Synthesis of Triazole Compounds

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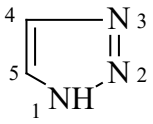
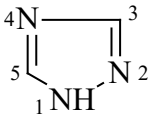
Synthesis of Triazole Compounds

Compounds containing three nitrogen atoms in a five-membered ring are called "Triazoles". Triazoles have two isomers. These are 1,2,3-triazole (v-triazole) and 1,2,4-triazole (sim-triazole) rings. Triazoles are generally resistant to reducers and oxidizers (Ikizler, 1996).



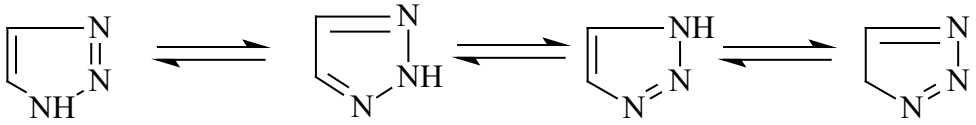
1,2,3-Triazole
(v-Trizole)



1,2,4-Triazole
(sim-Trizole)

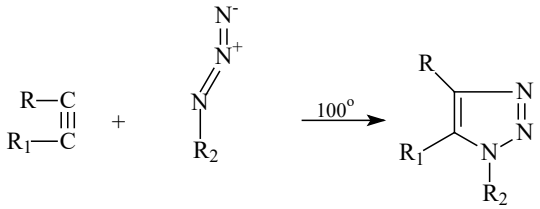
Synthesis of 1,2,3-Triazoles

The 1,2,3-triazole boiling point is 206°. The tautomeric forms of the 1,2,3-triazole ring are (Ikizler, 1996):



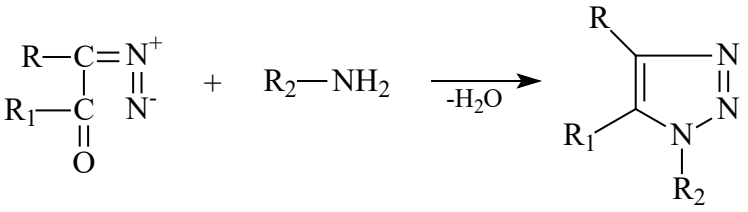
Some methods used to obtain 1,2,3-triazole and its derivatives (Aykut İkizler, 1996):

From Alkynes and Azides (Ikizler, 1996):

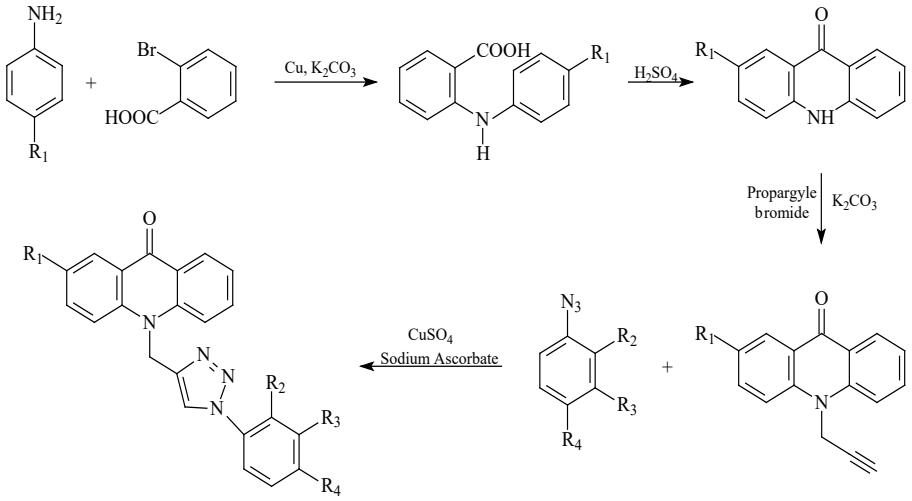


1,2,3-Triazole Derivative

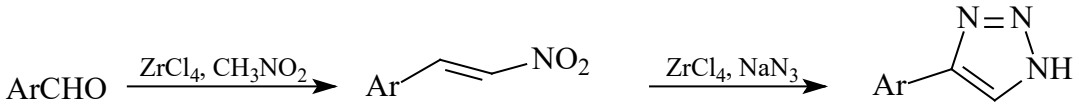
From Diazoketones (Ikizler, 1996):



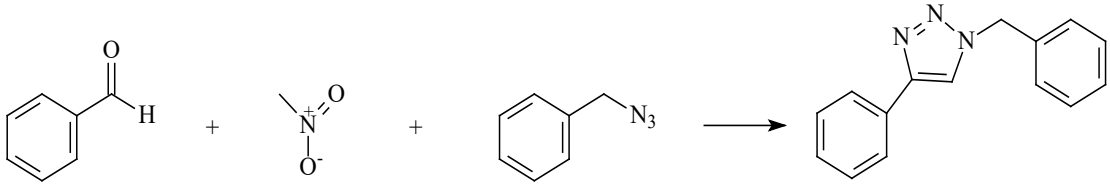
Synthesis of 1,2,3-triazole derivatives from acridone by the cycloaddition reaction between aromatic azides and *N*-propargyl acridones was obtained by the following reaction (Aarjane, Slassi, & Amine, 2021)



Vinyl nitrate is formed as a result of the reaction of the aldehyde compound with CH_3NO_2 in the presence of $ZrCl_4$. It was observed that this compound reacted with NaN_3 in the presence of $ZrCl_4$ at room temperature to form 1,2,3-triazole compound (Sridhar et al., 2017).

