REWIEW ARTICLE

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Utility of cyclohexanethiols in organic synthesis

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Abstract: Publications on the preparations of cyclohexanethiols and its reactions are reviewed for the first time.

Keywords: Cyclohexanethiols; disulphides; displacement reactions

CONTENT

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General information

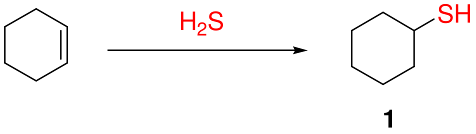
Cyclohexanethiol commonly named cyclohexyl mercaptan used as starting material for manufacture of biologically active compounds such as inhibitors of prostaglandin and leukotriene; canine COX-2 inhibitors; phosphodiesterase inhibitors, …etc. In the present article the methods for the production of cyclohexanethiol and its reactions are reviewed. The main purpose of this review is to present a survey of the literature on cyclohexanethiol chemistry till mid 2008.

1. Synthesis

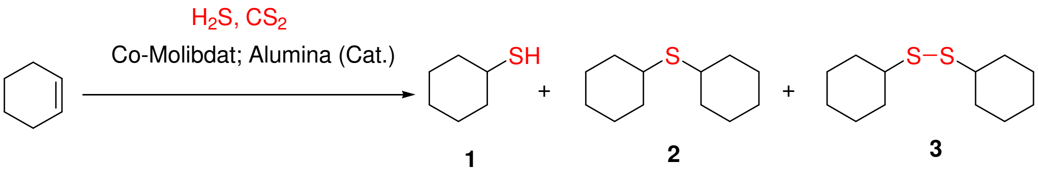
1.1. Synthesis of cyclohexanethiol

1.1.1. From cyclohexene

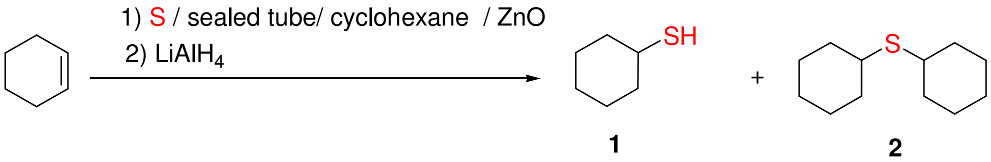
Cyclohexanethiol **1** was prepared by Markovnikov addition of hydrogen sulfide to cyclohexene.[1]



Cyclohexene react with hydrogen sulphide and carbon disulphide (as a promoter) over Co molybdate on alumina to give 70.6-93.7% conversion to products containing 62.5-69.4% cyclohexanethiol **1** and small amounts of cyclohexyl sulfide **2** and disulfide **3**. Without carbon disulphide, the conversion was 24.6-85.3% with 22.6-75.8% content of **1.**[2, 3]

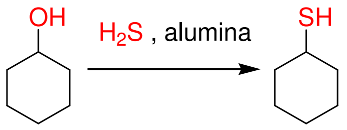


Cyclohexene was treated with sulfur at 140°C in sealed tube in the presence of cyclohexane and, optionally, zinc oxide. The products were reduced to **1** and monosulfide **2** with $LiAlH_4$, the yield of cyclohexanethiol **1** depended on the amount of zinc oxide and the reaction time.[4]



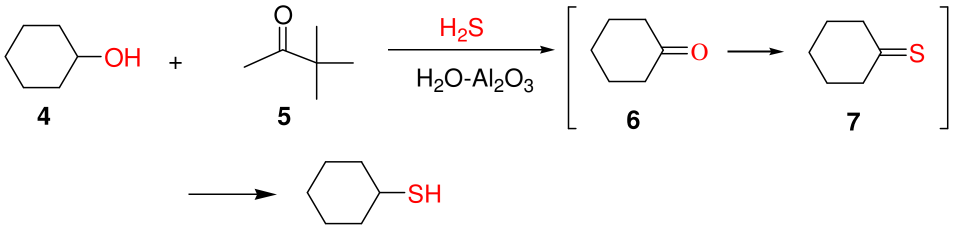
1.1.2. From cyclohexanol

Cyclohexanol **4** was converted into cyclohexanethiol **1** by treatment with hydrogen sulfide in the presence of a catalyst blend containing a hydrotreating catalyst and a dehydration catalyst (e.g., alumina). The mercaptan product contains <30% unreacted alcohol.[5]



4 1

The thiolation of cyclohexanol **4** with hydrogen sulphide in the presence of pinacolone **5** and a H_2O-Al_2O_3 catalyst gives thiol. The increased yield of cyclohexanethiol **1** involves 3 consecutive reactions: (1) H transfer from **4** to **5**, (2) thiolation of cyclohexanone **6** to cyclohexanethione **7**, and (3) H transfer from **4** to the thione **7** with formation of **1**.[6]

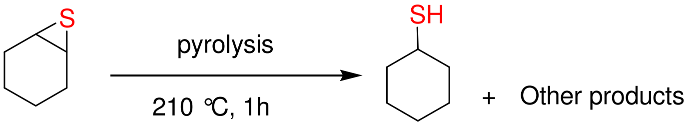


4 5 6 7

1

1.1.3. From 1,2-epithiocyclohexane

Cyclohexanethiol **1** was obtained, in 6% yield, by the pyrolysis of 1,2-epithiocyclohexane **8** at 210°C for 1h.[7]



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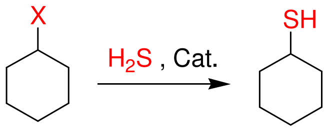
1.1.4. From cyclohexyl halide

Cyclohexanethiol **1** was prepared from cyclohexyl halide by reaction with hydrogen sulfide in presence of ammonia[8] or $Pd(OAc)_2$/(1-dicyclohexylphosphino-2-(1-di-tert-butylphosphino)ethyl)ferrocene (Josiphos) as catalyst.[9]



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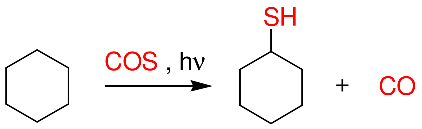
1.1.5. By photolysis

Photolysis of carbonyl sulfide (COS) in cyclohexane afforded cyclohexanethiol **1**.[10]



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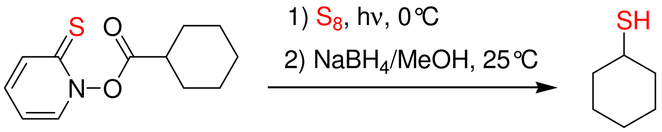
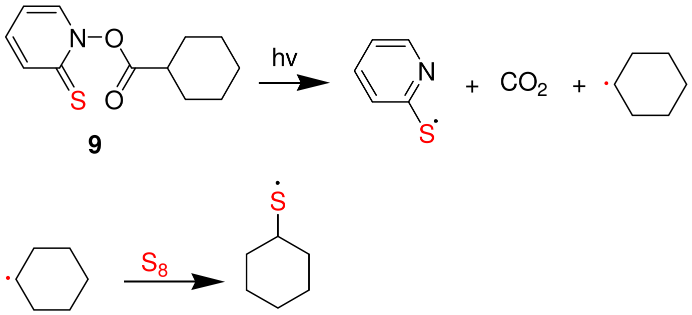
Photolysis of N-hydroxy-2-thiopyridone ester (Barton ester) **9** utilizing carbon radicals and elemental sulfur (NaBH$_4$/MeOH/sulfur) gave cyclohexanethiol **1** 94%.[11]



9 1

The free radical mechanism involve initiation resulted from the irradiation of the Barton PTOC ester causing homolysis of the oxygen-nitrogen bond affording the alkyl radical), carbon dioxide and the thiopyridyl radical. The mechanism include propagation steps, the key step is the reaction of a carbon-centered radical with S$_{8.}$[11]



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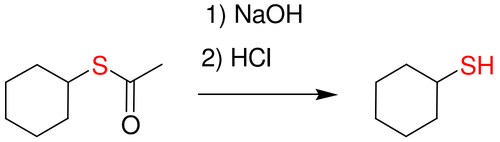
1.1.6. By hydrolysis of cyclohexyl thiolacetate

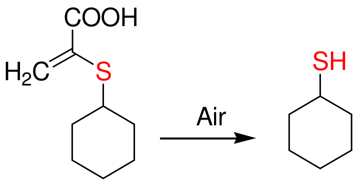
Hydrolysis of cyclohexyl thiolacetate **10** with sodium hydroxide, and acidification gave cyclohexanethiol **1** in 81% yield.[12]



10 1

1.1.7. By decomposition of 2-(cyclohexylthio)acrylic acid

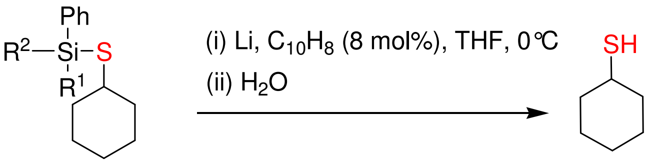
Decomposition of 2-(cyclohexylthio)acrylic acid **11** in air afforded cyclohexanethiol **1.** [13]



11 **1**

1.1.8. From silyl protected thiol

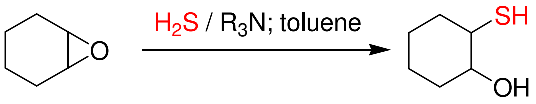
The reaction of silyl protected thiol **12** with lithium powder and a catalytic amount of naphthalene, in THF, led, after hydrolysis, to the recovery of the free cyclohexanethiol **1** in 51% yield. At least a Ph group was required in the silyl protecting group for the success of the reaction.[14]



12 **1**

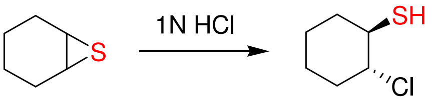
1.2. Synthesis of *O*-substituted cyclohexanethiols

2-Mercaptocyclohexanol **14** was prepared, in 86% yield, by treating a small excess of hydrogen sulphide with a 1,2-epoxycyclohexane **13** in the presence of a trialkylamine of basic ionization constant 10-3 to 10-7 at 0-150°C in toluene.[15]



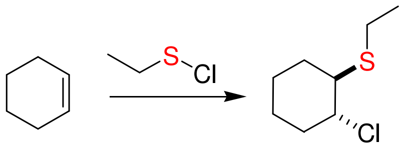
13 **14**

Trans-2-chlorocyclohexanethiol **16** was obtained by treatment of cyclohexane episulfide **15** with 1N HCl.[16]



15 **16**

Addition of ethylsulfenyl chloride to cyclohexene gave trans-1-chloro-2-ethylthiocyclohexane **17**. Passage of trans-2-acetylthiocyclohexanol **18** across silicon dioxide gave trans-2-acetoxycyclohexanethiol **19.**[16]



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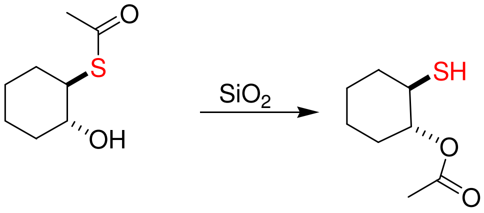
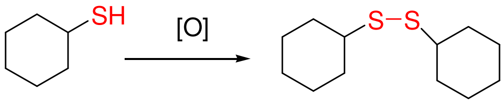


