Chemistry lab safety information resources for academic user

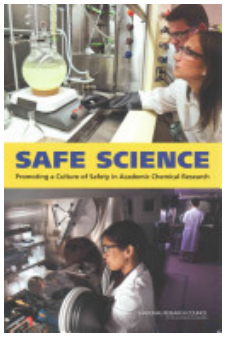
Grace Baysinger (graceb@stanford.edu)

Chemistry & Chemical Engineering Librarian, Stanford University

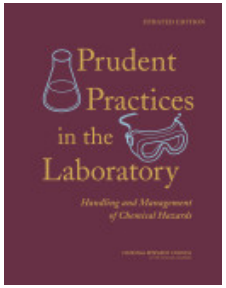
Current Topics in Chemical Safety Information (CHAS)

Boston, MA, 18 June 2015

Start Here



Safe Science: Promoting a Culture of Safety In Academic Chemical Research. Washington, D.C. : National Academies Press, [2014]
http://www.nap.edu/catalog.php?record_id=18706



Prudent Practices In the Laboratory: Handling and Management of Chemical Hazards. Updated version. Washington, D.C.: National Academies Press, 2011. http://books.nap.edu/catalog.php?record_id=12654

Outline of Topics

- Chemical Safety Data
- Reactivity, Reactions, and Protocols

Chemical Safety Data

Looking for data

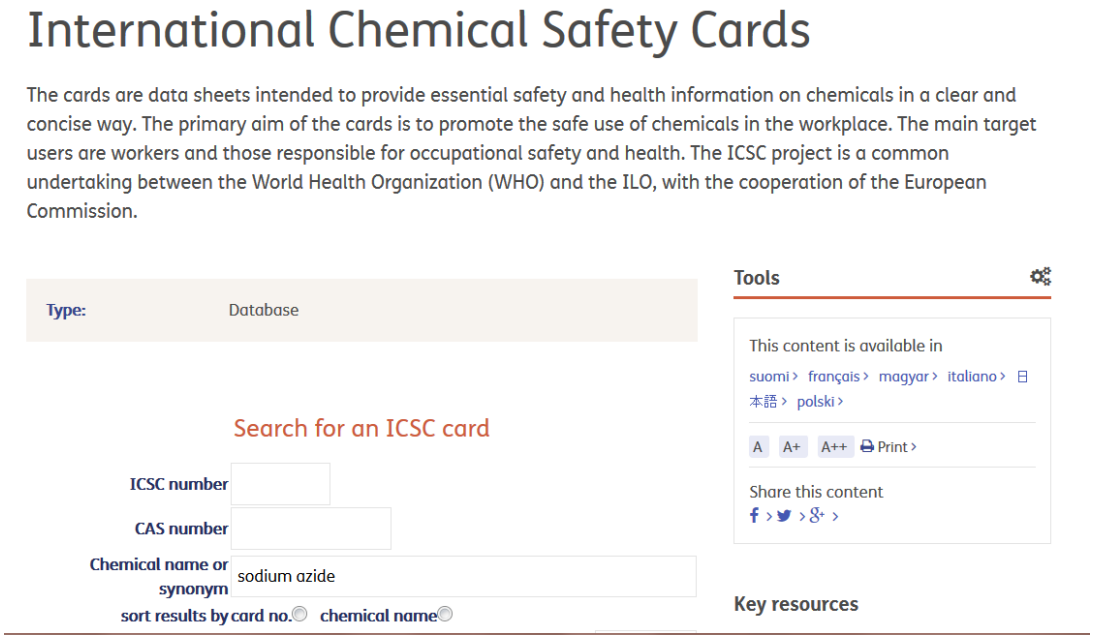
- Caveats
  - NA
  - Provenance
  - Experimental or predicted
- Searching
  - Name or CAS Registry Number
  - Class, Group, or Type
  - Molecular Formula (Hill System Order)
    - Organic: Carbon, Hydrogen & alphabetical for all remaining elements
    - Inorganic: Alphabetical by element symbol
  - Properties
    - Browse vs. search

Safety Data: International Chemical Safety Cards

Promoting safe use of chemicals in the work environment.

More than 1,700 cards are available in English. All are peer reviewed.

The National Institute of Occupational Health and Safety is a participating institution.



International Chemical Safety Card for Sodium Azide

[EN - FI - FR - HU - IT - JA - PL]

SODIUM AZIDE	**ICSC: 0950** Peer-Review Status: 04.07.1997 Validated

Azide
Azium

CAS #: 26628-22-8 RTECS #: VY8050000
UN #: 1687
EC #: 011-004-00-7
EINECS #: 247-852-1

Formula: NaN_3
Molecular mass: 65.02

TYPES OF HAZARD / EXPOSURE	ACUTE HAZARDS / SYMPTOMS	PREVENTION	FIRST AID / FIRE-FIGHTING
FIRE		NO contact with acids or heavy metals.	Use dry sand, special powder.
EXPLOSION	Risk of fire and explosion on contact with acids or metals.	Do NOT expose to friction or shock.	In case of fire: keep drums, etc., cool by spraying with water.
EXPOSURE		**STRICT HYGIENE!**	
Inhalation	Cough. Headache. Shortness of breath. Unconsciousness. Nasal congestion. Blurred vision. Slowing of heart rate. Fall in blood pressure.	Use local exhaust or breathing protection.	Fresh air, rest. Artificial respiration may be needed. Refer for medical attention.
Skin	MAY BE ABSORBED! Redness. Blisters.	Protective gloves.	Remove contaminated clothes. Rinse skin with plenty of water or shower.
Eyes	Redness. Pain.	Wear safety goggles or eye protection in combination with breathing protection.	First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then refer for medical attention.
Ingestion	Abdominal pain. Nausea. Sweating. Further see Inhalation.	Do not eat, drink, or smoke during work.	Rinse mouth. Do NOT induce vomiting. Give one or two glasses of water to drink. Rest. Refer for medical attention .

International Chemical Safety Card for Sodium Azide cont.

SPILLAGE DISPOSAL	PACKAGING & LABELLING
Evacuate danger area! Consult an expert! Sweep spilled substance into covered plastic containers. If appropriate, moisten first to prevent dusting. Carefully collect remainder. Then store and dispose of according to local regulations. Personal protection: complete protective clothing including self-contained breathing apparatus.	Do not transport with food and feedstuffs. **EC Classification** Symbol: T+, N; R: 28-32-50/53; S: (1/2)-28-45-60-61 **UN Classification** UN Hazard Class: 6.1; UN Pack Group: II **GHS Classification**

EMERGENCY RESPONSE	SAFE STORAGE
Transport Emergency Card: TEC (R)-61G12B.	Fireproof. Separated from acids, food and feedstuffs, metals, lead and lead compounds.

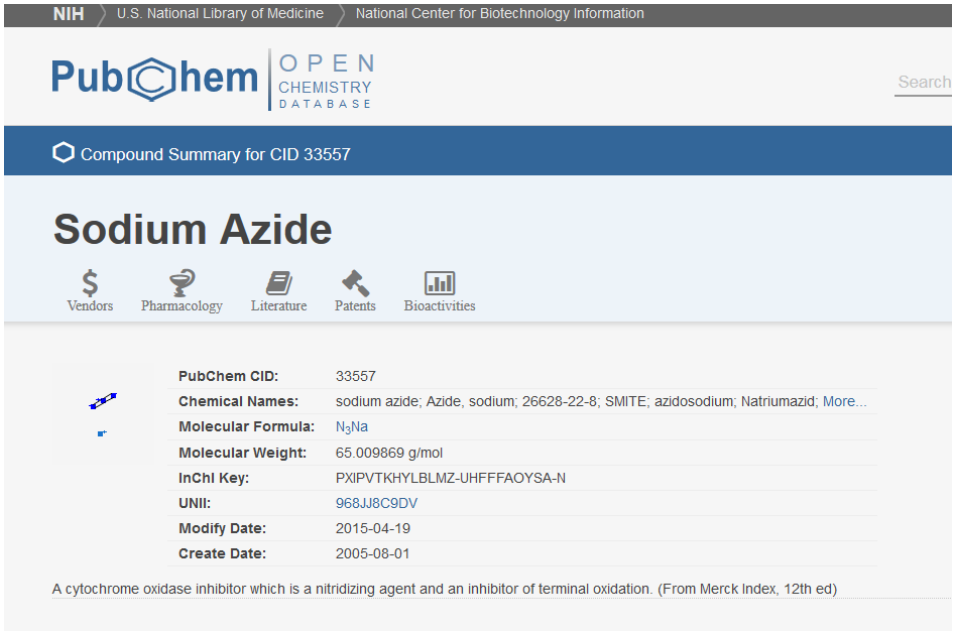
IMPORTANT DATA	
Physical State; Appearance ODOURLESS COLOURLESS HEXAGONAL CRYSTALS. **Physical dangers** **Chemical dangers** May explode on heating above melting point, especially on rapid heating. This generates fire and explosion hazard. The solution in water is a weak base. Reacts with copper, lead, silver, mercury and carbon disulfide. This produces particularly shock-sensitive compounds. Reacts with acids. This produces toxic and explosive hydrogen azide. **Occupational exposure limits** TLV: 0.29mg/m³ (ceiling value); A4 (not classifiable as a human carcinogen); (ACGIH 2005).	**Routes of exposure** The substance can be absorbed into the body by inhalation, through the skin and by ingestion. **Inhalation risk** Evaporation at 20°C is negligible; a harmful concentration of airborne particles can, however, be reached quickly. **Effects of short-term exposure** The substance is irritating to the eyes, skin and respiratory tract. Exposure slightly above the OEL could cause effects on the nervous system. **Effects of long-term or repeated exposure**

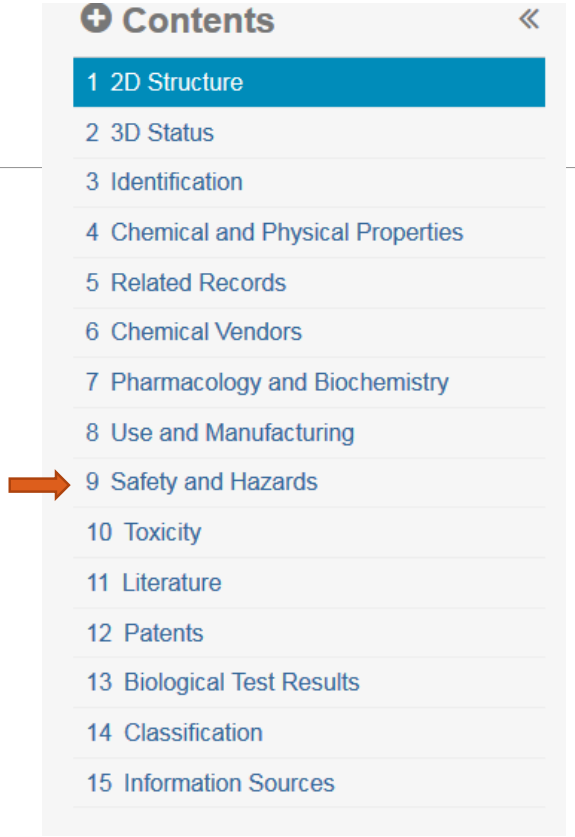
PHYSICAL PROPERTIES	ENVIRONMENTAL DATA
Decomposes at 275°C Relative density (water = 1): 1.8475 Solubility in water, g/100ml at 17°C: 41.7 (good)	

PubChem


NIH
U.S. National Library of Medicine
National Center for Biotechnology Information
PubChem
OPEN
CHEMISTRY
DATABASE
SEARCH 1.0 βETA
Current System
Compounds
Bioassays
Patents
Bioactivities
Targets

PubChem – ID plus ToC for Sodium Azide





PubChem – excerpt from entry on Sodium Azide

9.1.5 Inhalation Hazard

Cough. Headache. Shortness of breath. Unconsciousness. Nasal congestion. Blurred vision. Slowing of heart rate. Fall in blood pressure. *from ILO-ICSC [5]*

9.1.6 Eye Hazard

Redness. Pain. *from ILO-ICSC [5]*

9.1.7 Ingestion Hazard

Abdominal pain. Nausea. Sweating. Further see Inhalation. *from ILO-ICSC [5]*

9.1.8 Fire Potential

NOT CONSIDERED FLAMMABLE UNLESS HEATED ABOVE 300 DEG C.

