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Functional Groups

X—C≡X, X=C=X, X₂C=X, CX₄ Compounds

Nitriles, Isocyanides, and Derivatives

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Amides and Derivatives, Peptides, Lactams

Thio-, Seleno-, and Tellurocarboxylic Acids, Imidic Acids, Ortho Acids

Ketenes

Ketene Acetals, Yne—X Compounds

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Heteroatom Analogues of Aldehydes and Ketones

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Fused Five-Membered Hetarenes with One Heteroatom

Five-Membered Hetarenes with One Chalcogen and One Additional Heteroatom

Five-Membered Hetarenes with Two Nitrogen or Phosphorus Atoms

Five-Membered Hetarenes with Three or More Heteroatoms

Six-Membered Hetarenes with One Chalcogen

Six-Membered Hetarenes with One Nitrogen or Phosphorus Atom

Six-Membered Heteroatom Analogues

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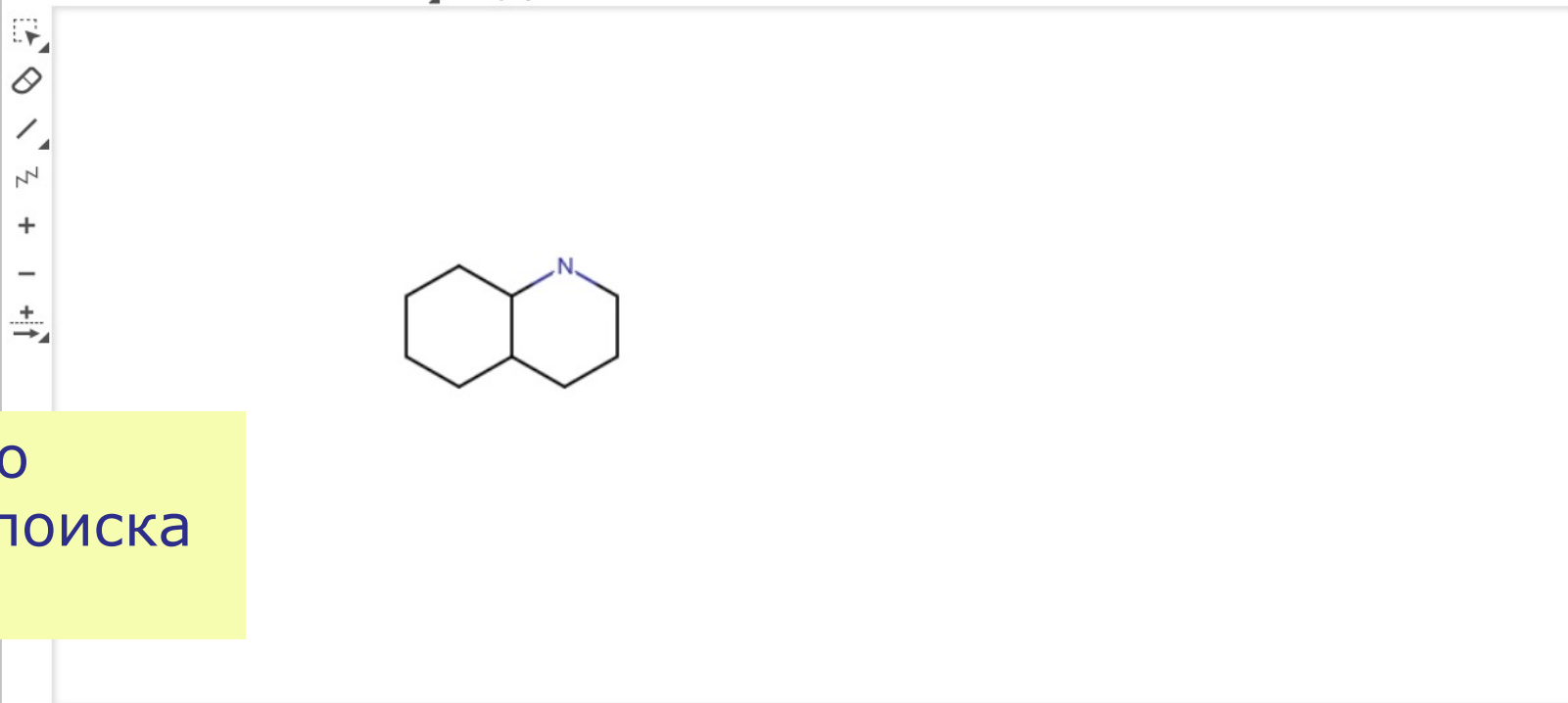
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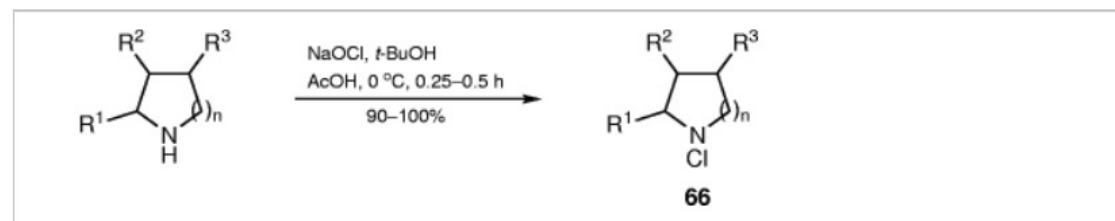
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40.4.2.1.5.2 Variation 2: From Azacyclanes Using Hypochlorites