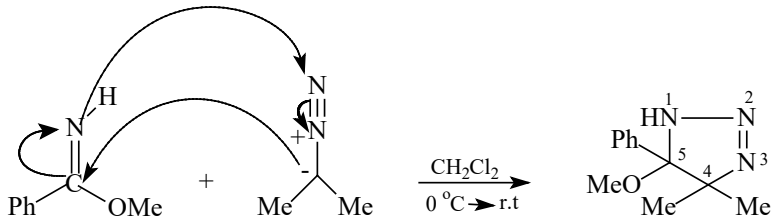


The 1,2,3-triazole triazole was obtained as a result of the reaction of aldehyde, nitromethane and benzyl azide under the catalysis of Fe_2O_3@MgO@ch.OAc in EtOH (Mohammadkhani & Heydari, 2021).

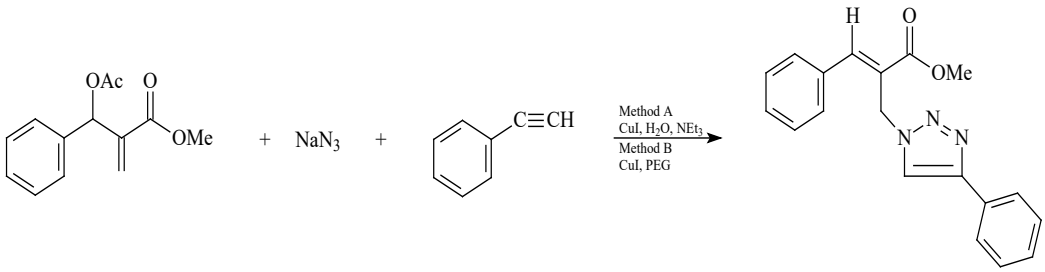


2-diazopropane reacts with methyl benzene carboximidoate in dichloromethane at

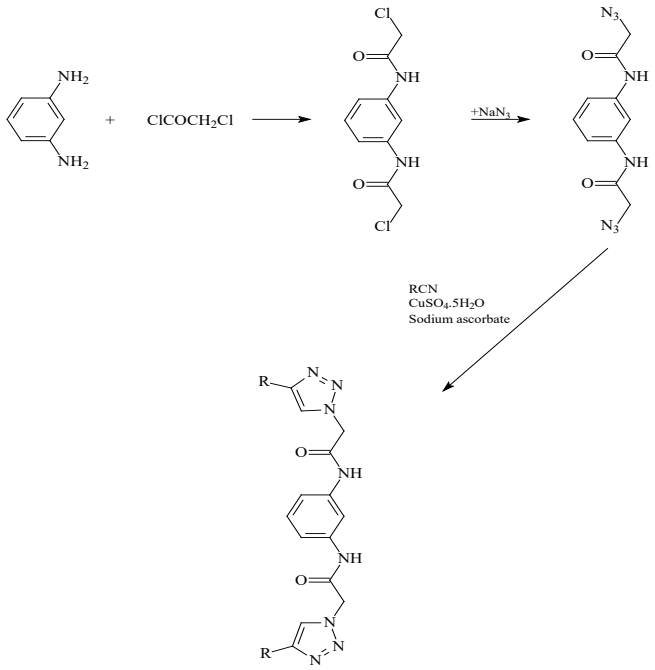
0°C, and after reaction 5-methoxy-4,4-dimethyl-5-phenyl-4,5-dihydro-1*H*-[1,2,3]-triazole occurs. This compound consists of regioselective 1,3-dipolar cycloaddition of 2-diazopropane to the imidate C=N bond (Hamdi et al., 2006).



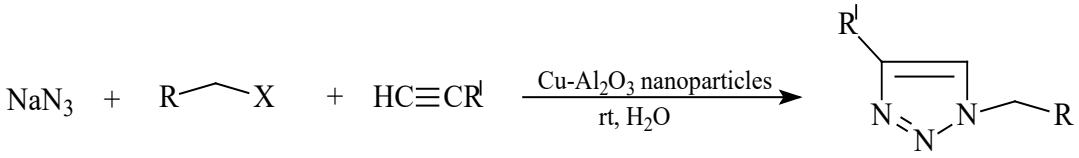
1,4-disubstituted 1,2,3-triazoles can be synthesized in one step by reacting Baylis-Hillman acetates, sodium azide, and terminal alkynes in water or poly(ethylene glycol) [PEG] (Sreedhar et al., 2006).