Weed Science Society of America. Herbicide Handbook. 5th ed. Champaign, Illinois: Weed Science Society of America, 1983., p. 439

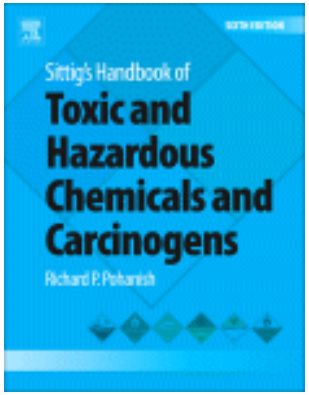
from HSDB [1]

9.2 Safety and Hazard Properties

9.2.1 Flammability

Combustible Solid (if heated above 572°F). *from NIOSH-PocketGuide [7]*

Sittig's Handbook of Toxic and Hazardous Chemicals and Carcinogens



One of the most reliable, easy-to-use and essential reference works on hazardous materials.

Providing a vast array of critical information on the 2,100 most heavily used, transported, and regulated chemical substances of both occupational and environmental concern.

Arranged alphabetically by name of substance.

Available in print and online at Stanford.

Sittig's: Excerpts from entry for Sodium Azide

Sodium azide **S:0390**

Molecular Formula: N_3Na
Common Formula: NaN_3
Synonyms: AI3-50436; Axium; Azida sodico (Spanish); Azide; Azium; Azoture de sodium (French); Dazoe; Hydrazoic acid, Sodium salt; Kazoe; Natriumazid (German); NCI-C06462; Smite; Sodium salt of hydrazoic acid
CAS Registry Number: 26628-22-8; *(alt.)* 12136-89-9

Description: Sodium azide is a colorless to white, odorless, crystalline solid. Combustible solid above 300°C. Molecular weight = 65.02; Specific gravity (H_2O:1) = 1.85 at 25°C; Boiling point = (decomposes); Freezing/Melting point = (the solid crystals decompose with the evolution of nitrogen gas, leaving a residue of sodium oxide) 275°C. Hazard Identification (based on NFPA-704 M Rating System): Health 4, Flammability 0, Reactivity 2. Soluble in water; reaction; solubility = 42% at 17°C.

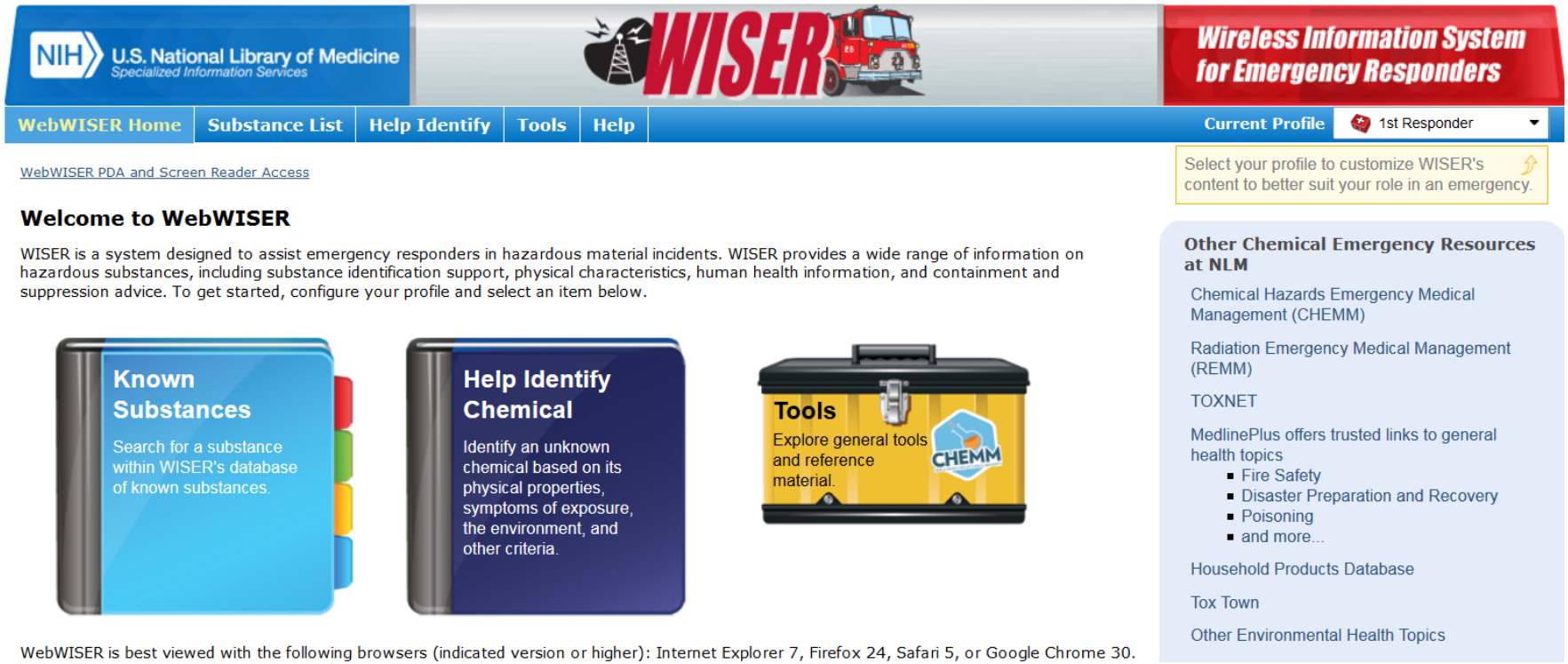
Incompatibilities: Reacts explosively and/or forms explosive and/or shock-sensitive compounds with acids and many metals. Contact with water forms hydrazoic acid. Combustible solid (if heated above 300°C). May explode when heated above its melting point, especially if heating is rapid. Reacts with acids, producing toxic, shock-sensitive, and explosive hydrogen azide. It forms explosive compounds with phosgene, brass, zinc, trifluoroacrylol fluoride, and nitrogen-diluted bromine vapor. Reacts with benzoyl chloride and potassium hydroxide, bromine, carbon disulfide, copper, lead, nitric acid, barium carbonate, sulfuric acid, chromium(II) hypochlorite, dimethyl sulfate, dibromomalononitrile, silver, mercury. Over a period of time, sodium azide may react with copper, lead, brass, or solder in plumbing systems to form an accumulation of the *highly explosive* and shock-sensitive compounds of lead azide and copper azide.

Sittig's: Excerpts from entry for Sodium Azide cont.

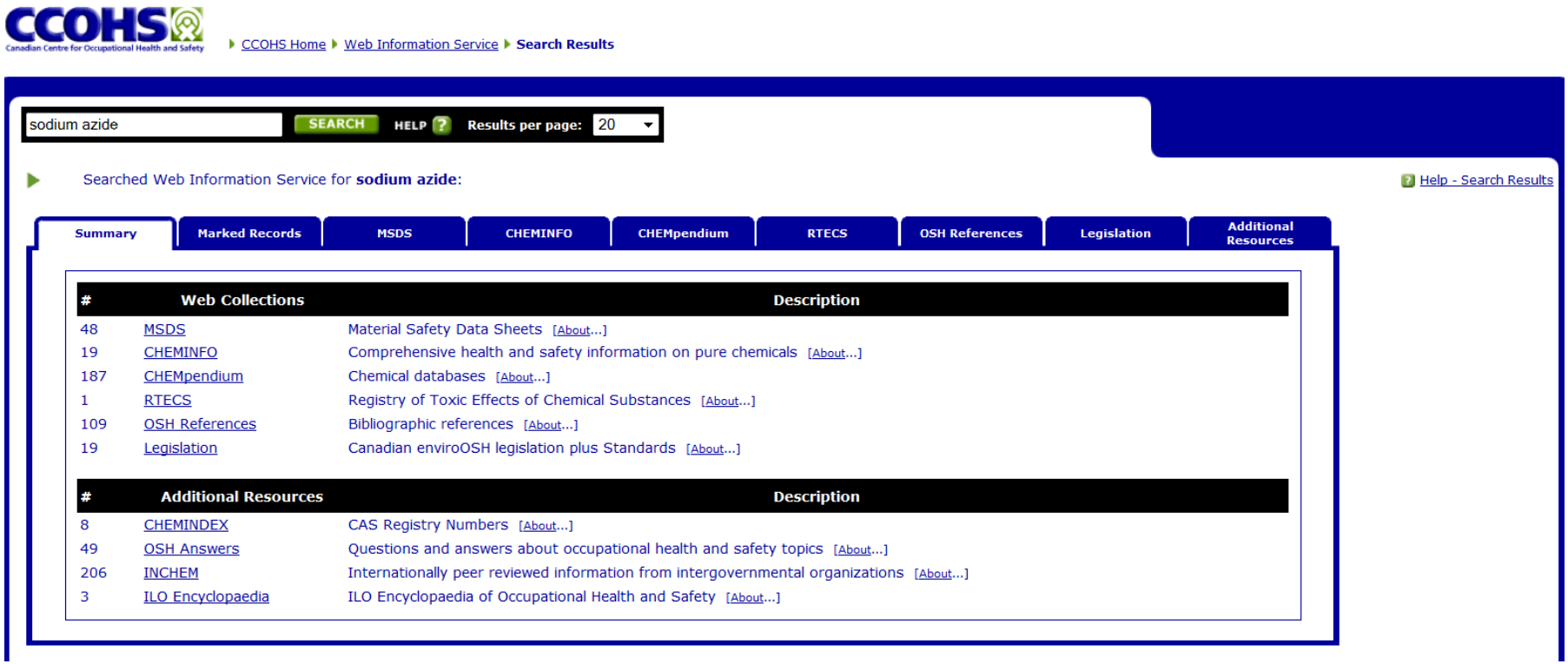
Personal Protective Methods: Wear protective gloves and clothing to prevent any reasonable probability of skin contact. Safety equipment suppliers/manufacturers can provide recommendations on the most protective glove/clothing material for your operation. All protective clothing (suits, gloves, footwear, headgear) should be clean, available each day, and put on before work. Contact lenses should not be worn when working with this chemical. Wear dust-proof goggles and face shield when working with powders or dust, unless full face-piece respiratory protection is worn. Where sodium azide may be present in solution, wear splash-proof chemical goggles and face shield, unless full face-piece respiratory protection is worn. Employees should wash immediately with soap when skin is wet or contaminated. Provide emergency showers and eyewash.

