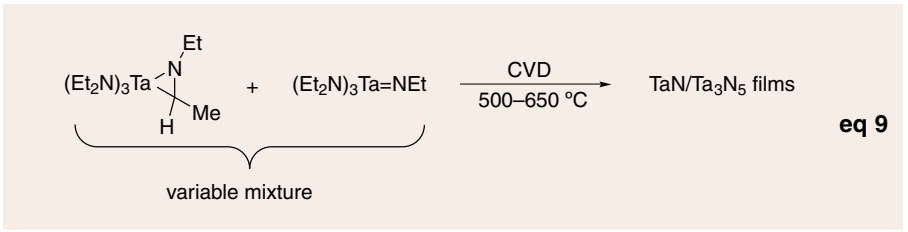
Several additional routes to imido complexes of the formula $(R_2N)_3Ta{=}NR$ have been reported. Treatment of $TaCl_5$ with lithium dimethylamide (4 equiv) and lithium *tert*-butylamide (1 equiv) afforded $(Me_2N)_3Ta{=}NBu^t$ in 40% yield as colorless crystals with a melting point of 68–69 °C (**eq 6**).[23] A crystal structure determination demonstrated that the complex was monomeric. The complexes $(Et_2N)_3Ta{=}NR$ (R = *t*-Bu, *i*-Pr, *n*-Pr) were prepared by treatment of $Ta(NR)Cl_3py_2$ with lithium diethylamide (3 equiv; **eq 7**).[24] The diethylamido complexes are liquids with boiling points of about 60 °C (0.1 torr).

2.1.3. Film Depositions Using Tantalum Amide Based Precursors

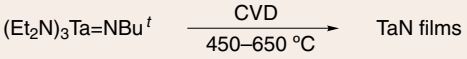
In an earlier work, Sugiyama reported that "$Ta(NEt_2)_5$" functions as a single-source precursor to tantalum nitride films, although the phase was not identified (**eq 8**).[25] The chemical nature of the precursor was not discussed. Consistent with the work of Bradley[19] and the later report by Sugiyama,[20] the "$Ta(NEt_2)_5$" precursor actually consisted of a mixture of $Ta(EtNCHCH_3)(NEt_2)_3$ and $(Et_2N)_3Ta{=}NEt$.

Recently, it was reported that a mixture of $Ta(EtNCHCH_3)(NEt_2)_3$ and $(Et_2N)_3Ta{=}NEt$ could be used as a precursor to tantalum nitride films.[26,27] Films were deposited with this precursor mixture at low pressure with substrate temperatures of 500–650 °C (**eq 9**). The bubbler containing $Ta(EtNCHCH_3)(NEt_2)_3$ and $(Et_2N)_3Ta{=}NEt$ was heated to 60–100 °C to effect vapor transport with argon carrier gas. Based on Bradley's[19] and Sugiyama's work,[20] it is likely that $(Et_2N)_3Ta{=}NEt$ was the major species that

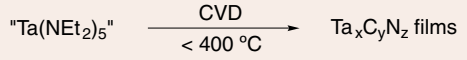




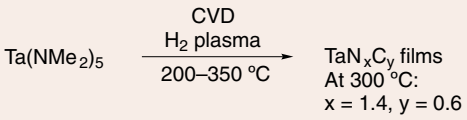
eq 9



eq 10



eq 11



eq 12

was transported to the deposition chamber. The films thus deposited showed X-ray diffraction patterns consistent with cubic TaN, although some diffraction spectra also revealed weak and broad reflections assignable to tetragonal Ta_3N_5. Analysis of the films by wavelength dispersive spectroscopy revealed that the films were slightly nitrogen-rich (N/Ta 1.1–1.2) and contained a minimum of 15–20% carbon. The carbon content of the films dramatically increased (C/Ta ratios as high as 3) upon raising the deposition temperature from 500 ºC to 650 ºC, increasing the pressure at which the depositions were carried out, or increasing the temperature at which the precursor mixture was held. The Ta/N ratio did not vary upon changing the deposition parameters; the constant composition was attributed to the fixed Ta/N stoichiometry associated with the strong tantalum–nitrogen imido bond. A subsequent study reported that addition of hydrogen to the carrier gas mixture decreased the carbon content in the films to a constant level of 15–20%, relative to tantalum, under all deposition conditions.[26] It was proposed that the hydrogen in the carrier gas leads to an increase in surface-bound hydride species that can react with surface-bound hydrocarbon fragments to afford volatile neutral hydrocarbons that are swept away from the film-growth environment.

The complex $(Et_2N)_3Ta{=}NBu^t$ has also been evaluated as a precursor to TaN films (**eq 10**).[28-30] The motivation for using $(Et_2N)_3Ta{=}NBu^t$, as opposed to the mixture of $Ta(EtNCHCH_3)(NEt_2)_3$ and $(Et_2N)_3Ta{=}NEt$ described above, was to have a single pure precursor that did not undergo decomposition at temperatures required for vapor transport. Film depositions were carried out at substrate temperatures of 450–650 ºC and pressures of about 0.02 torr.[28,29] The bubbler containing $(Et_2N)_3Ta{=}NBu^t$ was heated to 30–50 ºC to effect vapor transport. The growth rate of TaN films was constant at about 20 Å/min between 450 and 650 ºC. The resistivity of the films was 10^4–10^5 μΩ•cm at 450 ºC, but dropped with increasing substrate temperature to about 900 μΩ•cm at 650 ºC. The X-ray diffraction patterns of films deposited at 500–650 ºC were consistent with the cubic TaN phase, and were made up of randomly oriented crystallites. The film deposited at 500 ºC exhibited very broad reflections in the X-ray diffraction spectrum, due to an average grain size of 9.2 nm. Analysis of a film deposited at 600 ºC by X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectrometry (RBS) revealed a nitrogen-rich composition (N/Ta 1.1–1.3) with about 10% carbon and 5–10% oxygen. The carbon was present as carbide, indicating direct tantalum–carbon bonds. A film deposited at 450 ºC had a composition of $Ta_{1.0}N_{1.4}C_{0.7}O_{0.2}$. The conformality of the films was measured in trenches with aspect ratios of 1.75:1 to 2.00:1. At 450 ºC, the conformality was 100%, while at 650 ºC the values were 25–40%.

A W/CVD-TaN/Si contact structure was fabricated. No tungsten encroachment was found at the bottom of the contact hole, and the structure adhered well as demonstrated by a Scotch™ tape test. An Al/CVD-TaN/Si structure was fabricated as another test for the barrier properties of the TaN layer. The failure temperature of the TaN barrier was found to be 550–600 ºC. The barrier-layer performance of CVD-TaN, deposited using $(Et_2N)_3Ta{=}NBu^t$, against copper diffusion was compared with that of PVD-TaN.[30] It was found that the Cu/CVD-TaN/Si structure survived without copper diffusion up to about 550 ºC, while the Cu/PVD-TaN/Si structure did not fail until about 600 ºC. The increased performance of the PVD-TaN was attributed to its small grain size (20 nm) and preferred (111) crystallographic orientation. In contrast, the CVD-TaN possessed a larger grain size (50–70 nm) and a preferred (200) crystallographic orientation.

Recent work has examined the low-temperature deposition (≤ 400 ºC) of tantalum nitride films using a precursor that was claimed to be "$Ta(NEt_2)_5$".[31] Films were deposited with substrate temperatures of 275–400 ºC, a reactor pressure of 1 torr, and a vapor transport bubbler temperature of 60 ºC (**eq 11**). As noted earlier, 60 ºC is a sufficient temperature to cause the conversion of $Ta(NEt_2)_5$ to $Ta(EtNCHCH_3)(NEt_2)_3$ and $(Et_2N)_3Ta{=}NEt$;[19,20] thus, there is some ambiguity as to the nature of the source compound in this work. Films deposited in this study exhibited resistivities of about 6000 μΩ•cm at 400 ºC; the resistivities increased with decreasing deposition temperature. A film deposited at 400 ºC had a carbon-rich composition of $Ta_{1.0}C_{1.0}N_{0.3}O_{0.1}$, in which the carbon was present predominantly as carbide (XPS analysis). The X-ray diffraction pattern showed a very broad reflection at $2\theta = 35°$ that could be attributed to the (111) plane of TaC or TaN. It was proposed that the film consisted of a Ta(CN) phase, rather than a mixture of TaC and TaN, due to the very high resistivity of the film and the very low resistivities of TaC and TaN. Analysis of a film deposited at 350 ºC by transmission electron microscopy revealed an average grain size of about 30 Å.

Han et al. have recently reported the deposition of amorphous films derived from activation of $Ta(NMe_2)_5$ with a remote hydrogen plasma (**eq 12**).[32] Depositions were conducted on silicon substrates at 200–350 ºC and ~1 torr. $Ta(NMe_2)_5$ was maintained in a bubbler held at 80 ºC and was carried by argon. A film deposited at 300 ºC had a stoichiometry of $Ta_{1.0}N_{1.4}C_{0.6}$, demonstrating that the film was both nitrogen- and carbon-rich. XPS indicated that the carbon was present predominantly in carbide form, with the remainder being attributed to hydrocarbons. It was suggested that the hydrocarbon residues originated from incomplete decomposition of the precursor. The films were found to be amorphous by X-ray diffraction and electron microscopy. The lowest film resistivities were 2000 μΩ•cm, and were obtained at a substrate temperature

of 350 °C. The step coverage for films deposited in contact holes with an aspect ratio of 3:1 was nearly 100%. The as-deposited films remained amorphous up to 1000 °C, at which temperature crystallization ensued. These films served as effective barriers against the diffusion of platinum into silicon substrates at temperatures of up to 700 °C. A subsequent study found that use of a remote ammonia plasma instead of the remote hydrogen plasma led to a lower nitrogen and carbon content in the films.[33] For example, a film deposited at 300 °C with the remote ammonia plasma had a stoichiometry of $Ta_{1.0}N_{1.1}C_{0.51}$, and an X-ray diffraction spectrum that revealed the presence of cubic TaN with a preferred orientation along the (111) axis. Films deposited with the ammonia plasma showed larger crystallites, an observation that is consistent with the sharp reflections seen in the X-ray diffraction spectrum.

To summarize, amido precursors that have been evaluated as precursors to tantalum nitride films include $Ta(NMe_2)_5$, mixtures of $Ta(EtNCHCH_3)(NEt_2)_3$ and $(Et_2N)_3Ta{=}NEt$, and $(Et_2N)_3Ta{=}NBu^t$. Several groups have claimed to use "$Ta(NEt_2)_5$" as a source compound, but it has been demonstrated that "$Ta(NEt_2)_5$" is unstable at ambient temperature and decomposes to variable mixtures of $Ta(EtNCHCH_3)(NEt_2)_3$ and $(Et_2N)_3Ta{=}NEt$. Use of "$Ta(NEt_2)_5$", mixtures of $Ta(EtNCHCH_3)(NEt_2)_3$ and $(Et_2N)_3Ta{=}NEt$, or $(Et_2N)_3Ta{=}NBu^t$ as precursors yields cubic TaN films, but these films contain a minimum of 15–20% carbon relative to tantalum. Additionally, mixtures of cubic TaN and tetragonal Ta_3N_5 phases have been observed in some depositions using these precursors. The CVD process using $Ta(NMe_2)_5$ and ammonia yields Ta_3N_5 films. Activation of $Ta(NMe_2)_5$ with a remote hydrogen plasma leads to carbon-contaminated Ta_3N_5 films, while use of the same tantalum source with a remote ammonia plasma gives carbon-rich TaN films.

2.1.4. Precursors and Film-Deposition Processes for Niobium Nitride Films

Although cubic NbN is a metallic nitride that is isostructural with TaN, the low-temperature CVD routes to NbN have been studied less than those to TaN. The chemistry of niobium dialkylamide complexes is different from that observed for tantalum dialkylamides,[34-36] and reflects the greater ease with which Nb(V) is reduced to Nb(IV).[15] Like $Ta(NMe_2)_5$, $Nb(NMe_2)_5$ can be prepared as a brown solid upon treatment of $NbCl_5$ with lithium dimethylamide (**eq 13**).[34] $Nb(NMe_2)_5$ sublimes at 100 °C/0.1 torr, but partial decomposition (30–40%) is observed during the sublimation. Upon treatment of $NbCl_5$ with lithium diethylamide, lithium di-*n*-propylamide, or lithium di-*n*-butylamide, however, complexes of the formula $Nb(NR_2)_4$ (R = Et, *n*-Pr, *n*-Bu) are obtained as dark-red liquids in 76–81% yields after distillation (**eq 14**). There was no evidence for the formation of $Nb(EtNCHCH_3)(NEt_2)_3$ and $(Et_2N)_3Nb{=}NEt$ during the preparation of $Nb(NR_2)_4$. Imido complexes of the formula $(Et_2N)_3Nb{=}NR$ (R = *t*-Bu, *i*-Pr, *n*-Pr) have been prepared in about 30% yields by treatment of $Nb(NR)Cl_3py_2$ (py = pyridine) with lithium diethylamide (**eq 15**).[37] The complexes are yellow liquids that distill at about 60 °C/0.1 torr.

As in the case of TaN, routes to NbN films using $NbCl_5$ as the niobium source proceeded only at high temperatures.[16] The CVD process involving the gas-phase reaction of $Nb(NEt_2)_4$ or $Nb(NMe_2)_5$ with ammonia yielded amorphous niobium(IV) nitride (Nb_3N_4) films, rather than the NbN phase (**eq 16**).[18] Sugiyama and coworkers reported that use of "$Nb(NEt_2)_5$" as a single-source precursor led to the deposition of NbN or Nb_4N_3 films at substrate temperatures of > 500 °C (**eq 17**).[25] However, no further details were given on the properties of the film. As noted previously, "$Nb(NEt_2)_5$" is not a stable complex, and the authors were most likely using $Nb(NEt_2)_4$ as the source compound. The complex $(Et_2N)_3Nb{=}NPr^n$ was also evaluated as a precursor to NbN films (**eq 18**).[37] A film deposited with a substrate temperature of 550 °C and a reactor pressure of 0.01 torr had a stoichiometry of $Nb_{1.0}N_{0.7}C_{0.2}O_{0.2}$. The X-ray diffraction spectrum was consistent with the cubic NbN phase. XPS studies indicated that the carbon and oxygen in the film were present as carbide and oxide, respectively.

2.1.5. Low-Temperature Film Depositions Using Tantalum Pentabromide

Cubic TaN films have been deposited with $TaBr_5$ as the tantalum source using plasma-assisted CVD (**eq 19**).[38] $TaBr_5$ was chosen as the tantalum source, since it was hypothesized that the weaker tantalum–bromine bonds, as compared to the stronger tantalum–chlorine bonds in $TaCl_5$, would lead to lower-temperature depositions of TaN. Moreover, the larger size of the bromide ion, as compared to the chloride ion, would lead to a very low diffusion constant for bromine in the film, assuring that any residual bromine in the TaN film does not interfere with the properties of the barrier structure. The plasma-assisted CVD was carried out at 350–450 °C and 0.9–1.6 torr using a mixture of nitrogen and

$$NbCl_5 + 5\ LiNMe_2 \xrightarrow{-5\ LiCl} Nb(NMe_2)_5 \qquad \textbf{eq 13}$$

$$NbCl_5 + 5\ LiNR_2 \xrightarrow[76–81\%]{-5\ LiCl} Nb(NR_2)_4,\ R = Et,\ n\text{-}Pr,\ n\text{-}Bu \qquad \textbf{eq 14}$$

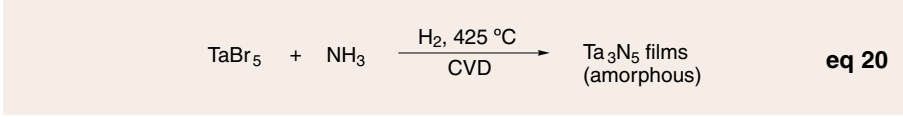
$$Nb(NR)Cl_3py_2 + 3\ LiNEt_2 \xrightarrow[30\%]{-3\ LiCl} (Et_2N)_3Nb{=}NR,\ R = t\text{-}Bu,\ i\text{-}Pr,\ n\text{-}Pr \qquad \textbf{eq 15}$$

$$Nb(NR_2)_x + NH_3 \xrightarrow[200–400\ °C]{CVD} Nb_3N_4\ films \qquad \textbf{eq 16}$$
R = Me, x = 5
R = Et, x = 4

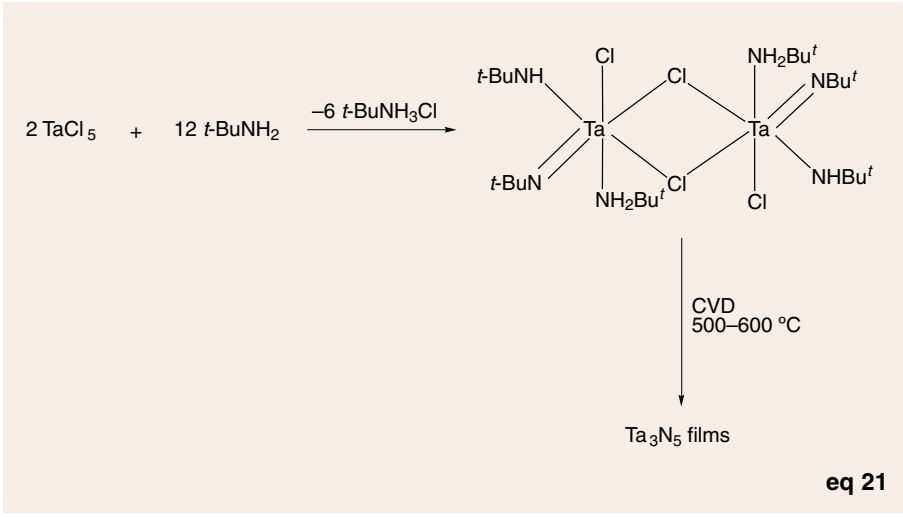
$$"Nb(NEt_2)_5" \xrightarrow[> 500\ °C]{CVD} NbN\ or\ Nb_4N_3\ films \qquad \textbf{eq 17}$$

$$n\text{-}PrN{=}Nb(NEt_2)_3 \xrightarrow[550\ °C]{CVD} NbN\ films \qquad \textbf{eq 18}$$

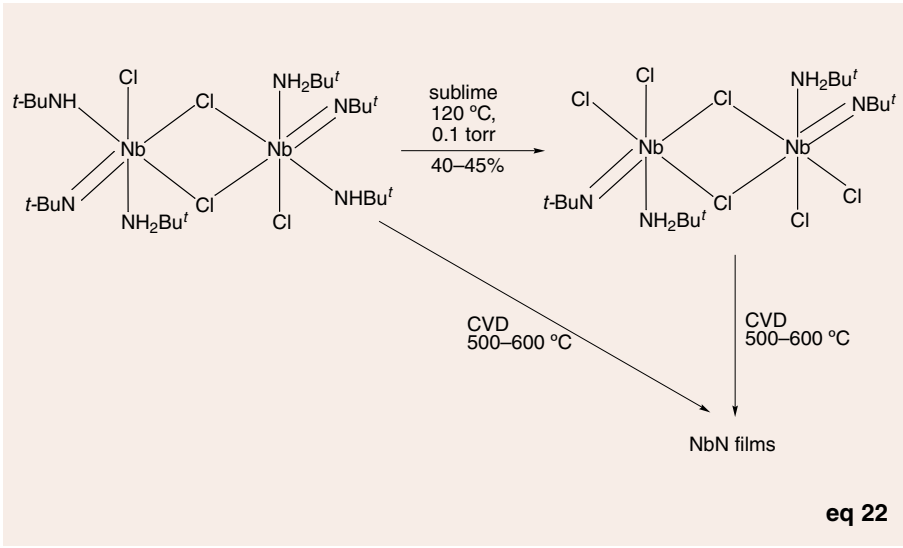
$$TaBr_5 \xrightarrow[N_2/H_2\ plasma\ 350–450\ °C]{CVD} TaN\ films \qquad \textbf{eq 19}$$



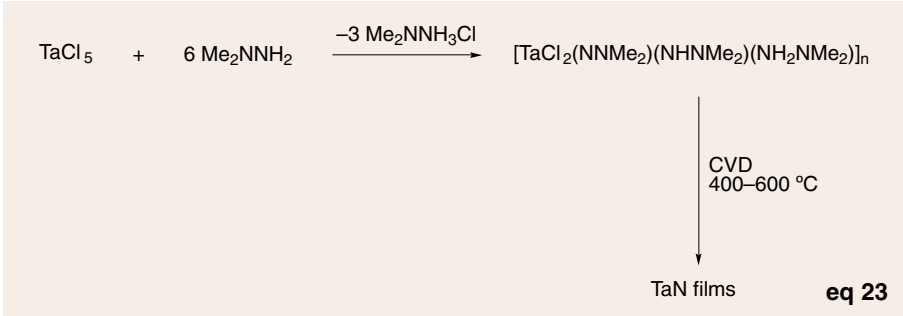
eq 20



eq 21



eq 22



eq 23

hydrogen as the plasma gas. X-ray diffraction spectra indicated that cubic TaN was obtained. The stoichiometry of the films was $Ta_{1.0}N_{1.0}$ with < 3% bromine, as determined by Auger spectroscopy and RBS. The resistivity of the films was as low as 150 μΩ•cm, which is similar to values for high-quality TaN films obtained by PVD methods.[11] The step coverage in a 0.3-μm-diameter trench with an aspect ratio of 4.5:1 was 95%. Accordingly, excellent-quality TaN films are obtained at low substrate temperatures from this process.