N,N'-(1,3-phenylene)bis(2-chloroacetamide) compound is formed as a result of the reaction of m-phenylenediamine with chloroacetyl chloride. As a result of the reaction of this compound with sodium azide, the compound *N,N'*-(1,3-phenylene)bis(2-azidoacetamide) is obtained. In the treatment of this compound with alkyne compounds and sodium ascorbate under the catalysis of $CuSO_4.5H_2O$ in DMF, bis-1,2,3-triazole compound is formed (Nural et al., 2021).

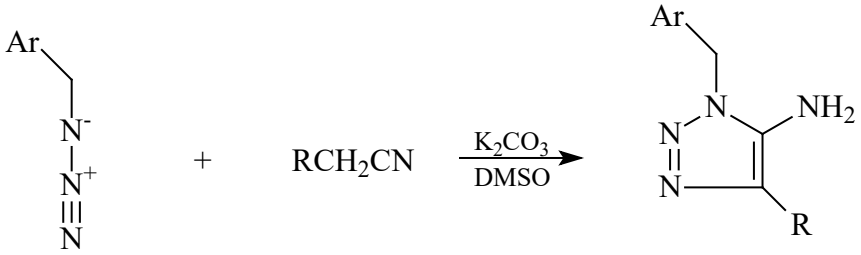


1,2,3-triazoles are produced in one-pot using Cu-Al_2O_3 nanoparticles at room temperature with sodium azide of aliphatic/aromatic alkynes of alkyl/allyl halides (Kantam et al., 2006).

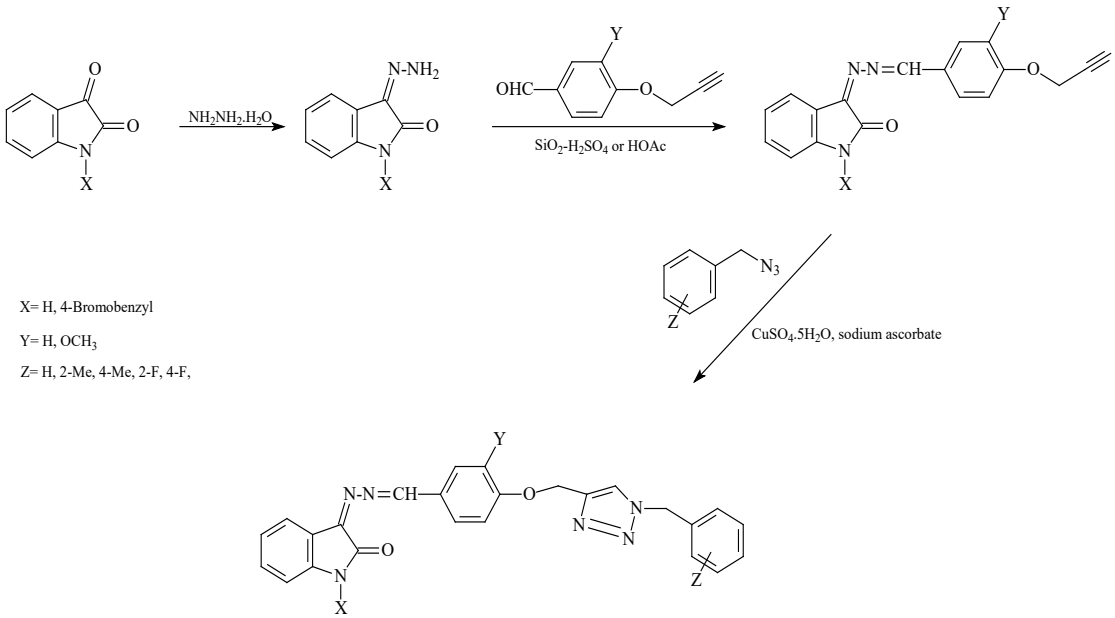


R= Alkyl, allyl
X= Cl, Br, I
R'= Aromatic, aliphatic

It has been shown that benzyl-1*H*-1,2,3-triazole compounds are formed by the reaction of benzyl azides and active methylene compounds with anhydrous potassium carbonate in DMSO under mild conditions (Cottrell et al., 1991).