18 **19**

2. Application of cyclohexathiols in organic synthesis

2.1. Oxidation to disulphides

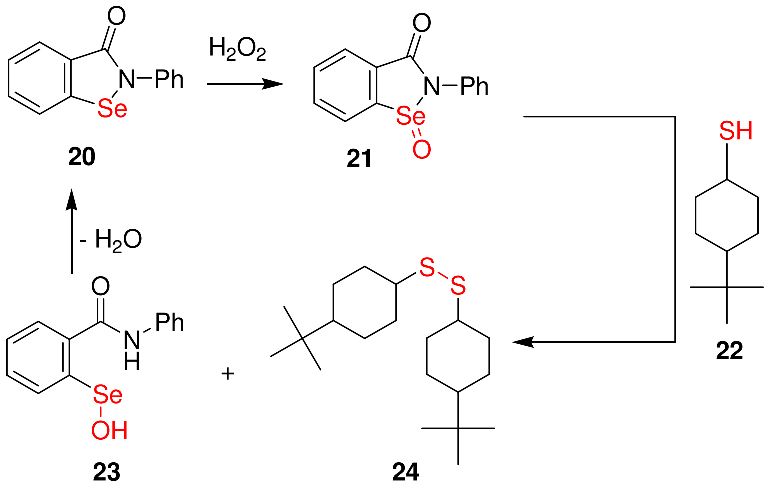
Cyclohexanethiol **1** was oxidized into the corresponding disulphide **10** by using different catalysts such as tetramethylammonium fluorochromate[17]; Ni-nanoparticles [18]; permanganates[19], ferric chloride[20], hydrogen peroxide[21], halogens[22], and bis(trimethylsilyl) chromate (BTSC) in acetonitrile.[23] tributylammonium chlorochromate[24]; tungstate sulfuric acid in combination with various oxidants[25]; Silica chloride catalyst[26]; tribromoisocyanuric acid (TBCA) and Oxone-MX systems[27]; 1,3-dibromo-5,5-dimethylhydantoin (DBDMH)[28]; 1,4-Diazabicyclo[2.2.2]octane-di-N-oxide-di-perhydrate[29]; γ-picolinium chlorochromate and its silica gel supported[30]; aerobic oxidation catalyzed by trichlorooxyvanadium in the presence of mol. sieves 3A[31]; ammonium dichromate in the presence of silica chloride and wet SiO_2 in solution[32]; quinolinium fluorochromate (QFC) on silica-gel[33]; Ti(IV) catalyst as $TiCl_3(O_3SCF_3)$ and $TiO(O_2CCF_3)_2$[34]; $(NO_3)_3CeBrO_3$ in boiling aceteonitrile[35]; Benzyltriphenylphosphoniumperoxymonosulfate[36]; ammonium persulfate[37]; pyridinium chlorochromate[38]; DMSO and chromatog. neutral alumina[39]; $Cu(NO_3)_2.N_2O_4$[40]; bromine[41]; ethylenebis(N-methylimidazolium)chlorochromate (EBMICC)[42]; quinolinium tribromide (QTB) or molybdate sulfuric acid (MSA)[43, 44], potassium permanganate supported on alumina under solvent-free conditions[45]; benzyltriphenylphosphonium peroxodisulfate (BTPPD)[46, 47], hexamethyldisilazane (HMDS) in DMSO[48], hydrogen peroxide in the presence of a catalytic amount of NaI or iodine[21], Fe(III) / NaI in the presence of air[20], trimethylchlorosilane (TMSCl) and cyanuric chloride (CC)[49], cationic rhodium(I)/PPh_3 complex-catalyzed $[Rh(cod)_2]BF_4/8PPh_3$[50], 2,6-dicarboxypyridiniumchlorochromate[51], SO_2Cl_2[52], Bismuth(III)nitrate pentahydrate $Bi(NO_3)_3{\cdot}5H_2O$[53], urea- hydrogen peroxide (UHP)and maleic anhydride as mediator[54], sodium periodate (10%)[55], molecular oxygen in subcritical water[56], trichloronitromethane[57], iodine in wet acetonitrile[58], tetramethylammonium chlorochromate[59], N-Bromophthalimide (NBPI)[60], o-xylylenebis(triphenylphosphonium tribromide)[61], Mn(III)-salophen in the presence of urea hydrogen peroxide[62], 3-carboxypyridinium trichloroacetatochromate (CPTCAC)[63], N-bromosaccharin under microwave irradiation[64], tetramethylammonium fluorochromate.[65]



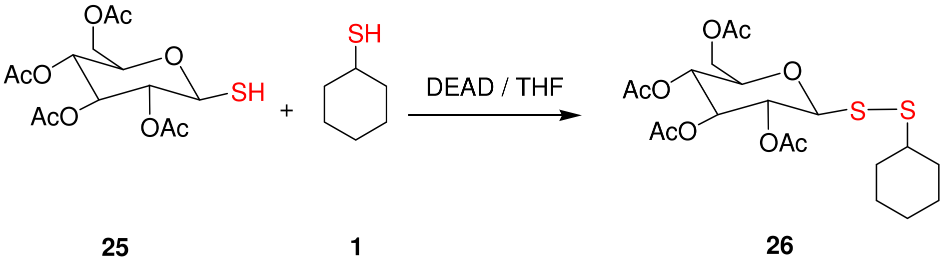
1 **10**

On the other hand, dicyclohexyldisulfide **10** can be prepared also by reaction of chlorocyclohexane with sodium sulfide.[66]

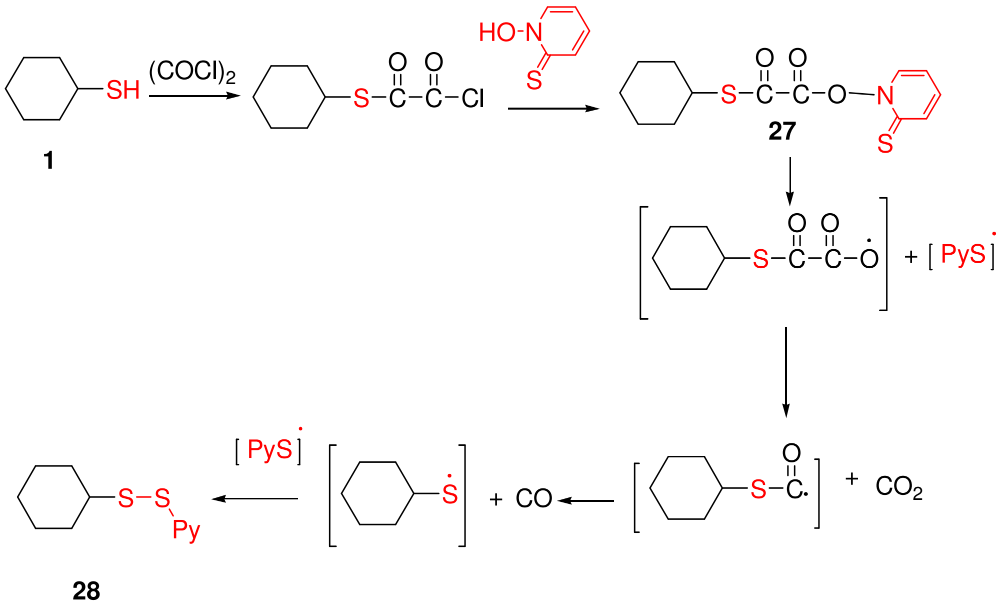
The selenium heterocycle 2-phenyl-1,2-benzisoselenazol-3(2H)-one, **20** (Ebselen, PZ **51)** is a remarkably good catalyst for the oxidation of thiol to disulphide by hydroperoxides. Ebselen **20** is readily oxidized to the corresponding oxide **21** by hydrogen peroxide. The rapid reactions of Ebselen oxide **21** with thiol **22** have been reported to give Ebselen hydroxide **23** and the corresponding disulfide **24** in 86% yield.[67]



One-pot synthesis of glycosyl disulfide **26**, in 46% yield, using diethyl azodicarboxylate (DEAD) was carried out starting from cyclohexanethiol **1** and 1-thiosugar **25**.[68]

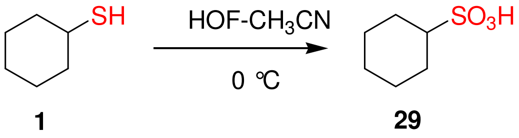


Barton's method, which is a radical decarboxyaltion reaction of thiohydroxamic ester (O-acyl derivatives of N-hydroxy-2-thiopyridone) **27** prepared from carboxylic acid chlorides and N-hydroxy-2-thiopyridine, can be used in the synthesis of disulphide **28** in 40% yield.[11]



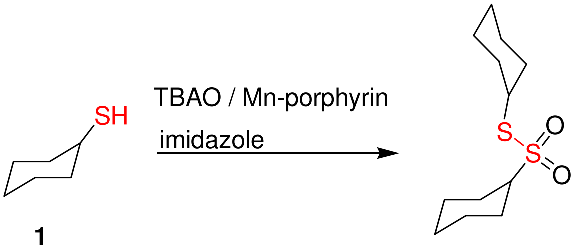
2.2. Oxidation to sulfonic acid

Sulfonic acids serve as important molecules in organic chemistry. For example, the sulfonic group, in either its acidic or salt form, is capable of solubilizing substances in water thus increasing their usefulness especially in the organic dye industry.[69] These acids are also frequently used as catalysts in organic chemistry, for instance, in esterification of amino acids and peptides.[70, 71] Most aliphatic sulfonic acids are made by oxidation of thiols.[72-74] Therefore, cyclohexanethiol **1** was oxidized to the corresponding sulfonic acid **29**, in 96% yield, using HOF-CH_3CN. The HOF-CH_3CN complex, easily prepared by bubbling dilutes fluorine through aqueous acetonitrile.[75]



2.3. Oxidation to thiosulfonate

The immediate oxidation of cyclohexanethiol **1** using tetrabutylammonium peroxymonosulfate (TBAO) in the presence of manganese meso-tetraphenylporphyrin (Mn-porphyrin) and imidazole gave thiosulfonate **30** in 93% yield. The molar ratio for thiol/TBAO/Im/Mn(TPP)OAc is 100:150:40:1.[76]



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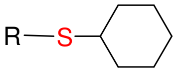
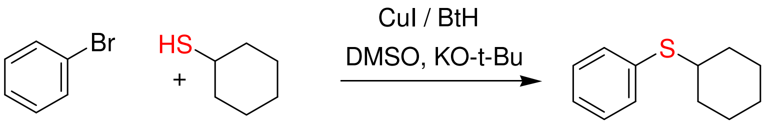
2.4. Coupling with aryl halides

Reaction of cyclohexanethiol **1** and borohydride exchange resin (BER) with alkyl halides or epoxides in methanol affords unsymmetrical sulfides **31** (R = alkyl, cycloalkyl, aryl).[77]



31

Copper-catalyzed coupling of bromobenzene with cyclohexanethiol using benzotriazole (BtH) as ligand produces cyclohexyl(phenyl)sulfane **32** in 98% yield.[78]