The thermal CVD reaction using $TaBr_5$, ammonia, and hydrogen as source compounds has also been reported (**eq 20**).[39,40] Amorphous films with a composition of $Ta_{1.00}N_{1.83}$ were obtained at 425 °C and 0.4 torr. The resistivity of the films was about 2500 μΩ•cm. Upon annealing at 650–700 °C, the films crystallized to the hexagonal Ta_3N_5 phase. Since the stoichiometry of the amorphous film was close to that expected for Ta_3N_5, and this phase crystallizes predominantly upon annealing, it is likely that the amorphous material corresponds predominantly to Ta_3N_5. The amorphous $Ta_{1.00}N_{1.83}$ films were evaluated as barrier materials against copper diffusion into silicon substrates, and were found to fail above 550 °C.

2.1.6. Synthesis and Evaluation of Precursors Derived from Tantalum Pentachloride

Our group has explored the use of compounds derived from the treatment of niobium and tantalum pentachlorides with primary amines and 1,1-dialkylhydrazines as precursors to metal nitride phases.[41,42] As first reported by Nielson and coworkers,[43] treatment of $TaCl_5$ with *tert*-butylamine affords the dimeric, chloride-bridged imido complex $[TaCl_2(NBu^t)(NHBu^t)(NH_2Bu^t)]_2$ (**eq 21**). We found that this complex existed as three major and two minor isomers in chloroform solution, apparently due to the isomerism of the nitrogen ligands about the coordination sphere of the dimeric unit.[41] $[TaCl_2(NBu^t)(NHBu^t)(NH_2Bu^t)]_2$ sublimed at 120 °C/0.1 torr without decomposition, and was evaluated as a precursor to tantalum nitride films.[42] Sublimation of this precursor into a hot-walled CVD reactor held at 500 or 600 °C led to the deposition of yellow-brown films on glass and silicon substrates; these films were identified as Ta_3N_5 by their X-ray powder diffraction patterns. Interestingly, the analogous niobium complex, $[NbCl_2(NBu^t)(NHBu^t)(NH_2Bu^t)]_2$, afforded cubic NbN films in the same reactor at substrate temperatures of ≥ 500 °C (**eq 22**).[42] However, $[NbCl_2(NBu^t)(NHBu^t)(NH_2Bu^t)]_2$ decomposes to $[NbCl_3(NBu^t)(NH_2Bu^t)]_2$ upon sublimation,[41] thus, the basic chemical behaviors of the niobium and tantalum precursors are quite different.

A tantalum complex of the formulation $[TaCl_2(NNMe_2)(NHNMe_2)(NH_2NMe_2)]_n$ was prepared in quantitative yield by treatment of $TaCl_5$ with 1,1-dimethylhydrazine in dichloromethane (**eq 23**).[42,44] This complex sublimed at 150–175 °C/0.1 torr without decomposition. Slow sublimation of this complex into a hot-walled CVD reactor held at 400, 500, or 600 °C resulted in the formation of silver-colored TaN films. The films were smooth and highly adherent, as demonstrated by a Scotch™ tape test.

The X-ray diffraction spectra of the films revealed the cubic TaN phase with preferred orientation along the (200) plane. XPS and RBS measurements gave a stoichiometry of about $Ta_{1.0}N_{1.1}$, with an oxygen content of about 6% and a carbon content below the detection limits of these techniques (< 5%). Electron micrographs showed a smooth surface, with particle sizes between 50–200 Å. The resistivity of a film deposited at 600 ºC was 2.1 x 10^5 μΩ•cm.

2.2. Ternary Nitride Films

In recent years, the amorphous ternary nitrides M–Si–N (M = Ti, Ta, Mo, W) have been demonstrated as excellent barrier materials between copper and silicon for use in microelectronics devices.[12,13,45-49] The advantage of these amorphous materials over TiN, TaN, and other crystalline nitrides is the lack of grain boundaries to provide fast diffusion pathways for copper atoms to migrate into the silicon substrate. The failure of M–Si–N barrier materials is associated with crystallization, which supports the idea that copper atoms and other metal atoms migrate along grain boundaries. The first work in this area was reported by Nicolet,[12] who found that amorphous Ta–Si–N films fabricated by sputtering served as barriers between copper and silicon. Most of the work reported to date has used M–Si–N films that are deposited using PVD methods.[45,46] PVD methods are generally "line-of-sight" in nature, and do not afford high conformal coverage of shaped features on substrates. As noted earlier, barrier materials for microelectronics applications must be applied with excellent conformal coverage to silicon substrates to avoid copper diffusion into the silicon substrate and concomitant device failure. Accordingly, there has been significant interest in the development of CVD processes for the deposition of M–Si–N films.

To date, there have been no reports of CVD routes to Ta–Si–N films. This lack of activity reflects in large part the absence of a good low-temperature thermal CVD route to TaN films. Nicolet has found that Ta–Si–N has the highest barrier failure temperature of any ternary nitride that has been studied (900 ºC), so there is keen interest in CVD routes to this material.[12,45] The potential importance of Ta–Si–N barrier materials provides a strong impetus for new research in this area.

While Ta–Si–N was found to have the highest barrier failure temperature, Ti–Si–N films have barrier properties that approach those exhibited by Ta–Si–N.[12,45] For example, Nicolet found that a Ti–Si–N structure failed at 850 ºC, which is very close to the failure temperature of a Cu/Ta–Si–N/Si structure (900 ºC).[12c] Since the CVD reaction of $Ti(NR_2)_4$ with ammonia has been developed as a low-temperature process for TiN films,[9] a basis exists for the exploration of Ti–Si–N films by CVD.

$$Ti(NEt_2)_4 + NH_3 + SiH_4 \xrightarrow[\text{CVD}]{450\ ^\circ C} Ti_{1.00}N_xSi_y \quad x = 1.10\text{–}1.20,\ y = 0.06 \qquad \textbf{eq 24}$$

$$TiCl_4 + SiH_4 \xrightarrow[\text{CVD}]{N_2/H_2\ \text{plasma},\ 550\text{–}570\ ^\circ C} Ti_{1.00}N_xSi_y \quad x = 1.0,\ y = 0.00\text{–}0.26 \qquad \textbf{eq 25}$$

$$Ti(NEt_2)_4 + NH_3 + SiH_4 \xrightarrow[\text{CVD}]{300\text{–}450\ ^\circ C} Ti_{1.00}N_xSi_y \quad x = \text{ca } 1.1,\ y = 0.00\text{–}0.25 \qquad \textbf{eq 26}$$

The first description of a CVD route to Ti–Si–N films was reported by Raaijmakers.[47] The standard CVD process for the low-temperature deposition of conformal TiN—$Ti(NEt_2)_4$ plus ammonia at 450 ºC—was modified by the addition of silane (SiH_4). Deposition on silicon substrates at 450 ºC led to highly adherent Ti–Si–N films that contained about 6% silicon (**eq 24**). In addition, low carbon (0.5%) and oxygen (1%) levels were observed. The film was amorphous by X-ray diffraction. While TiN films deposited from $Ti(NEt_2)_4$ and ammonia possessed resistivities of about 270 μΩ•cm, the amorphous Ti–Si–N film was found to have a resistivity of 9400 μΩ•cm.

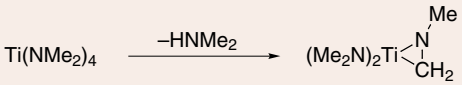
Ti–Si–N films with a silicon content of 16% were fabricated by a plasma-assisted CVD process involving $TiCl_4$, nitrogen, hydrogen, and SiH_4 as the reactants (**eq 25**).[48] The reactants were activated by a dc glow discharge, and the films were deposited on steel substrates that were heated to 500 ºC. The films were crystalline by X-ray diffraction, and exhibited preferred growth along the (200) plane. Unlike TiN deposited from $TiCl_4$, nitrogen, and hydrogen by plasma-assisted CVD, the Ti–Si–N film containing 16% silicon did not reveal a detectable columnar structure in cross-section electron micrographs. Additionally, the grain size in the Ti–Si–N films was smaller than that of TiN films deposited by plasma-assisted CVD. Interestingly, the Ti–Si–N films were harder and more resistant to oxidation by the ambient atmosphere than TiN films prepared by plasma-assisted CVD. A recent report has described the thermal CVD of Ti–Si–N films from $TiCl_4$, ammonia, and SiH_2Cl_2 or $TiCl_4$, nitrogen, hydrogen, and SiH_2Cl_2.[49]

Smith and Custer have described the deposition of Ti–Si–N films containing variable amounts of silicon through the thermal CVD reaction between $Ti(NEt_2)_4$, ammonia, and SiH_4 (**eq 26**).[13] Films were grown in a warm-walled reactor with silicon substrate temperatures between 300–450 ºC and a working pressure of 20 torr. The films were nitrogen-rich, and contained 0–25% silicon, depending on the amount of SiH_4 added to the reactant stream. The only contaminants observed in the films were carbon (<1.5%) and hydrogen (5–15%). Film resistivity increased exponentially with increasing silicon content. The lowest film resistivities were obtained with a substrate temperature of 350 ºC, and ranged between 400 μΩ•cm for pure TiN to 1 Ω•cm for Ti–Si–N containing 25% silicon. It was suggested that the low resistivities observed at 350 ºC were due to the nitrogen content in the films being the closest to the idealized value of 1:1 for TiN. Higher-resistivity films deposited at 300, 400, or 450 ºC possessed 8–15% excess nitrogen. Transmission electron microscopy demonstrated that the films consisted of about 6-nm nanocrystallites of TiN embedded in an amorphous Ti–Si–N matrix. Deposition of $Ti_{0.46}N_{0.51}Si_{0.03}$ films with resistivities of ≤ 800 μΩ•cm on shaped substrates at 350 ºC afforded step coverages of 60% on a 0.2-μm feature with an aspect ratio of 6:1, 75% on a 0.35-μm feature with an aspect ratio of 3:1, and 35–40% on a 0.1-μm feature with an aspect ratio of 10:1. Accordingly, this process provides very good conformal coverage and may provide acceptable films of barrier material in sub-0.18 μm features.

Table 1. Summary of Current CVD Techniques for Depositing Metal Nitride Films

Precursor(s)	Deposition Temp. (°C)	Deposition Pressure (torr)	Film Deposited[a]	Ref.
"$Ta(NEt_2)_5$"	500	not given	unidentified	25
$Ta(EtNCHCH_3)(NEt_2)_3$ + $(NEt_2)_3Ta{=}NEt$	500–650	0.3–1.0	cubic TaN + Ta_3N_5	26,27
$(NEt_2)_3Ta{=}NBu^t$	450–650	0.02	cubic TaN	28–30
"$Ta(NEt_2)_5$"	275–400	1	TaN_xC_y	31
$Ta(NMe_2)_5$ / H_2 or NH_3 plasma	200–350	1	TaN_xC_y	32
$Nb(NEt_2)_4$ or $Nb(NMe_2)_5$ + NH_3	200–450	760	Nb_3N_4	18
"$Nb(NEt_2)_5$"	500	not given	NbN or Nb_4N_3	25
$(NEt_2)_3Nb{=}NPr^i$	550	0.01	cubic NbN	37
$TaBr_5$, N_2/H_2 plasma	350–450	0.9–1.6	cubic TaN	38
$TaBr_5$ + NH_3 + H_2	425	0.4	Ta_3N_5	39,40
$[TaCl_2(NBu^t)(NHBu^t)(NH_2Bu^t)]_2$	500–600	0.1	Ta_3N_5	42
$[NbCl_2(NBu^t)(NHBu^t)(NH_2Bu^t)]_2$	500–600	0.1	cubic NbN	42
$[TaCl_2(NNMe_2)(NHNMe_2)(NH_2NMe_2)]_2$	400–600	0.1	cubic TaN	42,44
$Ti(NEt_2)_4$ + NH_3 + SiH_4	300–450	20	Ti–Si–N	13,47
$TiCl_4$ + N_2 + H_2 + SiH_4 dc glow discharge	850–1100	0.2	Ti–Si–N	48,49

[a] The compositions and properties of the films obtained are critically dependent on the nature of the source compound and the deposition conditions.



eq 27

3. Conclusions and Prospects

This account has summarized the current state of film depositions by CVD techniques for TaN, Ta–Si–N, and related nitride materials that are candidates for advanced barrier layers between copper and silicon in future generations of microelectronics devices (**Table 1**). Precursors that have been used to deposit the cubic TaN phase under thermal CVD conditions include a mixture of imino and imido complexes derived from the decomposition of $Ta(NEt_2)_5$, imido complexes of the formula $(Et_2N)_3Ta{=}NR$, as well as imido complexes derived from treatment of $TaCl_5$ with primary alkylamines. Serious drawbacks of complexes bearing diethylamido ligands include variable selectivity for the cubic TaN phase over the tetragonal Ta_3N_5 phase, incorporation of significant amounts (15–20 atom %) of carbon and oxygen into the film, and film resistivities that are too high for use as barrier layers (generally > 2000 μΩ•cm). The incorporation of carbon into TiN films from $Ti(NR_2)_4$ precursors has been proposed to occur through intramolecular β-hydrogen activation, which leads to a species with a direct titanium–carbon bond (**eq 27**).[50] It is necessary to add a large excess of ammonia to the $Ti(NR_2)_4$ precursor stream to reduce the carbon incorporation in the resultant films to low levels (< 10%).[9] Since a similar process is operant in the formation of $Ta(EtNCHCH_3)(NEt_2)_3$ from $Ta(NEt_2)_5$,[20] it is likely that carbon incorporation in TaN films derived from dialkylamido-based precursors occurs through intermediate species with tantalum–carbon bonds. Intramolecular β-hydrogen activation appears to be a characteristic reaction path for early transition-metal dialkylamido complexes; therefore, it is likely that significant carbon incorporation will be observed when such compounds are used in CVD. Because MN film resistivity increases dramatically with impurity incorporation, TaN films with resistivities below 1000 μΩ•cm may not be accessible from these precursors. Addition of ammonia to precursor streams of tantalum dialkylamido compounds may lower the carbon content, but it is very likely that the high-resistivity Ta_3N_5 phase would result—in analogy with the CVD of Ta_3N_5 films from $Ta(NMe_2)_5$ and ammonia.[18]

While the resistivity of the TaN films deposited from $[TaCl_2(NNMe_2)(NHNMe_2)(NH_2NMe_2)]_n$ is too high for barrier-layer applications, the deposition of high-purity cubic TaN films in a thermal CVD process at temperatures as low as 400 °C is significant. Additionally, the fact that $[TaCl_2(NNMe_2)(NHNMe_2)(NH_2NMe_2)]_n$ leads to TaN films at substrate temperatures that are up to 600 °C lower than that observed for $[TaCl_2(NBu^t)(NHBu^t)(NH_2Bu^t)]_2$ argues that hydrazido ligands are powerful reducing agents that greatly facilitate the Ta(V)–Ta(III) reduction.[44] The reducing ability of hydrazine-derived ligands could be used to devise new classes of precursors for the low-temperature CVD of TaN.

The plasma-assisted process involving $TaBr_5$, nitrogen, and hydrogen provides the

highest-quality TaN films that are available from any CVD route reported to date.[39] The TaN films are stoichiometric, have resistivities that are comparable to high-quality films obtained by PVD methods,[11] can be deposited with excellent conformal coverage in high-aspect-ratio features, and are deposited at temperatures that are compatible with microelectronics device manufacturing (≤ 400 ºC). Potential drawbacks include the necessity of the plasma processing as well as the presence of small amounts of bromine in the films. Plasma-assisted CVD requires more expensive and elaborate deposition equipment than thermal CVD, and there is potential for damage of the microelectronics device being fabricated due to the highly energetic chemical species that are generated through the plasma activation. The presence of bromine atoms or hydrogen bromide in the films could lead to degradation of the interface between the TaN films and the copper or silicon layers. The use of the plasma is essential to obtaining TaN films, since the thermal CVD process involving $TaBr_5$ and ammonia affords Ta_3N_5 films instead.[40]

The lack of a low-temperature thermal CVD process to high-quality TaN films has so far prevented the development of a CVD process to amorphous Ta–Si–N films. The analogous material Ti–Si–N has been deposited by CVD through modification of two existing processes to TiN films by adding SiH_4 or SiH_2Cl_2 to the precursor streams.[13,47,48] The process using $Ti(NEt_2)_4$, ammonia, and SiH_4 provides low-resistivity, highly conformal Ti–Si–N coatings with properties that appear to be acceptable for barrier-layer applications.[13,47]

The development of new precursors for the deposition of metal nitride films for barrier layer applications presents many challenges for the chemist. To be useful in semiconductor manufacturing, new processes to metal nitride films must afford high-purity, low-resistivity, and highly conformal coatings at deposition temperatures of ≤ 400 ºC. Furthermore, new precursors must be prepared in high yields and high purities by efficient syntheses, and should be liquids at ambient temperature in order to maintain constant surface areas for achieving steady vapor transport from stainless steel bubblers used to contain source compounds. To address these goals, it will be necessary to identify ligands that lead to minimum carbon incorporation in the metal nitride films, and which help to promote reduction to the Ta(III) oxidation state, while still providing high-quality TaN and related thin-film materials. Advances in deposition techniques would also aid in the fabrication of new tantalum-based barrier materials.

4. Acknowledgments

The author is grateful to grants from the National Science Foundation, Army Research Office, Defense Advanced Research Projects Agency, and Office of Naval Research, that have supported source-compound-development studies in his laboratory. Careful proofreading and many helpful suggestions for the final draft by Professor Stephanie L. Brock and Mr. Karl R. Gust are greatly appreciated.

5. References and Notes

(1) For an overview of the area, see *Refractory Materials*; Margrave, J.L., Ed.; Academic Press: New York, NY, 1971.

(2) For selected leading references, see: (a) Guu, Y.Y.; Lin, J.F.; Chen, K.C. *Surf. Coating Technol*. **1997**, *302*, 193. (b) He, J.L.; Lin, Y.H.; Chen, K.C. *Wear* **1997**, *208*, 36. (c) Münz, W.D.; Hofmann, D.; Hartig, K. *Thin Solid Films* **1982**, *96*, 79.

(3) For leading references, see: (a) Erola, M.; Keinonen, J.; Anttila, A.; Koskinen, J. *Solar Energy Mater*. **1985**, *12*, 353. (b) Schlegel, A.; Wachert, P.; Nickl, J.J.; Lingg, H. *J. Phys. C: Solid State Phys*. **1977**, *10*, 4889.

(4) Buhl, R.; Pulker, H.K.; Moll, E. *Thin Solid Films* **1981**, *80*, 265.

(5) For leading references, see: (a) Ernsberger, C.; Nickerson, J.; Miller, A.; Banks, D. *J. Vac. Sci. Technol. A* **1985**, *3*, 2303. (b) Wittmer, M.; Studer, B.; Melchior, H. *J. Appl. Phys*. **1981**, *52*, 5722.

(6) For examples, see: (a) Nicolet, M.-A. *Thin Solid Films* **1978**, *52*, 415. (b) Ting, C.Y. *J. Vac. Sci. Technol*. **1982**, *21*, 14.

(7) For a review of barrier materials, see Wang, S.-Q. *MRS Bull*. **1994**, *19*, 30.

(8) For other relevant reviews, see: (a) *Advanced Metallization for ULSI Applications in 1994*; Blumenthal, R.; Janssen, G., Eds.; Materials Research Society: Pittsburgh, PA, 1995. (b) Roberts, B.; Harrus, A.; Jackson, R.L. *Solid State Technol*. **1995**, 69. (c) Murarka, S.P.; Gutmann, R.J.; Kaloyeros, A.E.; Lanford, W.A. *Thin Solid Films* **1993**, *236*, 257. (d) Li, J.; Shacham-Diamand, Y.; Mayer, J.W. *Mater. Sci. Rep*. **1992**, *9*, 1.

(9) For reviews of titanium nitride thin films, see: (a) Musher, J.N.; Gordon, R.G. *J. Electrochem. Soc*. **1996**, *143*, 736. (b) Musher, J.N.; Gordon, R.G. *J. Mater. Res*. **1996**, *11*, 989. (c) Hoffman, D.M. *Polyhedron* **1994**, *13*, 1169.

(10) For a study of TiN barrier layer failure mechanism, see Wang, S.-Q.; Raaijmakers, I.; Burrow, B.J.; Suthar, S.; Redkar, S.; Kim, K.-B. *J. Appl. Phys*. **1990**, *68*, 5176.

(11) (a) Oku, T.; Kawakami, E.; Uekubo, M.; Takahiro, K.; Yamaguchi, S.; Murakami, M. *Appl. Surf. Sci*. **1996**, *99*, 265. For other PVD routes to TaN films, see: (b) Radhakrishnan, K.; Ing, N.G.; Gopalakrishnan, R. *Mater. Sci. Eng*. **1999**, *B57*, 224. (c) Cekada, M.; Panjan, P.; Navinsek, B.; Cvelbar, F. *Vacuum* **1999**, *52*, 461. (d) Wang, M.T.; Lin, Y.C.; Chen, M.C. *J. Electrochem. Soc*. **1998**, *145*, 2538. (e) Chuang, J.-C.; Chen, M.C. *J. Electrochem. Soc*. **1998**, *145*, 3170. (f) Chuang, J.-C.; Chen, M.C. *Thin Solid Films* **1998**, *322*, 213. (g) Stavrev, M.; Fischer, D.; Preuss, A.; Wenzel, C.; Mattern, N. *Microelectron. Eng*. **1997**, *33*, 269. (h) Stavrev, M.; Fischer, D.; Wenzel, C.; Heiser, T. *Microelectron. Eng*. **1997**, *37/38*, 245. (i) Stavrev, M.; Fischer, D.; Wenzel, C.; Drescher, K.; Mattern, N. *Thin Solid Films* **1997**, *307*, 79. (j) Min, K.-H.; Chun, K.-C.; Kim, K.-B. *J. Vac. Sci. Technol*. **1996**, *B14*, 3263. (k) Lovejoy, M.L.; Patrizi, G.A.; Rieger, D.J.; Barbour, J.C. *Thin Solid Films* **1996**, *290/291*, 513. (l) Jia, Q.X.; Ebihara, K.; Ikegami, T.; Anderson, W.A. *Appl. Phys. A* **1994**, *58*, 487. (m) Walter, K.C.; Fetherston, R.P.; Sridharan, K.; Chen, A.; Shamim, M.M.; Conrad, J.R. *Mater. Res. Bull*. **1994**, *29*, 827. (n) Sun, X.; Kolawa, E.; Chen, J.-S.; Reid, J.S.; Nicolet, M.-A. *Thin Solid Films* **1993**, *236*, 347. (o) Noya, A.; Sasaki, K.; Takeyama, M. *Jpn. J. Appl. Phys*. **1993**, *32*, 911. (p) Katz, A.; Pearton, S.J.; Nakahara, S.; Baiocchi, F.A.; Lane, E.; Kolvalchick, J. *J. Appl. Phys*. **1993**, *73*, 5208. (q) Olowolafe, J.O.; Mogab, C.J.; Gregory, R.B.; Kottke, M. *J. Appl. Phys*. **1992**, *72*, 4099. (r) Holloway, K.; Pryer, P.M.; Cabral, C., Jr.; Harper, J.M.E.; Bailey, P.J.; Kelleher, K.H. *J. Appl. Phys*. **1992**, *71*, 5433. (s) Farooq, M.A.; Murarka, S.P.; Chang, C.C.; Baiocchi, F.A. *J. Appl. Phys*. **1989**, *65*, 3017.