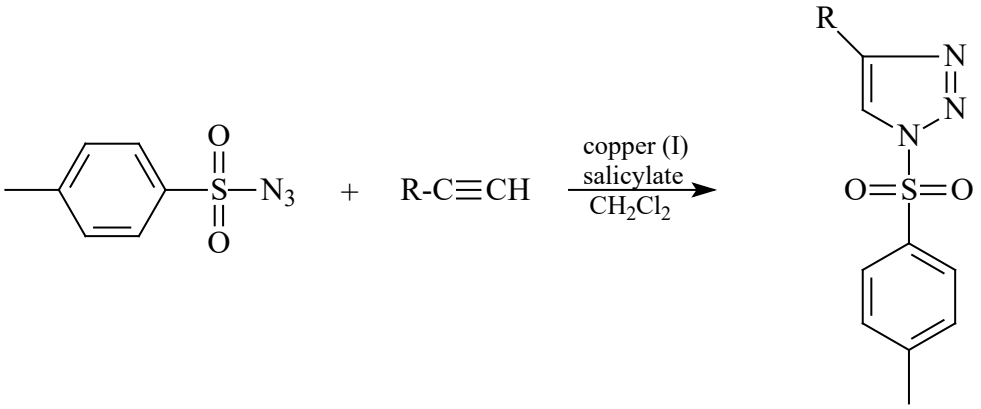


Isatin or its 4-bromobenzyl derivative reacts with hydrazine hydrate to form hydrazineylideneindolinone. Then, prop-2-yn-1-yloxybenzylidene-hydrazineylideneindolinone derivative is obtained by reaction of this compound with aldehyde in the presence of catalytic amount of SiO_2-H_2SO_4 or acetic acid under microwave irradiation. Finally, this compound leads to the formation of 1,2,3-triazole derived compound by click reaction with benzyl azide (Shareghi-Boroujeni et al., 2021).

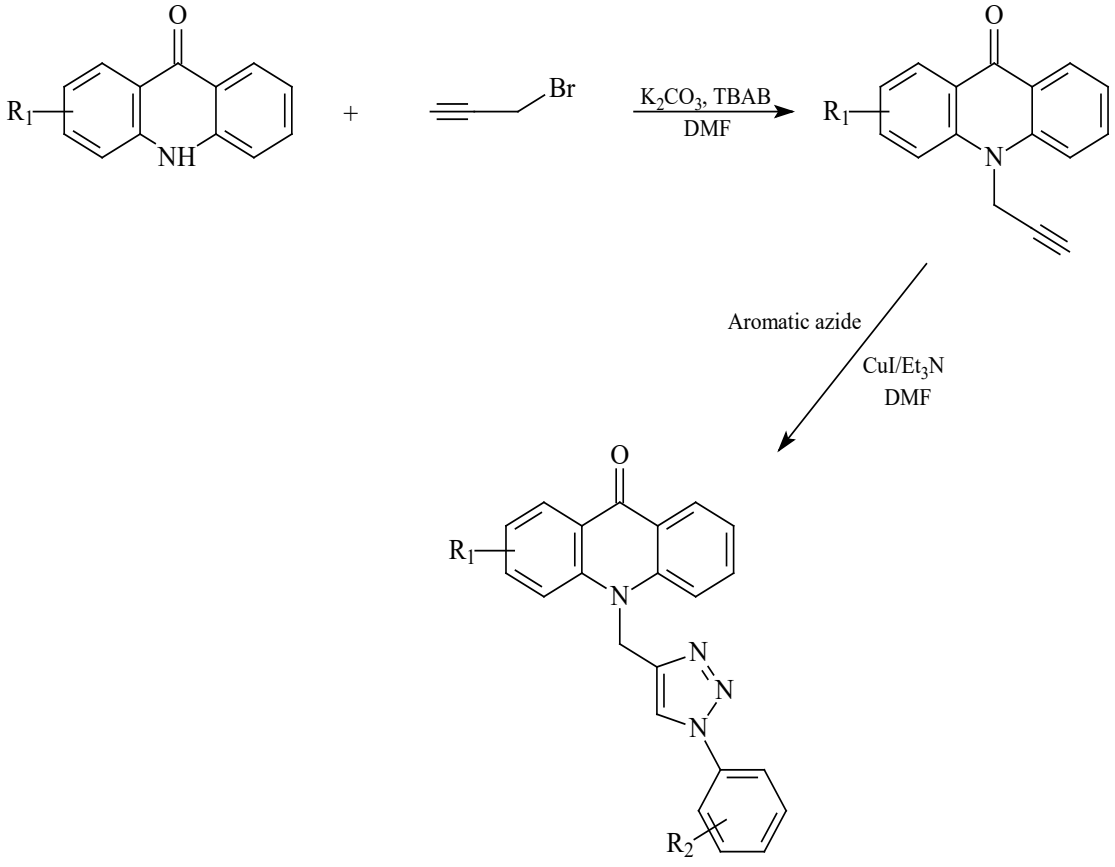


X= H, 4-Bromobenzyl
Y= H, OCH_3
Z= H, 2-Me, 4-Me, 2-F, 4-F,

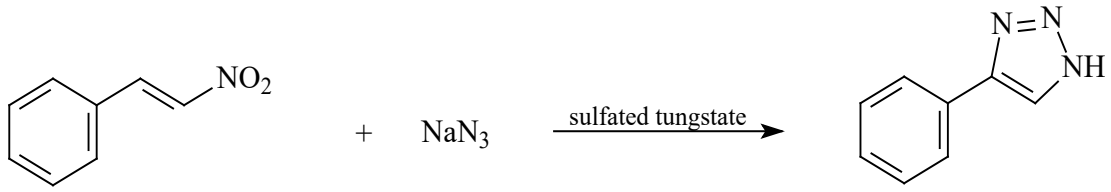
The copper-catalyzed azide-alkyne cycloaddition of *p*-toluenesulfonyl azide with an alkyne provides the appropriate compound 1-sulfonyl-1,2,3-triazole (Jose Garcia-Vanegas et al., 2021).