Respirator Selection: Where there is potential for exposures over 0.1 ppm as a dust, fume, or mist, use a NIOSH/MSHA- or European Standard EN149-approved full face-piece respirator with a high-efficiency particulate filter. Greater protection is provided by a powered air-purifying respirator. *Where there is potential for high exposures*, or for exposures to hydrazoic acid vapor, use a NIOSH/MSHA- or European Standard EN149-approved supplied-air respirator with a full face-piece operated in the positive-pressure mode, or with a full face-piece, hood, or helmet in the continuous-flow mode; or use a NIOSH/MSHA- or European Standard EN149-approved self-contained breathing apparatus with a full face-piece operated in pressure-demand or other positive-pressure mode.

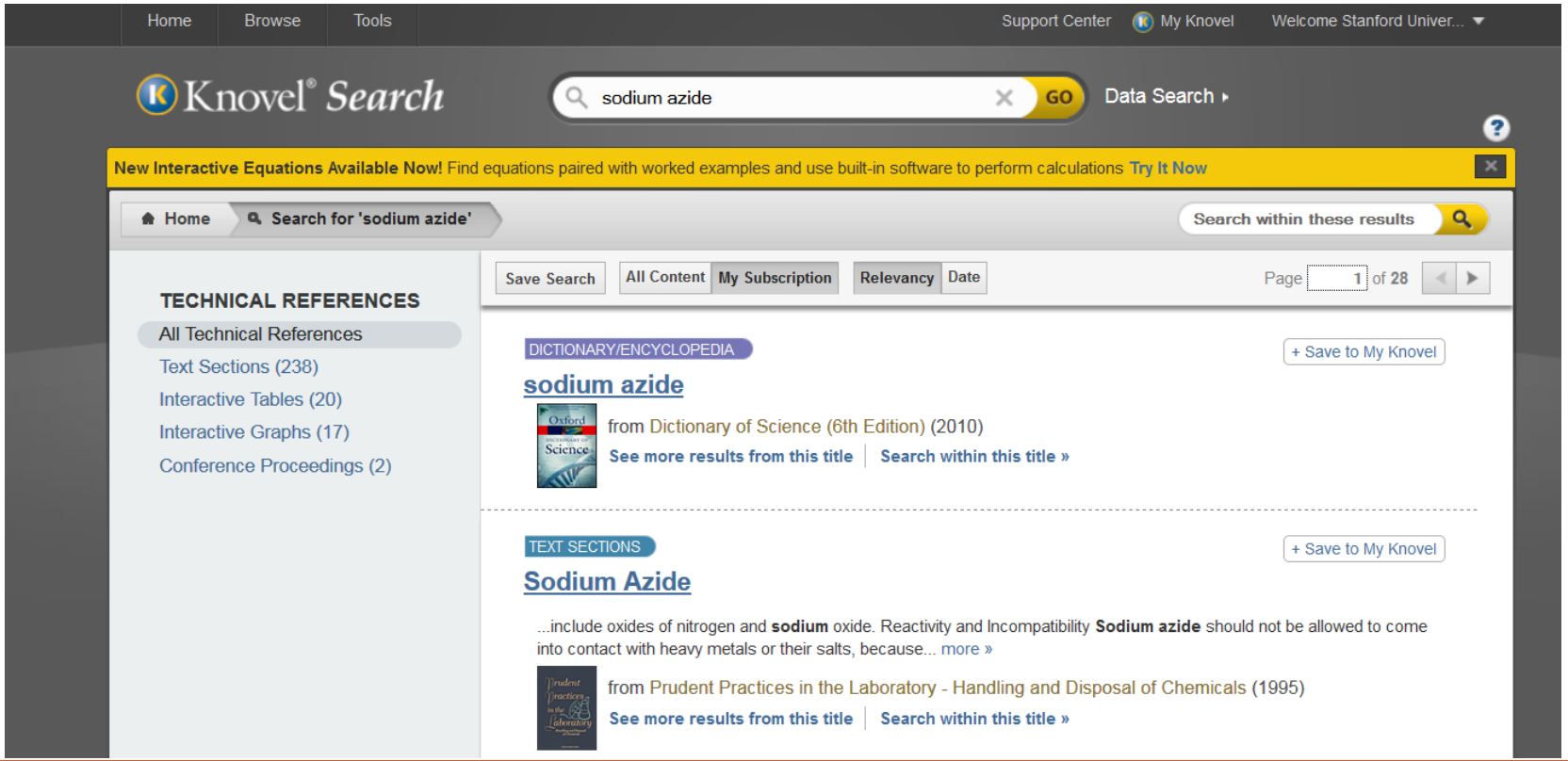
WebWISER


NIH U.S. National Library of Medicine
Specialized Information Services
WISER
Wireless Information System for Emergency Responders
WebWISER Home
Substance List
Help Identify
Tools
Help
Current Profile
1st Responder
WebWISER PDA and Screen Reader Access
Select your profile to customize WISER's content to better suit your role in an emergency.
Welcome to WebWISER
WISER is a system designed to assist emergency responders in hazardous material incidents. WISER provides a wide range of information on hazardous substances, including substance identification support, physical characteristics, human health information, and containment and suppression advice. To get started, configure your profile and select an item below.
Known Substances
Search for a substance within WISER's database of known substances.
Help Identify Chemical
Identify an unknown chemical based on its physical properties, symptoms of exposure, the environment, and other criteria.
Tools
Explore general tools and reference material.
CHEMM
Other Chemical Emergency Resources at NLM
Chemical Hazards Emergency Medical Management (CHEMM)
Radiation Emergency Medical Management (REMM)
TOXNET
MedlinePlus offers trusted links to general health topics
Fire Safety
Disaster Preparation and Recovery
Poisoning
and more...
Household Products Database
Tox Town
Other Environmental Health Topics
WebWISER is best viewed with the following browsers (indicated version or higher): Internet Explorer 7, Firefox 24, Safari 5, or Google Chrome 30.

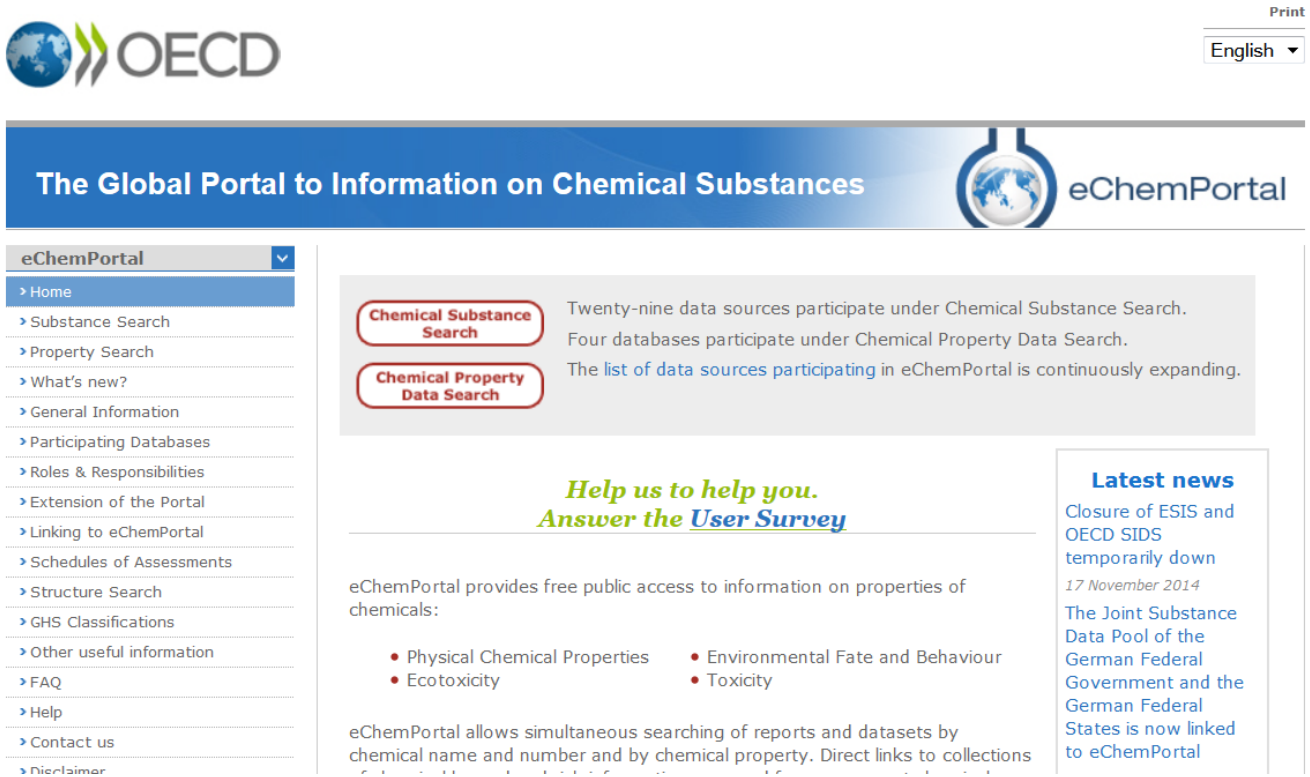
CCOHS Web Information Service



Knovel


Home
Browse
Tools
Support Center
My Knovel
Welcome Stanford Univer...
Knovel® Search
sodium azide
GO
Data Search
New Interactive Equations Available Now! Find equations paired with worked examples and use built-in software to perform calculations Try It Now
Home
Search for 'sodium azide'
Search within these results
TECHNICAL REFERENCES
All Technical References
Text Sections (238)
Interactive Tables (20)
Interactive Graphs (17)
Conference Proceedings (2)
Save Search
All Content
My Subscription
Relevancy
Date
Page 1 of 28
DICTIONARY/ENCYCLOPEDIA
+ Save to My Knovel
sodium azide
from Dictionary of Science (6th Edition) (2010)
See more results from this title
Search within this title »
TEXT SECTIONS
+ Save to My Knovel
Sodium Azide
...include oxides of nitrogen and sodium oxide. Reactivity and Incompatibility Sodium azide should not be allowed to come into contact with heavy metals or their salts, because... more »
from Prudent Practices in the Laboratory - Handling and Disposal of Chemicals (1995)
See more results from this title
Search within this title »

eChemPortal

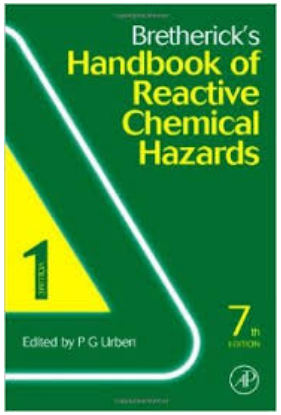


More Resources

- **Canadian Centre for Occupational Health and Safety. Web Information Service** - metasearch for chemical hazard information from many sources.
- **Knovel** – site contains 2,000+ handbooks. Browse or search the Safety and Industrial Hygiene section. Provided by Knovel.
- **Encyclopedia of Reagents for Organic Synthesis** – includes safety information. Provided by Wiley.
- **Hazardous Substances Data Bank** - HSDB has comprehensive, peer-reviewed toxicology data for about 5,000 potentially hazardous chemicals. Provided by NLM.
- **eChemPortal** - provides free public access to information on properties of chemicals: Physical Chemical Properties, Ecotoxicity, Environmental Fate and Behavior, and Toxicity. Provided by the OECD.