(12) (a) Reid, J.S.; Kolawa, E.; Ruiz, R.P.; Nicolet, M.-A. *Thin Solid Films* **1993**, *236*, 319. (b) Kolawa, E.; Chen, J.S.; Reid, J.S.; Pokela, P.J.; Nicolet, M.-A. *J. Appl. Phys*. **1991**, *70*, 1369. (c) Reid, J.S.; Sun, X.; Kolawa, E.; Nicolet, M.-A. *IEEE Electron Device Lett*. **1994**, *15*, 298. (d) Reid, J.S.; Kolawa, E.; Garland, C.M.; Nicolet, M.A.; Cardone, F.; Gupta, D.; Ruiz, R.P. *J. Appl. Phys*. **1996**, *79*, 1109.

(13) Smith, P.M.; Custer, J.S. *Appl. Phys. Lett*. **1997**, *70*, 3116.

(14) Brown, D. The Chemistry of Niobium and Tantalum. In *Comprehensive Inorganic Chemistry*; Bailar, J.C., Jr., Emeléus, H.J., Nyholm, R., Trotman-Dickenson, A.F., Eds.; Pergamon Press: Oxford, UK, 1973; Vol. 3, pp 553–622.

(15) *Handbook of Chemistry and Physics*, 76th ed.; Lide, D.R., Ed.; CRC Press: Boca Raton, Florida, 1996; pp **8**–23 to **8**–26.

(16) Hieber, K. *Thin Solid Films* **1974**, *24*, 157.

(17) Takahashi, T.; Itoh, H.; Ozeki, S. *J. Less Common Met*. **1977**, *52*, 29.

(18) Fix, R.; Gordon, R.G.; Hoffman, D.M. *Chem. Mater*. **1993**, *5*, 614.

(19) (a) Bradley, D.C.; Thomas, I.M. *Can. J. Chem*. **1962**, *40*, 1355. Preparation of $Ta(NMe_2)_5$ according to the original procedure can, upon isolation, lead to detonation through a rapid, exothermic, solid-state methathesis reaction between $LiNMe_2$ and $TaCl_5$. As a result, ***extreme care must be exercised during its synthesis***. (b) For an improved synthesis of $Ta(NMe_2)_5$, see Riley, P.N.; Parker, J.R.; Fanwick, P.E.; Rothwell, I.P. *Organometallics* **1999**, *18*, 3579.

(20) Takahashi, Y.; Onoyama, N.; Ishikawa, Y.; Motojima, S.; Sugiyama, K. *Chem. Lett*. **1978**, 525.

(21) For a discussion, see Hubert-Pfalzgraf, L.G.; Postel, M.; Riess, J.G. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R.D., McCleverty, J.A., Eds.; Pergamon Press: Oxford, UK, 1987; p 652.
(22) For a recent description of a Ta(IV) amido chloro complex, see Hoffman, D.M.; Suh, S. *J. Chem. Soc., Chem. Commun*. **1993**, 714.
(23) Nugent, W.A.; Harlow, R.L. *J. Chem. Soc., Chem. Commun*. **1978**, 579.
(24) Chiu, H.-T.; Chuang, S.-H.; Tsai, C.-E.; Lee, G.-H.; Peng, S.-M. *Polyhedron* **1998**, *17*, 2187.
(25) Sugiyama, K.; Pac, S.; Takahashi, Y.; Motojima, S. *J. Electrochem. Soc*. **1975**, *122*, 1545.
(26) Chiu, H.-T.; Chang, W.P. *J. Mater. Sci. Lett*. **1992**, *11*, 96.
(27) Chiu, H.-T.; Chang, W.P. *J. Mater. Sci. Lett*. **1992**, *11*, 570.
(28) Tsai, M.H.; Sun, S.C.; Chiu, H.T.; Tsai, C.E.; Chuang, S.H. *Appl. Phys. Lett*. **1995**, *67*, 1128.
(29) Tsai, M.H.; Sun, S.C.; Lee, C.P.; Chiu, H.T.; Tsai, C.E.; Chuang, S.H.; Wu, S.C. *Thin Solid Films* **1995**, *270*, 531.
(30) Tsai, M.H.; Sun, S.C.; Tsai, C.E.; Chuang, S.H.; Chiu, H.T. *J. Appl. Phys*. **1996**, *79*, 6932.
(31) Jun, G.-C.; Cho, S.-L.; Kum, K.-B.; Shin, H.-K.; Kim, D.-H. *Jpn. J. Appl. Phys*. **1998**, *37*, L30.
(32) Han, C.-H.; Cho, K.-N.; Oh, J.-E.; Paek, S.-H.; Park, C.-S.; Lee, S.-I.; Lee, M.Y.; Lee, J.G. *Jpn. J. Appl. Phys*. **1998**, *37*, 2646.
(33) Cho, K.-N.; Han, C.-H.; Noh, K.-B.; Oh, J.E.; Paek, S.-H.; Park, C.-S.; Lee, S.-I.; Lee, M.Y.; Lee, J.G. *Jpn. J. Appl. Phys*. **1998**, *37*, 6502.
(34) Bradley, D.C.; Thomas, I.M. *Can. J. Chem*. **1962**, *40*, 449.
(35) Bradley, D.C.; Gitlitz, M.H. *J. Chem. Soc. (A)* **1969**, 980.
(36) Bradley, D.C.; Chisholm, M.H. *J. Chem. Soc. (A)* **1971**, 1511.
(37) Chiu, H.-T.; Lin, J.-C.; Chuang, S.-H.; Lee, G.-H.; Peng, S.-M. *J. Chin. Chem. Soc*. **1998**, *45*, 355.
(38) Chen, X.; Frisch, H.L.; Kaloyeros, A.E.; Arkles, B.; Sullivan, J. *J. Vac. Sci. Technol. B* **1999**, *17*, 182.
(39) Kaloyeros, A.E.; Chen, X.; Stark, T.; Kumar, K.; Seo, S.-C.; Peterson, G.G.; Frisch, H.L.; Arkles, B.; Sullivan, J. *J. Electrochem. Soc*. **1999**, *146*, 170.
(40) Chen, X.; Peterson, G.G.; Goldberg, C.; Nuesca, G.; Frisch, H.L.; Kaloyeros, A.E.; Arkles, B.; Sullivan, J. *J. Mater. Res*. **1999**, *14*, 2043.
(41) Jayaratne, K.C.; Yap, G.P.A.; Haggerty, B.S.; Rheingold, A.L.; Winter, C.H. *Inorg. Chem*. **1996**, *35*, 4910.
(42) Winter, C.H.; Jayaratne, K.C.; Proscia, J.W. *Mater. Res. Soc. Symp. Proc*. **1994**, *327*, 103.
(43) For leading references, see: (a) Jones, T.C.; Nielson, A.J.; Rickard, C.E.F. *J. Chem. Soc., Chem. Commun*. **1984**, 205. (b) Bates, P.A.; Nielson, A.J.; Waters, J.M. *Polyhedron* **1985**, *4*, 1391. (c) Nielson, A.J. *Polyhedron* **1988**, *7*, 67.
(44) Scheper, J.T.; McKarns, P.J.; Lewkebandara, T.S.; Winter, C.H. *Solid-State Electron.* **1999**, *2*, 149.
(45) (a) Angyal, M.S.; Shacham-Diamand, Y.; Reid, J.S.; Nicolet, M.-A. *Appl. Phys. Lett*. **1995**, *67*, 2152. (b) Kacsich, T.; Kolawa, E.; Fleurial, J.P.; Caillat, T.; Nicolet, M.-A. *J. Phys. D: Appl. Phys*. **1998**, *31*, 2406. (c) Fleming, J.G.; Roherty-Osmun, E.; Smith, P.M.; Custer, J.S.; Kim, Y.-D.; Kacsich, T.; Nicolet, M.-A.; Galewski, C.J. *Thin Solid Films* **1998**, *320*, 10.
(46) Vaz, F.; Rebouta, L.; da Silva, R.M.C.; da Silva, M.F.; Soares, J.C. *Vacuum* **1999**, *52*, 209.
(47) Raaijmakers, I.J. *Thin Solid Films* **1994**, *247*, 85.
(48) He, J.-W.; Bai, C.-D.; Xu, K.-W.; Hu, N.-S. *Surf. Coat. Technol*. **1995**, *74-75*, 387.
(49) Llauro, G.; Hillel, R.; Sibieude, F. *Adv. Mater. CVD* **1998**, *4*, 247.
(50) Fix, R.M.; Gordon, R.G.; Hoffman, D.M. *Chem. Mater*. **1990**, *2*, 235.

Scotch is a trademark of 3M Co.

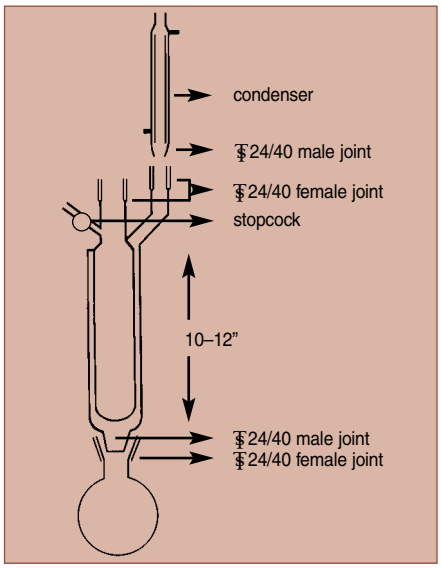
About the Author

Charles H. Winter was born in 1959 in Grand Rapids, Michigan, and grew up in Portage, Michigan, where he attended public schools. He obtained a B.S. degree from Hope College in 1982. While at Hope College, he was introduced to organometallic chemistry through undergraduate research with Professor Michael P. Doyle. He then went on to the University of Minnesota, and obtained his doctoral degree in 1986 under the direction of the late Professor Paul G. Gassman. After an NIH postdoctoral fellowship with Professor John A. Gladysz at the University of Utah, he joined the faculty at Wayne State University in 1988. He is now Professor of Chemistry.

Professor Winter's research interests include synthetic inorganic and organometallic chemistry, as well as chemical vapor deposition. A particular research emphasis in his laboratory is the development of new source compounds for use in CVD processes. Materials systems for which new precursors are being developed include group 4 and 5 nitrides for application as barrier materials in microelectronics devices, lanthanide compounds for application in infrared photonic devices, and magnesium compounds for devices that emit blue and green light. In the area of compound semiconductors, the development of precursors that are designed to decompose under X-ray irradiation is also underway. In addition to research directed toward CVD, Professor Winter maintains significant basic research projects involving the synthesis and properties of metal complexes with new nitrogen-donor ligands, metallocenes and aromatic compounds substituted with unusual main group elements, as well as fundamental chemistry of the group 13 elements. He has been a mentor to 22 doctoral students and is the author of more than 95 publications.

Lab Notes, continued from page 2.

Balki's Modified Abderhalden Drying Apparatus



An innovative and convenient apparatus has been designed, which is especially useful for manipulating air-sensitive compounds.

Because of its horizontal construction, the traditional Abderhalden drying apparatus has certain disadvantages, such as the possibility of sample spillage and the inconvenience of drying liquid samples (that cannot be distilled).

In this modified apparatus, the sample—which is most often stored in a slim, screw-cap vial—is conveniently lowered into the apparatus with the help of long tweezers, forceps (Cat. No. Z22,560-6 or Z22,561-4), or a copper wire that is tied around the neck of the vial.

This modified Abderhalden drying apparatus is very advantageous to use in many applications: It makes it convenient to add or remove solvent or solid materials, and is ideal for carrying out reactions in NMR tubes and for preparing NMR samples after drying the solid samples in the NMR tubes. We have also been successful in growing single crystals of air-sensitive samples using this setup.

I hope that this modification to a widely used apparatus will prove helpful to research scientists all over the world.

Maravanji S. Balakrishna, Ph.D.
Department of Chemistry
Tulane University
New Orleans, LA 70118

Current Address:
Department of Chemistry
Indian Institute of Technology
Powai, Mumbai 400 076, INDIA
E-mail: krishna@chem.iitb.ernet.in

Products for the Deposition of Metal Nitride Films

The following Aldrich products are mentioned in Dr. Winter's review. For more information, please call us at *800-231-8327* (USA) or your local Sigma-Aldrich office, or visit our Web site at *www.sigma-aldrich.com*. Larger quantities are available through Sigma-Aldrich Fine Chemicals. Please call *800-336-9719* (USA) or your local office for availability.

Niobium, Tantalum, and Silicon Compounds

$NbCl_5$ $TaBr_5$ $TaCl_5$ $Ta(NMe_2)_5$ SiH_2Cl_2 SiH_4

51,069-6 **Niobium(V) chloride**, 99.999%, anhydrous, powder
33,660-2 **Niobium(V) chloride**, 99.9+%
21,579-1 **Niobium(V) chloride**, 99%
40,046-7 **Tantalum(V) bromide**, -8 mesh, 98%
51,068-8 **Tantalum(V) chloride**, 99.999%, anhydrous, powder
40,047-5 **Tantalum(V) chloride**, 99.99%
21,863-4 **Tantalum(V) chloride**, 99.8%
49,686-3 **Pentakis(dimethylamino)tantalum**, 99.9%
(packaged in ampules)
33,339-5 **Dichlorosilane**, 99.99+%
29,522-1 **Dichlorosilane**, 97+%
33,389-1 **Silane**, 99.998+%, electronic grade
29,567-1 **Silane**, 99.9%

Titanium Compounds

$Ti(NMe_2)_4$ $Ti(NEt_2)_4$ $TiCl_4$

46,985-8 **Tetrakis(dimethylamino)titanium**, 99.999%
46,986-6 **Tetrakis(diethylamino)titanium**, 99.999%
25,431-2 **Titanium(IV) chloride**, 99.995+%
20,856-6 **Titanium(IV) chloride**, 99.9%
24,986-6 **Titanium(IV) chloride**, 1.0*M* solution in dichloromethane

34,569-5 **Titanium(IV) chloride**, 1.0*M* solution in toluene
40,498-5 **Titanium(IV) chloride**, *ca.* 0.09*M* solution in 20% hydrochloric acid

Featuring:

- Anhydrous Metal Halides
- Boron Reagents
- Chiral Products
- Conducting Polymers
- High-Purity Gases for CVD
- High-Purity Solvents
- Isocyanates
- Laboratory Equipment
- Metallocenes
- MOCVD Precursors
- Organic Building Blocks
- Organosilicon Compounds
- Reagents for Suzuki Coupling
- Resins for Combichem
- Rieke® Organozinc Reagents
- Silsesquioxanes
- Stable Isotopes

Aldrich's Latest *Masterpiece.*

The 2000-2001 Aldrich Handbook of Fine Chemicals and Laboratory Equipment is now available. The Aldrich Handbook remains the benchmark for chemical catalogs.

We call it a Handbook because it is loaded with the technical information you use on a daily basis in your research. The 2000-2001 version allows you access to 35,000 products, with 3,000 new listings, plus a complete selection of Laboratory Equipment, including custom glassware from the Aldrich Glass Shop.

If you have not yet received a Handbook, request your **FREE** copy today by e-mailing **sams-usa@sial.com**, or calling our Technical Service Department at **800-231-8327**.

Rieke is a registered trademark of Rieke Metals, Inc.

ALDRICH®

CHEMISTS HELPING CHEMISTS

WWW.SIGMA-ALDRICH.COM/ALDRICH

Special Interest Groups

In an effort to better serve our customer base, Aldrich offers a number of specialty catalogs and brochures. These pieces highlight specific groupings of products with relevant references and technical information. Please look for more publications, such as our *Products for NMR Spectroscopy* brochure, that highlight Aldrich's expertise in additional arenas.

Isocyanates

Widely used in organic synthesis and combinatorial applications, here we present all our isocyanates, as well as some popular isothiocyanates. In addition, the brochure highlights our Small Sample Service and several of the polymeric isocyanates in our collection.

Arylboronic Acids

Suzuki couplings are of great importance in synthetic and combinatorial methodologies. Aldrich offers the most comprehensive list of arylboronic acids and diboron esters available. Transition-metal catalysts for Suzuki coupling are also presented.

Rieke® Organozinc Reagents

Available exclusively from Aldrich, these reagents are stable as solutions in THF. They are often employed in cross-coupling reactions, Michael additions, and electrophilic amination reactions.

Glassware—Innovative Solutions for Research

Publicizes the extensive collection of glassware that Aldrich supplies and produces. We also welcome any custom requests you may have!

Rieke is a registered trademark of Rieke® Metals, Inc.

To receive any of these publications, please copy the ad, fill in the information below, and fax it to **414-298-7960** or email us at **awatson@sial.com**

Name	
Company	
Address	
City	**State**
Postal Code	**Country**
Phone	**Email**

Please check the following boxes for the publications you would like to receive.

- ☐ **Isocyanates (CZU)**
- ☐ **Arylboronic Acids (CMX)**
- ☐ **Rieke® Organozinc Reagents (CUS)**
- ☐ **Glassware—Innovative Solutions for Research (CLG)**

ALDRICH®

Synthetic Applications of Indium Trichloride Catalyzed Reactions

*G. Babu and P. T. Perumal**
Organic Chemistry Division
Central Leather Research Institute
Adyar, Chennai 600 020, India
E-mail: ptperumal@hotmail.com

Outline

1. Introduction
2. Synthetic Applications
   2.1. The Diels–Alder Reaction
   2.2. The Aldol Reaction
   2.3. The Friedel–Crafts Reaction
   2.4. Miscellaneous Reactions
3. Conclusion
4. Acknowledgements
5. References

1. Introduction

Lewis acids play a vital role in organic reactions. The Lewis acids most frequently encountered in organic synthesis are $AlCl_3$, BF_3•Et_2O, $ZnCl_2$, $TiCl_4$, and $SnCl_4$. Recently, lanthanide triflates have gained a lot of attention as Lewis acids for organic reactions.[1] Although indium belongs to the same group in the periodic table as boron and aluminum, the utility of indium trichloride as a Lewis acid for organic reactions has not been exploited to a greater extent largely because of its mild Lewis acid character. Recently, it has been proven that indium trichloride is a mild Lewis acid which is stable in an aqueous medium, and that it effectively catalyzes the aldol, Diels–Alder, and Friedel–Crafts reactions. This short review focuses on the effectiveness of indium trichloride as a Lewis acid in organic synthesis, and covers the literature of the past decade. The synthetic applications of indium trichloride prior to 1990 were surveyed by Fedorov and Fedorov[2a] and by Boghosian and Papatheodorou.[2b]

2. Synthetic Applications

2.1. The Diels–Alder Reaction

The Diels–Alder reaction is one of the most powerful methods for the regio- and stereospecific preparation of carbocyclic and heterocyclic ring systems. Lewis acids increase the rate of the reaction and its regio-, endo-, and π-face selectivities by coordination with the dienophile, i.e., with a conjugated C=O or C=N group.

Loh and coworkers[3] have reported that indium trichloride catalyzes the Diels–Alder reaction between cyclopentadiene and acrylates in water (**eq 1**), and have shown that the catalyst can be easily recovered from water and reused after the reaction has been completed.