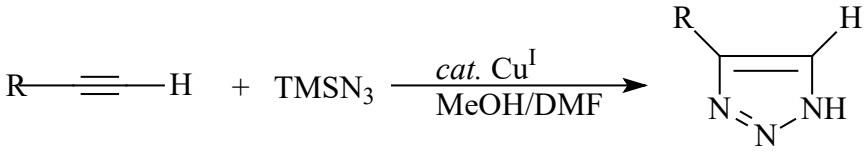
10-(prop-2-yn-1-yl)acridone derivatives were synthesized by reacting acridon and propargyl bromide in a mixture of tetra-n-butylammonium bromide (TBAB) in anhydrous potassium carbonate and DMF under microwave irradiation. It was determined that 1,2,3-triazole derivatives were obtained in the presence of CuI and triethylamine by using microwave assisted and conventional heating methods by 1,3-dipolar cycloaddition reaction between 10-(prop-2-yn-1-yl)acridone derivatives and aromatic azides (Aarjane, Slassi, Tazi, et al., 2021).



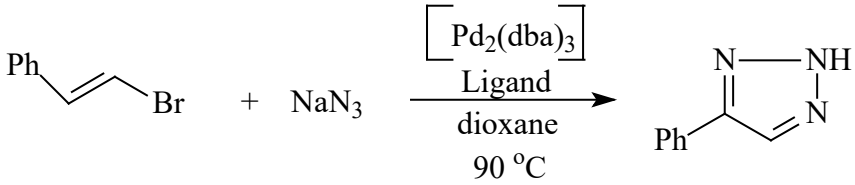
It was determined that 4-phenyl-NH-1,2,3-triazole compound was formed as a result of the reaction of a nitro styrene and sulfated tungstate with NaN_3 (Autade & Akamanchi, 2019).



N-unsubstituted 1,2,3-triazoles are obtained by the copper-catalyzed [3+2] cycloaddition reaction of nonactivated terminal alkynes and trimethylsilyl azide (Jin et al., 2004).



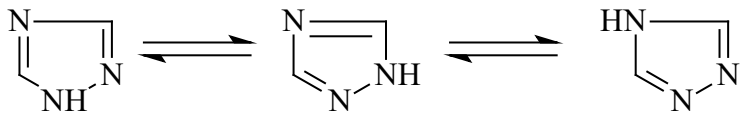
1*H*-1,2,3-triazoles were obtained from the reaction of an azide with an alkenyl halide under Pd^0 catalysis (Barluenga et al., 2006).



dba = trans, trans-dibenzylideneacetone

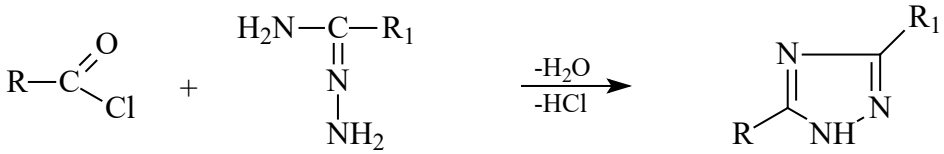
Synthesis of 1,2,4-Triazoles

1,2,4-triazole has a melting point of 121°. The tautomer shapes are as follows (Ikizler, 1996):

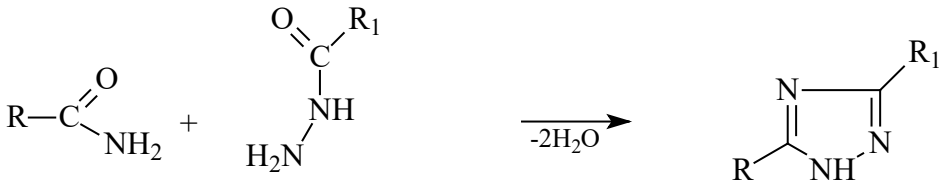


Methods used in the preparation of 1,2,4-triazole and its derivatives (Aykut İkizler, 1996):

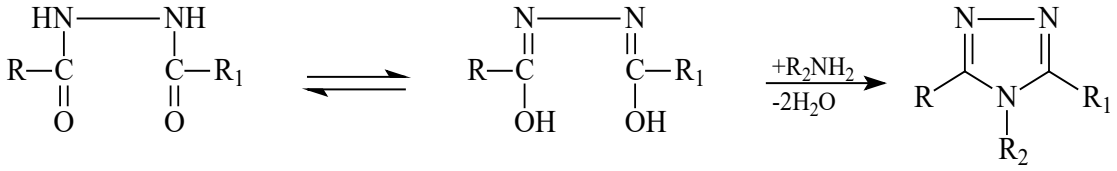
From Amidrazones (Ikizler, 1996):



From Heating of Acylhydrazines and Amides (Ikizler, 1996):

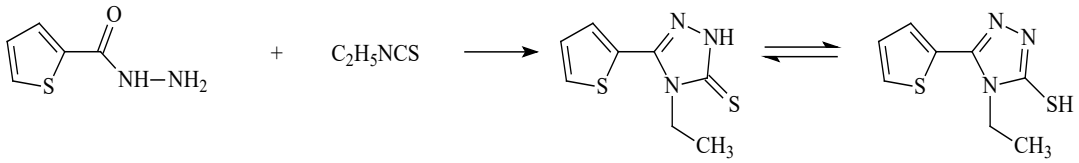


From Diacylhydrazines (Ikizler, 1996):