Reactivity, Reactions, and Protocols

Reactivity Information – Bretherick's Volume 1



Bretherick's Handbook of Reactive Chemical Hazards (print + online as PDF)

Two volume set. V.1=Specific Chemicals. V. 2=Class, Group, & Topic.

Find stability of single compound:

- Elements and substances are arranged by molecular formula in volume 1.
- Use Volume 1, Appendix 4 (Index of Chemical Names & Synonyms). Browse by name and find entry number.
- In the online version, search entry number followed by name (example: 4753. Sodium Azide). Open PDF for chapter in search results and then use Cntrl-F to locate entry.

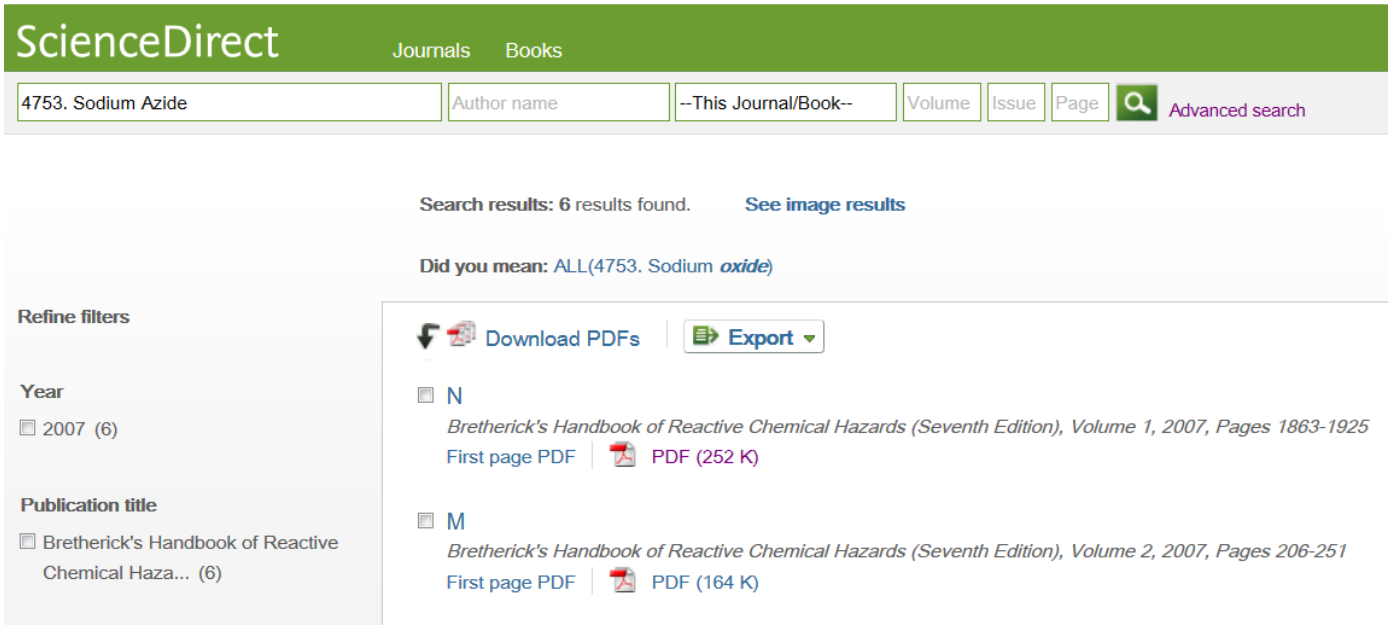
Find data on possible violent interaction between two or more compounds.

- Determine which compound is more reactive (using above method).
- Browse sub-entries for that compound (e.g. Sodium Azide, Barium Carbonate).

For more information about specific chemicals, see:

- Appendix 2: Fire-related data
- Appendix 5: CAS Registry Number Index

Search Results in the Online Version of Bretherick's



Bretherick's entry on Sodium Azide (in Vol. 1)

4753. Sodium azide
[26628-22-8] **N_3Na**

$Na^+ \quad N^-=N^+=N^-$

HCS 1980, 827

1. Mellor, 1940, Vol. 8, 345
2. Lambert, B., *School Sci. Rev.*, 1927, **8**(31), 218
3. Anon., *Jahresber.*, 1981, 77—79
4. Anon., *Safety*, 1982, (3), 2
5. Grewer, T. *et al., Exothermic Decomposition*, Technical Report 01VD 159/0329 for Federal German Ministry for Res. Technol., Bonn. 1986
6. www.chemsafety. gov/circ. US Chem. Safety & Haz. Investigation Board, CSB 2001-5086
7. Hagenbuch, J-P. *Chimia*, 2003, **57**(12), 773

Insensitive to impact, it decomposes, sometimes explosively, above its m.p. [1], particularly if heated rapidly [2]. Although used in aqueous solutions as a preservative in pharmaceutical preparations, application of freeze-drying techniques to such solutions has led to problems arising from volatilisation of traces of hydrazoic acid from non-neutral solutions, condensation in metal lines, traps or filters, and formation of heavy metal azides in contact with lead, copper or zinc components in the drying plant [3,4]. An explosion is reported when cutting into a pipe previously used to transport the powdered azide [air may have been involved as an oxidant – Ed.] [6]. A study of risks inherent in industrial use of sodium azide at hundred kg scale is reported. For reagent use, keeping the mix buffered to alkalinity is important [7]

Energy of exothermic decomposition in range 230—260°C was measured as 0.76 kJ/g by DSC, and T_{ait24} was determined as 253°C by adiabatic Dewar tests, with an apparent energy of activation of 145 kJ/mol [5].

See Heavy metals, below

Acids
See Hydrogen azide

Ammonium chloride, Trichloroacetonitrile
See 5-Trichloromethyltetrazole

Barium carbonate
Henneburg, G. O. *et al., Can. J. Res.*, 1950, **28B**, 345
Interaction to form cyanide ion requires careful control of temperature at 630°C to prevent explosions.

Bromine
See Bromine: Metal azides

Reactivity - Bretherick's Volume 2

Volume 2: Class, Group and Topic

- Appendix 3: Alphabetical Index
- Appendix 4: Classified by Type Index
  - Chemical Classes
  - Inorganic chemical groups
  - Organometallic chemical groups
  - Organic chemical groups
  - Hybrid chemical groups
  - Hazard Assessment and prediction topics
  - Miscellaneous topics
  - Performance materials topics
  - Phenomenon topics
  - Specific reaction hazards
  - Substances (not simple chemical entities, often of natural origin)
  - Technique topics
  - Unit operation or process topics

METAL AZIDES **MN_3**

1. Mellor, 1940, Vol. 8, Suppl. 2, 16—54
2. *Energetic Materials*, Fair, H. D. and Walker, R. F. (Eds.), Vols. 1 and 2, New York, Plenum, 1977

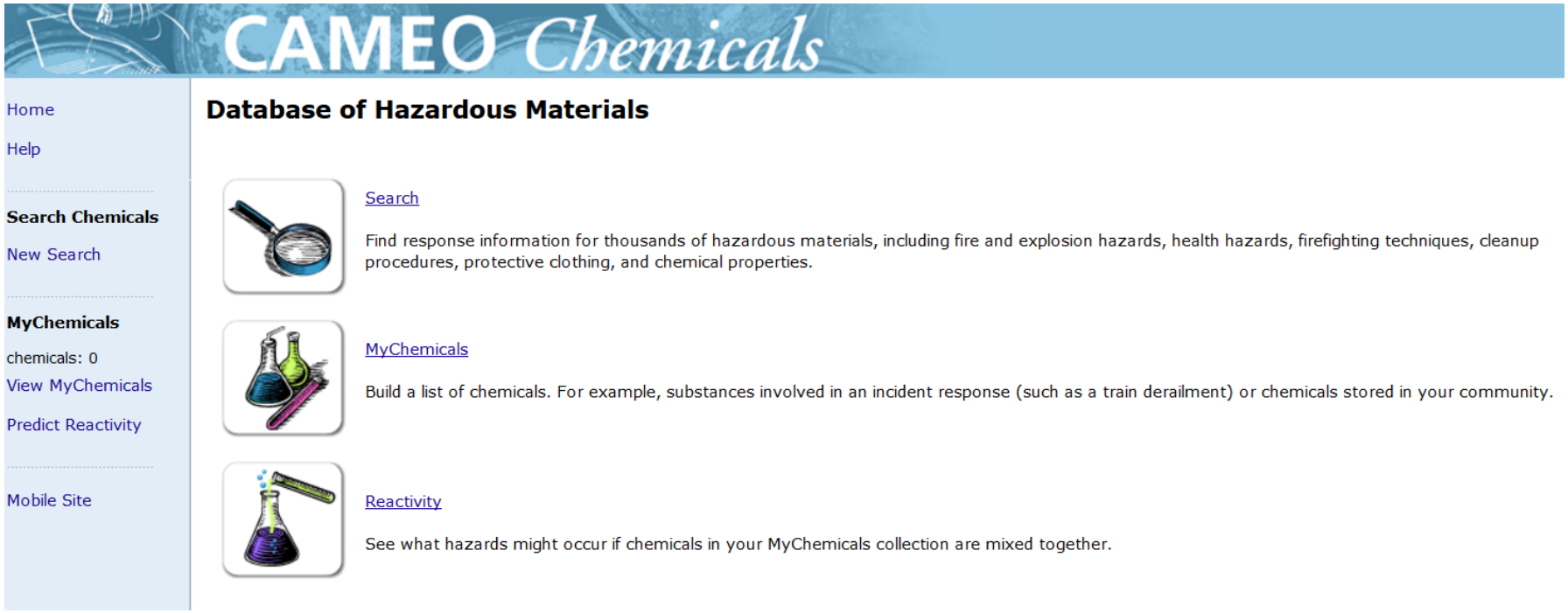
This large and well documented group of explosive compounds contains some which are widely used industrially [1]. The text gives a thorough treatment of all aspects of the physics and chemistry (Vol. 1) and of the applications (Vol. 2) of this important group of energetic compounds [2] and individually indexed compounds are:

Aluminium azide, 0082
* Azidogermane, 4410
Barium azide, 0214
* Bis(2-aminoethyl)aminecobalt(III) azide, 1769
* Bis(cyclopentadienyl)tungsten diazide oxide, 3279

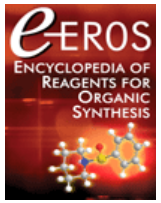
Organic Chemical Groups

ACETYLENIC COMPOUNDS, 2
ACETYLENIC PEROXIDES, 5
ACRYLIC MONOMERS, 6
O-ACYLHYDROXAMIC ACIDS, 9
ACYL HYPOHALITES, 10
ACYL NITRATES, 10
ACYL NITRITES, 10
ALDEHYDES, 12

CAMEO Chemicals



e-EROS: Encyclopedia of Reagents for Organic Synthesis



- *e-EROS* has in-depth information on reagents and catalysts for all chemists planning or working on organic syntheses.
- *e-EROS* gives detailed information on more than 4,500 reagents and catalysts, and every year more than 200 new or updated articles are added in order to keep the Database up-to-date.
- Search by Reagent Name or Chemical Structure. Entries include safety information.