The imino Diels–Alder reaction is a powerful tool for the synthesis of quinoline and pyridine derivatives. Although Lewis acids often promote the reaction, more than stoichiometric amounts of the acids are required due to the strong coordination of the acids to the nitrogen atoms.[4] In contrast, only a catalytic amount of anhydrous indium trichloride (20 mol %) is needed for the reaction of Schiff bases with cyclopentadiene to afford cyclopentaquinolines (**eq 2**).[5] The use of indium trichloride enhances the rate of the reaction and improves its yield as compared to other Lewis acids (**Table 1**).[6,7] Indium trichloride also catalyzes the Diels–Alder reaction of *N*-benzylidene-1-naphthylamine with cyclopentadiene to afford benzo[*h*]-cyclopenta[*c*]quinoline (**eq 3**).[5]

The pyranoquinoline moiety is present in many alkaloids such as flindersine, oricine and veprisine (**Figure 1**). Pyranoquinoline derivatives possess a wide range of biological activities, such as psychotropic, antiallergic, anti-inflammatory, and estrogenic activities, and are potential pharmaceuticals. Pyranoquinoline derivatives have been synthesized by the BF_3•Et_2O,[8] acetic acid,[9] or ytterbium triflate catalyzed[10] Diels–Alder reaction of *N*-benzylideneaniline with 3,4-dihydro-2*H*-pyran; the yields, however, are low. On the other hand, indium trichloride catalyzes the Diels–Alder reaction of Schiff bases with 3,4-dihydro-2*H*-pyran and affords the corresponding pyranoquinoline derivatives in good-to-moderate yields. Indium trichloride coordinates with the Schiff bases yielding endo/exo products, the ratio of which is determined largely by the electronic effects of the substituents in the Schiff bases (**eq 4**).[11] A comparison of the results obtained with indium trichloride with those obtained with other catalysts is given in **Table 2**. The reaction of 3,4-dihydro-2*H*-pyran with *N*-benzylidene-1-naphthylamine in the presence of 20 mol % indium trichloride provides benzo[*h*]pyrano[3,2-*c*]quinolines (**eq 5**).[11]

Schiff bases react with indene in the presence of indium trichloride affording only the endo isomer of indeno[2,1-*c*]quinolines in

moderate yields (**eq 6** and **Table 3**);[11] in the absence of indium trichloride, the reaction does not proceed at all. The endo isomer is obtained as a result of the likely secondary orbital interactions of diene and dienophile. Similarly, *N*-benzylidene-1-naphthylamine reacts with indene to provide benzo[*h*]-indeno[2,1-*c*]quinoline in 50% yield (**eq 7**).[11]

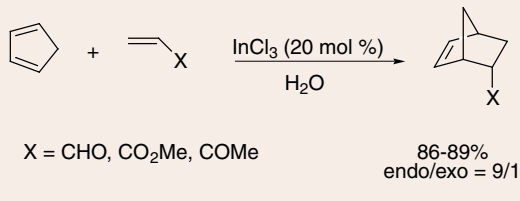
The Diels–Alder reaction of benzo[*b*]-thienylimines with cyclopentadiene and 3,4-dihydro-2*H*-pyran in the presence of anhydrous indium trichloride provides benzo[*b*]thienyl-substituted quinoline derivatives (**Scheme 1**),[12] a class of biologically active agents, in good yields and endo stereoselectivities. The addition is also regioselective with respect to the dihydropyran ring. Similarly, the reaction of imines with enamides leads to the biologically important pyrolloquinolines regioselectively and in moderate yields (**eq 8**).[13]

Azabicyclo[2.2.2]octanones have been prepared in moderate yields and regio- and stereoselectivities by the Diels–Alder reaction of either *N*-tosylimines with 2-trialkylsilyl-oxy-1,3-cyclohexadiene (**eq 9**),[14] or imino-carbamates with 1,3-cyclohexadiene (**eq 10**)[15] in the presence of BF_3•Et_2O. By comparison, the Diels–Alder reaction of Schiff bases with 2-cyclohexenone in the presence of indium trichloride provides a facile route to azabicyclo[2.2.2]octanones (**eq 11** and **Table 4**).[16] Azabicyclononan-8-ones have been similarly prepared in good yields (**eq 12**).[16] Azabicyclooctanones and azabicyclononanones are of interest as precursors of naturally occurring piperidine alkaloids of the prosopis family.[17]

2.2. The Aldol Reaction

The aldol reaction is one of the most important carbon–carbon bond forming reactions for acyclic stereocontrol. Mukaiyama and coworkers[18] have reported that aldehydes smoothly react with trimethylsilyl enol ethers, in the presence of TMSCl and indium trichloride, to produce the corresponding aldol adducts in high yields (**eq 13**).

Catalytic amounts of *tert*-butyldimethyl-silyl chloride (TBSCl) and indium trichloride also promote aldol reactions. The conventional Mukaiyama aldol reaction requires strictly anhydrous and nonprotic conditions.[19] Kobayashi has shown that lanthanide triflates are excellent catalysts for the Mukaiyama aldol reaction in aqueous media (THF-H_2O).[20,21] However, efforts to carry out the experiment in water alone afforded only low yields of the products. Loh and coworkers[22] have demonstrated for the first time that indium trichloride catalyzes the Mukaiyama-type reaction of silyl enol ethers and

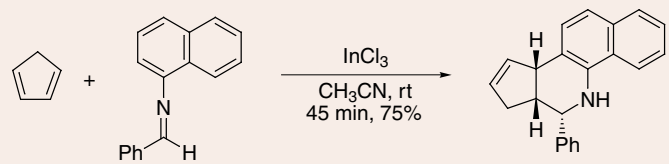


eq 1

eq 2

Table 1. Reaction of Schiff Bases with Cyclopentadiene

Entry	Schiff Base	R^1	R^2	R^3	Catalyst	Time, h	Product	Yield, %	Ref.
1	**1a**	H	H	H	TFA	2	**2a**	71	6
					$Yb(OTf)_3$	20		85	7
					$InCl_3$	0.5		75	5
2	**1b**	H	NO_2	H	TFA	3	**2b**	98	6
					$InCl_3$	0.5		95	5
3	**1c**	H	OCH_3	H	$Yb(OTf)_3$	20	**2c**	38	7
					$InCl_3$	0.75		58	5
4	**1d**	H	Cl	H	$Yb(OTf)_3$	20	**2d**	85	7
					$InCl_3$	0.5		84	5



eq 3

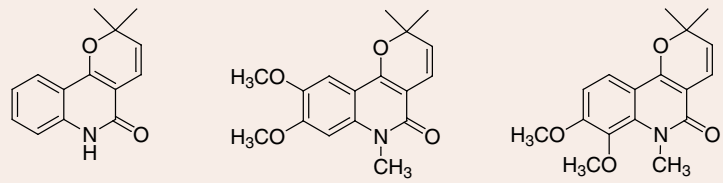
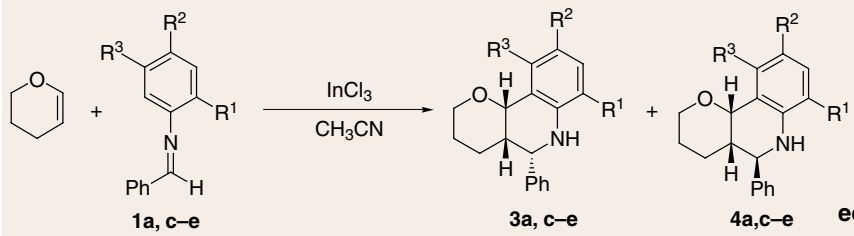


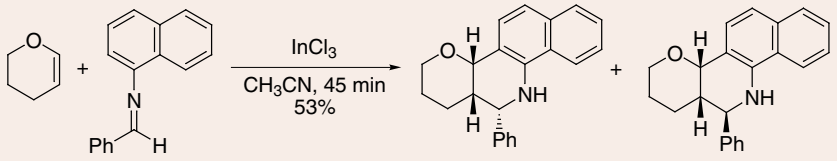
Figure 1



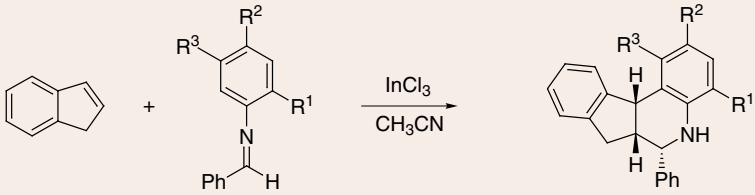
eq 4

Table 2. Reaction of Schiff Bases with 3,4-Dihydro-2*H*-pyran

Entry	Schiff Base	R^1	R^2	R^3	Catalyst	Time, h	Product Ratio 3:4	Overall Yield, %	Ref.
1	**1a**	H	H	H	BF_3•Et_2O	12	100:0	25	8
					$InCl_3$	0.5	41:59	80	11
2	**1c**	H	OCH_3	H	$Yb(OTf)_3$	9	37:63	54	10
					$InCl_3$	4	58:42	70	11
3	**1d**	H	Cl	H	$InCl_3$	0.5	34:66	50	11
4	**1e**	H	CH_3	H	$InCl_3$	2	68:32	70	11



eq 5

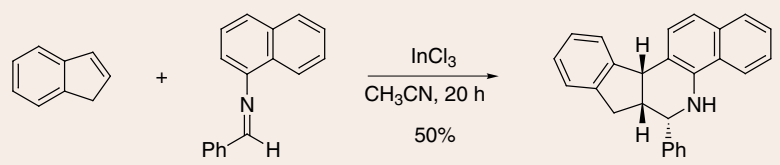


1a, c, d, f, g **5a, c, d, f, g**

eq 6

Table 3. Reaction of Schiff Bases with Indene in the Presence of 20 mol % $InCl_3$

Entry	Schiff Base	R^1	R^2	R^3	Time, h	Product	Yield, %
1	**1a**	H	H	H	6	**5a**	40
2	**1c**	H	OCH_3	H	24	**5c**	30
3	**1d**	H	Cl	H	6	**5d**	48
4	**1f**	CH_3	Cl	H	12	**5f**	48
5	**1g**	CH_3	H	CH_3	9, reflux	**5g**	65



eq 7

aldehydes in water (**eq 14**). Recently, Kobayashi[23] has reported that the indium trichloride catalyzed aldol reaction of silyl enol ethers with aldehydes proceeds smoothly in water without using any cosolvents when a small amount of surfactant is present (**eq 15**). Because of its high coordination number and fast coordination–dissociation equilibrium, $InCl_3$ is stable in aqueous media and thereby effectively catalyzes the aqueous aldol reaction.[3] In contrast, other Lewis acids, such as BF_3•Et_2O and $AlCl_3$, react with water to yield the corresponding hydroxide derivatives.

The aldol–Mannich-type reaction is among the most fundamental methods for the synthesis of β-amino ketones and esters. The uncatalyzed synthesis of β-amino ketones and esters by the aldol–Mannich-type reaction gives products in low yields due to severe side reactions such as deamination. Unfortunately, most of the Lewis acids used in aldol–Mannich-type reactions are not stable and decompose or deactivate in the presence of water, which is a by-product of imine formation, or as a result of direct attack by the free amine present. Loh's group[24] has reported that indium trichloride catalyzes the formation of β-amino esters, in better yields, by reaction of an aldehyde, an amine, and an ester-derived silyl enol ether (**eq 16**). The reaction of a ketone-derived silyl enol ether with an aldehyde and an amine affords β-amino ketones in good-to-moderate yields (**eq 17**).[24]

2.3. The Friedel–Crafts Reaction

Indium trichloride catalyzes the acylation of anisole at room temperature, and the yield of the reaction is improved significantly by the addition of silver perchlorate (**eq 18**).[25] The combination of $InCl_3$ and $AgClO_4$ is believed to generate the active catalyst species, $InCl_2(ClO_4)$ or $InCl(ClO_4)_2$, which reacts with the anhydride to form an acyl cation intermediate that is stabilized by the perchlorate anion. This acylium ion intermediate then reacts with aromatics to give the desired ketone. In combination with chlorodimethylsilane, indium trichloride catalyzes the reductive Friedel–Crafts alkylation of aromatics (**eq 19**).[26,27] This transformation is especially valuable in light of the difficulty with which these alkylated aromatics have traditionally been prepared. The tolerance of ester and ether groups, which are frequently used as alkylating reagents, is perhaps due to the weak Lewis acidity of $InCl_3$. In the general systems reported, the alkylations involving esters and ethers give different results that are dependent on the acidity of the catalyst.[28]

2.4. Miscellaneous Reactions

Tetrahydropyrans have been prepared by the indium trichloride mediated Prins-type cyclization in high yields and with high stereoselectivity (**eq 20**).[29] Tetrahydropyrans are useful for the construction of various important carbohydrates and natural products. They have been prepared in the past by the titanium tetrachloride or aluminum trichloride catalyzed reactions of alkoxyallylsilanes with aldehydes, or by the related cross-coupling between homoallyl alcohols and aldehydes.[30]

Sigma-Aldrich Laboratory Equipment

SUMMER
2000

Aldrich Kugelrohr

Short-Path Distillation Apparatus

Kugelrohr

Büchi
Distillation Ovens

KNF Vacuum
Pumps

IKA
Stirrers/Mixers

Eppendorf
Thermomixers

Electronic
Incubators/
Ice Cubes

Easy-Read
Thermometers

IR Thermometer

PLUS:
FREE OFFER
INSIDE

ALDRICH®

Aldrich Kugelrohr
Short-Path Distillation Apparatus

- Distills heat-sensitive compounds
- Distills liquids and low-melting solids from polymers and tars
- Distills with minimal holdup and sample loss
- Removes color and particulates
- Can be used for sublimation/solvent evaporation

Kugelrohr apparatus shown with KNF Laboport vacuum pump (see page 4).

"Distills the Most Difficult Materials"

Step 1

Oven flask is filled one-third full with distillable material, placed carefully in oven, and connected to the horizontal receiving flasks outside the oven.

Step 2

Connect the glassware to the rotary drive and the drive to a vacuum pump.* Switch the vacuum drive on to turn the distillation train 360° to speed distillation, ensure even heating, and prevent bumping. Start the vacuum pump.

*Use of a vacuum trap between the rotary drive and the pump is recommended to protect the pump. See the Equipment Section of the 2000-2001 Aldrich Handbook for vacuum traps.

Step 3

When the correct vacuum is attained, set the distillation temperature on the air-bath oven and begin distillation. The digital temperature controller displays both "set" and "actual" air-bath temperature.

Step 4

Collect distillate in the horizontal ball-tubes outside of oven. An ice-filled polypropylene cooling tray quickly condenses distillate in receiving ball-tubes.

Specifications:

Micro to macro distillation capability

- ❑ Accommodates flask sizes 10mL to 1L

Air-bath oven

- ❑ SS wall with leakproof seal at the base contains spills
- ❑ Grounded heating element prevents electrical shock
- ❑ Detachable power cord, on/off switch, adjustable rubber feet, and interchangeable Teflon bearing set for flasks with ₮14/40 and ₮24/40 joints

Distill under vacuum to 0.05mm Hg

- ❑ Single-speed rotary drive is optimized for Kugelrohr distillations
- ❑ Detachable power cord, on/off switch, adjustable rubber feet, built-in stabilizing clamp

Automatic temperature controller

- ❑ Maintains oven temperature up to 220°C, ±1°C
- ❑ Type-K thermocouple ensures fast, accurate temperature measurements inside of oven
- ❑ Automatically turns off power to oven if thermocouple fails or disconnects

CE Compliant

Kugelrohr Short-Path Distillation Apparatus

Includes the following components:

air-bath oven with digital temperature controller, glassware set consisting of a straight tube with hose connection, 25 and 100mL round-bottom oven flasks, 25 and 100mL single bulb ball-tube flasks with ₮14/20 joints, and rotary drive.

Volts	Cat. No.
115	**Z40,113-7**
230	**Z40,114-5**

Please see the Equipment Section of the 2000-2001 Aldrich Handbook for a complete listing of Kugelrohr accessory glassware and parts.

Büchi
Distillation Ovens

Model B580 GKR

The small size flasks in this ball-tube oven make it an ideal system for high temperature distillation of small quantities of liquid, for separating solvents from non-volative, oily components in a mixture, or for evaporating quantities of sample that are too small for rotary evaporators. Includes 3 x 20mL ball-tube assembly, ball-tube drive unit, and 60mL rotation drying flask.

Volts	Cat. No.
115	Z41,222-8
230	Z31,916-3

Accessory ball tubes with vapor ducts

No. Balls x Volume (mL)	Cat. No.
2 x 40	Z31,920-1
3 x 20	Z31,922-8
4 x 10	Z31,923-6

- Variable rotation speed: 0 to 50rpm
- Cooling device cold trap can be cooled down to –80°C
- Ball-tubes with 2, 3, or 4 balls are available
- External ball-tube drive unit for constant rotation
- Linear drying tube holds up to 60mL of solids
- CE compliant

KNF
LABOPORT

Solid Teflon Deep-Vacuum Pumps

Vacuum pump shown with optional baseplate and KNF Precision vacuum controller

"Provides the Deepest Vacuum Available in a Dry Diaphragm Pump"

- 1.5 torr performance
- Excellent for use with all solvents
- Solid Teflon pump heads with Kalrez valves
- Dry operation, uses no oil and is maintenance-free
- CE compliant

Specifications:

- Pumping speed: 34L/min
- Max. vacuum: 1.5 torr (29.88in. Hg)
- Max. pressure: 15psig
- Head/valves: Teflon/Kalrez
- Compact cast-alloy case with carrying handle
- Totally-enclosed, fan-cooled, ball-bearing motor
- Hose connections: 3/8 in. i.d. barbs
- Dim.: 33 L x 17 W x 22in. H
- Wt: 27lb (12.2kg)

Volts	Cat. No.
115	Z28,820-9
230	Z28,821-7

Baseplate for units
Z28,833-0

See the Equipment Section in the 2000-2001 Aldrich Handbook for more KNF vacuum pumps and accessories.

IKAMAG
Stirring Hot Plates

Model RCT

Low profile, enclosed construction with a connection for the IKATRON electronic thermometer listed separately, below. 90 H x 160 W x 280mm D. Wt = 2.4kg. CE compliant.

- 20L stirring cap.
- Speed range: 0 to 1,100rpm
- Temp. range: ambient to 300°C/572°F
- AlSi plate; diam: 135mm
- Safety circuit fixed at 370°C/698°F

Volts	Cat. No.
115	**Z40,351-2**
230	**Z40,352-0**

Model RCT stirring hot plate shown with optional vertical support rod, boss head clamp, and IKATRON electronic thermometer

IKATRON Electronic Thermometer

Fuzzy logic and 2-point control for optimal control of hot plate temperature. Connects to above hot plates or any unit with a DIN 12878 socket. Includes a 250 L x 3mm diam., PT 1000, SS temperature probe. Dim.: 96 H x 50 W x 35mm D. Wt = 0.2kg.

Z40,353-9

- Digital display
- Measuring range: -10 to 400°C with adjustable safety circuit between 100 and 400°C
- Control precision: ± 0.2°C
- No temperature overshoot

Accessories for Stirring Hot Plates and Electronic Thermometer

Probe extension cable, 2.5m, for the remote connection of IKATRON electronic thermometer to sensor probe.
Z40,355-5

Vertical support rod, SS, threads into top of stirrer base
Z40,356-3

Boss head clamp
Z40,357-1

Adjustable stand support rod, R380
Attaches to side groove of stirring hot plate allowing adjustment to any desired setting along stirrer. Several support rods can be attached to stirrer simultaneously.
Z40,360-1

IKA
Dual-Speed Mixers

Two speed ranges for stirring applications up to 20L (in terms of H_2O) of material. 292 H x 88 W x 188mm D. Wt = 2.9kg. Order stirring shafts separately; see listings in the Aldrich Handbook. CE compliant.

- Two speed ranges:
  60 to 500rpm
  240 to 2,000rpm
- Viscosity max.: 10,000cps
- Max. torque: 185Ncm
- Adjustable chuck; range: 0.5 to 10mm

	Analog	*w/Digital speed display*
Volts	**Cat. No.**	**Cat. No.**
115	**Z40,395-4**	**Z40,397-0**
230	**Z40,396-2**	**Z40,398-9**

Eppendorf Thermomixers

This new thermomixer combines heating and shaking of 24 x 1.5mL samples at a time to ease user workload. Incubation and mixing may also be performed independently. Autoclavable and freezer-safe rack with 24 numbered positions make processing and transporting samples quick and easy. Short-mix function for quick "vortex" applications.

- Mixing speed: 300 to 1,400rpm
- Mixing stroke: 3mm
- Temp. control range: - 4°C above ambient up to 99°C in 1°C increments
- Temp. accuracy: ± 1°C at 0 to 45°C; ± 2°C above 45°C
- Dim.: 6.5 W x 9.5 D x 5.3in. H
- CE compliant

Volts	Cat. No.
115	**T 1317**
220	**T 1442**

Echotherm Chilling Incubators

Ideal for benchtop use in any laboratory. The unit is designed for standard incubations, culture growth, enzyme reactions, and more. Chill or heat samples with the precise control of 0.1°C selectability. Includes two electropolished steel racks, power cord, and manual. Chamber dim.: 9½ x 9½ x 14in. Overall dim.: 15½ x 16½ x 22½ in. Weight: 45lb.

- Temp. range: 4 to 70°C
- No CFCs; Peltier based cooling
- Digital controls
- Timer with alarm and Auto-off
- UL, CSA, and CE certified

Volts	Cat. No.
115	**Z40,096-3**
230	**Z40,097-1**

Electronic Ice Cubes

Chill samples as low as -10°C on the bench or in the field. Plate surface will go to 0°C in two minutes. Plate dim.: 2⅞ x 4⅜ in. Overall dim.: 3½ x 6½ x 4¾ in. Weight: 6lb.

- Freeze 96-well plates and centrifuge tubes
- No CFCs; Peltier based cooling
- UL, CSA, and CE certified

Volts	Cat. No.
115	**Z40,099-8**
230	**Z40,100-5**

Accessories for Electronic Ice Cubes

Cover for 96-well plates	**Z40,106-4**
Cover for blocks	**Z40,105-6**
Al block for 0.2mL centrifuge tubes	**Z40,101-3**
Al block for 0.5mL centrifuge tubes	**Z40,102-1**
Al block for 1.5mL centrifuge tubes	**Z40,104-8**

Easy-Read Thermometers

Easy-to-read thermometers with black printing on a bright yellow background. Filled with contrasting black, non-hazardous, Enviro-Safe liquid. Calibrated with NIST, DKD standards.