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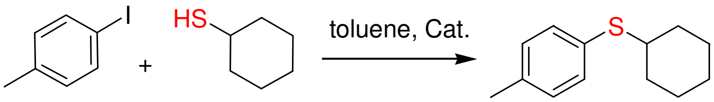
32

Cyclohexyl(p-tolyl)sulfane **33** was prepared in 94% yield by coupling of cyclohexanethiol **1** with 1-iodo-4-methylbenzene in toluene in the presence of bases, CuI and 2,9-dimethyl-1,10-phenanthroline (neocuproin) or Co-Catalyst.[79, 80]



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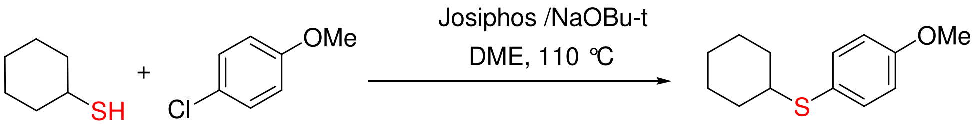
33

$Pd(OAc)_2$/(1-dicyclohexylphosphino-2-(1-di-tert-butylphosphino)ethyl)ferrocene (Josiphos) catalyzed coupling reaction of cyclohexanethiol **1** with 4-chloroanisole in the presence of NaOBu-*t* base in DME at 110 °C gave 98% cyclohexyl(4-methoxyphenyl)sulfane **34**.[9]



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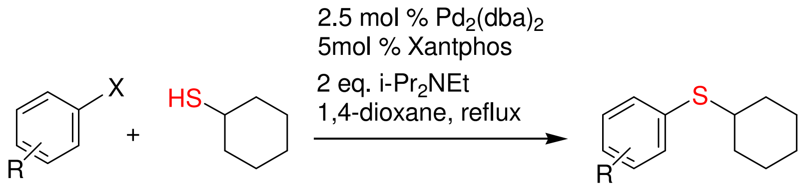
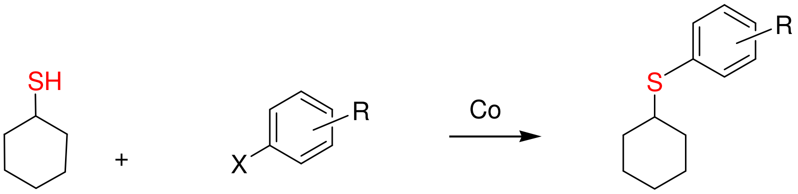
34

Palladium-catalyzed carbon-sulfur bond formation was performed with the reaction of aryl bromides, triflates, and activated aryl chloride, and cyclohexanethiol **1** to afford thioether **35**.[81, 82]



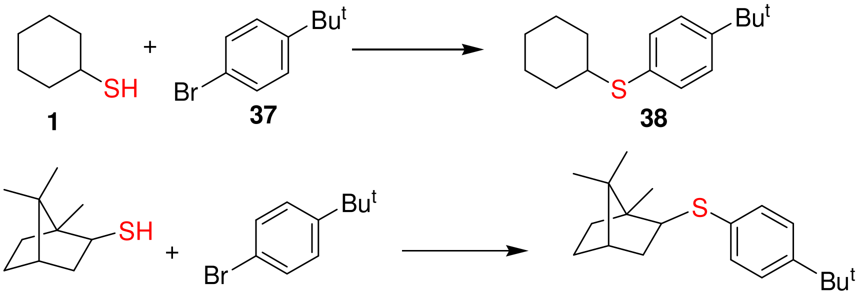
1 **35**

A cobalt-catalyzed coupling of aryl halides with cyclohexanethiol **1** was reported to give a variety of aryl sulfides **36** in excellent yields under mild reaction conditions.[83]



1 **36**

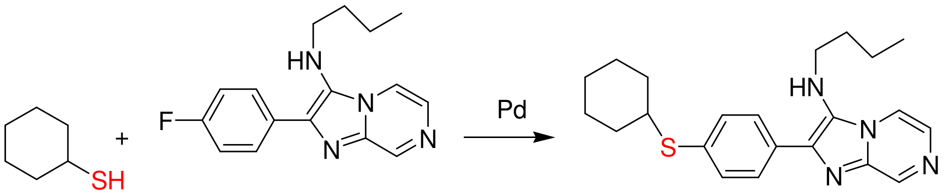
The cross-coupling of cyclohexanethiol **1** and 1-tert-butyl-4-bromobenzene **37** mediated by a $Pd_2(dba)_3$/Xantphos catalytic system in refluxing xylene (140°C) afforded the corresponding aryl thioethers **38** and **39** in 94 and 59 % yields respectively.[84]



1 **37** **38**

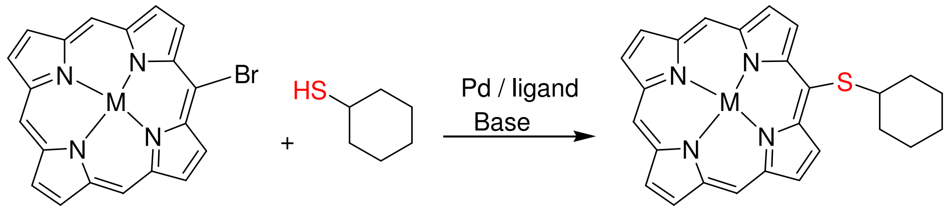
39

Microwave Pd-catalyzed cross-coupling reaction cyclohexanethiol with N-butyl-2-(4-fluorophenyl)imidazo[1,2-*a*]pyrazin-3-amine **40** afforded N-butyl-2-(4-(cyclohexylthio)phenyl)imidazo[1,2-*a*]pyrazin-3-amine **41**.[85]



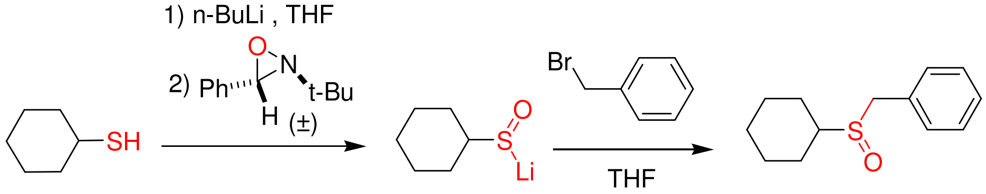
1 **40** **41**

Porphyrins are a unique class of heteroaromatic macrocycles that have found wide applications in many fields, including catalysis, medicine, and materials.[86] In addition to diverse characteristics resulting from versatile metal coordination ability of the central nitrogen core, the physical, chemical, and biological properties of porphyrins can be systematically regulated through introduction of peripheral substituents having varied electronic, steric, and conformational environments.[85] Thus, cyclohexyl sulfanyl-substituted porphyrin **43** was efficiently synthesized from direct reactions of *meso*-brominated porphyrin **42** with cyclohexanethiol **1** via palladium-mediated C-S bond formation (M = H_2 or Zn).[87]



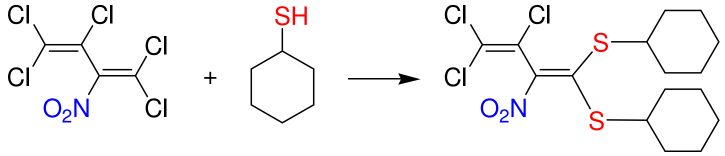
42 **1** **43**

Cyclohexanethiol **1** was efficiently converted into the corresponding sulfenate **44**, in 42% yield, by smooth oxidition with trans-(±)-2-tert-butyl-3-phenyloxaziridine at room temperature. Subsequent electrophilic quench with benzyl bromide led to sulfoxide **45**.[88]



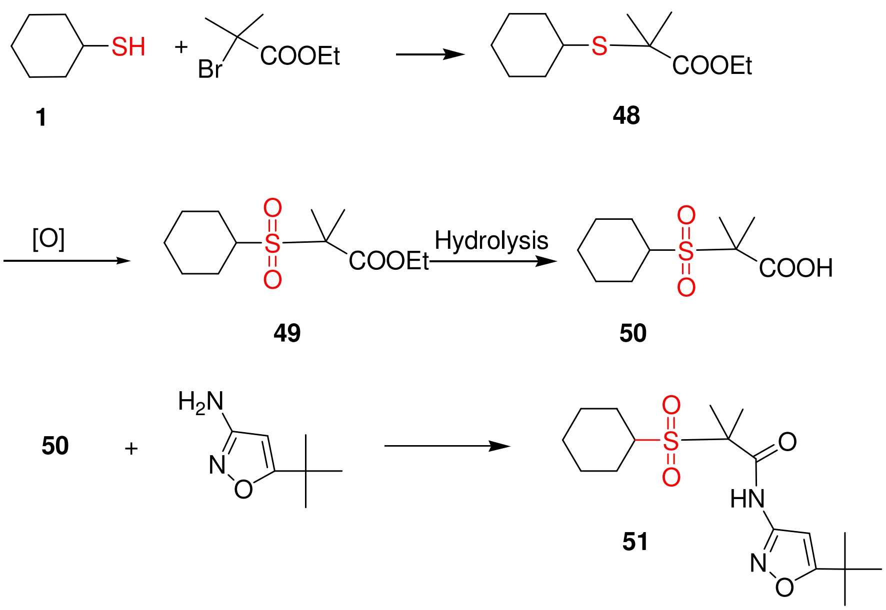
1 **44** **45**

1,1,2,4,4-Pentachloro-3-nitrobuta-1,3-diene **46** reacts with cyclohexanethiol **1** to yield dithioacetal **47**.[89]