Sodium Azide[1]

NaN_3

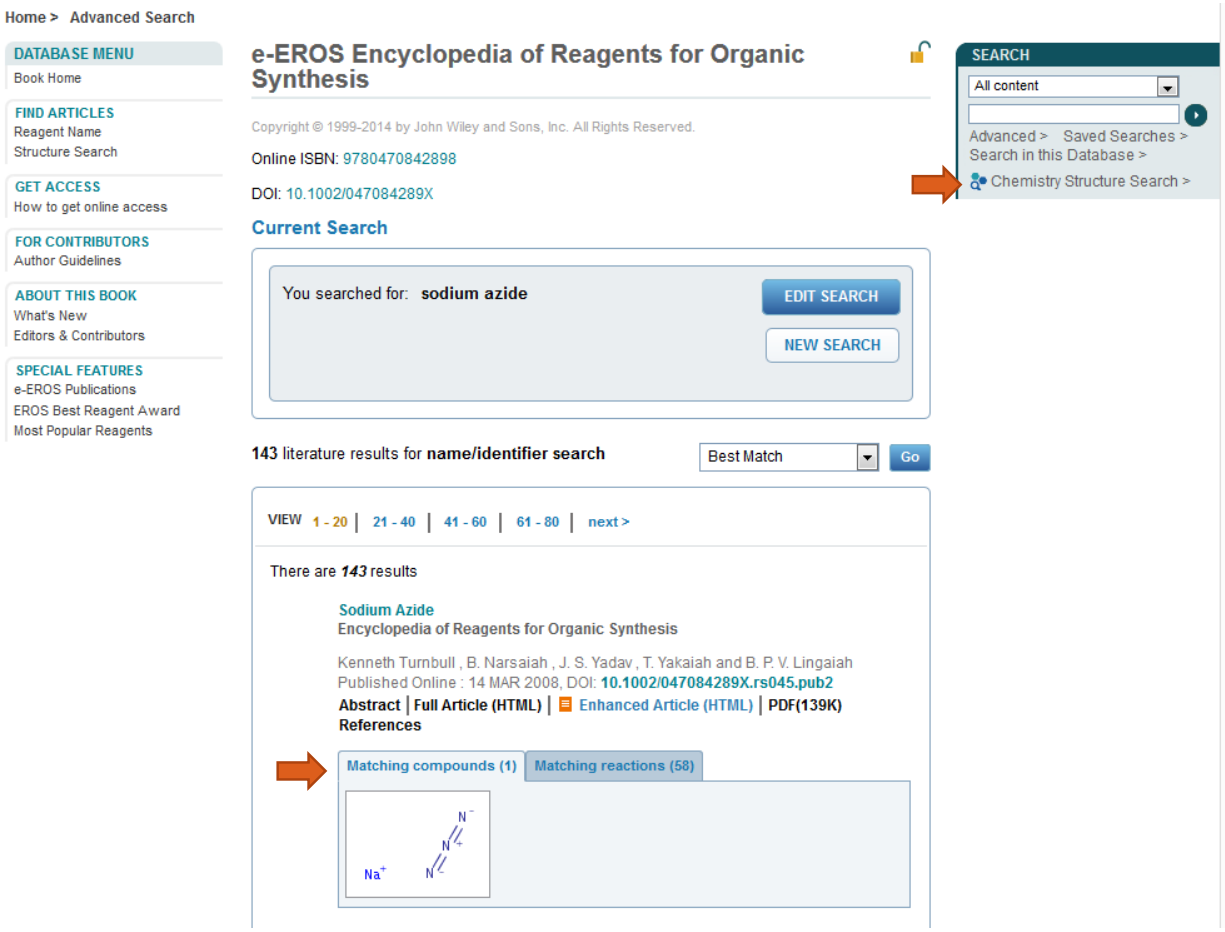
[26628-22-8] N_3Na (MW 65.02)
InChI = 1/N3.Na/c1-3-2;/q-1;+1
InChIKey = PXIPVTKHYLBLMZ-UHFFFAOYAH

(nucleophilic azide source for organoazide preparation;[2] precursor to reagents such as hydrazoic acid,[3] halogen azides,[4] trimethylsilyl azide,[5] tosyl azide,[6] and diphenyl phosphorazidate[7])

Physical Data: dec ca. 300 °C; *d* 1.850 g cm^{-3}.
Solubility: sol water (39 g/100 g at 0 °C, 55 g/100 g 100 °C); slightly sol alcohol; insol ether.
Form Supplied in: white solid; widely available.
Handling, Storage, and Precautions: while relatively insensitive to impact, the solid can decompose explosively above its melting point. It forms highly explosive azides with metals such as Cu, Pb, Hg, Ag, Au, their alloys and compounds, and reacts with acids to form hydrazoic acid (HN_3) which is a toxic, spontaneously explosive gas. Explosive *gem*-diazides can be formed in CH_2Cl_2 or other chlorinated solvents and shock or heat sensitive metal azidothioformates in CS_2. All work with NaN_3 and other azides should be conducted on a very small scale behind a shield, in a fume hood. Excess NaN_3 on flasks, paper, etc. can be destroyed in a fume hood by soaking with acidified ***Sodium Nitrite*** or by oxidation with ***Cerium(IV) Ammonium Nitrate***.[8]