Range	L (mm)	Immersion level 76mm Cat. No.	Immersion level Total Cat. No.
-20 to 110°C	200	Z42,335-1*	Z42,337-8
-20 to 150°C	200	Z42,338-6*	Z42,339-4
-20 to 110°C	300	Z42,341-6	Z42,340-8
-20 to 150°C	300	Z42,343-2	Z42,342-4
-10 to 225°C	350	–	Z42,350-5
-10 to 260°C	350	Z42,351-3	–
0 to 230°F	300	Z42,345-9	Z42,344-0
0 to 300°F	300	Z42,347-5	Z42,346-7
20 to 435°F	350	–	Z42,348-3
20 to 500°F	350	Z42,349-1	–

*50mm immersion level

Easy-Read Pocket Thermometers

Easy-to-read total immersion pocket thermometers with non-hazardous, biodegradable black liquid fill. Thermometers are 145mm L, 160mm L with aluminum case. An armor option is available, providing extra shielding for the thermometer.

Range	Div.	Without armor Cat. No.	With armor Cat. No.
-5 to 50°C	1°C	Z42,356-4	Z42,359-9
-10 to 110°C	1°C	Z42,355-6	Z42,358-0
20 to 120°F	2°F	Z42,357-2	Z42,360-2
0 to 220°F	2°F	Z42,354-8	Z42,352-1

Non-Contact Mini Infrared Thermometer

"Measures temperature in difficult to reach or unsafe areas"

- Built-in laser pointer to improve aim
- Measures to 315°C (600°F) without contact
- Large digital display with backlighting
- Switchable °C/°F temperature units
- Pocket size meter complete with 9V battery

Z42,281-9

Specifications:

Range:	0 to 315°C or 0 to 600°F
Accuracy:	±2% of reading or 4°F / 2°C (whichever is greater)
Resolution:	1°C or 1°F
Field of view:	6:1 (at 6in. distance measures 1in. target)
Dim.:	6.7 L x 1.7 W x 1.6in. D (170 x 44 x 40mm)

Galileo Thermometers

These fascinating and functional instruments indicate temperature by colorful glass spheres that rise and fall according to changes in temperature of the clear liquid contained in each unit. Based on Galileo Galilei's discovery that as a liquid's temperature increases, its buoyancy decreases.

- ❍ Calibrated multi-colored glass spheres, in °F or °C
- ❍ The lowest floating sphere indicates temperature
- ❍ All-glass, hand blown body filled with harmless clear liquid

RECEIVE A FREE DESKTOP GALILEO THERMOMETER* WITH ANY ORDER OF $300 OR MORE FROM THIS BROCHURE.

Model	H (in./cm)	Temp. range (°F)	Temp. range (°C)	No. spheres	*Fahrenheit* Cat. No.	*Celsius* Cat. No.
Desktop	11/28	64-80	18-26	5	**Z42,263-0**	**Z34,139-8**
Classic	13.5/34	64-80	18-26	5	**Z42,262-2**	**Z34,140-1**
Majestic	17/43	64-76	18-24	7	**Z42,261-4**	**Z34,142-8**
Grande	24/61	62-82	18-27	11	**Z42,260-6**	**Z34,143-6**

Ordering Information

Call: 800-558-9160
Outside USA and Canada: 414-273-3850
Fax: 800-962-4979
Outside USA and Canada: 414-273-4979
Laboratory Equipment mailing address:
P.O. Box 2060
Milwaukee, WI 53201 USA

*To receive a FREE desktop Galileo thermometer, please specify Fahrenheit or Celsius scale and send your qualifying purchase order number to: cwozniak@sial.com.

For Development/Manufacturing Quantities
Contact your local Sigma-Aldrich office
and ask for Sigma-Aldrich Fine Chemicals

SIGMA-ALDRICH

World Headquarters • 3050 Spruce St., St. Louis, MO 63103 • (314) 771-5750 • http://www.sigma-aldrich.com

The SIGMA-ALDRICH Family

SIGMA	ALDRICH	Fluka	Riedel-de Haën	SUPELCO
Biochemicals and Reagents for Life Science Research	Organics and Inorganics for Chemical Synthesis	Specialty Chemicals and Analytical Reagents for Research	Laboratory Chemicals and Reagents for Research and Analysis	Chromatography Products for Analysis and Purification

Sigma-Aldrich Fine Chemicals is the development and manufacturing division of Sigma-Aldrich, Inc

Indium trichloride is also very efficient in effecting the rearrangement of epoxides to the corresponding carbonyl compounds highly regioselectively (**eq 21**).[31]

Mukaiyama et al.[32] have reported that TMSCl and indium trichloride catalyze the reaction of *O*-trimethylsilyl monothioacetals with triethylsilane and silylated carbon nucleophiles to afford the corresponding sulfide derivatives (**eq 22**). These sulfides are of interest because they are not only used as protecting groups, but also as electrophiles in various coupling reactions, especially carbon–carbon bond forming reactions.

Indium trichloride is used as a catalyst for the polymerization of biphenylylchlorophthalide,[33] with *tert*-butylhydroperoxide for vinyl monomers,[34] methyl methacrylates,[35] chlorophthalides[36] and *tert*-butylacetylene.[37] Zhun et al.[38] have reported that treatment of $Me_nPhSiCl_{3-n}$ (n = 0–2) with chlorine in the presence of indium trichloride affords (chlorophenyl)silanes. Indium trichloride also catalyzes the dehydrochlorination of dichloroethane,[39] is used as a promoter for the hydrochlorination of low-molecular-weight polyisobutylenes[40] and the allylation of carbonyl compounds.[41]

Bisindolylmethanes have been prepared in excellent yields by the electrophilic substitution reaction of indole with aldehydes or Schiff bases in the presence of indium trichloride (**Scheme 2**).[42] The reaction is thought to proceed via an electrophilic substitution step of indole with the aromatic aldehydes or Schiff bases. These bisindoles are of current interest as potent CNS depressants.[43]

3. Conclusion

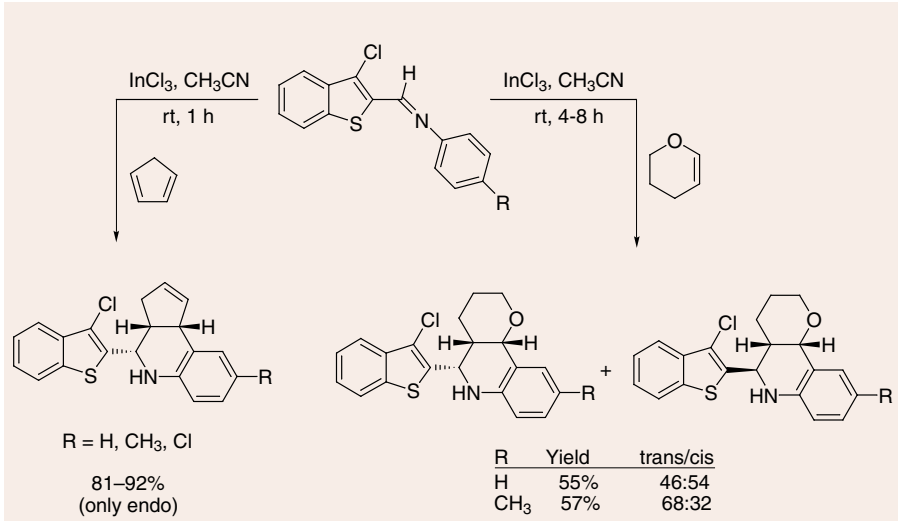
It is evident from the above reports that indium trichloride has emerged as a mild Lewis acid for effecting a variety of chemical transformations in a chemo-, regio-, and stereoselective fashion. Because indium trichloride is catalytically active both in aqueous and organic solvents, it is the mild Lewis acid of choice in a number of synthetic organic reactions.

4. Acknowledgements

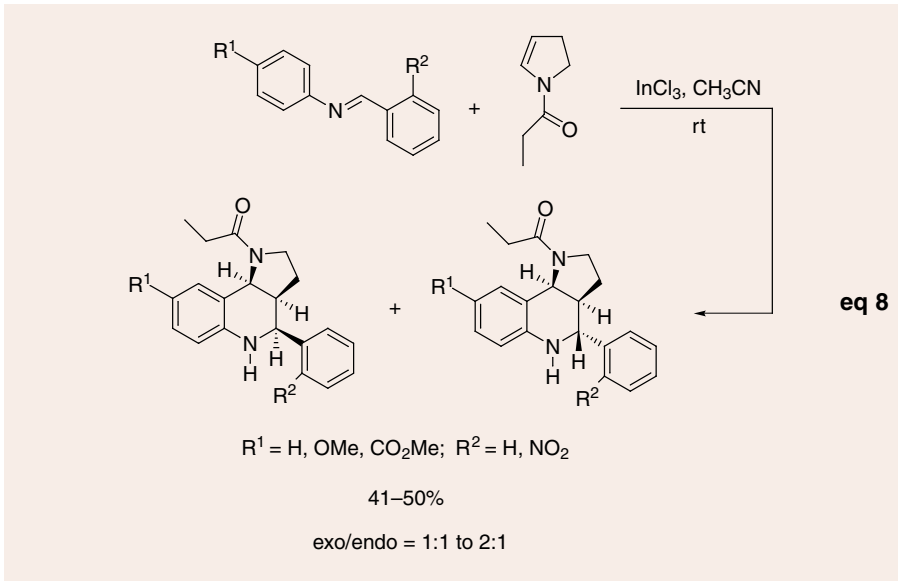
We thank all those who have contributed to the chemistry reviewed here and whose names appear in the cited references. We also thank the Council of Scientific and Industrial Research, India, for financial support.

5. References

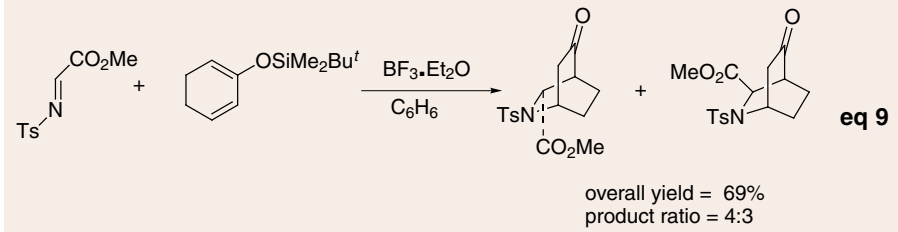
(1) (a) Kobayashi, S.; Hachiya, I.; Takahori, T.; Araki, M.; Ishitani, H. *Tetrahedron Lett*. **1992**, *33*, 6815. (b) Kobayashi, S.; Hachiya, I.; Araki, M.; Ishitani, H. *Tetrahedron Lett*. **1993**, *34*, 3755.



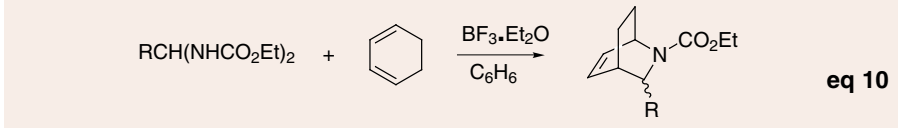
Scheme 1



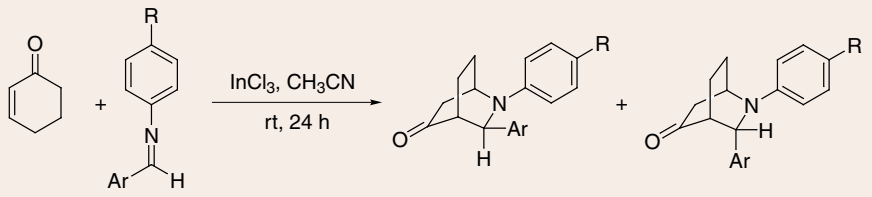
eq 8



eq 9



eq 10

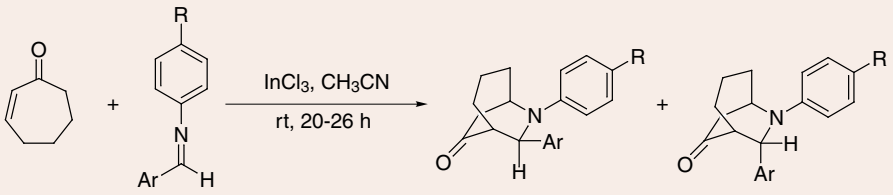


1a–e, h, i **6a–e, h, i** **7a–e, h, i**

eq 11

Table 4. Diels–Alder Reaction of Schiff Bases with 2-Cyclohexenone

Entry	Schiff Base	R	Ar	Product Ratio 6:7	Combined Yield (%)
1	**1a**	H	C_6H_5	69:31	65
2	**1b**	NO_2	C_6H_5	67:33	70
3	**1c**	OCH_3	C_6H_5	68:32	60
4	**1d**	Cl	C_6H_5	73:27	68
5	**1e**	CH_3	C_6H_5	73:27	62
6	**1h**	H	4-Cl-C_6H_4	48:52	65
7	**1i**	Cl	4-Cl-C_6H_4	47:53	74



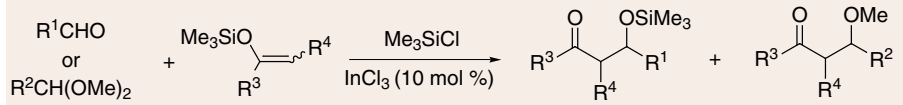
R = H, CH_3, OCH_3, Cl

Ar = C_6H_5, 4-ClC_6H_4

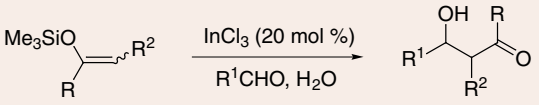
48–78%

exo/endo = 39/61 to 65/35

eq 12

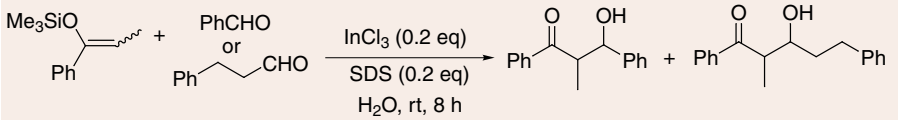


eq 13



85–96%

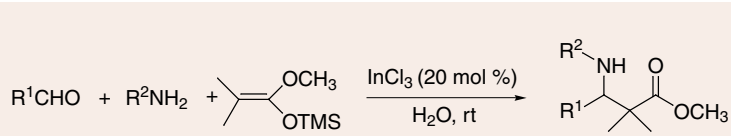
eq 14



SDS = Sodium dodecylsulfate 75% 54%

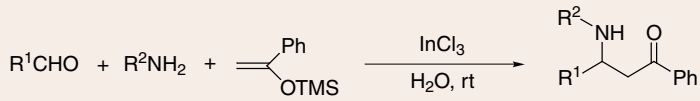
eq 15

(2) (a) Fedorov, P. I.; Fedorov, P. P. *Zh. Neorg. Khim*. **1974**, *19*, 215; *Chem. Abstr*. **1974**, *80*, 87863. (b) Boghosian, S.; Papatheodorou, G.N. *Handb. Phys. Chem. Rare Earths* **1996**, *23*, 435; *Chem. Abstr*. **1997**, *126*, 138990z.
(3) Loh, T.-P.; Pei, J.; Lin, M. *Chem. Commun*. **1996**, 2315.
(4) (a) Weinreb, S. M. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, UK, 1991; Vol. 5, p 401. (b) Boger, D. L.; Weinreb, S. M. *Hetero Diels–Alder Methodology in Organic Synthesis*; Academic Press: New York, NY, 1987; Chapters 2 and 9.
(5) (a) Babu, G.; Perumal, P. T. *Tetrahedron Lett*. **1997**, *38*, 5025. (b) Babu, G.; Nagarajan, R.; Natarajan, R.; Perumal, P. T. *Synthesis* **2000**, in press.
(6) Grieco, P. A.; Bahsas, A. *Tetrahedron Lett*. **1988**, *29*, 5855.
(7) Kobayashi, S.; Ishitani, H.; Nagayama, S. *Synthesis* **1995**, 1195.
(8) Kametani, T.; Takeda, H.; Suzuki, Y.; Honda, T. *Synth. Commun*. **1985**, *15*, 499.
(9) Gilchrist, T. L.; Stannard, A.-M. *Tetrahedron Lett*. **1988**, *29*, 3585.
(10) Makioka, Y.; Shindo, T.; Taniguchi, Y.; Takaki, K.; Fujiwara, Y. *Synthesis* **1995**, 801.
(11) Babu, G.; Perumal, P. T. *Tetrahedron Lett*. **1998**, *39*, 3225.
(12) Babu, G.; Perumal, P. T. *Tetrahedron* **1999**, *55*, 4793.
(13) Hadden, M.; Stevenson, P. J. *Tetrahedron Lett*. **1999**, *40*, 1215.
(14) (a) Holmes, A. B.; Thompson, J.; Baxter, A. J. G.; Dixon, J. *J. Chem. Soc., Chem. Commun*. **1985**, 37. (b) Birkinshaw, T. N.; Tabor, A. B.; Holmes, A. B.; Kaye, P.; Mayne, P. M.; Raithby, P. R. *J. Chem. Soc., Chem. Commun*. **1988**, 1599. (c) Birkinshaw, T. N.; Tabor, A. B.; Holmes, A. B.; Raithby, P. R. *J. Chem. Soc., Chem. Commun*. **1988**, 1601.
(15) Krow, G.; Rodebaugh, R.; Carmosin, R.; Figures, W.; Pannella, H.; DeVicaris, G.; Grippi, M. *J. Am. Chem. Soc*. **1973**, *95*, 5273.
(16) Babu, G.; Perumal, P. T. *Tetrahedron* **1998**, *54*, 1627.
(17) (a) Holmes, A. B.; Raithby, P. R.; Thompson, J.; Baxter, A. J. G.; Dixon, J. *J. Chem. Soc., Chem. Commun*. **1983**, 1490. (b) Holmes, A. B.; Thompson, J.; Baxter, A. J. G.; Dixon, J. *J. Chem. Soc., Chem. Commun*. **1985**, 37. (c) Birkinshaw, T.N.; Holmes, A.B. *Tetrahedron Lett*. **1987**, *28*, 813.
(18) Mukaiyama, T.; Ohno, T.; Han, J. S.; Kobayashi, S. *Chem. Lett*. **1991**, 949.
(19) Mukaiyama, T. *Org. React*. **1982**, *28*, 203.
(20) Kobayashi, S.; Hachiya, I. *J. Org. Chem*. **1994**, *59*, 3590.
(21) Kobayashi, S. *Chem. Lett*. **1991**, 2187.
(22) Loh, T.-P.; Pei, J.; Cao, G.-Q. *Chem. Commun*. **1996**, 1819.
(23) Kobayashi, S.; Busujima, T.; Nagayama, S. *Tetrahedron Lett*. **1998**, *39*, 1579.
(24) Loh, T.-P.; Wei, L.-L. *Tetrahedron Lett*. **1998**, *39*, 323.
(25) Mukaiyama, T.; Ohno, T.; Nishimura, T.; Suda, S.; Kobayashi, S. *Chem. Lett*. **1991**, 1059.
(26) Miyai, T.; Onishi, Y.; Baba, A. *Tetrahedron Lett*. **1998**, *39*, 6291.



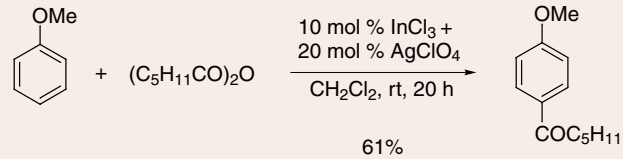
R^1 = H, Ph, 2-Py; R^2 = Ph, 4-ClC_6H_4, 4-$CH_3OC_6H_4$ 21–92%

eq 16

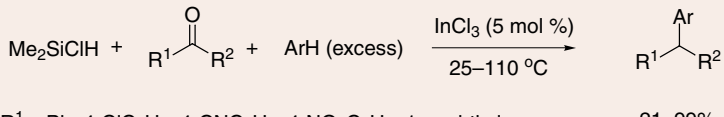


R^1 = H, Ph, 2-Py; R^2 = H, Ph, 4-ClC_6H_4, 4-$CH_3OC_6H_4$ 40–94%

eq 17



eq 18

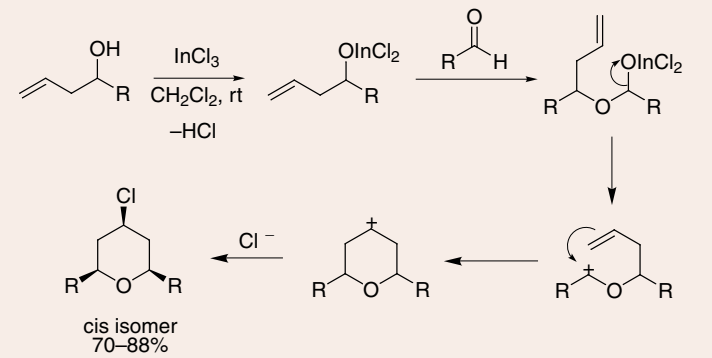


R^1 = Ph, 4-ClC_6H_4, 4-CNC_6H_4, 4-$NO_2C_6H_4$, 1-naphthyl, 2-naphthyl, -$(CH_2)_4$-, -$(CH_2)_5$-, Me, *n*-C_5H_{11}

R^2 = H, Me; Ar = Ph, *p*-tolyl, *p*-xylyl

21–99%

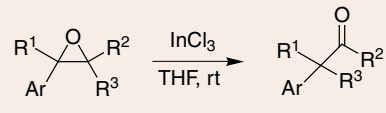
eq 19



cis isomer
70–88%

R = Ph, 4-$CH_3C_6H_4$, 3-$CH_3C_6H_4$, 2-$CH_3C_6H_4$, 4-ClC_6H_4, 4-FC_6H_4, 4-C_2H_5-C_6H_4, *n*-C_7H_{15}

eq 20

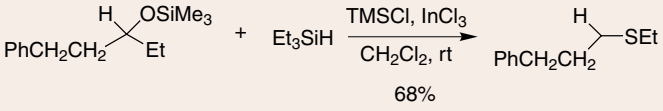


65–91%

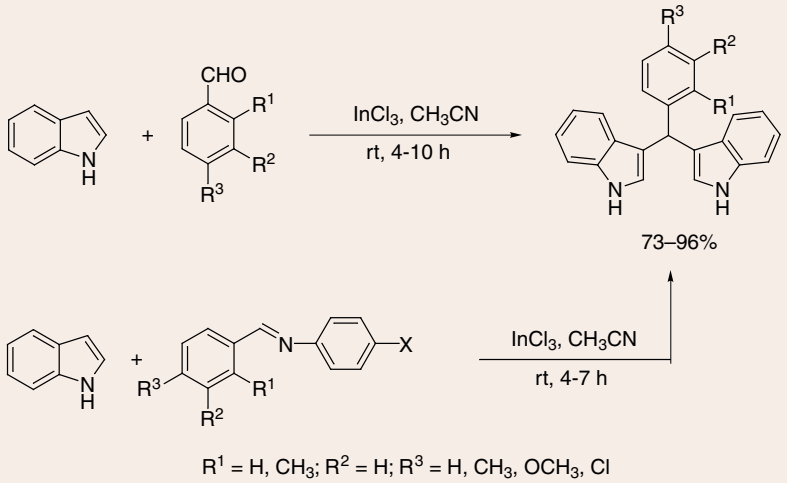
R^1, R^2, R^3 = H, alkyl, Ph

Ar = Ph, 4-$CH_3OC_6H_4$, 3,4-$(CH_3O)_2C_6H_3$, 2-naphthyl

eq 21



eq 22



Scheme 2

(27) Miyai, T.; Onishi, Y.; Baba, A. *Tetrahedron* **1999**, *55*, 1017.