Wille, U., *Science of Synthesis*, (2009) 40, 917.

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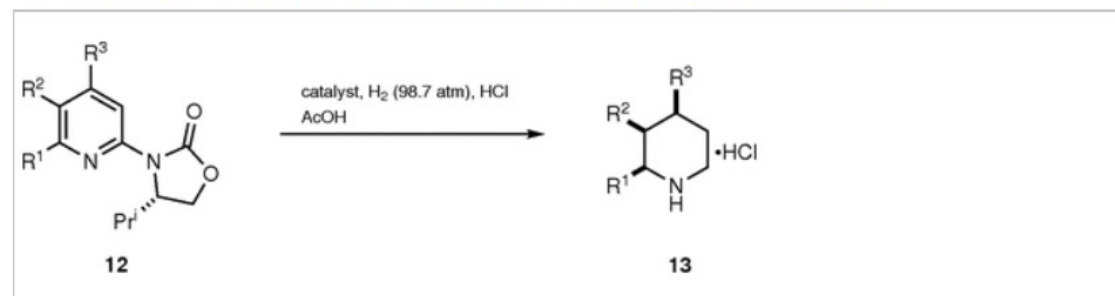
 Reduction of Hetarenes

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1.4.1.3 Reduction of Pyridine Derivatives

Chen, Z.-P.; Zhou, Y.-G., *Science of Synthesis: Catalytic Reduction in Organic Synthesis*, (2017) 1, 157.

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Kikelj, D.; Urleb, U., *Science of Synthesis*, (2002) **11**, 627.Product Class 17: **Thiazoles****Thiazoles** and Their Reduced FormsHantzsch was the first to firmly establish **thiazoles** as the products obtained from reactions between thiourea and ...of **thiazoles**...
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 Thiazoles (Update 2010) #2 of 395
11.17.6 Thiazoles (Update 2010)
Koutentis, P. A.; Ioannidou, H. A., *Science of Synthesis Knowledge Updates*, (2010) **1**, 267.**Thiazoles** (Update 2010)The present review covers the synthesis and modification of aromatic **thiazoles**, e.g. of heterosubstituted **thiazoles** (**Thiazoles** and Their Tautomeric Forms...**thiazoles**...
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 4,5-Dihydroglycopyranoso[2,1-d]-1,3-thiazoles #3 of 395
29.14.5 Product Subclass 5: 4,5-Dihydroglycopyranoso[2,1-d]-1,3-thiazoles
Turnbull, W. B.; Fascione, M. A.; Stalford, S. A., *Science of Synthesis*, (2007) **29**, 932.]-1,3-**thiazoles**]-1,3-**thiazoles** and -oxazoles
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11.17.4 Synthesis from Other Thiazoles


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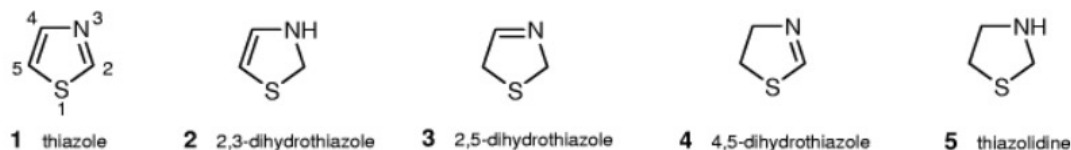
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11.17 Product Class 17: **Thiazoles**

DOI: 10.1055/sos-SD-011-00783

Kikelj, D.; Urleb, U., *Science of Synthesis*, (2002) **11**, 627.**General Introduction**

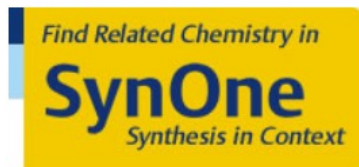
IUPAC uses the name 1,3-thiazole, for the heterocycle **1**, although the term thiazole is recommended by CAS and more commonly used. Very early on Greek letters were employed to assign the atoms in the thiazole ring,^[1] but this system has long since disappeared in favor of a conventional numbering system. All three dihydrothiazoles (thiazolines) **2**, **3**, and **4** are known. Thiazolidine (**5**) is also known as 2,3,4,5-tetrahydrothiazole (**Scheme 1**).