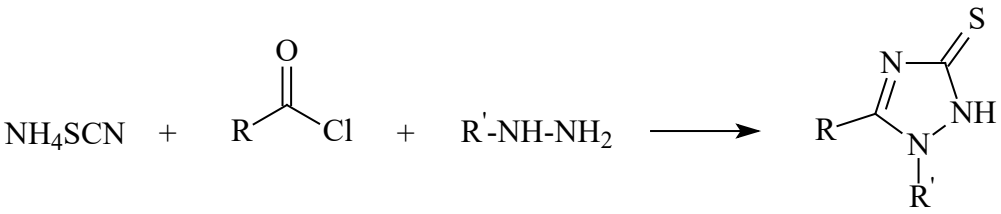


1,2,4-triazole derivatives are obtained from the reaction of diacylhydrazines with primary amines (Ikizler, 1996).

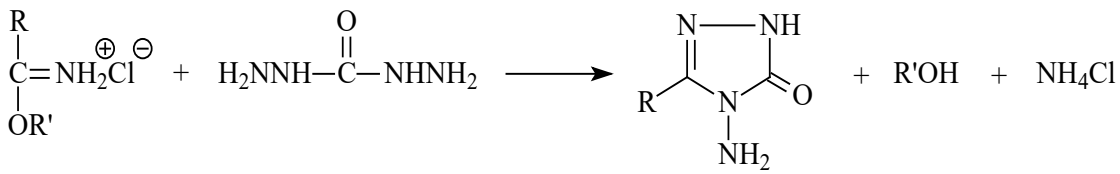
It has been shown that 4-ethyl-5-(thiophene-2-yl)-4*H*-1,2,4-triazole-3-thiol compound is synthesized as a result of the reaction of thiophene-2-carbohydrazide and ethyl isothiocyanate (Koparir et al., 2022).



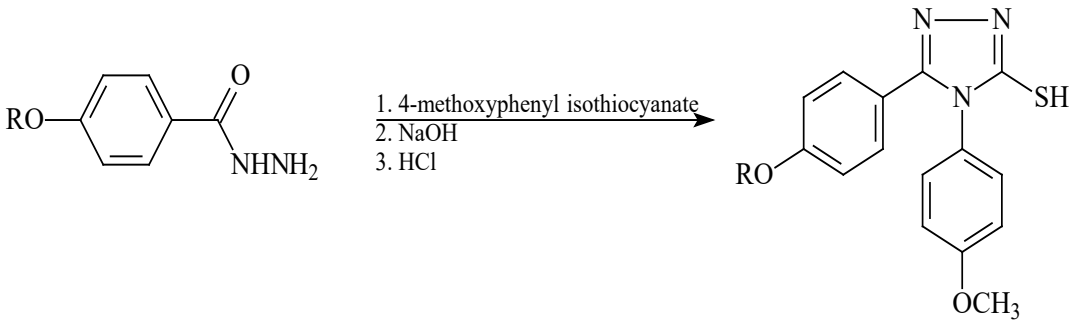
As a result of the reaction of ammonium thiocyanate, acyl chloride and arylhydrazine, 1,2,4-triazole derivative was synthesized (Yavari et al., 2010).



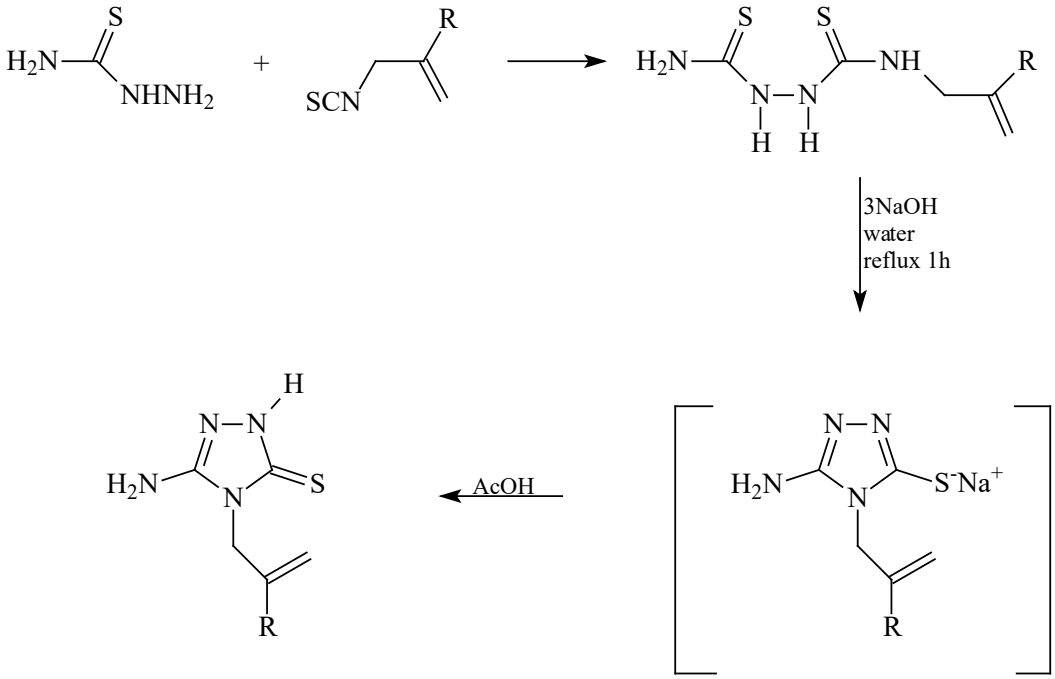
Some methods have been developed for the synthesis of 4-amino-derived 1,2,4-triazol-5-one compounds. In one of these methods, the reaction of iminoester hydrochlorides obtained from nitriles with carbohydrazide is predicted (Milcent & Redeuilh, 1979).