(28) (a) Olah, G. A.; Krishnamurti, R.; Surya Prakash, G. K. In *Comprehensive Organic Synthesis*; Pergamon Press: Oxford, UK, 1991; Vol. 3, pp 293–335. (b) Price, C. C. *Org. React*. **1959**, *3*, 1.

(29) Yang, J.; Viswanathan, G.S.; Li, C.-J. *Tetrahedron Lett*. **1999**, *40*, 1627.

(30) (a) Wei, Z. Y.; Li, J. S.; Wang, D.; Chan, T. H. *Tetrahedron Lett*. **1987**, *28*, 3441. (b) Perron, F.; Albizati, K. F. *J. Org. Chem*. **1987**, *52*, 4128. (c) Wei, Z. Y.; Wang, D.; Li, J. S.; Chan, T. H. *J. Org. Chem*. **1989**, *54*, 5768. (d) Coppi, L.; Ricci, A.; Taddei, M. *J. Org. Chem*. **1988**, *53*, 911. (e) Rychnovsky, S. D.; Hu, Y.; Ellsworth, B. *Tetrahedron Lett*. **1998**, *39*, 7271.

(31) Ranu, B. C.; Jana, U. *J. Org. Chem*. **1998**, *63*, 8212.

(32) Mukaiyama, T.; Ohno, T.; Nishimura, T.; Han, J. S.; Kobayashi, S. *Bull. Chem. Soc. Jpn*. **1991**, *64*, 2524.

(33) Kovardakov, V. A.; Zolotukhin, M. G.; Salazkin, S. N.; Rafikov, S. R. *Deposited Doc*. **1983**, VINITI 5606-83, 77 pp; *Chem. Abstr*. **1985**, *102*, 149883x.

(34) Aleksandrov, Yu. A.; Semchikov, Yu. D.; Lelekov, V. E.; Mazanova, L. M.; Makin, G. I.; Sokolova, V. A. *Vysokomol. Soedin., Ser. B* **1985**, *27*, 683; *Chem. Abstr*. **1986**, *104*, 34373e.

(35) Aleksandrov, Yu. A.; Lelekov, V. E.; Makin, G. I.; Mazanova, L. M.; Semchikov, Yu. D.; Katkova, M. A. *Zh. Obshch. Khim*. **1987**, *57*, 1798; *Chem. Abstr*. **1987**, *107*, 176536w.

(36) Zolotukhin, M. G.; Sedova, E. A.; Sorokina, Yu. L.; Salazkin, S. N.; Sangalov, Yu. A.; Sultanova, V. S.; Panasenko, A. A.; Khalivov, L. M.; Muslukhov, R. M. *Makromol. Chem*. **1990**, *191*, 1477.

(37) Liaw, D. J.; Lin, C. L. *J. Polym. Sci., Part A: Polym. Chem*. **1993**, *31*, 3151.

(38) Zhun, V. I.; Tsvetkov, A. L.; Sukhikh, A. S.; Sheludyakov, V. D. *Zh. Obshch. Khim*. **1990**, *60*, 1104; *Chem. Abstr*. **1990**, *113*, 212074d.

(39) Czarny, Z.; Oszczudlowski, J. *React. Kinet. Catl. Lett*. **1984**, *25*, 195.

(40) Yasman, Yu. B.; Khudaiberdina, Z. I.; Sangalov, Yu. A.; Minsker, K. S.; Prokof'ev, K. V. *Khim. Tekhnol. Topl. Masel* **1984**, *30*; *Chem. Abstr*. **1984**, *101*, 210506z.

(41) Araki, S.; Jin, S.; Idou, Y.; Butsugan, Y. *Bull. Chem. Soc. Jpn*. **1992**, *65*, 1736.

(42) Babu, G.; Sridhar, N.; Perumal, P. T. *Synth. Commun*. **2000**, in press.

(43) Porszasz, J.; Gibiszer-Porszasz, K.; Foldeak, S.; Matkovics, B. *Experientia* **1965**, *21*, 93.

About the Authors

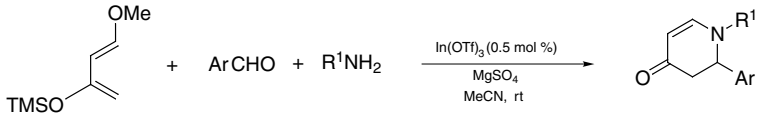
Dr. G. Babu received his M.Sc. degree in Chemistry from Loyola College, University of Madras, and, in August 1993, joined the organic chemistry laboratory of Dr. P.T. Perumal at the Central Leather Research Institute. He was awarded the Ph.D. degree in January 1999 by the University of Madras. His research work involved the synthesis of heterocyclic compounds through Diels–Alder reactions catalyzed by indium trichloride, and the microwave-accelerated synthesis of furfurylidene chalcones. Currently, he is working as a Postdoctral Fellow with Professor A. Wada, Kobe Pharmaceutical University, Japan, on the synthesis of retenoic acid analogs.

Dr. P. T. Perumal obtained his Ph.D. degree in 1981 from the Indian Institute of Science, Bangalore, under the guidance of Prof. M. V. Bhatt. He then worked as a Postdoctoral Research Associate with Prof. H. C. Brown at Purdue University until 1983. After returning to India, he worked briefly as a Scientist at the Indian Institute of Chemical Technology, Hyderabad, and later moved to the Central Leather Research Institute (CLRI), Chennai. He was a Visiting Scientist at the University of Miami in 1989–1990 and the University of Florida in 1990–1991. He has authored more than 60 publications and trained five Ph.D. students. Currently, he is working on natural biocides and the synthesis of heterocyclic compounds and peptidomimetic antimicrobial agents.

Lewis Acids in Organic Synthesis

The preceding review highlights the use of indium(III) chloride as a Lewis Acid. Other Lewis acids also facilitate organic reactions and can often be used in just catalytic amounts. The reactivity and selectivity vary, depending upon reaction conditions and the reagent chosen. Presented here are some examples of the applications in organic synthesis of the triflate (trifluoromethanesulfonate) salts of three popular Lewis acids. A selection of Aldrich products that are mentioned in the review is also included. For additional information, please call our Technical Services Department at **800-231-8327** (USA) or your local Sigma-Aldrich office. Larger quantities are available through Sigma-Aldrich Fine Chemicals. Please call **800-336-9719** (USA) or your local office for availability.

Indium

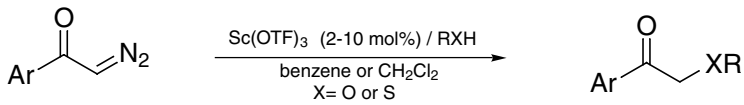


Indium triflate has several applications including catalysis of Friedel–Crafts alkylations[1] and acylations,[2] and is shown here to catalyze the hetero-Diels–Alder reaction. Frost[3] has prepared a series of aryl-substituted tetrahydropyridines, via the imines derived from aryl aldehydes, with a catalyst loading as low as 0.5 mol %.

(1) Miyai, T. et al. *Tetrahedron* **1999**, *55*, 1017. (2) Chauhan, K. K. et al. *Synlett* **1999**, 1743. (3) Ali, T. et al. *Tetrahedron Lett.* **1999**, *40*, 5621.

44,215-1 **Indium(III) trifluoromethanesulfonate** *(Indium triflate)*

Scandium

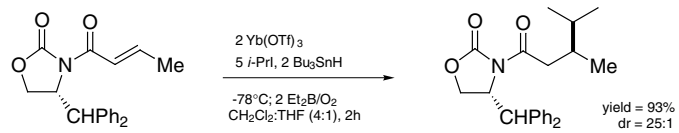


Scandium triflate catalyzes, among other reactions, the intermolecular carbene–heteroatom bond insertion in alcohols and thiols leading to the preparation of α-alkoxy, α-alkylthio, and α-phenylthio aryl ketones.

Pansare, S. V. et al. *Tetrahedron Lett.* **1999**, *40*, 5255. *For a brief review on this catalyst, see* Longbottom, D. *Synlett* **1999**, 2023.

41,821-8 **Scandium trifluoromethanesulfonate**, 99% *(Scandium triflate)*

Ytterbium



Lewis acid assisted diastereoselective free radical conjugate additions compete favorably with their ionic counterparts. In the reaction shown here, Sibi reports that ytterbium triflate gives a 25:1 diastereomeric ratio (dr) using 2 equiv of the Lewis acid and a 20:1 dr at 0.1 equiv. Also, moderate amounts of water seem to have little effect on the outcome of the reaction.

Sibi, M. P. et al. *J. Am. Chem. Soc.* **1999**, *121*, 7517.

43,059-5 **Ytterbium(III) trifluoromethanesulfonate**, 99.99% *(Ytterbium triflate)*

40,532-9 **Ytterbium(III) trifluoromethanesulfonate hydrate**

These products, mentioned in the review, as well as a complete selection of other Lewis acids are available from stock. To place your order, please call **800-558-9160** (USA), fax **800-962-9591** (USA), or visit our Web site at **www.sigma-aldrich.com**.

19,050-0 *tert*-**Butyldimethylsilyl chloride**, 99%
37,295-1 *tert*-**Butyldimethylsilyl chloride**, 1.0*M* solution in tetrahydrofuran
38,442-9 *tert*-**Butyldimethylsilyl chloride**, 1.0*M* solution in dichloromethane
44,612-2 **Butyldimethylsilyl chloride**, 98%
47,346-4 *tert*-**Butyldimethylsilyl chloride**, 50 wt. % solution in toluene
14,420-7 **Chlorodimethylsilane**, 98%
38,441-0 **Chlorotrimethylsilane**, 1.0*M* solution in tetrahydrofuran
38,652-9 **Chlorotrimethylsilane**, redistilled, 99+%
C7,285-4 **Chlorotrimethylsilane**, 98%
20,344-0 **Indium(III) chloride**, 99.999%
33,406-5 **Indium(III) chloride**, 98%
33,407-3 **Indium(III) chloride tetrahydrate**, 97%
42,941-4 **Indium(III) chloride**, anhydrous, powder, 99.999+%
22,654-8 **Silver perchlorate hydrate**, 99%
44,923-7 **Silver perchlorate**, 99.9%

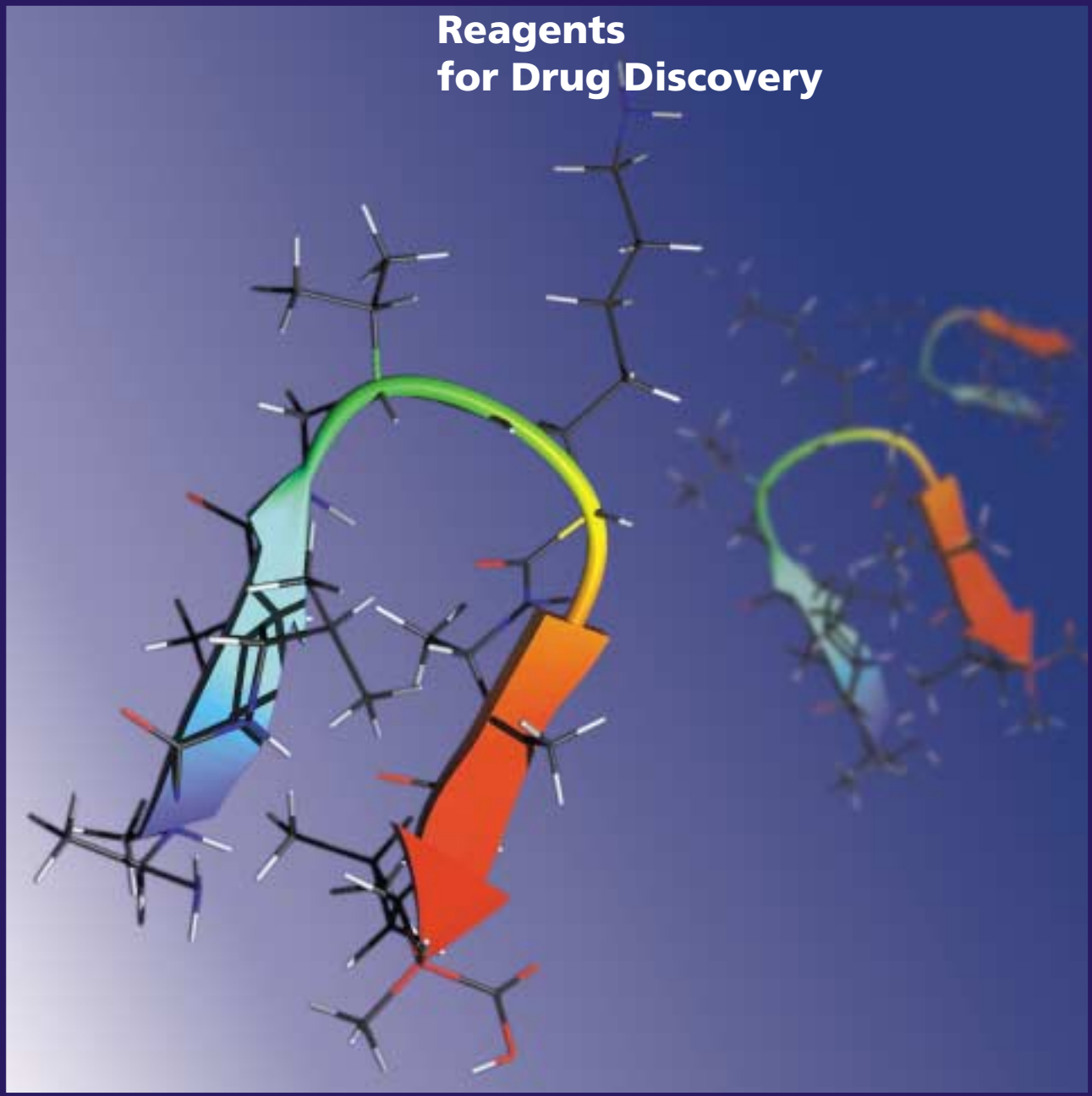
Request your new catalog TODAY!

Fluka

Chemika

Peptide and Peptidomimetic Synthesis

Reagents for Drug Discovery



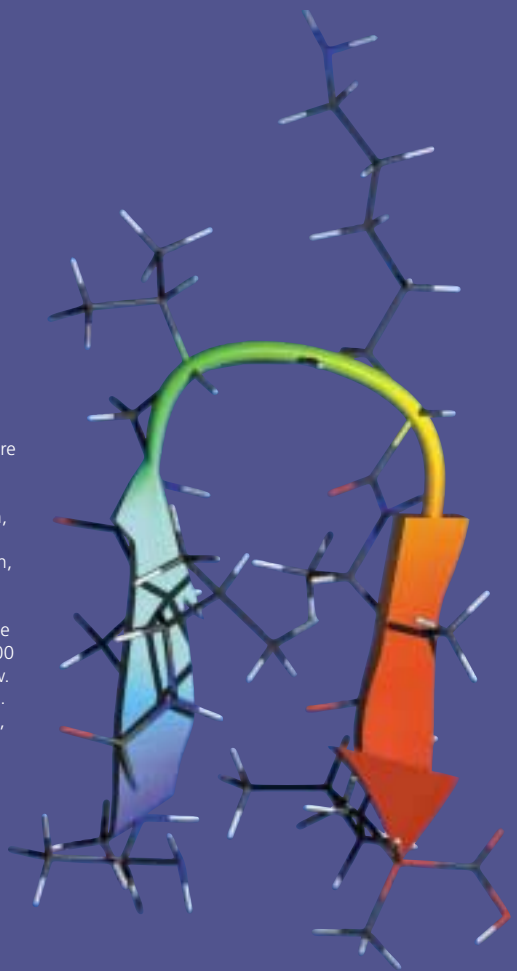
The Solution for Drug Discovery...

Peptide and Peptidomimetic Synthesis

One-Stop-Shopping at Fluka

- All basic reagents and auxiliaries for solution and solid phase synthesis
- Focus: largest selection of specialty amino acids for peptidomimetic synthesis
- Custom synthesis of building blocks

Discover our unique product range!



Hairpin structure of a ß-peptide determined by Dieter Seebach, Stefan Abele, Karl Gademann, Bernhard Jaun

Angew. Chemie 1999, 111, 1700 – 1703; Angew. Chemie Int. Ed. Engl. 1999, 38, 1595 – 1597

Fluka

Your Competent Partner for Peptide Synthesis

www.sigma-aldrich.com

Please tear out this page and fax it back to us at 1-800-200-1096 (USA) or 314-286-8345 to receive your FREE catalogs.

Yes, please send me the following free copies:

Fluka Peptide Synthesis Catalog (cju)	☐
Fluka/RdH Main Catalog (003)	☐

What are your areas of interest?

Peptides (pept)	☐
Peptide Synthesis Reagents (psyn)	☐
Peptides/Amino Acids (peam)	☐
Amino Acids Analysis (aaar)	☐
Amino Acids & Derivatives (aaad)	☐
Combinatorial Chemistry (coch)	☐
Drug Design (drug)	☐
Pharmaceutical Chemistry (phfo)	☐
Pharmaceutical R&D (phrd)	☐
Medicinal Chemistry (medc)	☐
Custom Peptide Synthesis (ppsy)	☐
Custom Peptide Antisera (ppan)	☐
Peptide HPLC Analysis (ppal)	☐

Please indicate full address

First Name

Second Name

Position

Organisation / Company

Department

Building

Street Address

Town

Postal Code

Country

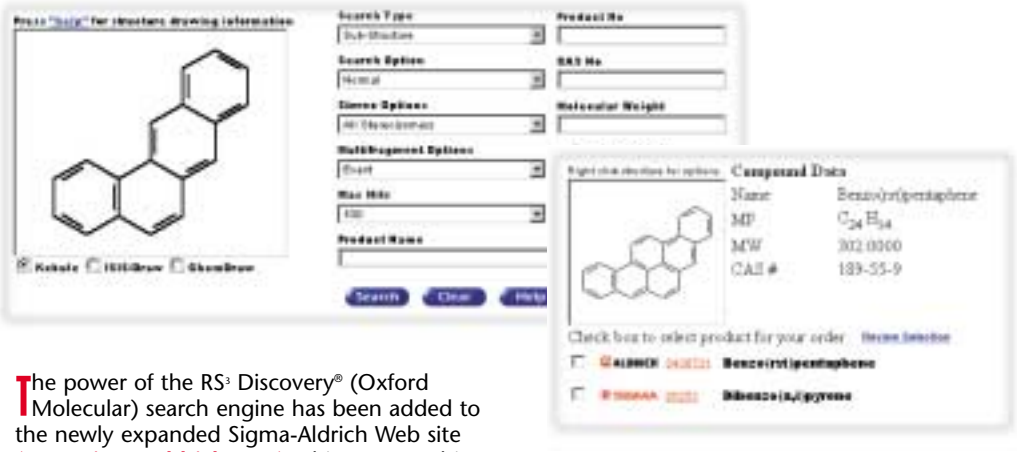
Phone No.

Fax No.

E-mail

Signature

Sigma-Aldrich Web Site Teamed with Oxford Molecular Software Revolutionizes On-line Structure Search and Procurement



The power of the RS³ Discovery® (Oxford Molecular) search engine has been added to the newly expanded Sigma-Aldrich Web site (www.sigma-aldrich.com). This new combination of unique software with one of the world's largest chemical databases (over 130,000 compounds) allows users to search, view, and order new compounds with unheard-of speed and efficiency.

Now you can customize queries in terms of a multitude of definitive search parameters including:

Search Types
Structure
Substructure
Similarity

Search Options
(options change based on search type selected above)
Normal
Tautomer
Salt
Tautomer Salt

Stereo Option
All Stereoisomers
Enantiomers/match unknown
Enantiomers
Exact/match unknown
Exact

Multifragmented Options
Any/Overlap Allowed
Any
Same/Overlap Allowed
Same
Different
Exact
(Note: help screens are available on-line to assist in the searching process.)