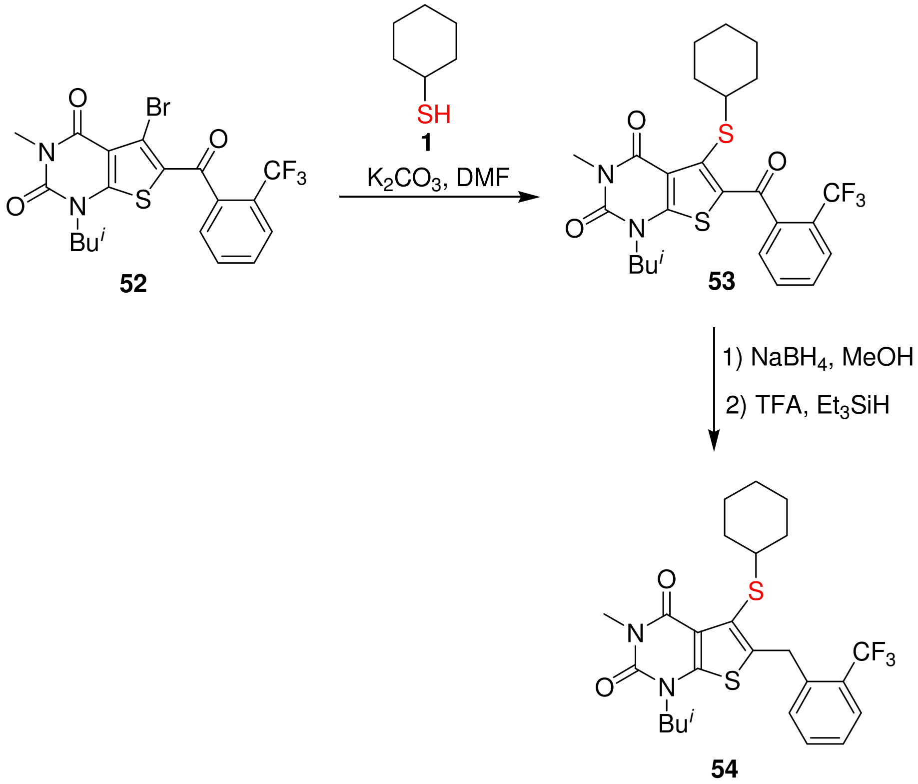


46 **1** **47**

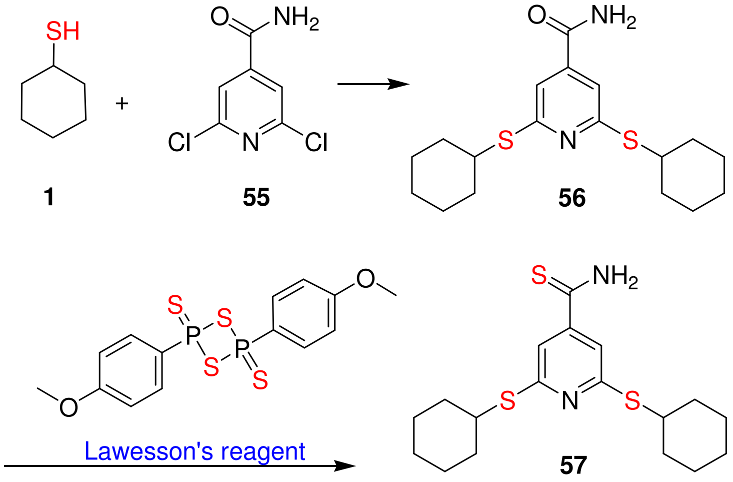
Substitution of ethyl α-bromoisobutyrate with cyclohexanethiol **1** afforded 2-cyclohexylsulfanyl-2-methylpropionic acid ethyl ester **48**, which underwent oxidation to give 2-cyclohexylsulfonyl-2-methylpropionic acid ethyl ester **49**. Hydrolysis of the later ester **49** gave 2-cyclohexylsulfonyl-2-methylpropionic acid **50**, which underwent amidation with 3-amino-5-*tert*-butylisoxazole to give 2-sulfonyl carboxamide **51** which modulate the CB_2 receptor.[90]



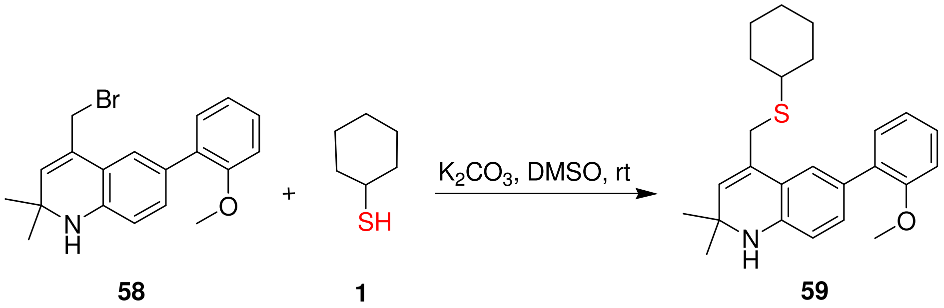
When 6-(2`-trifluromethyl)benzoyl-5-bromo-1,3-dimethylthieno[2,3-d]pyrimidine-2,4(1*H*,3*H*)-dione **52** was treated with cyclohexanethiol **1** afforded 6-2`-trifluromethyl)benzoyl-5-(cyclohexylthio)-1,3-dimethylthieno[2,3-*d*]pyrimidine-2,4(1H,3H)-dione **53** which then reduced with sodium borohydride followed by reduction with TFA and triethylsilane to give 6-(2-(trifluoromethyl)benzyl)-5-(cyclohexylthio)-1,3-dimethylthieno[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dione derivative **54** in 90% yield**.**[91]



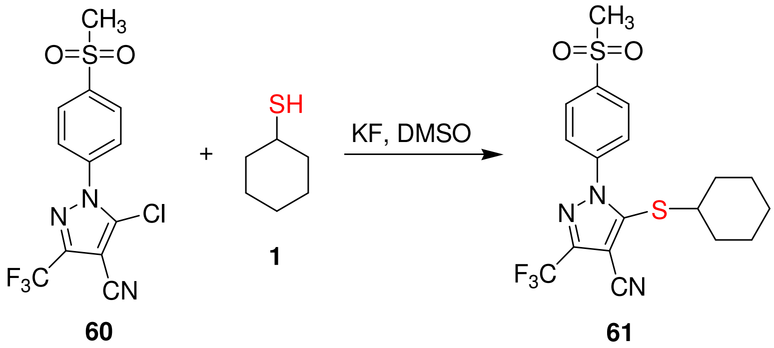
2,6-Bis(cyclohexylthio)-4-pyridinecarboxamide **56** was prepared by treatment of 2,6-dichloro-4-pyridinecarboxamide **55** with cyclohexanethiol **1**. Subsequent reaction with Lawesson's reagent gave the corresponding thioamide **57**.[92]



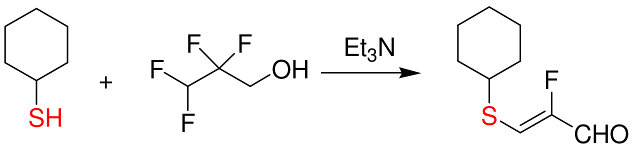
4-((Cyclohexylthio)methyl)-1,2-dihydro-6-(2-methoxyphenyl)-2,2-dimethylquinoline **58** was formed, in 75% yield, by reaction of cyclohexanethiol **1** with 4-(bromomethyl)-1,2-dihydro-6-(2-methoxyphenyl)-2,2-dimethylquinoline **59** using potassium carbonate in dimethylsulphoxide.[93]



When 5-chloro pyrazole derivative **60** reacted with cyclohexanethiol **1** under potassium or cesium fluoride-mediated reaction, or under base promoted reaction, provided thioether **61**.[94]

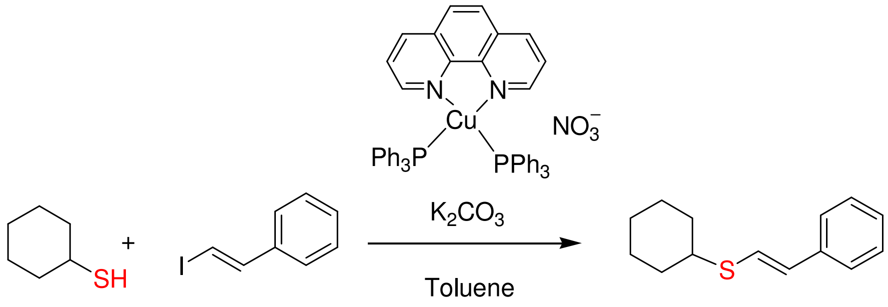


(Z)-3-(Cyclohexylthio)-2-fluoroacrylaldehyde **63** was available from 2,2,3,3-tetrafluoropropanol **62**, reacted smoothly with cyclohexanethiol **1** in the presence of triethylamine at ambient temperature for 3 h. in good yield.[95]



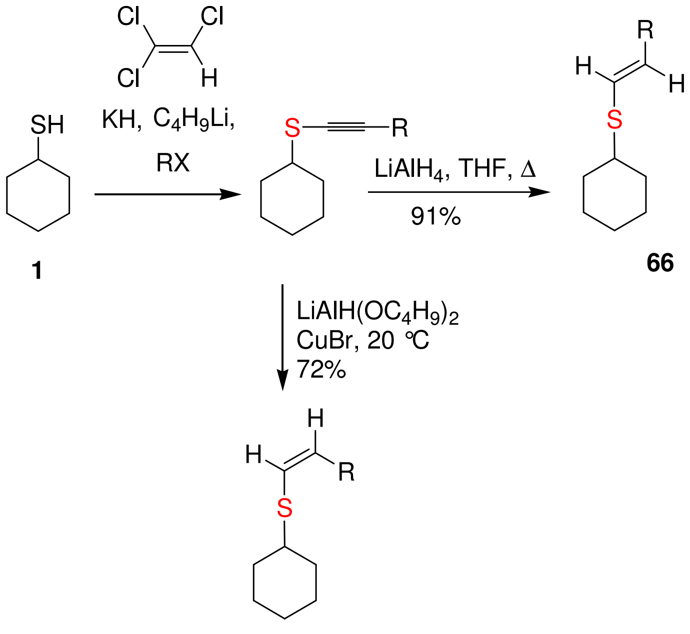
1 **62** **63**

Copper-catalyzed cross-coupling of cyclohexanethiol **1** with *trans*-α-iodostyrene **64** afforded cyclohexyl(styryl)sulfane **65** in 95% yield.[96]



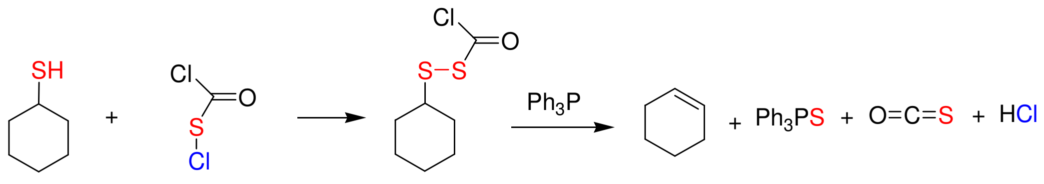
1 **64** **65**

A one-pot preparation of the compounds **66** and **67**, with 85-93% yields, involving the reaction of cyclohexanethiol **1** with trichloroethylene and alkyl halides mediated by potassium hydride and butyllithium, followed by reduction with lithium aluminum hydride.[97]



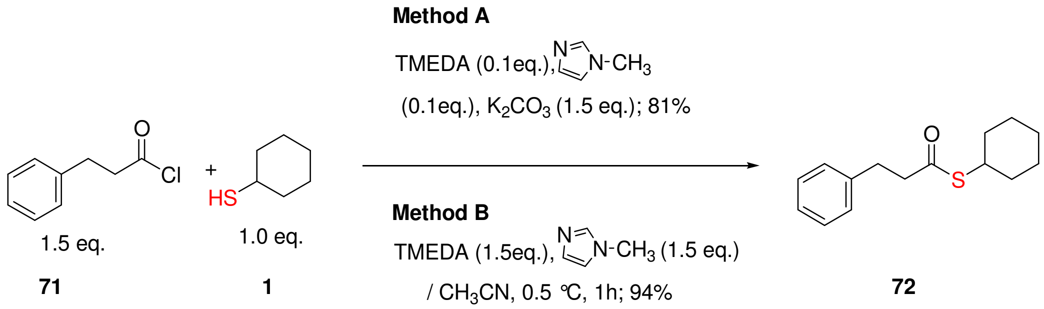
67

Cyclohexanethiol **1** reacted with chlorocarbonylsulfenyl chloride **68** below 0 °C to give about 80% disulphide **69**, which treated with triphenylphosphine at -35 °C gave cyclohexene **70** and Ph$_3$PS.[98]