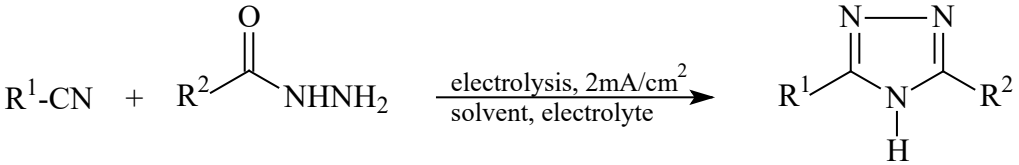
3-mercapto-1,2,4-triazole derivatives are obtained by the reaction of 4-alkyloxybenzohydrazides with 4-methoxyphenyl isothiocyanates (Al-Mansury et al., 2021).



1-alkenyl-2,5-dithiourea is formed by the reaction of thiosemicarbazide with allyl isothiocyanate or methallyl isothiocyanate. Heating this compound in sodium hydroxide solution forms 4-alkenyl-5-amino-1,2,4-triazole-3-thiolate sodium salts. Direct acidification of the reaction mixture yields 4-alkenyl-5-amino-1,2,4-triazol-3-thiones (Fizer et al., 2022).

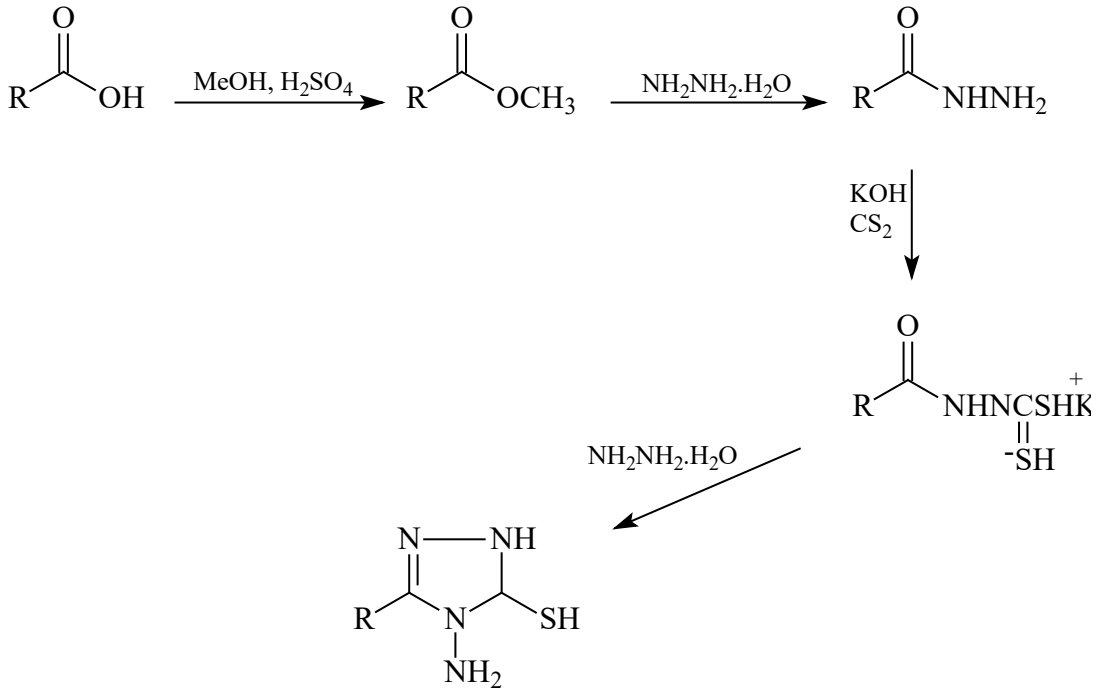


Electrochemically, one-pot direct synthesis of 3,5-disubstituted 1,2,4-triazoles from nitrile and hydrazide using KI as a redox catalyst was carried out (Singh et al., 2020).