Scheme 1 **Thiazoles** and Their Reduced Forms

Hantzsch was the first to firmly establish **thiazoles** as the products obtained from reactions between thiourea and α -halo carbonyl compounds,^[2] although earlier claims for these compounds had been made.^[3] The history of thiazole has been reviewed^[4] and there are several excellent surveys which deal with the recent chemistry of **thiazoles**.^[4–10]

Although thiazole itself is not found in nature, the thiazole ring occurs in a number of natural products including peptide alkaloids and cyclopeptides incorporating unusual amino acids. Some exhibit important antibiotic^[11–13] and antifungal properties;^[14] in addition, antineoplastic and cytotoxic activity^[15] is shown by thiazole natural products isolated from marine species. Cyclopeptides incorporating thiazole and dihydrothiazole rings also have cytotoxic activity and several total syntheses of these compounds have been described.^[16] Related natural products include powerful cell growth inhibitor,^[17,18] and others that have an unusual mechanism of interaction with microtubules.^[19–25]

The most important natural product containing a thiazole ring is thiamine (vitamin B₁, **6**) (**Scheme 2**). Its mode of action may involve ylide intermediates.^[26] Conformational analyses of some thiamine-related compounds have also been reported.^[27]

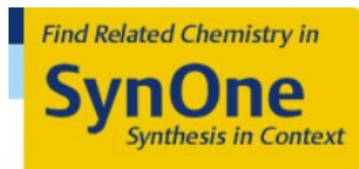


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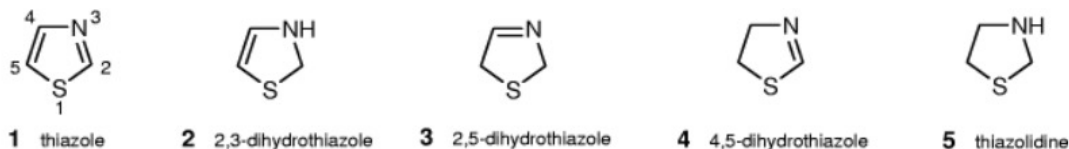
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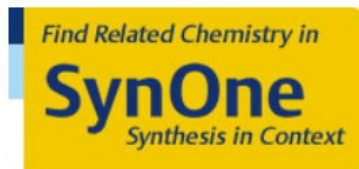
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11.17.3.1 Method 1: By Dehydration and Dehydroamination of Dihydrothiazoles

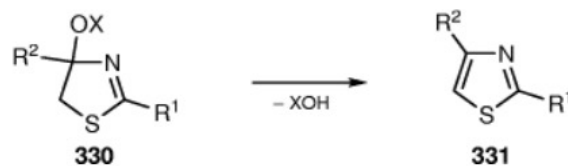
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Kikelj, D.; Urleb, U., *Science of Synthesis*, (2002) **11**, 725.

Many ring cyclizations, which occur under mild reaction conditions, first give dihydrothiazoles having a leaving group (e.g., hydroxy, amino) frequently bound to C4 or C5. ^[319–321,704] Normally such products undergo ready elimination to form **thiazoles**, but sometimes this is not the case and then thermolysis, or treatment with acids, is required. For example, the aromatization of thiazol-3(2H)-amine under acidic reaction conditions (2 M H₂SO₄) gives the corresponding **thiazoles** in moderate yields. ^[400] When chiral substituents are present and the rate of acid-catalyzed aromatization is slow racemic products may form. ^[705]

The dehydration step in the synthesis of 2-substituted **thiazoles** **331** (X = H) from the corresponding 4,5-dihydrothiazol-4-ols **330** is accomplished by reaction with thionyl chloride, sulfuryl chloride, phosphoryl chloride, phosphorus trichloride, or phosphorus pentachloride, ^[706] together with many other reagents (**Scheme 128**). ^[319,363,704,707–710] 4-Alkoxy-4,5-dihydrothiazoles **330** (X = alkyl) also give **thiazoles** by the elimination of the appropriate alcohol. ^[105,363]

Scheme 128 Aromatization of 4,5-Dihydrothiazoles by the Elimination of a C4 Hydroxy or Alkoxy Group ^[105,305,363,704,707–710]



R ¹	R ²	OX	Reagent	Solvent	Temp, Time	Yield ^a (%)	mp or bp ^a (°C)/Torr	Ref
OPh	H	OEt	TsOH	DMF	125–130°C, 10 min	96	84–85/1	[363]
CH ₂ NMe ₂	CH ₂ Cl	OH	SOCl ₂	ClCH ₂ CH ₂ Cl	65–70°C, 30 min	76 ^b	139–141	[706]

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