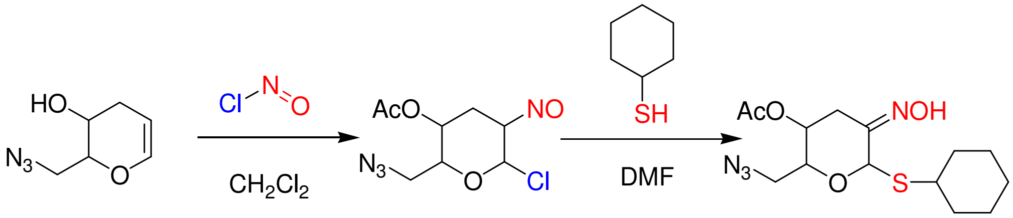
1 **68** **69** **70**

Thioesterification between acid chloride **71** and cyclohexanethiol **1** occurred in the presence of N-methylimidazole, and *N*,*N*,*N*\`,*N*\`-tetramethylethylenediamine (TMEDA) by two methods: Method A uses catalytic N-methylimidazole and TMEDA with an equimolar amount of K_2CO_3, whereas, Method B uses equimolar amounts of N-methylimidazole and TMEDA to afford S-cyclohexyl 3-phenylpropanethioate **72**.[99]



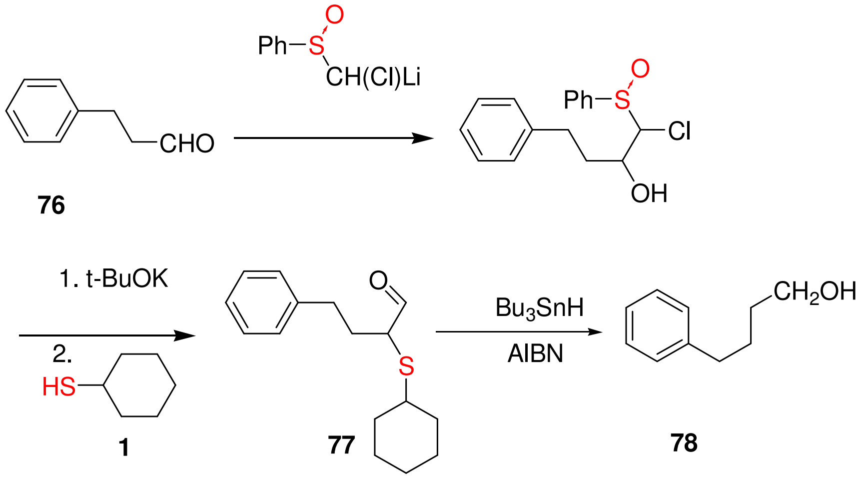
71 **1** **72**

Treatment of the glucal **73** with nitrosyl chloride in methylene chloride gave the dimeric 4-*O*-acetyl-6-azido-2,3,6-trideoxy-2-nitrosoa- D-ribo-hexopyranosyl chloride **74** in high yield. Condensation of the nitrosochloro adduct **74** with cyclohexanethiol **1** in DMF at 23°C in the presence of 2,2,6,6-tetramethylpiperidine (TMP, prepared from **73** and nitrosyl chloride) afforded cyclohexyl 4-*O*-acetyl-6-azido-2,3,6-trideoxy-2-hydroxyimino-1-thio-α-D-erythro-hexopyranoside **75** in 80% yield.[100]



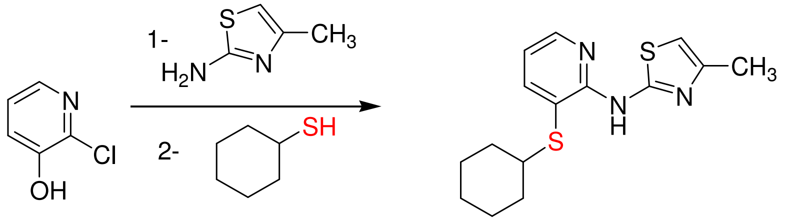
73 **74** **75**

A two-step and high-yield method for the synthesis of α-thio aldehydes **77** from aldehydes **76** with one-carbon elongation is realized by using chloromethyl Phenyl sulfoxide as a one-carbon homologating agent. The α-thio aldehyde **77** is easily converted to desulfurized alcohol **78** with Bu_3SnH and AIBN in refluxing benzene in good yield.[101]



76 **1** **77** **78**

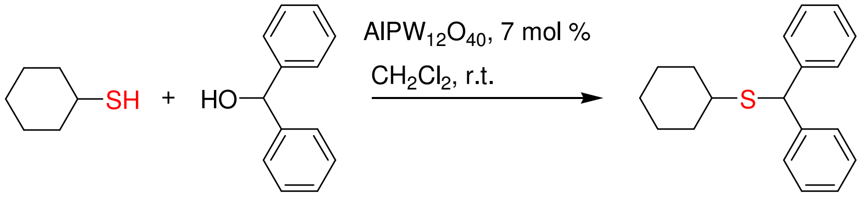
Pyridyl thiazolyl amines e.g. 3-(cyclohexylthio)-2-((4-methylthiazol-2-yl)methyl)pyridine **80** which used as glucokinase activators was prepared starting from 2-chloropyridin-3-ol **79.**[102, 103]



79 **80**

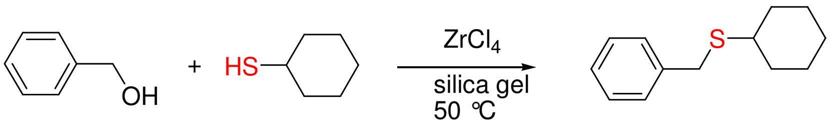
2.5. Reaction with alcohols, amines, carboxylic acids, and esters

Protection of cyclohexanethiol **1** with diphenylmethanol was achieved in high yield at room temperature using catalytic amounts of $AlPW_{12}O_{40}$ in dichloromethane to give benzhydryl(cyclohexyl)sulfane **81** with 95% yield.[104]



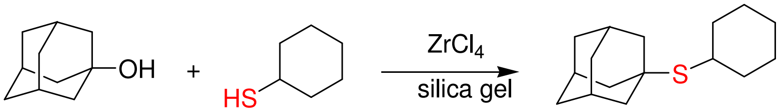
1 **81**

$ZrCl_4$ dispersed on dry silica gel allows the efficient preparation of thioether **82**, with 87% yield, by the reaction of cyclohexanethiol **1** with benzyl alcohol under solvent-free conditions.[105]



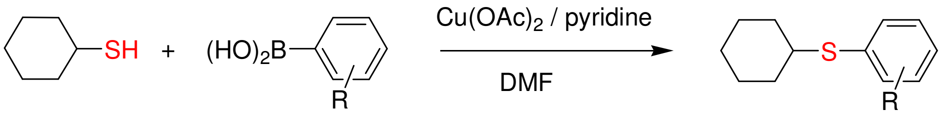
1 **82**

S-Alkylation of cyclohexanethiol **1** with tert-alcohol **83** using $ZrCl_4$ dispersed on dry silica gel under solvent-free conditions gave thioether **84** (95% yield).[105]



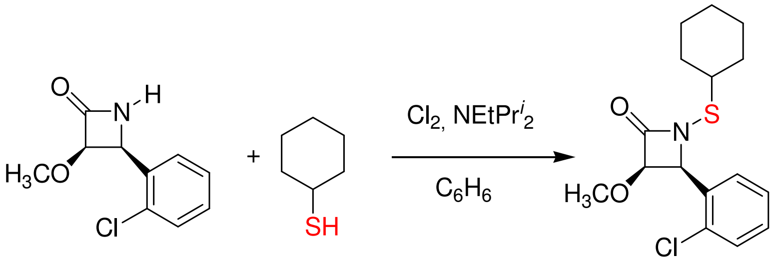
83 **1** **84**

The cross-coupling of aryl boronic acids **85** and cyclohexanethiol **1** mediated by copper(II) acetate and pyridine in anhydrous DMF affords aryl cyclohexyl sulfides **86** in good yield with a wide variety of substituted aryl boronic acids.[106]



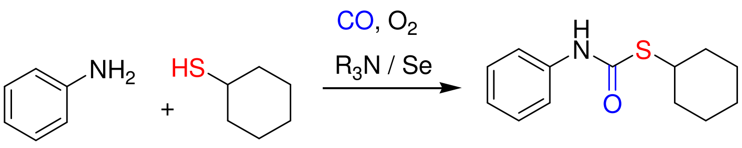
1 **85** **86**

(3R,4S)-4-(2-Chlorophenyl)-3-methoxyazetidin-2-one **87** was N-alkylthiolated using cyclohexanethiol **1** to give (3R,4S)-4-(2-chlorophenyl)-1-(cyclohexylthio)-3-methoxyazetidin-2-one **88**.[107]



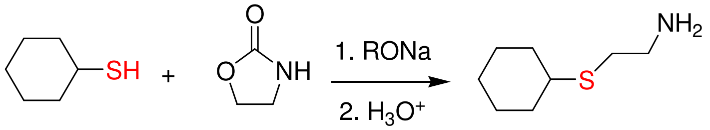
87 **1** **88**

Thiocarbamate **89** can be prepared by reacting aniline with cyclohexanethiol at molar ratio of 1:2 to 2:1 in CO and O_2 in the presence of organic amine and selenium. The organic amine may be triethylamine, tripropylamine, tributylamine, or 1,8-diazobicyclo[5.4.0]undec-7-ene.[108-112]



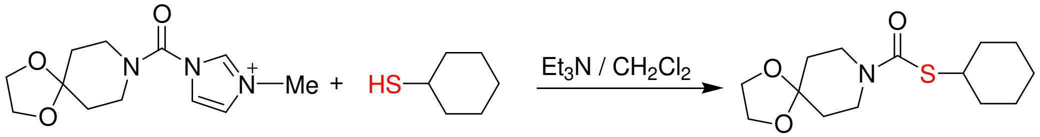
1 **89**

Cyclohexanethiol **1** reacted with 2-oxazolidinone **90** in the presence of alkoxide to give β-amino sulfide **91** in high yield.[113, 114]

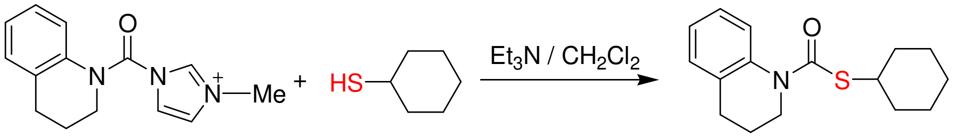


1 **90** **91**

Carbamoylimidazolium salts such as **92** and **93** act as efficient *N*,*N*-disubstituted carbamoylating reagents, when reacted with cyclohexanethiol **1** in methylenechloride and triethylamine afforded thioesters **94** and **95** respectively.[115, 116]