Similarity Options
Euclidean distance
Tanimoto coefficient
Fuzzy substructure

Searches can be further refined using CAS number or molecular weight. When selecting the molecular weight as a variable, the chemist has a choice of criteria. The system recognizes exact molecular weight, molecular weight ranges, and the use of logical operators such as ">" or "<". In addition, this new search engine interfaces with several of the most popularly used drawing tools including Kekulé™ (available free at the Sigma-Aldrich site, Oxford Molecular), ChemDraw™ (CambridgeSoft) or ISIS™/Draw (MDL Information Systems). A striking new feature is "hit-term" highlighting, where part of the user-drawn structure originally entered in the query is highlighted when search results are returned.

Once completed, the search will instantly yield all existing Sigma-Aldrich products that fall within the stated criteria. From there, on-line ordering is a snap with Sigma-Aldrich's PipeLine® e-commerce system, ranked as the best on-line chemical ordering site by a recent Chemical and Engineering News market position study.

What you need and what you need to know.
www.sigma-aldrich.com

"Sigma-Aldrich's product line is an essential resource for the research community. We believe that the addition of RS³ Discovery® greatly enhances the overall usability of the Sigma-Aldrich Web site and demonstrates Sigma-Aldrich's level of dedication to serving its customers."

Jeff Moore, Vice President of Cheminformatics for Oxford Molecular.

Purpald®: A Reagent That Turns Aldehydes Purple!

Harvey B. Hopps
Physical Sciences Department
Amarillo College
Amarillo, TX 79178-0001, USA
E-mail: hbhopps@actx.edu

Introduction

What was described as a new reagent for the qualitative detection of aldehydes has resulted in a host of methods for the quantitative determination of aldehydes. The story began when Dickinson and Jacobsen reported a new, sensitive, and specific test for the detection of aldehydes using 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (**1**).[1] Because its lengthy name did not give any indication of this important application, Aldrich offered this triazole under the trade name Purpald®, in order to highlight its utility in this respect.

While both aldehydes and ketones readily condense with **1**, only the aminal, **2a**, from an aldehyde can be oxidized to give the conjugated, purple-colored, bicyclic ring system, 6-mercapto-3-substituted-*s*-triazolo-[4,3-*b*]-*s*-tetrazine (**3**).

Qualitative Tests

Dickinson and Jacobsen's initial paper described a simple test that uses one drop of the aldehyde and about 150 mg of **1** in 2 mL of 1N NaOH. Aeration of the resulting solution produces an intense color within one minute. This test is both sensitive and specific for aldehydes. The reagent does not give purple condensation products with ketones, esters, amides, hydrazines, hydroxylamines, quinones, aminophenols, uric acid, or formic acid, which are known to interfere with the usual test reagents such as Fehling's solution, and Tollens' and Schiff's reagents. The test is sensitive to aldehydes at a concentration of 1 x 10^{-4} M. The authors examined the purple-colored solutions obtained from a variety of aldehydes and reported an absorption band in the visible region at 520–555 nm. Very hindered aldehydes may require longer reaction times. **Table 1** lists some representative aldehydes and reaction times necessary for color changes.[2]

Dickinson and Jacobsen mentioned in a footnote that acetic acid, known to contain 0.05% acetaldehyde, gave a positive test with **1**.[1] Recently, a student obtained a positive test with a sample of 95% 3-pentanone, which clearly indicated the presence of a low concentration of an aldehyde.[3] Therefore, care must be taken, if one is relying on the test, when dealing with samples of unknown purity. Other misleading results can be obtained when certain substances are oxidized to aldehydes under the test conditions. Durst and Gokel[4] reported that the use of ethylene glycol, known to be readily oxidized, as the solvent might give spurious results. They described the use of a phase-transfer catalyst to improve the test for lipophilic aldehydes, which have low solubilities in aqueous media. The oxidation of aminal **2** to **3** was also carried out using hydrogen peroxide[5] or periodate ion.[6,7] Rahn and Schlenk[8] observed a positive test from ozonides. Purpald® has been used to prepare filter paper test strips,[9] in TLC spray reagents,[8] and as a reagent for the post-column derivatization in high-pressure liquid chromatography.[5,10] The sensitivity limit of this reagent (a distinct purple solution is produced) is under 1 mg of Purpald® in 0.6 mL of dilute NaOH with 37% fomaldehyde solution.[3] At this level, the cost of Purpald® is less than that of the silver nitrate used in the Tollens' aldehyde test.

Quantitative Tests

Following their initial report, Jacobsen and Dickinson described the use of **1** in spectrophotometric quantitative assays of aldehydes.[11] They found that Beer's law was followed for 0.5–5 ppm formaldehyde within the limit of ± 3%. Also, the same ± 3% limit pertained to 5–20 ppm formaldehyde after suitable dilution. The colored product, **3**, from a group of aldehydes displayed a λ_{max} absorption between 532 and 549 nm. Nakano has described the detrimental effects of copper (II) and cobalt ions in the course of formaldehyde determinations.[12] The addition of EDTA markedly inhibited the interference of Cu(II) ion.

Applications

The spectrophotometric quantitative assays have led to a wide range of applications for Purpald®, including the detection of aldehydes in gases, liquids, and on solid surfaces. The detection of formaldehyde vapor has been extensively studied.[13-18] Quesenberry and Lee[6] described a rapid formaldehyde assay using Purpald® under periodation conditions, and attained the sensitivity level of as little as 1 nmol formaldehyde. Lambert et al.[16] described a solid reagent of Purpald®–acetone aminal on sodium bicarbonate, which responded to formaldehyde in the sub-ppm concentration range. Spreitzer and Jaeger[19] have reported a method for the determination of ppb amounts of formaldehyde in aqueous solution with Purpald®. Fujiwara et al.[20] reviewed the microscale determination of formaldehyde in vaccines with **1**. Mimura et al.[7] have compared the Purpald® method with the acetylacetone method for the detection of formaldehyde. The presence of formaldehyde on the surface of natural wood[21] and boards bonded with urea–formaldehyde resin[22] has been detected using Purpald®.

Other aldehydes that have been detected by using **1** include: aldehydes in disinfectant

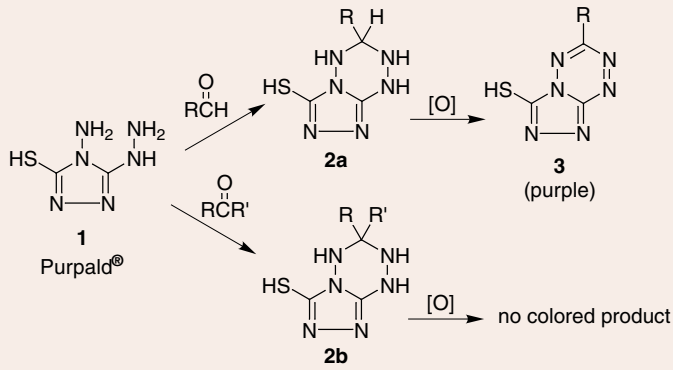


Table 1. Reactions of Representative Aldehydes with 1[2]

Aldehyde	Color	Time
5-Hydroxypentanal	purple	<30 sec
Crotonaldehyde	purple	—
trans-Cinnamaldehyde	purple	<5 min
α-Methylcinnamaldehyde	purple	<10 min
β-Phenylcinnamaldehyde	purple	—
Benzaldehyde	purple	<1 min
2-Nitrobenzaldehyde	purple-brown	<30 sec
4-Acetamidobenzaldehyde	purple-brown	<5 min
2-Chloro-6-nitrobenzaldehyde	purple	<5 min
10-Methylanthracene-9-carboxaldehyde	purple	very slow

solutions,[23] acetaldehyde on the surface of fruit,[24] semialdehydes,[25] invert sugars,[26,27] and lipid aldehydes.[8] A number of reports have also described analytical procedures, which utilize the formation of an aldehyde and its subsequent quantitative spectrophotometric measurement using Purpald®. For example, Sugano and co-workers[28] analyzed hydrogen peroxide in serum by adding methanol and the enzyme necessary to catalyze the peroxide oxidation of methanol to formaldehyde. Formaldehyde concentrations were then determined with Purpald®. Additional examples of substances analyzed in this way include: methanol,[29,30] sugars and glycols,[31] serum triglycerides,[32] diprophylline which contains a glycol moiety,[33] glafenine,[34] clindamycin,[35] uric acid,[36] and methylenebisthiocyanate.[37] Multistep processes, which ultimately produce an aldehyde, include the assay of acyl-CoA synthetase,[38] catalase activity in tissue,[39] and D-amino acid oxidase.[40]

Conclusion

This interesting reagent came to light shortly after it was mentioned for the qualitative detection of aldehydes in "Brownstein's Closet" section of *CHEMTECH*.[41] Naturally, it was prepared and offered by Aldrich. The anticipated use as a quantitative reagent has not been forthcoming; however, it has been widely employed as a quantitative spectrophotometric reagent. Recently, Brandl[42] has suggested that Purpald® will replace the Tollens' test for aldehydes in the student laboratory. Purpald® is both sensitive and specific for aldehydes. The test is fast and easy to perform, and avoids the potentially explosive silver salts associated with the Tollens' test. The toxicity of Purpald® has not been determined.

References

(1) Dickinson, R.G.; Jacobsen, N.W. *Chem. Commun*. **1970**, 1719.

(2) These tests were performed in the Aldrich Quality Control Laboratories.

(3) Hopps, H.B.; Stephens, R.L., Jr., Amarillo College, Amarillo, TX. Personal observation, 1999.

(4) Durst, H.D.; Gokel, G.W. *J. Chem. Ed*. **1978**, *55*, 206.

(5) Del Nozal, M.J.; Bernal, J.L.; Hernandez, V.; Toribio, L.; Mendez, R. *J. Liq. Chromatogr*. **1993**, *16*, 1105.

(6) Quesenberry, M.S.; Lee, Y.C. *Anal. Biochem*. **1996**, *234*, 50.

(7) Mimura, H.; Kaneko, M.; Nishiyama, N.; Fukui, S.; Kanno, S. *Eisei Kagaku* **1976**, *22*, 39; *Chem. Abstr*. **1976**, *85*, 71809m.

(8) Rahn, C.H.; Schlenk, H. *Lipids* **1973**, *8*, 612.

(9) Fischer, W.; Langkau, H. Ger. Offen. 2, 809, 475, 06 Sep 1979, 7 pp; *Chem. Abstr*. **1979**, *91*, 203901w.

(10) Kerr, T.M.; Mike, J.H. *J. Chromatogr., A*. **1998**, *813*, 213.

(11) Jacobsen, N.W.; Dickinson, R.G. *Anal. Chem*. **1974**, *46*, 298.

(12) Nakano, K. *Jpn. J. Toxicol. Environ. Health* **1995**, *41*, 381; *Chem. Abstr*. **1996**, *124*, 44376k.

(13) Kawachi, T.; Moriya, M.; Sato, Y. PCT Int. Appl. WO 98 30, 897, 16 Jul 1998, 32 pp; *Chem. Abstr*. **1998**, *129*, 126417s.

(14) Matsuhisa, K.; Ozeki, K. *Analyst (London)* **1986**, *111*, 1175.

(15) Lambert, J.L.; Chiang, Y.C. US. Patent 4, 511, 658, 16 Apr 1985, 3 pp; *Chem. Abstr*. **1985**, *103*, 10756k.

(16) Lambert, J.L.; Paukstelis, J.V.; Liaw, Y.L.; Chiang, Y.C. *Anal. Lett*. **1984**, *17*, 1987.

(17) Walker, R.F.; Guiver, R. *Am. Ind. Hyg. Assoc. J*. **1981**, *42*, 559.

(18) Izumikawa, M.; Asakono, K.; Ishiguro, S. *Kogai Kenkyusho Shiryo* **1977**, 99. *Chem. Abstr*. **1980**, *92*, 46522z.

(19) Spreitzer, H.; Jaeger, W. *Arch. Pharm*. **1990** *323*, 445.

(20) Fujiwara, M; Tomita, S.; Nishimura, T. *Nippon Saikingaku Zasshi* **1982**, *37*, 789.

(21) Kawamura, Y.; Funakoshi, K.; Sugita, T.; Yamada, T. *Shokuhin Eiseigaku Zasshi* **1995**, *36*, 731; *Chem. Abstr*. **1996**, *124*, 167700u.

(22) Harkin, J.M.; Obst, J.R.; Lehmann, W.F. *Forest Prod. J*. **1974**, *24*, 27.

(23) Zurek, G.; Karst, U. *Anal. Chim. Acta*. **1997**, *351*, 247.

(24) Agatsuma, M.; Ohshima, E. Fr. Demande 2, 513, 377, 25 Mar 1983, 20 pp; *Chem. Abstr*. **1983**, *99*, 18094n.

(25) Small, W.C.; Jones, M.E. *Anal. Biochem*. **1990**, *185*, 156.

(26) Reinefeld, E.; Emmerich, A.; Van Malland, H.; Miehe, D. *Zucker* **1976**, *29*, 657.

(27) Reinefeld, E.; Bliesener, K.M.; Van Malland, H.; Reichel, C. *Zucker* **1976**, *29*, 308.

(28) Sugano, T.; Sugiyama, M.; Nakagiri, Y.; Hayashi, Y.; Hirada, F. Jpn. Patent 77, 113, 292, 22 Sep 1977, 6 pp; *Chem. Abstr*. **1978**, *88*, 18676b.

(29) Fujimori, K.; Kitano, M.; Takenaka, N.; Bandow, H.; Maeda, Y. *Bunseki Kagaku* **1996**, *45*, 677; *Chem. Abstr*. **1996**, *125*, 103887y.

(30) Zhemchuzhin, S.G.; Kholodkova, L.G. U.S.S.R. Patent SU 1, 286, 969, 30 Jan 1987; *Chem. Abstr*. **1987**, *107*, 12164x.

(31) Avigad, G. *Anal. Biochem*. **1983**, *134*, 499.

(32) Fujiwara, M.; Tomita, S.; Tago, K.; Fukutake, K.; Nishimura, T. *Rinsho Byori* **1981**, *29*, 1151; *Chem. Abstr*. **1982**, *96*, 65147e.

(33) Abu-Shady, H.A.; Hassib, S.T.; Youssef, N.F. *Egypt. J. Pharm. Sci*. **1987**, *28*, 223.

(34) Hassib, S.T.; Romeih, F.A.; El-Sayed, N.M.; El-Zaher, A.A. *Bull. Fac. Pharm*. **1993**, *31*, 375.

(35) Mabrouk, M.M. *Al-Azhar J. Pharm. Sci*. **1997**, *19*, 121.

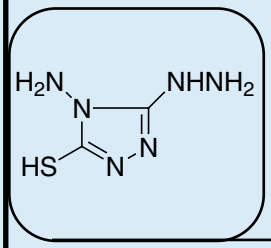
(36) Watanabe, T.; Suga, T. *Chem. Pharm. Bull.* **1978**, *26*, 1945.
(37) Hill, M.W.; Sharman, D.F. Int. Patent WO 91 15, 761, 17 Oct 1991, 15 pp; *Chem. Abstr.* **1992**, *116*, 50580y.
(38) Ichihara, K.; Shibasaki, Y. *J. Lipid Res.* **1991**, *32*, 1709.
(39) Johansson, L.H.; Borg, L.A.H. *Anal. Biochem.* **1988**, *174*, 331.
(40) Watanabe, T.; Motomura, Y.; Suga, T. *Anal. Biochem.* **1978**, *86*, 310.
(41) Brownstein, A. *CHEMTECH* **1971**, *1*, 134.
(42) Brandl, H. *Prax. Naturwiss., Chem.* **1991**, *40*, 25.

About the Author

Harvey B. Hopps received a B.A. degree from Occidental College in 1956, an M.S. degree from the University of Arizona in 1958, and a Ph.D. degree from Purdue University in 1962. After spending one year as postdoctoral scientist at New York University with Professor Kurt Mislow, he joined Aldrich as a group leader in research. He became Technical Services Manager in 1969, and Aldrich–Boranes Manager in 1972. He moved to Fumico, Inc. in 1981, and served as Head of Chemistry until he joined Amarillo College in 1996 as Instructor in the Physical Sciences Department, where he teaches organic and general chemistry. His interests include the local helium industry, fishing, and teaching fly-tying.

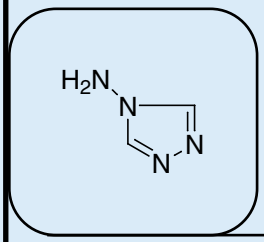
AMINOTRIAZOLES

Purpald®, an aminotriazole, was discussed in the previous article as a valuable agent for the colorimetric analysis of aldehydes. This product and other aminotriazoles also find utility in organic synthesis, especially for pharmaceuticals. See below for a few examples, and don't hesitate to call our Technical Services Department at **800-231-8327** (USA) or your local Sigma-Aldrich office for more information or to suggest new products. Larger quantities are available through Sigma-Aldrich Fine Chemicals. Please call **800-336-9719** (USA) or your local office for availability.



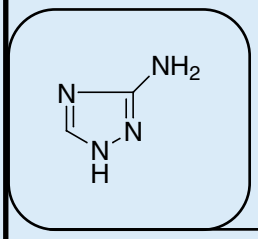
Purpald® continues to be useful as a complexation reagent for the spectrophotometric determination of aldehydes, e.g., in drug concentration analyses and in determining airborne formaldehyde. It was also used to prepare a series of antimicrobials.[1]

16,289-2 **Purpald®**, 99+% *(4-Amino-3-hydrazino-5-mercapto-1,2,4-triazole)*



This 4-aminotriazole was used in a study of anti-inflammatory COX-2 inhibitors[2] and in the preparation of fluconazole,[3] an antifungal.

A8,180-3 **4-Amino-1,2,4-triazole**, 99%



Several patents describe the use of 3-aminotriazole in the preparation of fungicides and herbicides. It was also used in the structure-activity analysis of angiotensin II receptor antagonists.[4]

A8,160-9 **3-Amino-1,2,4-triazole,** 95%

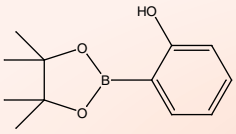
OTHER AMINOTRIAZOLE LISTINGS:

14,026-0 **3-Amino-5-mercapto-1,2,4-triazole**, 95%
19,068-3 **3-Amino-5-methylthio-1*H*-1,2,4-triazole**, 98%
28,207-3 **3-Amino-1,2,4-triazole-5-carboxylic acid hydrate**, 98%
34,152-5 **4-Amino-3,5-di-2-pyridyl-4*H*-1,2,4-triazole**, 97%
43,854-5 **4-Amino-5-(4-pyridyl)-4*H*-1,2,4-triazole-3-thiol**, 97%
43,855-3 **4-Amino-5-phenyl-4*H*-1,2,4-triazole-3-thiol**, 97%
D2,620-2 **3,5-Diamino-1,2,4-triazole**, 98%

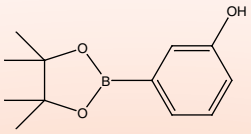
References:
(1) Dogan, H. N. et al. *Farmaco* **1998**, *52*, 565. (2) Song, Y. et al. *J. Med. Chem.* **1999**, *42*, 1151. (3) Narayanan, A. et al. *J. Heterocycl. Chem.* **1993**, *30*, 1405. (4) Shiota, T. et al. *Chem. Pharm. Bull.* **1999**, *47*, 928.

ARYLBORONIC ACID-PINACOL ESTERS

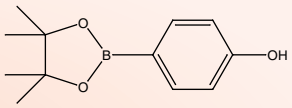
The synthesis of biaryl compounds via the Suzuki coupling reaction has become more commonplace now that many arylboronic acids are readily available. Several years ago, Miyaura demonstrated the utility of cyclic pinacol esters of arylboronic acids in Suzuki coupling reactions.[1,2] Aldrich offers the following arylboronic acid-pinacol esters[3] as part of a growing line of products used in the Suzuki coupling reaction and other synthetic and combinatorial methodologies. For a complete listing of Aldrich products, please request your **FREE** copy of the *2000–2001 Aldrich Handbook of Fine Chemicals and Laboratory Equipment* at **800-231-8327** (USA) or your local Sigma-Aldrich office, or visit us on the Web at **www.sigma-aldrich.com**.



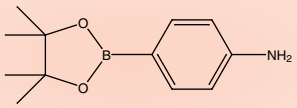
52,255-4



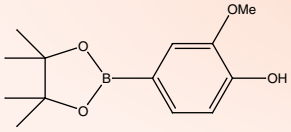
52,256-2



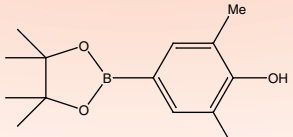
52,257-0



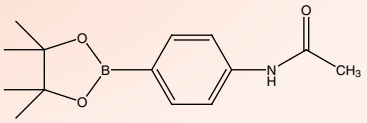
51,875-1



51,878-6



51,879-4



51,877-8

52,255-4 **2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol**
(2-Hydroxyphenylboronic acid, pinacol cyclic ester)

52,256-2 **3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol**
(3-Hydroxyphenylboronic acid, pinacol cyclic ester)

52,257-0 **4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol**, 97%
(4-Hydroxyphenylboronic acid, pinacol cyclic ester)

51,875-1 **4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)aniline**, 97%
4-Aminophenylboronic acid, pinacol cyclic ester)

51,878-6 **2-Methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol**, 98%
(4-Hydroxy-3-methoxyphenylboronic acid, pinacol cyclic ester)

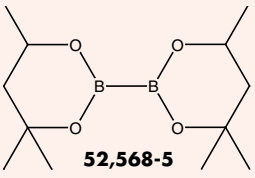
51,879-4 **2,6-Dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol**, 97%
(4-Hydroxy-3,5-dimethylphenylboronic acid, pinacol cyclic ester)

51,877-8 **4′-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)acetanilide**, 97%
(4-Acetamidophenylboronic acid, pinacol cyclic ester)

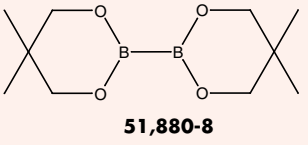
DIBORON ESTERS

NEW!