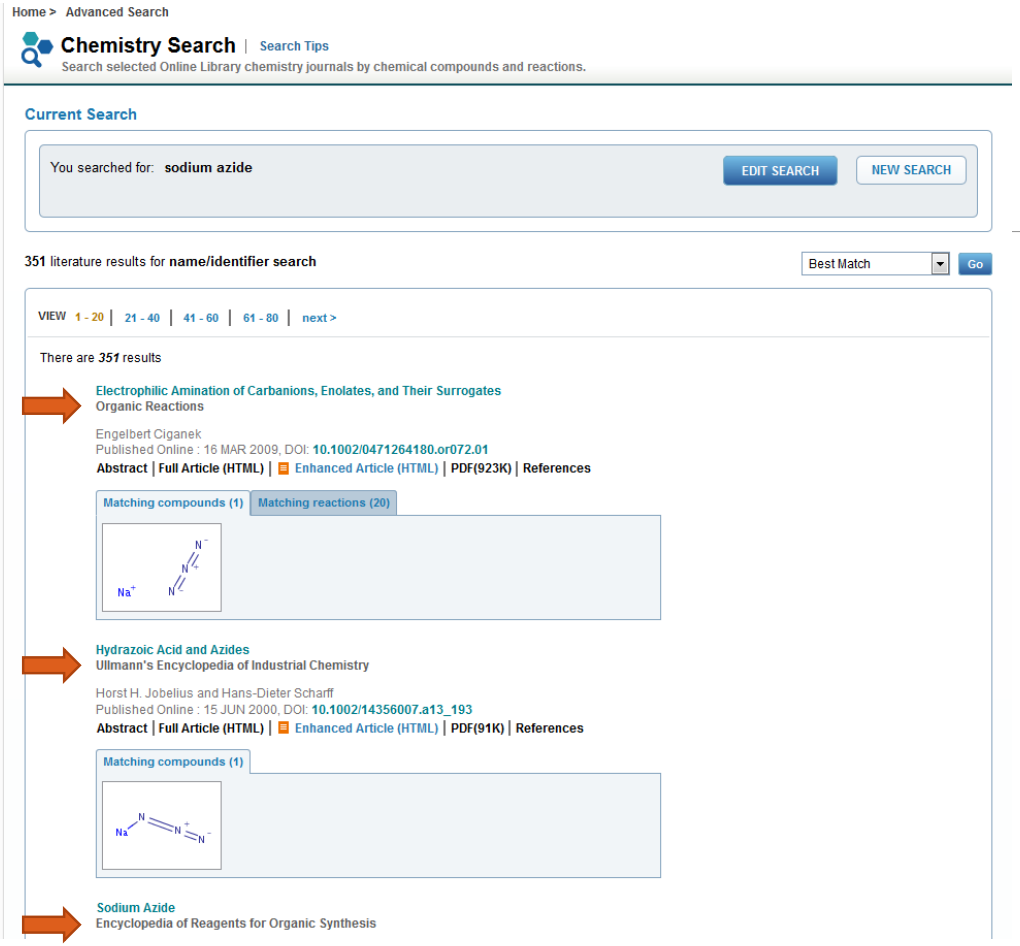
e-EROS – Structure Search page

e-EROS – **Search Results** using Name in Structure Search form

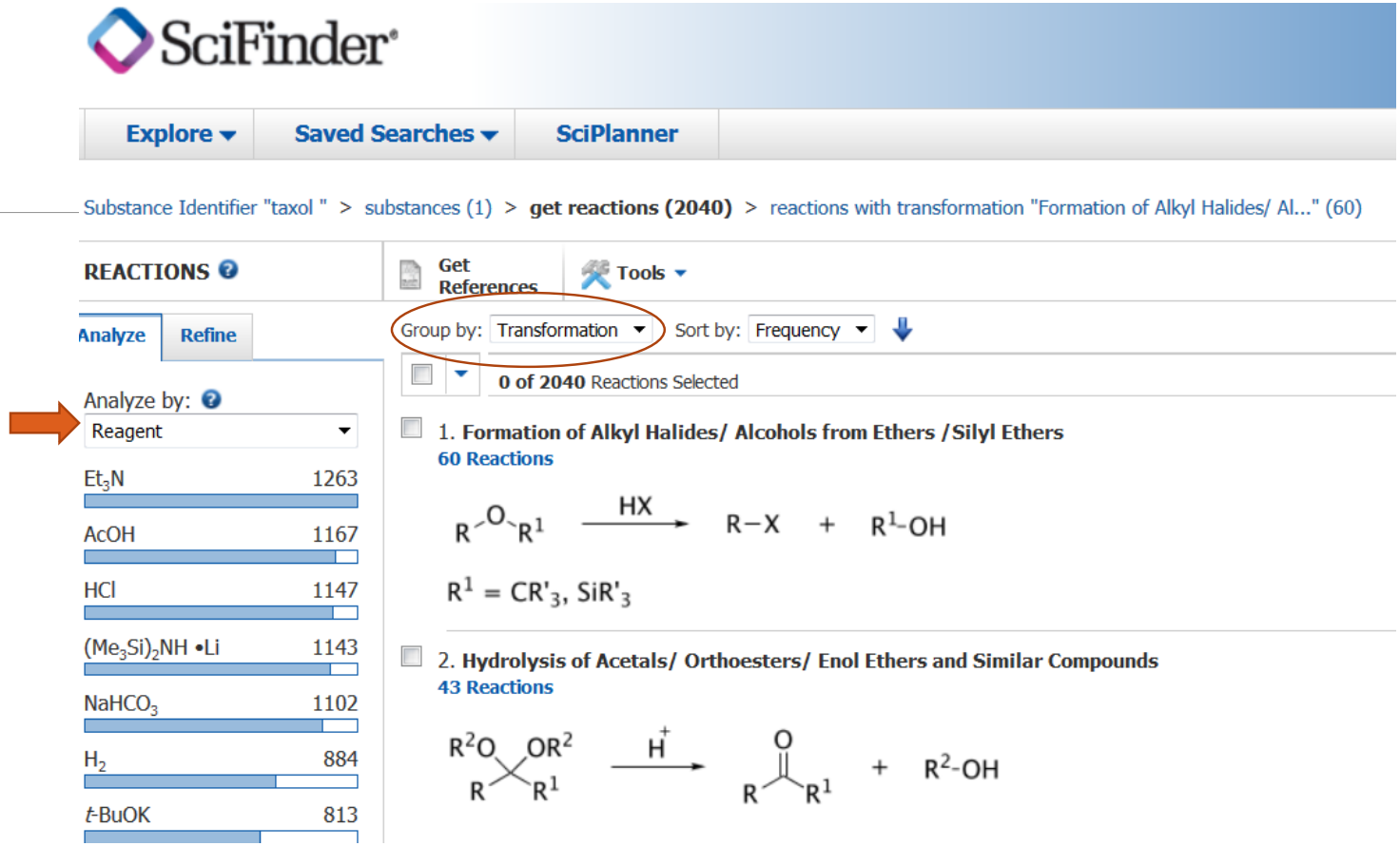


Wiley **Chemistry** Structure Search Results

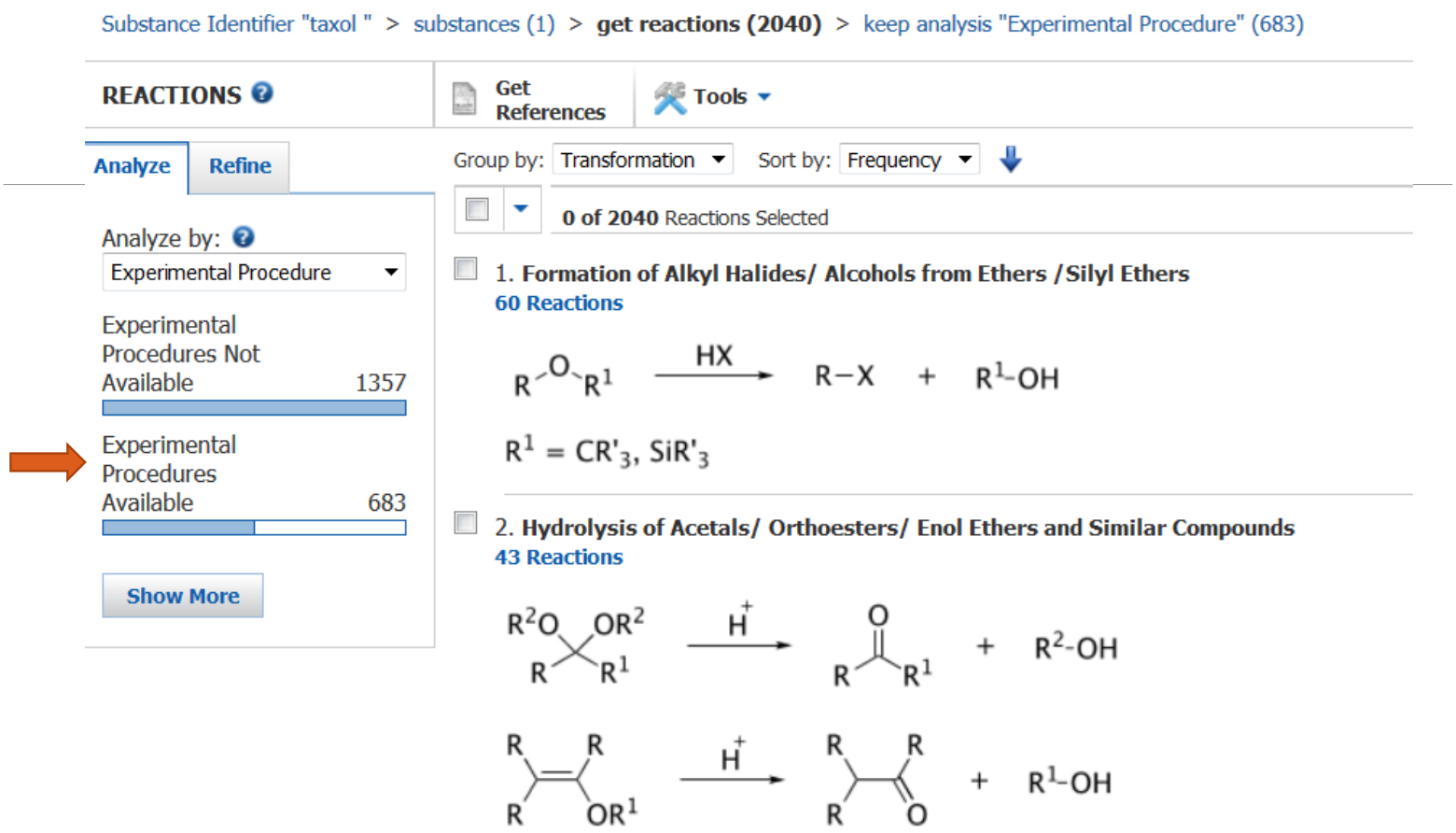
http://onlinelibrary.wiley.com/chemistry/search



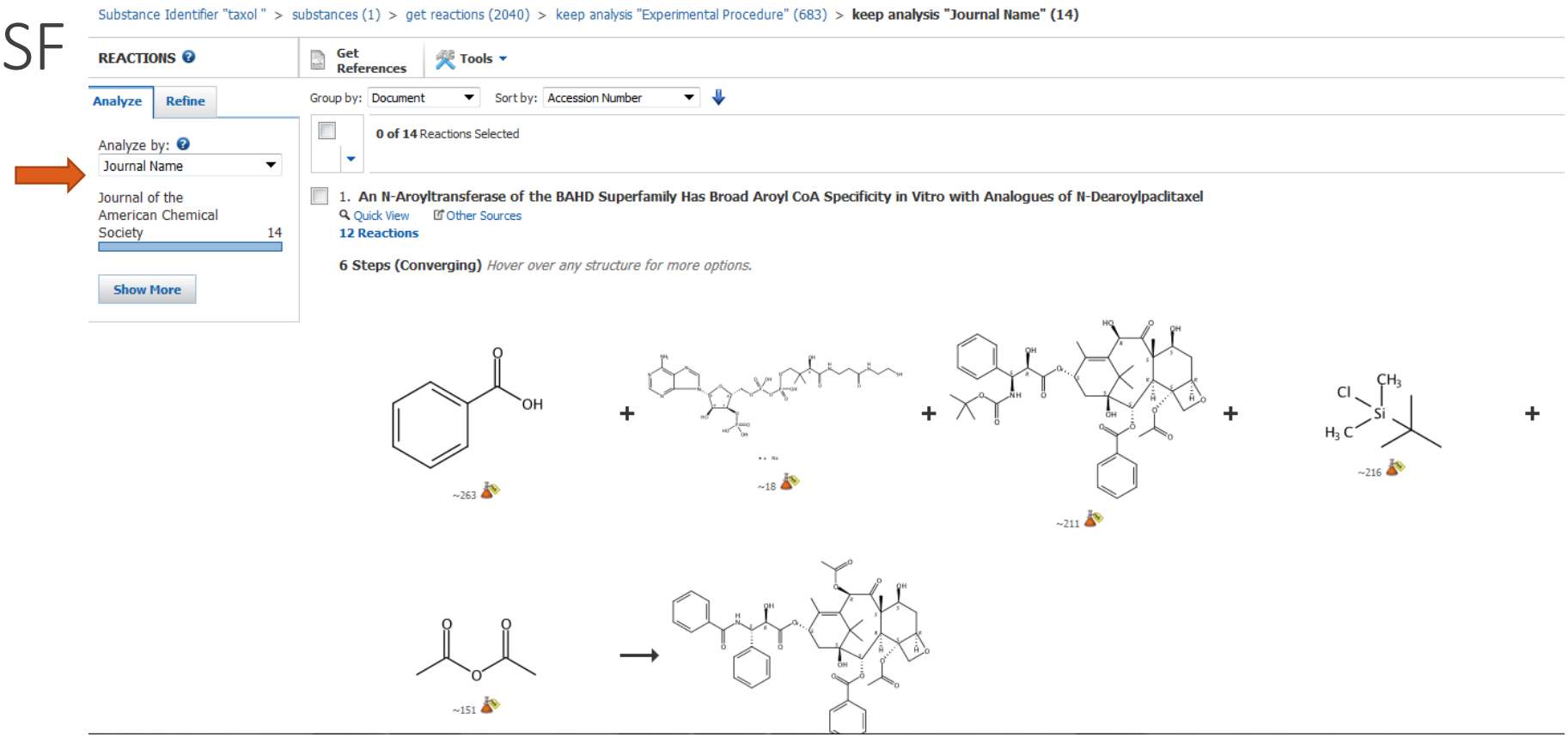
SciFinder


SciFinder
Explore
Saved Searches
SciPlanner
Substance Identifier "taxol " > substances (1) > get reactions (2040) > reactions with transformation "Formation of Alkyl Halides/ Al..." (60)
REACTIONS
Get References
Tools
Analyze
Refine
Group by: Transformation
Sort by: Frequency
Analyze by:
Reagent
Et3N 1263
AcOH 1167
HCl 1147
(Me3Si)2NH •Li 1143
NaHCO3 1102
H2 884
t-BuOK 813
0 of 2040 Reactions Selected
1. Formation of Alkyl Halides/ Alcohols from Ethers /Silyl Ethers
60 Reactions
HX
R−X + R1-OH
R1 = CR'3, SiR'3
2. Hydrolysis of Acetals/ Orthoesters/ Enol Ethers and Similar Compounds
43 Reactions
H+
+ R2-OH

SF


Substance Identifier "taxol " > substances (1) > get reactions (2040) > keep analysis "Experimental Procedure" (683)
REACTIONS
Get References
Tools
Analyze
Refine
Group by: Transformation
Sort by: Frequency
0 of 2040 Reactions Selected
Analyze by:
Experimental Procedure
Experimental Procedures Not Available 1357
Experimental Procedures Available 683
Show More
1. Formation of Alkyl Halides/ Alcohols from Ethers /Silyl Ethers
60 Reactions
HX
R−X + R1-OH
R1 = CR'3, SiR'3
2. Hydrolysis of Acetals/ Orthoesters/ Enol Ethers and Similar Compounds
43 Reactions
H+
+ R2-OH
H+
+ R1-OH

SF


Substance Identifier "taxol " > substances (1) > get reactions (2040) > keep analysis "Experimental Procedure" (683) > keep analysis "Journal Name" (14)
REACTIONS
Get References
Tools
Analyze
Refine
Analyze by:
Journal Name
Journal of the American Chemical Society 14
Show More
Group by: Document
Sort by: Accession Number
0 of 14 Reactions Selected
1. An N-Aroyltransferase of the BAHD Superfamily Has Broad Aroyl CoA Specificity in Vitro with Analogues of N-Dearoylpaclitaxel
Quick View
Other Sources
12 Reactions
6 Steps (Converging) Hover over any structure for more options.
~263
~18
~211
~216
~151