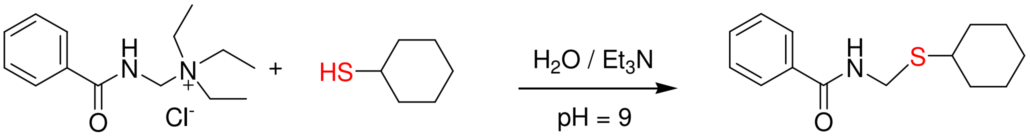


92 **1** **94**



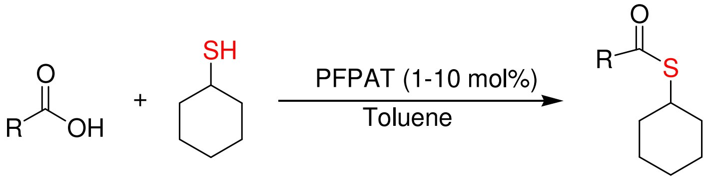
93 **1** **95**

Cyclohexanethiol **1** was benzamidomethylated in water solution at room temperature with (benzamidomethyl)triethylammonium chloride **96** in the presence of a small quantity of triethylamine (pH > 9) to afford benzamidomethyl thioether **97**.[117]



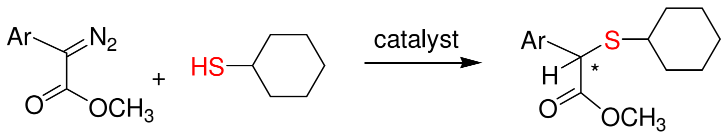
96 **1** **97**

A pentafluorophenylammonium triflate (PFPAT) catalyst (1–10 mol%) efficiently promoted thioesterification between a 1:1 mixture of carboxylic acids **98** and cyclohexanethiol **1** in good to excellent yield under mild reaction conditions to afford thioesters **99**.[118]



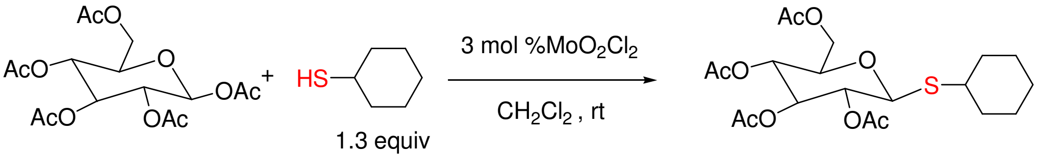
98 **1** **99**

Catalytic asymmetric S-H insertion of carbenoid generated from aryl diazoacetate **100** has been investigated with chiral Rh(II) and Cu(I) catalysts to afford chiral sulphide **101** in 72% yield.[119]



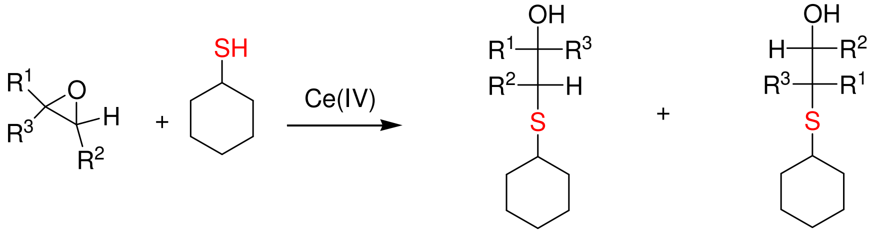
100 **1** **101**

MoO_2Cl_2 catalyzed thioglycosylation of *O*-acetylated glycoside **102** with cyclohexanethiol **1** in dichloromethane, leading cleanly to 1,2-trans-thioglycoside **103**, in 76% yield.[120]



102 **1** **103**

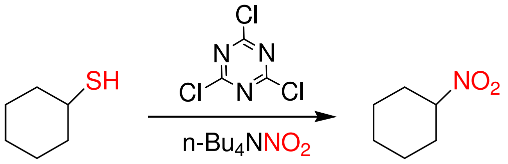
Tetrabutylammonium fluoride or ceric ammonium nitrate catalyze under mild conditions the opening of epoxides **104** [R_1 = e.g., $PhOCH_2$, $MeOCH_2$, CH_2:$CHCH_2OCH_2$, Ph_3COCH_2, C_6H_{13}, Ph; R_2, R_3 = H, Ph; R_1R_2 = $(CH_2)_4$] with cyclohexanethiol **1** to produce the corresponding β-hydroxy thioethers **105a** and **105b** in excellent yields (88-100%) and with high regioselectivity.[8, 121]



104 **1** **105a** **105b**

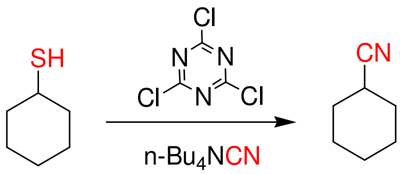
2.6. Displacement of SH group

Treatment of cyclohexanethiol **1** with 2,4,6-trichloro-1,3,5-triazine/n-Bu_4NNO_2 in acetonitrile afforded cyclohexylnitrite **106** with 92% yield.[122]



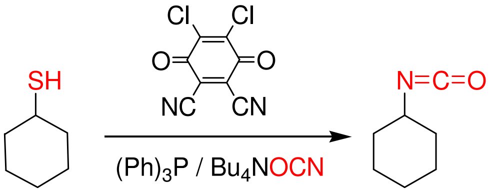
1 **106**

Cyclohexyl cyanide **107** was prepared in 93% yield by treatment of cyclohexanethiol **1** with 2,4,6-trichloro[1,3,5]triazine/n-Bu_4NCN in refluxing acetonitrile.[123]



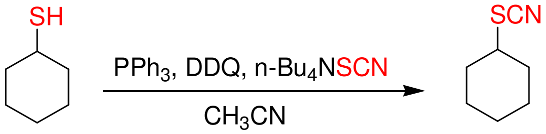
1 **107**

Cyclohexyl isocyanate **108** was prepared in 89% yield by treatment of cyclohexanethiol **1** with triphenylphosphine/2,3-dichloro-5,6-dicyanobenzoquinone/ Bu_4NOCN in acetonitrile.[124]



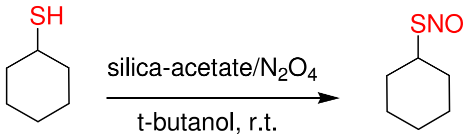
1 **108**

A combination of triphenylphosphine and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) provides a safe and easily available mixed reagent system for the conversion of cyclohexanethiol **1** to the corresponding thiocyanate **109** in 93% yield.[125]



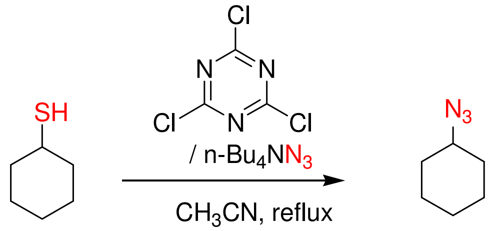
1 **109**

The use of silica-acetate/N_2O_4 complex provides the possibility of the conversion of cyclohexanethiol **1** into their corresponding thionitrite **110** in 90% yield without the formation of any disulfide or over-oxidized products in solvents such as diethyl ether, dichloromethane, ethyl acetate or t-butanol at room temperature.[126]



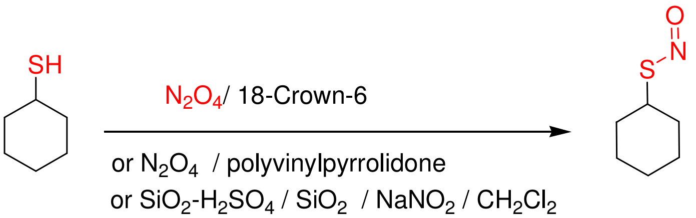
1 **110**

Cyclohexylazide **111** was prepared in 96% yield by treatment of cyclohexanethiol 1 with 2,4,6-trichloro[1,3,5]triazine/n-Bu_4NN_3 in acetonitrile.[127]



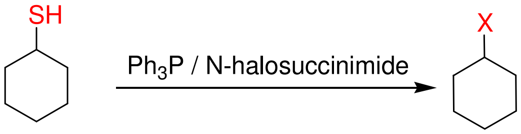
1 111

Complexation of gaseous N_2O_4 with 18-Crown-6 affords an ionic complex of NO+-18-crown-6-$H(NO_3)^{-2}$. This reagent is a nitrosating agent for conversion of cyclohexanethiol **1** to thionitrite **112**.[128, 129] On the other hand, gaseous N_2O_4 was immobilized on polyvinylpyrrolidone to give a stable polymeric reagent, cyclohexanethiol **1** was converted to S-nitrosothiol (thionitrite) **112** using this nitrosating agent in n-hexane or $CHCl_3$ at 10 °C.[130] In the same sense, cyclohexanethiol **1** can be readily converted to the corresponding thionitrite **112**, in 97% yield, with a combination of SiO_2-H_2SO_4, wet SiO_2 and sodium nitrite in methylenechloride at room temperature.[131]



1 112

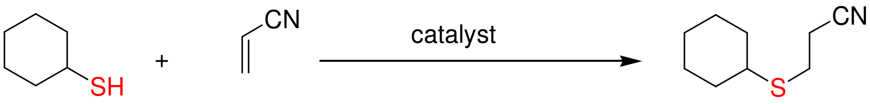
Cyclohexanethiol **1** is efficiently converted to alkyl halides **113** in high yields when treated with triphenylphosphine/N-halosuccinimide (X = Br, Cl, I) in dichloromethane at room temperature.[132]



1 113

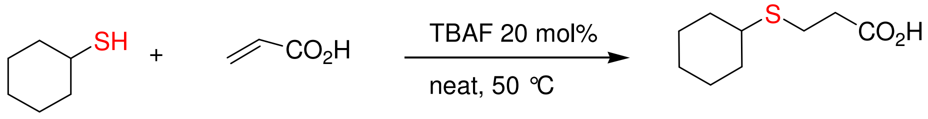
2.7. Addition to unsaturated compounds

Mg-Al-O-Bu-*t*-Hydrotalcite is a mild and efficient catalyst for the cyanoethylation of cyclohexanethiol **1** to afford, in 53% yield, 3-(cyclohexylthio)propanenitrile **114**.[133, 134]



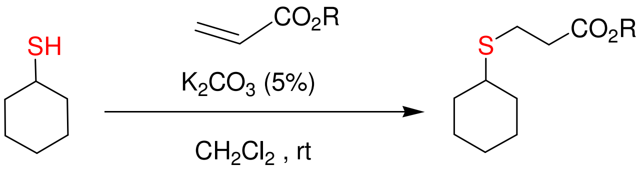
1 114

3-(Cyclohexylthio)propanoic acid **115** was obtained in 98% yield by proceeding through 1,2-addition of cyclohexanethiol **1** to acrylic acid utilizing tetrabutylammonium fluoride (TBAF) as catalyst.[135]