Aldrich is pleased to offer two new diboron esters to help develop the chemistry surrounding the Suzuki coupling reaction.[3] These new diboron esters exhibit different solubility and reactivity characteristics than the analogous bis(pinacolato)diboron and bis(catecholato)diboron, also available from Aldrich.



52,568-5



51,880-8

52,568-5 **Bis(hexylene glycolato)diboron**, 96%
51,880-8 **Bis(neopentyl glycolato)diboron**, 97%

Also Available:

47,328-6 **Bis(catecholato)diboron**, 97%
47,329-4 **Bis(pinacolato)diboron**, 98%

References: (1) Ishiyama, T. et al. *Tetrahedron Lett.* **1997**, *38*, 3447. (2) Ishiyama, T. et al. *J. Org. Chem.* **1995**, *60*, 7508. (3) Patents pending, including WO/98/45265.

DEPENDABLE IN DISCOVERY… DEDICATED THROUGH COMMERCIALIZATION.

DEVELOPMENT AND cGMP CUSTOM MANUFACTURING FOR YOUR DISCOVERY PROJECT

www.sigma-aldrich.com/safc

- Air-sensitive reactions under nitrogen or argon atmospheres
- Friedel-Crafts reactions
- Grignard reactions
- High-pressure reactions
- Hydrogenation
- Low-temperature reactions to −110 °C
- Ozonolysis
- Phosgenation

Let Sigma-Aldrich development chemists take your discovery chemistry and devise commercially scaleable methods for manufacturing. We routinely develop and produce small-molecule organics under cGMP conditions in our kilo labs, pilot plants and commercial production facilities. Production volumes range from micrograms to multi-tons.

Sigma-Aldrich Fine Chemicals offers the pharmaceutical and industrial markets the most comprehensive range of complex, multi-step organic synthesis processes available.

Contact us. Discover how quickly we can help you bring your project to market.

SIGMA-ALDRICH
FINE CHEMICALS

1-800-325-3010

From the Aldrich Bookshelf

Tartaric and Malic Acids in Synthesis: A Source Book of Building Blocks, Ligands, Auxiliaries, and Resolving Agents

J. Gawronski and K. Gawronska, John Wiley & Sons, New York, NY, 1999, 591pp. Hardcover. Provides chemists with a concise, yet comprehensive, review of the chemical properties and synthetic applications of derivatives of tartaric and malic acids. Includes hundreds of reaction schemes and figures, more than 70 tables of data and references for 2,000 compounds, and over 2,500 references to primary, secondary, and patent literature sources.

Z42,244-4

Enantiocontrolled Synthesis of Fluoro-Organic Compounds: Stereochemical Challenges and Biomedical Targets

V. A. Soloshonok, Ed., John Wiley & Sons, Chichester, England, 1999, 690pp. Hardcover. Selective insertion of fluorine substituents in strategic positions of bioactive molecules is a powerful and versatile tool for the design of new drugs, diagnostic agents, agrochemicals, and biomedical probes. This is the first book to give a comprehensive overview of the preparative methods for enantiocontrolled synthesis of fluorine-containing compounds of biomedical importance.

Z42,243-6

Conducting Polymers, Fundamentals and Applications: A Practical Approach

P. Chandrasekhar, Kluwer Academic Publishers, Boston, MA, 1999, 760pp. Hardcover. Deals with the practical fundamentals and applications of conducting polymers. This book may be used as a basis for further work, as a reference, or as a text supplementing advanced undergraduate- or graduate-level courses.

Z42,253-3

Sax's Dangerous Properties of Industrial Materials

10th ed., R. J. Lewis, Sr., John Wiley & Sons, New York, NY, 1999, 4,000pp. Hardcover. Three-volume set outlines the hazards of more than 23,500 industrial and laboratory chemicals. Individual listings include DPIM number, physical properties, synonyms, CAS No., toxicity data, DOT hazard code, hazard rating, OSHA, ACGIH, and MAK exposure limits, as well as NIOSH REL limits, DOT classification, and safety profiles, including both carcinogenic and reproductive effects data.

3-volume set
Z42,239-8

Concise Polymeric Materials Encyclopedia

J. C. Salamone, CRC Press, Boca Raton, FL, 1998, 1760pp. Hardcover. Contains more than 1,100 articles providing a synopsis of the topics described. Featuring contributions from more than 1,800 scientists from all over the world, the book discusses a vast array of subjects related to the synthesis, properties, and applications of polymeric materials, development of modern catalysts in preparing new or modified polymers, modification of existing polymers by chemical and physical processes, and biologically oriented polymers.

Z42,237-1

The Combinatorial Index

B. A. Bunin, Academic Press, New York, NY, 1998, 322pp. Hardcover. This compendium of methods from the primary literature provides quick and convenient access to reliable synthetic transformations as well as information on linkers and analytical methods. Each synthetic procedure is preceded by a section entitled "Points of Interest", which highlights the strengths and weaknesses of the various studies. The index covers the use of solution-based synthesis for the generation of molecular diversity, and includes a structural appendix showing functional group transformations.

Z42,250-9

Lewis Acid Reagents: A Practical Approach

H. Yamamoto, Ed., Oxford University Press, New York, NY, 1999, 288pp. Hardcover. A laboratory manual providing step-by-step protocols for using Lewis acid reagents to catalyze organic synthesis processes. Discusses a variety of new selective organic syntheses that are now available using modified/designed reagents.

Z42,248-7

Combinatorial Chemistry

N.K. Terrett, Oxford University Press, New York, NY, 1998, 200pp. Softbound. Provides a concise and comprehensive overview of combinatorial techniques for academic and industrial researchers and students. Includes extensive reference sections for further reading.

Z41,256-2

Asymmetric Fluoroorganic Chemistry: Synthesis, Applications, and Future Directions

P. V. Ramachandran, Oxford University Press, New York, NY, 1999, 320pp. Hardcover. This book collects current work on the synthesis of fluoroorganic compounds beginning with a review of fluorine-containing chiral compounds of biomedical interest. Subsequent chapters address reagent- and substrate-controlled asymmetric synthesis, the synthesis of fluorine-containing target molecules, bio-organic synthesis, and asymmetric fluoroorganic compounds in materials chemistry and agrochemistry.

Z42,249-5

Reagent Chemicals

9th ed., American Chemical Society, Washington, DC, 1999, 768pp. Hardcover. Provides test procedures and other valuable information required to ensure that chemicals meet the latest ACS reagent specifications.

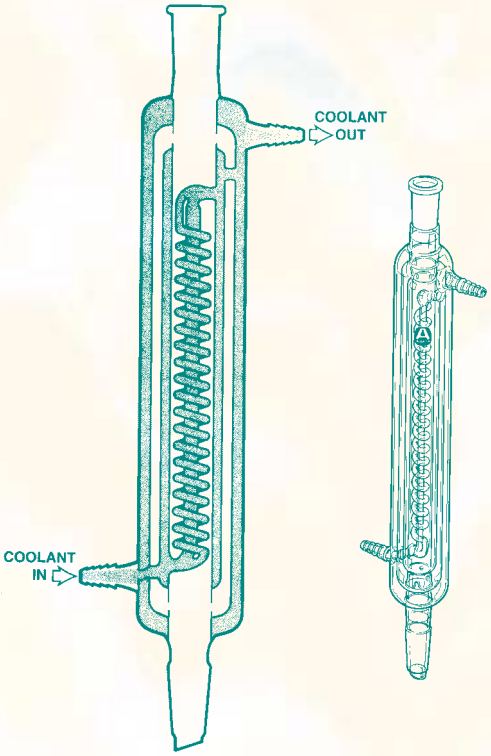
Z42,183-9

Scientific Glassware

Tested and Used in Aldrich Production Labs

ALDRICH TRIPLE-JACKET COIL CONDENSER

"Excellent for Lower-Boiling Solvents"



Cross-section of cooling surface area

Features:

- ✗ Triple jacketing provides maximum cooling surface area (1,230 cm^2)
- ✗ Does not flood as readily during reflux surges
- ✗ Minimizes loss of volatile components
- ✗ Highly efficient while extremely compact

H (mm)	Joint	Cat. No.
300	24/40	**Z42,227-4**

Tested and Used in Aldrich Production Labs

ALDRICH KOH & COLD TRAP SYSTEMS

"Efficient Removal of Solvent and Water Vapors"

Use Aldrich KOH and cold traps in tandem to eliminate solvent and water vapors, which can damage expensive vacuum pumps. Traps have a 50mm O-ring joint with pinch clamp.

Size	H (mm)	Trap i.d. (mm)	Cat. No.
KOH Traps			
Standard	450	50	**Z42,231-2**
Large	610	90	**Z42,232-0**
Cold Traps			
500mL bulb	460	50	**Z10,690-9**
1000mL bulb	475	50	**Z28,452-1**
Pyrex® glass wool			**Z25,589-0**
Potassium hydroxide, pellets, 85+% A.C.S. reagent			**22,147-3**

Pyrex is a registered trademark of Corning, Inc.

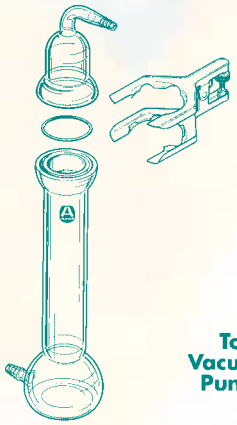
Features:

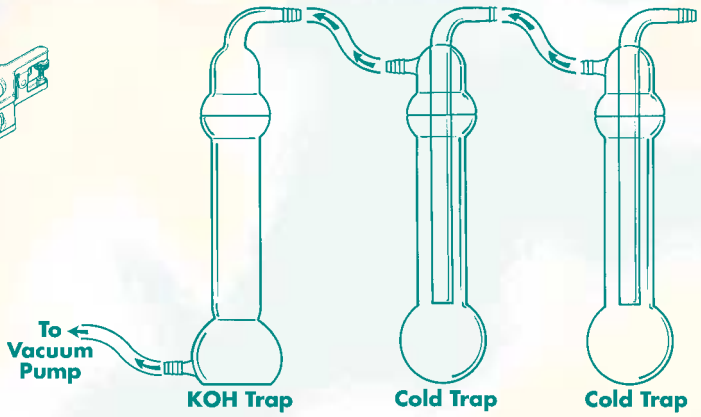
KOH traps

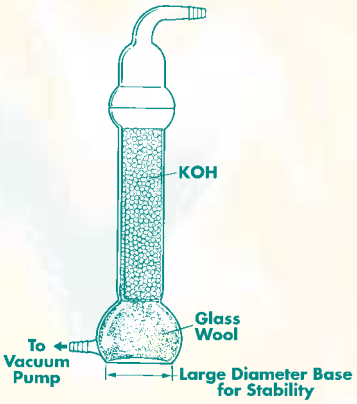
- ✗ Effective with multiple cold traps
- ✗ Flat-bottom design for maximum stability
- ✗ Glass wool chamber prevents KOH from entering pump

Cold traps

- ✗ Large capacity
- ✗ Removable cold finger







MODIFY ANY CATALOG ITEM TO MEET YOUR SPECIFIC NEEDS

LET THE ALDRICH GLASS SHOP HELP YOU WITH YOUR CUSTOM GLASSWARE: CONTACT US AT ALDGLASS@SIAL.COM

Sigma-Aldrich Worldwide Locations

Argentina
Sigma-Aldrich de Argentina, S.A.
Av. Pueyrredon 2446 Piso 5 "B"
C.P. C1119ACU C.A. de Buenos Aires
Argentina
Tel: (54-11) 4807-0321
Fax: (54-11) 4807-0346
E-mail: cservice@sigma-aldrich.com.ar

Australia
Sigma-Aldrich Pty., Limited
P.O. Box 970
Castle Hill, N.S.W. 1765
Free Tel: 1-800-800-097
Free Fax: 1-800-800-096
Tel: 61-2-9841-0555
Fax: 61-2-9841-0500
E-mail: ausmail@sial.com

Austria
Sigma-Aldrich Handels GmbH
Hebbelplatz 7
1100 Wien
Tel: 43 1 605 8110
Fax: 43 1 605 8120
E-mail: sigma@sigma.co.at

Belgium
Sigma-Aldrich nv/sa
K.Cardijnplein 8
B-2880 Bornem
Free Tel: 0800-147.47
Free Fax: 0800-147.45
Tel: 03 899.13.01
Fax: 03 899.13.11
E-mail: becustsv@eurnotes.sial.com

Brazil
Sigma-Aldrich Química Brasil Ltda.
Rua Sabará, 566- Cj. 53
01239-010 São Paulo, SP
Tel: 55-11-231-1866
Fax: 55-11-257-9079
E-mail: sigmabr@ibm.net

Canada
Sigma-Aldrich Canada Ltd.
2149 Winston Park Drive
Oakville, Ontario L6H 6J8
Free Tel: 800-565-1400
Free Fax: 800-265-3858
Tel: 905-829-9500
Fax: 905-829-9292
E-mail: canada@sial.com

Czech Republic
Sigma-Aldrich s.r.o.
Pobřežní 46
186 00 Praha 8
Tel: 00-420-2-2176 1300
Fax: 00-420-2-2176 3300
E-mail:
CZECustSV@eurnotes.sial.com

Denmark
Sigma-Aldrich Denmark A/S
Vejlegaardsvej 65 B
2665 Vallensbaek Strand
Tel: +45 43 56 59 10
Fax: +45 43 56 59 05
E-mail: denorder@eurnotes.sial.com

Eire
Sigma-Aldrich Ireland Ltd.
Airton Road
Tallaght
Dublin 24
Free Tel: 1 800 200 888
Free Fax: 1 800 600 222
Tel: 01 404 1900
Fax: 01 404 1910
E-mail: EICustsv@eurnotes.sial.com

Finland
Sigma-Aldrich Finland
YA-Kemia Oy
Teerisuonkuja 4
00700 Helsinki
Tel: (09) 350-9250
Fax: (09) 350-92555
E-mail: finorder@eurnotes.sial.com

France
Sigma-Aldrich Chimie S.a.r.l
L'Isle D'Abeau Chesnes
B.P. 701
38297 St.Quentin Fallavier
Cedex
Tel Numero Vert: 0800 21 14 08
Fax Numero Vert: 0800 03 10 52
E-mail: fradvsv@eurnotes.sial.com

Germany
(also SE Europe, the Baltics, Africa and the Middle East)
Sigma-Aldrich Chemie GmbH
Eschenstr. 5
82024 Taufkirchen
Freecall Tel: 0800-5155 000
Freecall Fax: 0800-6490 000
Tel: +49(0)89-6513-0
Fax: +49(0)89-6513-1169
Export Department:
Tel: +49(0)89-6513-1807
Fax: +49(0)89-6513-1877
E-mail: DeOrders@eurnotes.sial.com

Greece
Sigma-Aldrich (o.m) Ltd.
72 Argonafton Str.
16346 Ilioupoli, Athens
Tel: 30-1-9948010
Fax: 30-1-9943831
E-mail: GRCustSV@eurnotes.sial.com

Hungary
Sigma-Aldrich Kft
1399 Budapest
Pf. 701/400
Magyarország
Tel ingyenes: 06-80-355-355
Fax ingyenes: 06-80-344-344
Tel: 06-1-235-9055
Fax: 06-1-235-9050
E-mail: info@sigma.sial.hu

India
Sigma-Aldrich Corporation
Bangalore location:
Survey No. 31/1, Sitharamapalaya
Mahadevapura P.O.,
Bangalore 560048
Phone: 91 80 852 4222
Fax: 91 80 852 4214

New Delhi location:
Flat No. 4082, Sector B 5/6
Vasant Kunj, New Delhi 110070
Phone: (011) 689 9826
Fax: (011) 689 9827
E-mail: sigma@del2.vsnl.net.in

Israel
Sigma-Aldrich Israel Ltd.
Park Rabin, Rehovot 76100
Toll Free Tel: 1-800-70-2222
Tel: 972-8-948-4222
Fax: 972-8-948-4200
E-mail: sigisr@sigma.co.il

Italy
Sigma-Aldrich S.r.l.
Via Gallarate 154
20151 Milano
Numero Verde: 800-827018
Tel: 02-33417.310
Fax: 02-38010.737
E-mail: itorder@eurnotes.sial.com

Japan
Sigma-Aldrich Japan K.K.
Higashi Nihonbashi Sky Bldg.
1-1-7 Higashi Nihonbashi, Chuo-ku
Tokyo 103-0012
Tel: 81-3-5821-3111
Fax: 81-3-5821-3170

Korea
Sigma-Aldrich Korea
Samhan Camus Annex, 10th Floor
17-26 Yoido-dong, Yungdeungpo-ku
Seoul, South Korea
Toll Free Tel: 080-023-7111
Toll Free Fax: 080-023-8111
Tel: 82-2-783-5211
Fax: 82-2-783-5011
E-mail: order@sial.co.kr

Malaysia
Sigma-Aldrich (M) Sdn Bhd
60, 60-1 Jalan Awan Jawa
Taman Yarl
Off Jalan Kelang Lama
58200 Kuala Lumpur
Malaysia
Tel: 03-7824181
Fax: 03-7824067
E-mail: sigalm@po.jaring.my

Mexico
Sigma-Aldrich Química, S.A. de C.V.
Calle 6 Norte No. 107
Parque Industrial Toluca 2000
50200 Toluca, México
Teléfono sin costo: 01-800-007-5300
Teléfono en Toluca: (72)-76-1600
Fax sin costo: 01-800-712-9920
Fax en Toluca: (72)-76-1601
E-mail: mexico@sial.com

Netherlands
Sigma-Aldrich Chemie BV
Stationsplein 4 E
Postbus 27
NL-3330 AA Zwijndrecht
Tel Gratis: 0800 022 9088
Fax Gratis: 0800 022 9089
Tel: 078-620 54 11
Fax: 078-620 54 21
E-mail: nlcustsv@eurnotes.sial.com

Norway
Sigma-Aldrich Norway AS
Tevlingveien 23
1081 Oslo, Norway
Tel: 47 2317 6000
Fax: 47 2317 6010
E-mail: nororder@sial.com

Poland
Sigma-Aldrich Sp. z o.o.
Szelągowska 30
61-626 Poznań
Tel: (48-61) 823-24-81
Fax: (48-61) 823-27-81
E-mail: plcustsv@eurnotes.sial.com

Portugal
Sigma-Aldrich Quimica S.A.
(Sucursal em Portugal)
Aptdo. 131
2710 Sintra
Free Tel: 0800-202180
Free Fax: 0800-202178
E-mail, encomendas:
poorders@eurnotes.sial.com

Russia
Sigma-Aldrich Russia
TechCare Systems, Inc.
Makarenko Str. 2/21 Bldg. 1 Flat 22
Moscow 103062
Tel: 7-095-975-3321
Fax: 7-095-975-4792
E-mail: techcare@online.ru

Singapore
Sigma-Aldrich Pte., Ltd.
102E Pasir Panjang Road
#08-01, Citilink Warehouse
Singapore, 118529
Tel: (65) 271 1089
Fax: (65) 271 1571
E-mail: sapl@sialsea.com

South Africa
Sigma-Aldrich South Africa (Pty) Ltd.
Southern Life Industrial Park
Unit 16 & 17
CNR Kelly & Ackerman Streets
Jet Park, Boksburg 1459
Tel: (011) 397 8886
Fax: (011) 397 8859
E-mail: sigald@icon.co.za

Spain
Sigma-Aldrich Química S.A.
Aptdo. 161
28100 Alcobendas (Madrid)
Free Tel: 900-101376
Free Fax: 900-102028
Tel: 91-6619977
Fax: 91-6619642
E-mail, pedidos:
esorders@eurnotes.sial.com

Sweden
Sigma-Aldrich Sweden AB
Solkraftsvagen 14C
135 70 Stockholm
Tel (in Sweden only): 020-35 05 10
Fax (in Sweden only): 020-35 25 22
Outside Sweden Tel: 46-8-742 4200
Outside Sweden Fax: 46-8-742 4243
E-mail: sweorder@eurnotes.sial.com

Switzerland
Fluka Chemie GmbH
Postfach 260
CH-9471 Buchs
Tel: 081-755 27 23
Fax: 081-755 28 40
Swiss Free Call: 0800 80 00 80
E-mail: Fluka@sial.com

United Kingdom
Sigma-Aldrich Company Ltd.
The Old Brickyard
New Road
Gillingham
Dorset
SP8 4XT
Free Tel: 0800 717181
Free Fax: 0800 378785
Tel: (01747) 822211
Fax: (01747) 823779
E-mail: ukcustsv@eurnotes.sial.com

United States
Aldrich Chemical Company, Inc.
1001 West Saint Paul Avenue
Milwaukee, Wisconsin 53233
Toll Free Tel: 1-800-558-9160
Toll Free Fax: 1-800-962-9591
Tel: 414-273-3850
Fax: 414-273-4979
E-mail: aldrich@sial.com

Sigma Chemical Company
3050 Spruce Street
St. Louis, Missouri 63103
Toll Free Tel: 1-800-521-8956
Toll Free Fax: 1-800-325-5052
Tel: 314-771-5765
Fax: 314-771-5757
E-mail: sigma@sial.com

High-Hazard Chemicals

Such as Chlorosulfonic Acid, Epichlorohydrin, Allyl Chloride, and more...

Handled Safely and Conveniently

18 to 850L Returnable Containers

MINI·BULK™

MINIBULK is a trademark of Sigma-Aldrich Co.

For details, call **1-800-213-1206** (USA) or visit our Web site at **www.sigma-aldrich.com**

ALDRICH CHEMICAL COMPANY, INC.
P.O. BOX 355
MILWAUKEE, WISCONSIN 53201 USA

ALDRICH®

CHANGE SERVICE REQUESTED

F