SF

▾ Overview

Steps/Stages

1.1 R:Et_3N, S:THF, S:CH_2Cl_2, 10 min, 23°C
1.2 R:$ClCO_2Et$, 1 h, 23°C
1.3 R:$NaHCO_3$, S:H_2O, S:*t*-BuOH, 0.5 h, 23°C
1.4 R:HCl, S:H_2O, pH 3-5
1.1 R:1H-Imidazole, S:DMF, 18 h, 23°C
2.1 R:$CeCl_3 \cdot 7H_2O$, S:THF, rt; 1 h, rt
3.1 R:C_5H_5N, R:HF, S:THF, S:C_5H_5N, 0°C; 0°C → rt; 10 h, rt
4.1 R:HCO_2H, S:H_2O, S:MeCN, 0°C; 0°C → rt; 4 h, rt
4.2 R:$NaHCO_3$, S:H_2O, S:$CHCl_3$
5.1 R:Glycerol, C:476683-00-8, S:H_2O, pH 8
5.2 R:HCl, S:H_2O, 2.5 h, rt

Notes

regioselective, regioselective, incremental addition of pyridine and HF, enzymic, biotransformation, sodium phosphate buffered solution used, recombinant N-debenzoyl-2'-deoxypaclitaxel:N-benzoyltransferase from Taxus plants overexpressed in Escherichia coli used, kinetic study, Reactants: 5, Reagents: 10, Catalysts: 1, Solvents: 8, Steps: 6, Stages: 11, Most stages in any one step: 4

References

An N-Aroyltransferase of the BAHD Superfamily Has Broad Aroyl CoA Specificity in Vitro with Analogues of N-Dearoylpaclitaxel

Quick View Other Sources

By Nevarez, Danielle M. et al

From Journal of the American Chemical Society, 131(16), 5994-6002; 2009

▾ Experimental Procedure

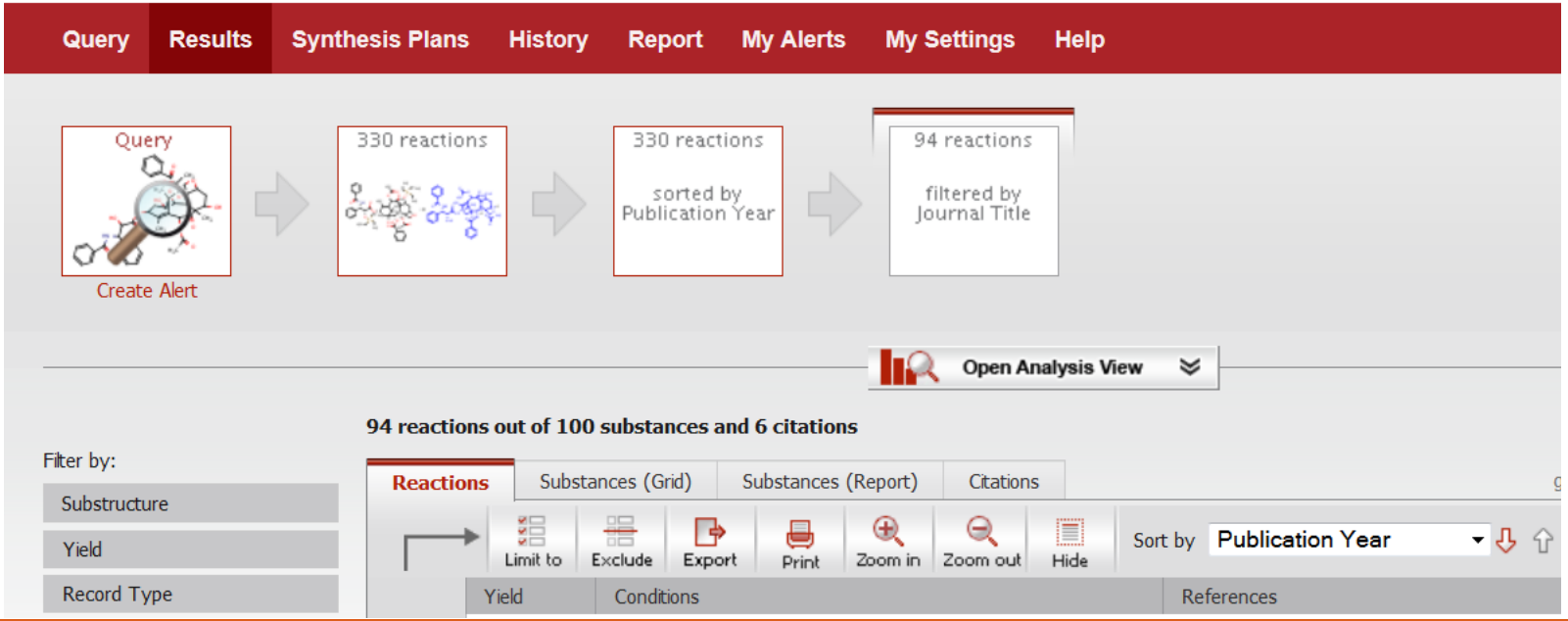
JACS

Sequence 1

Step 1

Synthesis of CoA Thioesters. Several aroyl CoA donors (heteroaroyls and variously substituted benzoyls) were synthesized *via* a previously described method that proceeds through a mixed ethyl carbonate anhydride.[29] Briefly, triethylamine (3.0 µL, 30 µmol) was added to a solution of the corresponding carboxylic acid (27 µmol) in 5:2 CH_2Cl_2/THF (v/v, 1.4 mL) under N_2 gas. The mixture was stirred for 10 min at 23 °C, ethyl chloroformate (2.9 µL, 30 µmol) was added in one portion, and the reaction was stirred for 1 h at 23 °C. The solvents were evaporated under reduced pressure, and the residue was dissolved in 0.5 mL of *tert*-butyl alcohol. Coenzyme A as the sodium salt (23 mg, 30 µmol dissolved in 0.5 mL of 0.4 M $NaHCO_3$) was added to the solution, and the mixture was stirred for 0.5 h at 23 °C, then quenched with dropwise addition of 1 M HCl, and adjusted to pH 3-5. The solvents were evaporated under vacuum, and the residue was dissolved in water (5 mL, pH 5) and loaded onto a C18 silica gel column (10% capped with TMS) that was washed with 100% MeOH (50 mL) and preequilibrated with distilled water (100 mL, pH 5). The sample was washed with water (100 mL, pH 5) and then eluted with 15% MeOH in water (50 mL, pH 5). The fractions containing aroyl CoA, as determined by TLC, were combined, and the solvent was evaporated to yield product (95-99% yield at 95-99% purity, assessed by ^1H NMR) (see Supporting Information).
Synthesis of benzoyl CoA. The product was isolated in >99% yield (99% pure by ^1H NMR). ESI-MS (negative ion mode), *m/z* : 870.1 (M-H) , 434.5 $(M-2H)^2$, 289.3 (M-3H)*3* . ^1H NMR (300 MHz, D_2O) δ: 0.58 (s, H-10'), 0.71 (s, H-11'), 2.27 (t, *J* = 7.2 Hz, H-4'), 2.98 (t, *J* = 7.2 Hz, H-1'), 3.27 (m,

Reaxys – Searched Taxol as a product, limited results to JACS and sorted by Year



Reaxys Search Results

90%

With hydrogenchloride **in** methanol; water
T=-5 - 30°C; 27 h;
Hide Experimental Procedure

Kung, Liang-Rern; Chang, Shih-Sheng; Fang, Tung-Shen; Lin, Shu-Fen; Chang, Cheng-Chang; Chen, Chia-Hui; Hung, Yi-Ting; Cheng, Ming-Ching
Patent: US2012/149925 A1, **2012** ;
Location in patent: Page/Page column 15 ;

Title/Abstract Full Text Show Details

22:
The crude T3 of EXAMPLE 14 in 22.5 mL MeOH was added 0.09 mL 32percent $HCl_{(aq)}$ at -55° C. and then the reaction mixture was stirred for 3 hours. As the reaction temperature was raised to 2030° C., the reaction mixture was stirred for 24 hours until the deprotection was completed. The reaction mixture was dried by rotavapor and then diluted with 40 mL CH_2Cl_2. After washed with 40 mL saturated sodium bicarbonate, the organic layer was dried by rotavapor to obtain the crude. The crude in 10 mL CH_2Cl_2 was slowly added 20 mL n-heptane to let paclitaxel precipitate. After filtration and dried the solid, 7.0 g paclitaxel (yield 90percent, LC purity 95percent) was obtained. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J=7.2 Hz, 2H), 7.75 (d, J=7.2 Hz, 2H), 7.63-7.56 (m, 1H), 7.53-7.47 (m, 5H), 7.43-7.34 (m, 5H), 7.00 (d, J=8.8 Hz, 1H), 6.27 (s, 1H), 6.25 (dd, J=8.0 and 9.2 Hz, 1H), 5.80 (dd, J=2.8 and 9.2 Hz, 1H), 5.68 (d, J=7.2 Hz, 1H), 4.95 (dd, J=1.6 and 9.6 Hz, 1H), 4.80 (dd, J=2.8 and 5.2 Hz, 1H), 4.42-4.37 (m, 1H), 4.31 (d, J=8.4 Hz, 1H), 4.20 (d, J=8.4 Hz, 1H), 3.80 (d, J=7.2 Hz, 1H), 3.58 (d, J=5.2 Hz, 1H), 2.58-2.50 (m, 1H), 2.47 (d, J=4.0 Hz, 1H), 2.38 (s, 3H), 2.36-2.27 (m, 2H), 2.23 (s, 3H), 1.91-1.84 (m, 1H), 1.79 (s, 3H), 1.68 (s, 3H), 1.24 (s, 3H), 1.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 172.7, 171.3, 170.3, 167.07 167.02, 142.0, 137.9, 133.7, 133.6, 133.1, 132.0, 130.2, 129.1, 129.0, 128.7, 128.4, 127.0, 84.4, 81.1, 79.0, 76.5, 75.5, 74.9, 73.2, 72.3, 72.2, 58.6, 55.0, 45.6 43.1 35.68, 35.62, 26.8, 22.6, 21.8, 20.8, 14.8, 9.5.