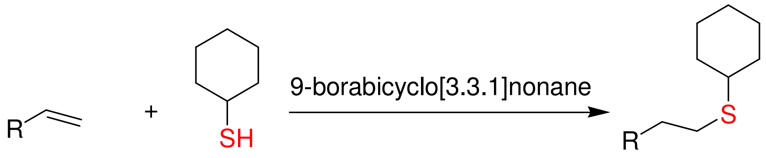
1 **115**

β-Sulfinylesters **116** was obtained, in 76% yield, by reaction of cyclohexanethiol **1** with acrylate.[136]



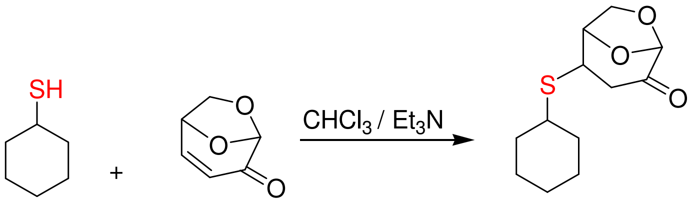
1 **116**

A catalytic amount of 9-borabicyclo[3.3.1]nonane (9-BBN) initiated the radicalic addition reaction of cyclohexanethiol **1** to terminal alkenes **117** to give dialkyl sulfides **118** in high yield.[137]



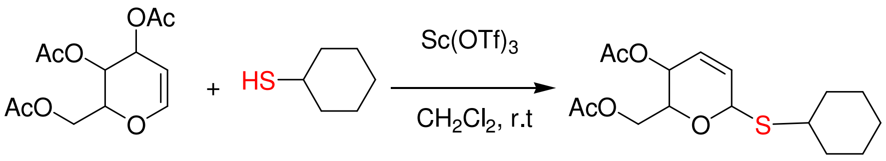
117 **1** **118**

Michael additions of cyclohexanethiol **1** to levoglucosenone **119** in chloroform in the presence of triethylamine gave addition product **120**.[138]



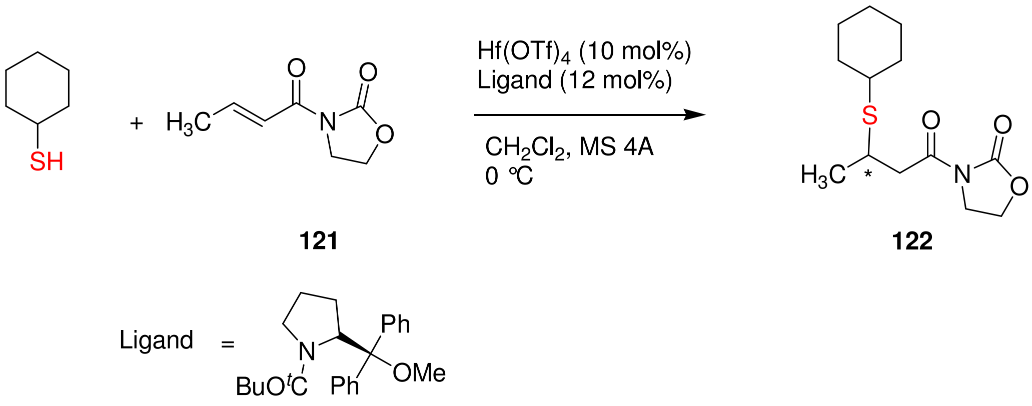
1 **119** **120**

The reaction of cyclohexanethiol **1** with tri-*O*-acetyl-*D*-glucal in the presence of 5% scandium triflate in dichloromethane at room temperature for 3–5 h gave the corresponding 2,3-nsaturated thioglycoside **120** in 81% yield.[139]



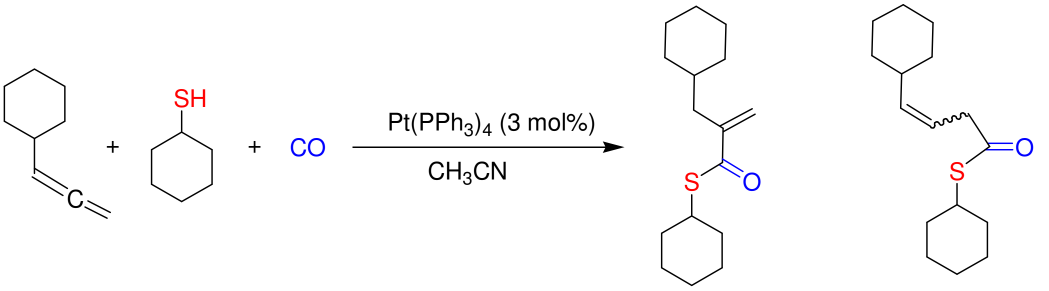
1 **120**

Asymmetric *Michael* reaction of cyclohexanethiol **1** with 3-(2-alkenoyl)-2-oxazolidinone **121** catalyzed by Lewis acid and chiral pyrrole ligands afforded addition product **122**.[140]



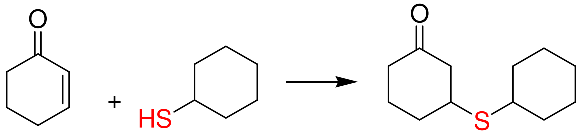
121 **122**

In the presence of a catalytic amount of tetrakis(triphenylphosphine)platinum(0), propa-1,2-dienylcyclohexane **123** undergo carbonylative thiolation with carbon monoxide and cyclohexanethiol **1** to provide the corresponding α,β- and β,γ-unsaturated thioesters **124** and **125** respectively in good yields.[141]



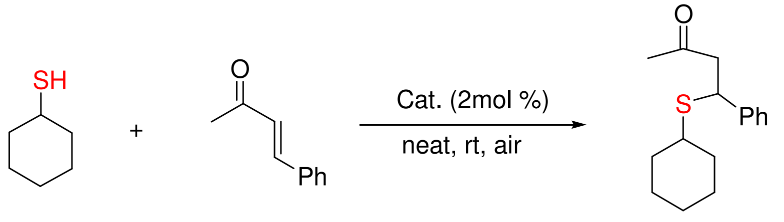
123 **1** **124** (39%) **125** (48%)

Reaction of cyclohexyl mercaptan **1** with α,β-unsaturated ketone **126** using a catalytic amount of iodine (5 mol %) or iron(III) chloride or sodium dodecyl sulfate generated the adduct **127** in 95% yield .[142-146]



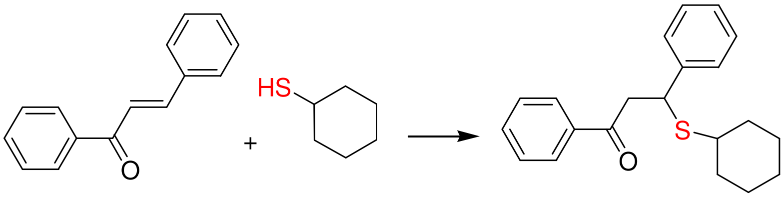
126 **1** **127**

The 1,4-addition of cyclohexanethiol **1** to α,β-unsaturated ketone **128** was completed rapidly in the presence of a catalytic amount (2–3 mol %) of anhydrous iron(III) chloride under solvent free conditions and an air atmosphere to give thioether **129** in high yield.[147]



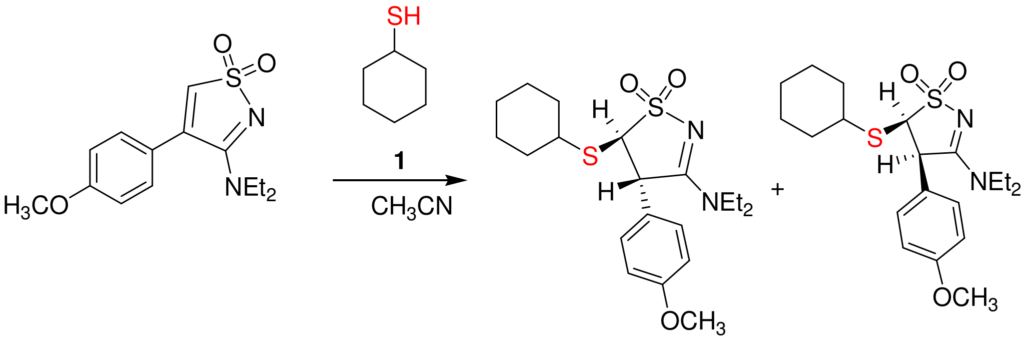
1 **128** **129**

Michael adduct **131** of chalcone **130** with cyclohexanethiol **1** was prepared in high yield.[147]



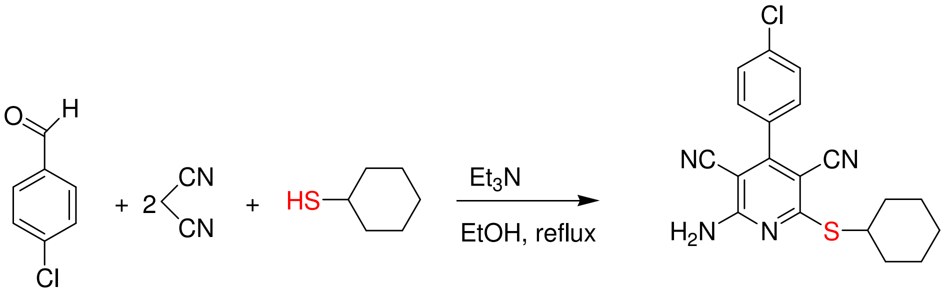
130 **1** **131**

Reactivity of 3-aminoisothiazole 1,1-dioxide with nucleophiles could be expected with attack at C-5 by a Michael-type reaction and formation of 4,5-dihydro derivatives. Thus, compound **132** was reacted with sulfur nucleophile such as mercaptan **1** in acetonitrile as the solvent at room temperature, compounds **133** (*trans*) and **134** *(cis)* were obtained in a ratio of about 2: 1.[148]



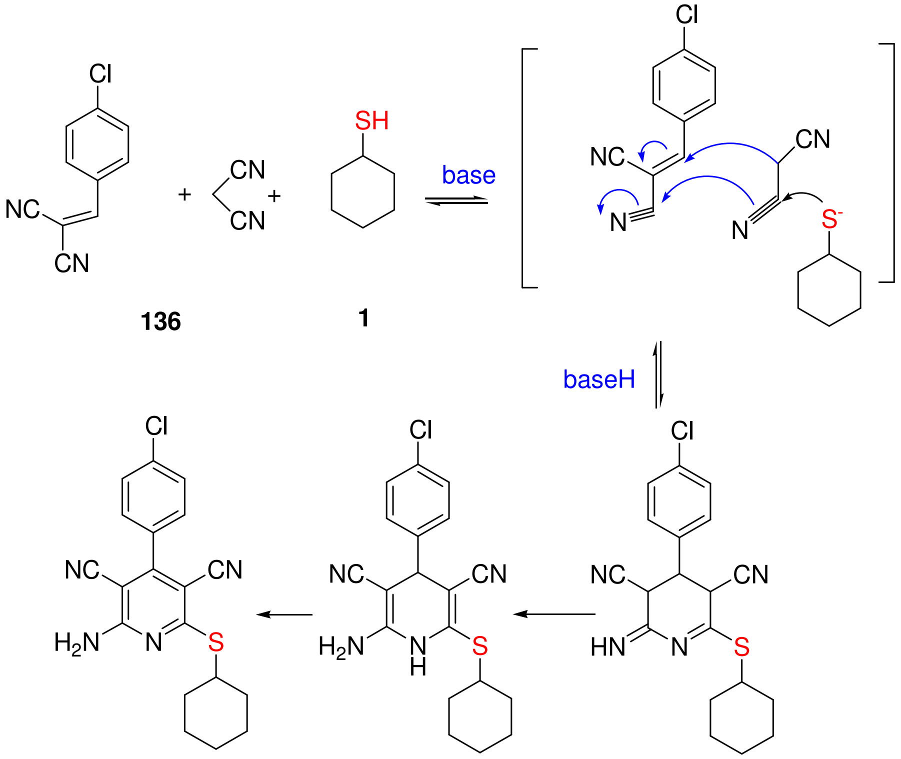
132 **133** **134**

Simply refluxing a solution of the three reactants (4-chlorobenzaldehyde, malononitrile and cyclohexanethiol **1** containing triethylamine in ethanol for 2.5-3 h followed by cooling to room-temperature resulted in precipitation of pyridine **135** in 31% yield.[149]