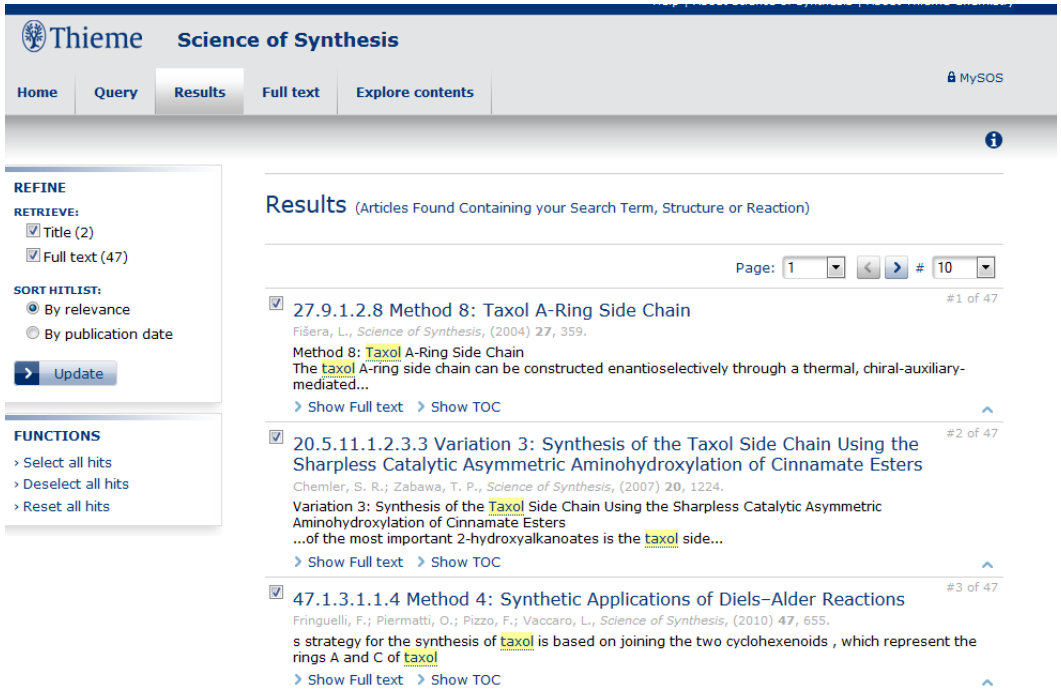
Hide Details

80%

With pyridine hydrogenfluoride **in** tetrahydrofuran
T=25°C; 1.25 h;

Nicolaou; Nantermet; Ueno; Guy
Journal of the Chemical Society - Series Chemical Communications, **1994** , # 3 p. 295 - 296
Title/Abstract Full Text View citing articles Show Details
Nicolaou; Nantermet; Ueno; Guy; Couladouros; Sorensen
Journal of the American Chemical Society, **1995** , vol. 117, # 2 p. 624 - 633
Title/Abstract Full Text View citing articles Show Details

Science of Synthesis Search Results after searching Taxol as a full-text term



Science of Synthesis – first hit in search results

NAVIGATION

Hit 1 of 47

Previous / Next

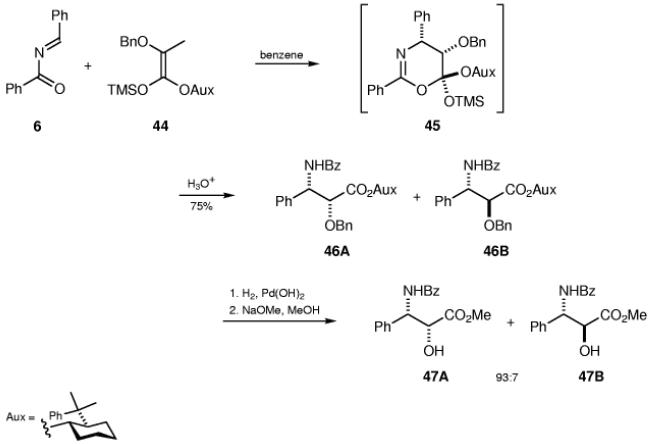
27.9.1.2.8 Method 8: Taxol A-Ring Side Chain

DOI: 10.1055/sos-SD-027-00352

Fišera, L., *Science of Synthesis*, (2004) **27**, 359.

Dihydrooxazines such as **47** can arise from inverse-electron-demand hetero-Diels–Alder reactions. [30] The taxol A-ring side chain can be constructed enantioselectively through a thermal, chiral-auxiliary-mediated variant of this cycloaddition. [31] Chiral-auxiliary-modified ketene acetal **44** and *N*-acylimine **6** are combined at room temperature to give a mixture of *cis*/*trans*-dihydrooxazine **45**, which are not isolated. After aqueous acid workup of the cycloaddition mixtures, *syn*- and *anti*-diastereomers **46A** and **46B** are obtained in a 75% combined yield. For the removal of the chiral auxiliary, the mixture of **46A** and **46B** is sequentially debenzylated by catalytic hydrogenation (quantitative) and transesterified with sodium methoxide in methanol (82%) to afford the taxol A-ring side chain methyl ester **47A** and the analogous *anti*-methyl ester diastereomer **47B** in a ratio of 93:7 (**Scheme 18**).

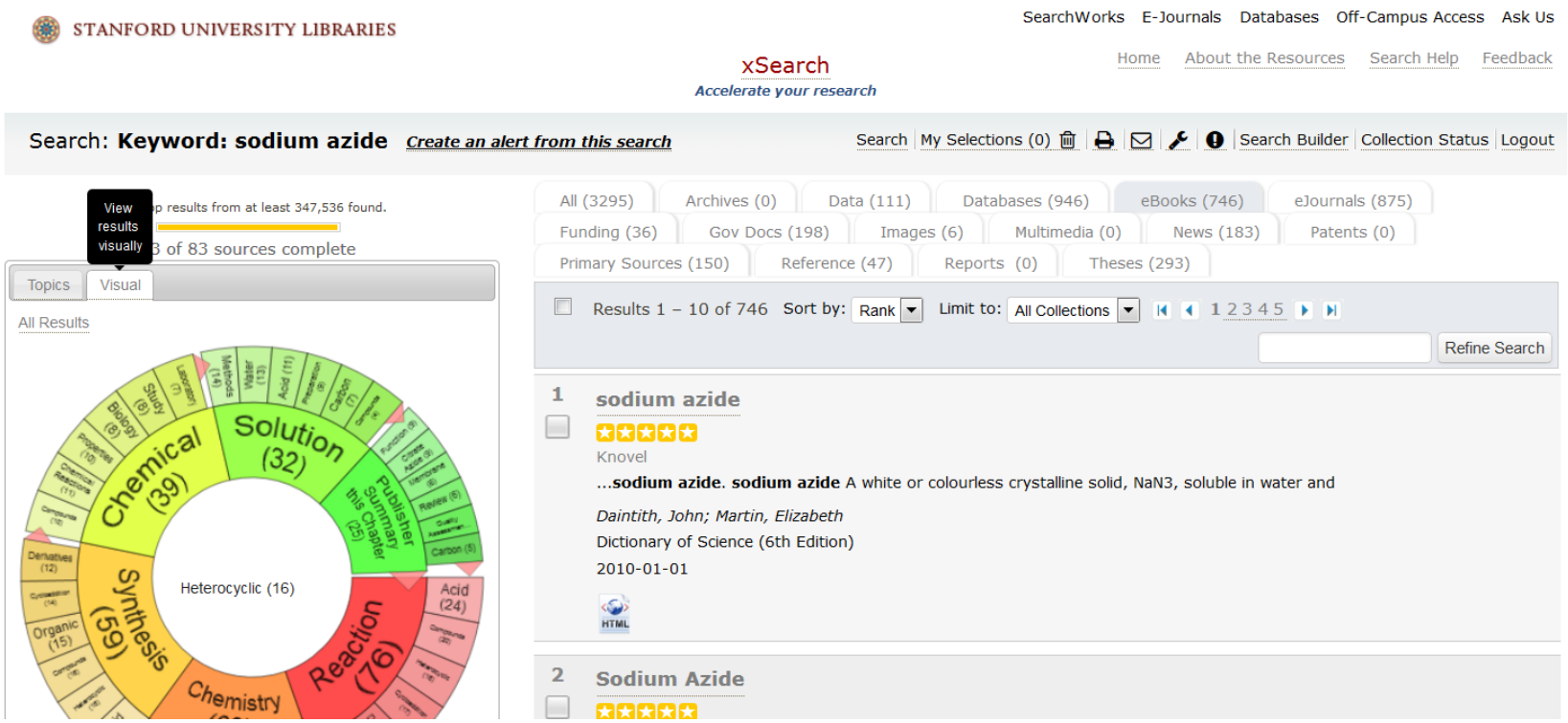
Scheme 18 Preparation of Taxol A-Ring Side Chain [31]



References

[30] Weinreb, S. M.; Scola, P. M., *Chem. Rev.*, (1989) **89**, 1525.
[31] Swindell, C. S.; Tao, M., *J. Org. Chem.*, (1993) **58**, 5889.

xSearch – Toxicology and Chemical Safety



xSearch Results on Sodium Azide cont.

Committee on Prudent Practices for Handling, Storage, and Disposal of Chemicals in Laboratories, National Research Council
Prudent Practices in the Laboratory - Handling and Disposal of Chemicals
1995-01-01

HTML

3

sodium azide

Knovel

...S47Last Update: Jan. 1999 **sodium azide** NaN3 N3Na Mol. Wt.: 65.01 CAS Registry No.: 26628-22-8 Synonyms: Nemazyd; Smite EINECS No.: 247-852-1 RTECS No.: VY 8050000 Uses In organic syntheses. Preparation of hydrazoic acid, lead **azide**, pure **sodium**. Differential selection of bacteria. Preservative. Propellant for automotive safety bags. Nematicide. Herbicide. Physical...

Gangolli, S.
Dictionary of Substances and Their Effects (DOSE, 3rd Electronic Edition)
2005-01-01

HTML

4

Sodium Azide

Knovel

...Substances Fact Sheet: **Sodium** Arsenite, Trenton, NJ (March 2002) **Sodium azide** S:0390 Molecular Formula: N3Na Common Formula: NaN3 Synonyms: AI3-50436; Axium; Azida sodico (Spanish); **Azide**; Azium; Azoture de **sodium** (French); Dazoe; Hydrazoic acid, **Sodium** salt; Kazoe; Natriumazid (German); NCI-C06462; Smite; **Sodium** salt of hydrazoic acid CAS Registry Number: 26628-22-8;...

Pohanish, Richard P.
Sittig's Handbook of Toxic and Hazardous Chemicals and Carcinogens (5th Edition)
2008-01-01

xSearch – Tentative List of Resources

ACToR (Aggregated Computational Toxicology Resource)

CAMEO Chemicals

Canadian Centre for Occupational Health and Safety. Web Information Service.

Chemical Safety Database

ChemID Plus Advanced

e-EROS : Encyclopedia of Reagents for Organic Synthesis - Chemical Name

Emergency Response Safety and Health Database

Hazardous Substances Data Bank

INCHEM

International Chemical Safety Cards (ICSC) database

Knovel

MSDSonline

NIOSH Pocket Guide to Chemical Hazards

Organic Reactions

Organic Syntheses

PubChem - Compound Search

Science of Synthesis

WebWISER-Known Substance List

Lab Safety Research Guide

Home
Training
Safety culture
Prudent practices
* Personal protection
* Electrical safety
* Laser safety
* Lab design

Handling & storage
* Standard operating procedures
* Biological materials
* Hazardous substances
* Reactive substances
* Reagents & solvents
* Nanomaterials
* Waste management
* Spills & emergencies
* Lessons learned

Undergrad lab safety
Websites (Organizations)
Find chemical safety data
Find reactions & protocols
Find safety articles & books
About using this guide

More resources

- **Lab Safety Research Guide: http://library.stanford.edu/guides/lab-safety**
- **The Safety Zone by C&EN: http://cenblog.org/the-safety-zone/**
- **ACS Division of Chemical Health & Safety: http://www.dchas.org/**
- **ACS Committee on Chemical Safety: http://www.acs.org/content/acs/en/about/governance/committees/chemicalsafety.html**
- **ACS Committee on Professional Training: http://www.acs.org/content/acs/en/about/governance/committees/training.html**

Acknowledgements

Stanford Environmental Health and Safety

Stanford Chemistry Department Safety Committee and

Chemistry Department Lab Group Safety Coordinators