1 **135**

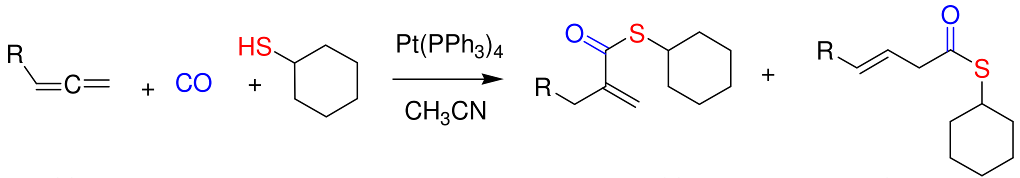
The mechanism involves the formation of arylidene malononitrile **136**, which reacts with malononitrile and cyclohexanethiol **1** to form dihydropyridine **137**, which then, auto-oxidized to substituted pyridine **135**.[149]



136 **1**

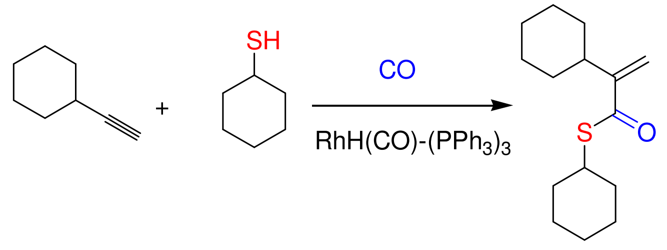
135 **137**

Unsaturated thioesters such as **139** and **140** (R = cyclohexyl, $BuCH_2CH_2$, $PhCH_2$) are prepared by carbonylative thiolation of allenes such as **138** (R = cyclohexyl, $BuCH_2CH_2$, $PhCH_2$) with carbon monoxide and cyclohexanethiol **1** in the presence of tetrakis(triphenylphosphine)platinum.[141]



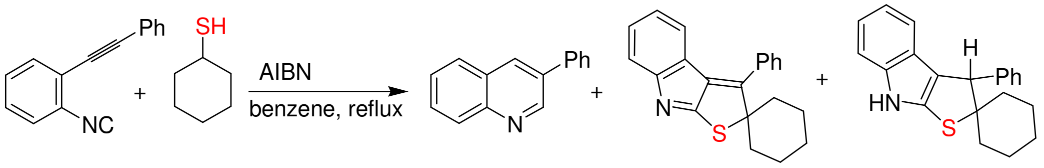
138 **1** **139** **140**

$Pt(PPh_3)_4$-catalyzed reaction of acetylene **141** with CO and cyclohexanethiol, and also, $RhH(CO)(PPh_3)_3$-catalyzed reaction, formyl and sulfide groups were introduced selectively into the terminal positions of acetylene to afford α,β-unsaturated carbonyl derivative **142** in 99% yield.[150, 151]



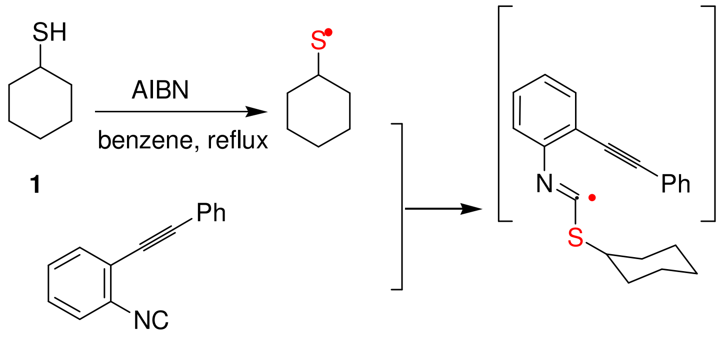
141 **1** **142**

2-(2-Phenylethynyl)phenyl isonitrile **143** react with cyclohexanethiol **1** in boiling benzene in the presence of azo-bis-*iso*-butyronitrile (AIBN) as a radical initiator. The reaction afforded the quinoline **144** (38%), the spiro-compound **145** (6%), and its dihydro-derivative **146** in 26% yield.[152]



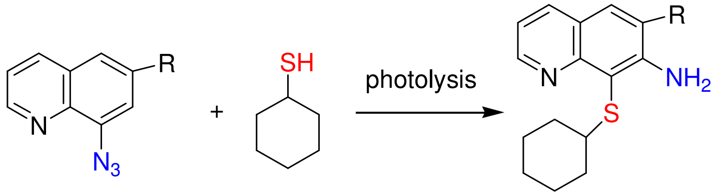
143 **1** **144** **145** **146**

In this case, **145** and **146** clearly result from H-abstraction from cyclohexanethiol **1** and addition of the resulting sulfanyl radical to isonitrile **143** to form the intermediate **147**.[152]



143 **147**

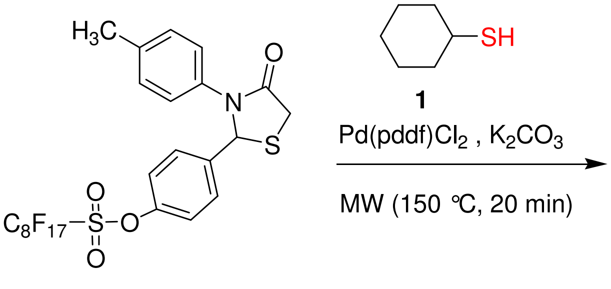
Photolysis of quinol **148** (R = H, OCH_3) with cyclohexanethiol **1** in dioxane for 5 h gave *O*-cyclohexylthioquinolylamine **149** in excellent yield.[153]



148 **1** **149**

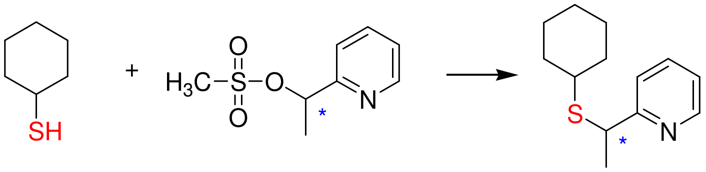
2.8. Different Reactions

4-Thiazolidinone-based palladium **150** coupling reaction with cyclohexanethiol **1** in 4:4:1 acetone/toluene/H_2O solvent and presence of potassium carbonate using a monomode microwave cavity (150°C, 20min) afforded 2-(4-(cyclohexylthio)Phenyl)-3-*p*-tolyl-1,3-thiazolidin-4-one **151**.[154]



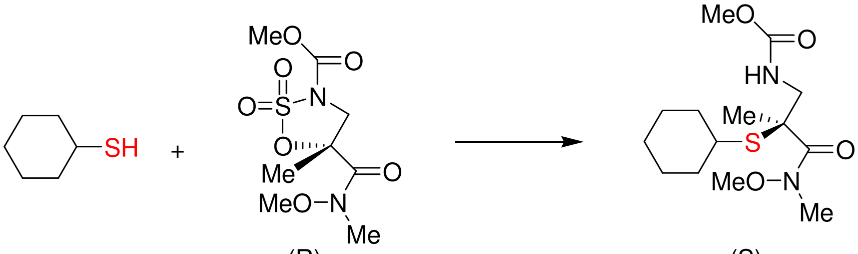
150 **151**

Nucleophilic substitution reaction of (R)-1-(2-pyridinyl)ethyl methanesulfonate **152** with cyclohexanethiol **1** gave substituted sulfide **153**.[155]



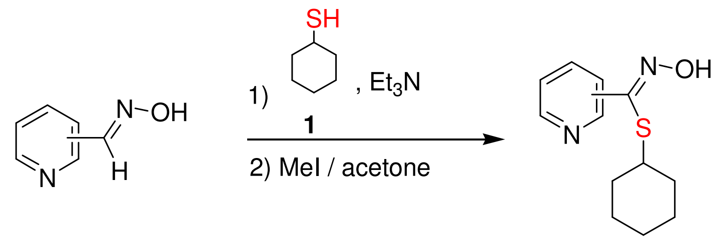
1 **152** **153**

S_N2 Reaction of cyclic sulfamidate (*R*) **154** with cyclohexanethiol **1** as S-nucleophile afforded the opening product **155** in 94% yield.[156]



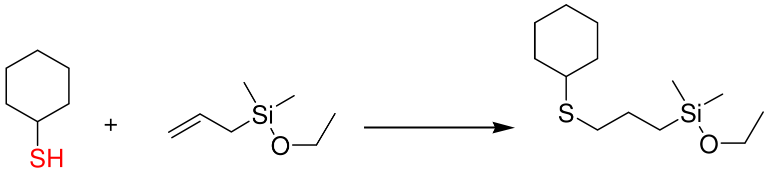
1 **154** **155**

N-Methylpyridinium thiohydroximic ester **157** was prepared by the reaction of 2-pyridinehydroxyimoyl chloride-HCl **156** with cyclohexanethiol **1** in ether in the presence of triethylamine followed by the quaternization with methyliodide in dry acetone.[157]



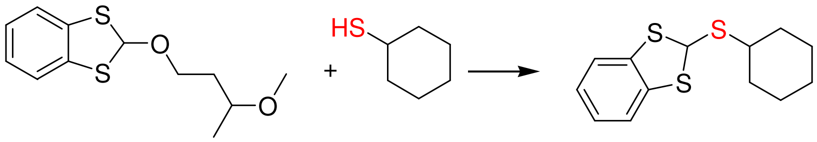
156 **157**

(3-(Cyclohexylthio)propyl)(ethoxy)dimethylsilane **159** useful for coupling agents in rubbers filled with siliceous material, was manufactured, in 98% yield, by reaction of allyldimethylethoxysilane **158** with cyclohexanethiol **1**.[158]



1 **158** **159**

2-(3-Methoxybutoxy)-1,3-benzodithiole **160** reacted readily with cyclohexanethiol **1** to give 2-(cyclohexylthio)benzo[*d*][1,3]dithiole **161** by replacement of the butoxy group of 2-(3-methylbutoxy)-1,3-benzodithiole by cyclohexylthio groups.[159]



160 **1** **161**

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