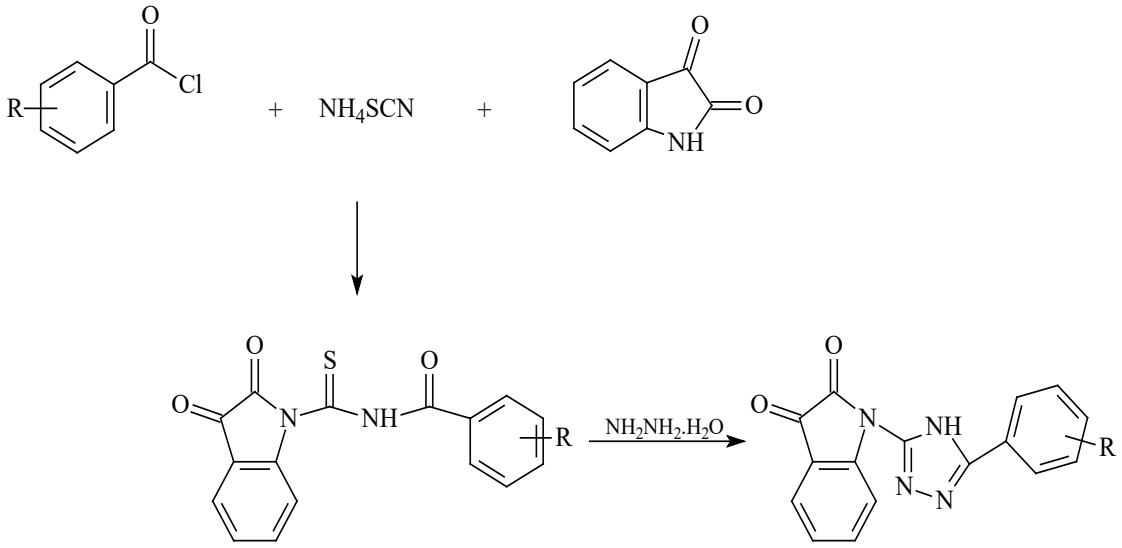


The following procedure has been followed for the synthesis of 1,2,4-triazole-derived compounds: The aromatic carboxylic acid is treated with methyl alcohol in the presence of sulfuric acid via Fischer esterification to form the aromatic acid ester. Subsequent treatment of this compound with hydrazine hydrate forms acid hydrazide. It gives dithiocarbazinic acid salts as a result of interaction with KOH and carbon disulfide. It

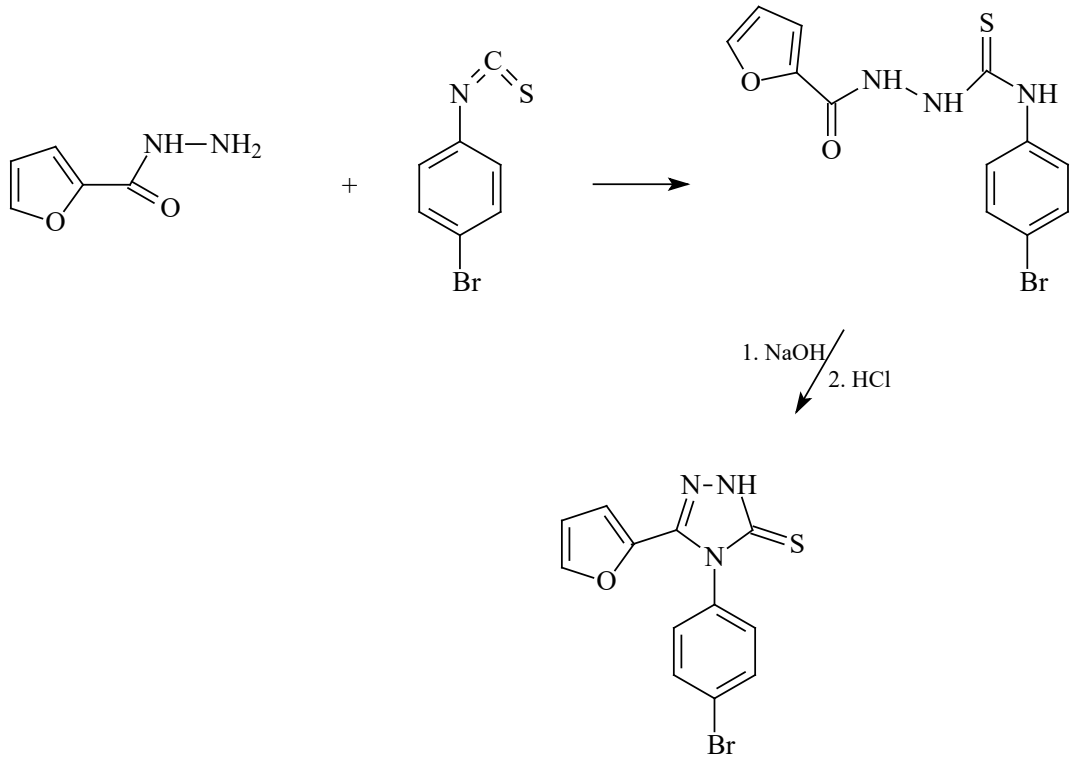
has been shown that 1,2,4-triazole-derived compound is formed in the interaction of this compound with hydrazine hydrate (Pathak et al., 2021).



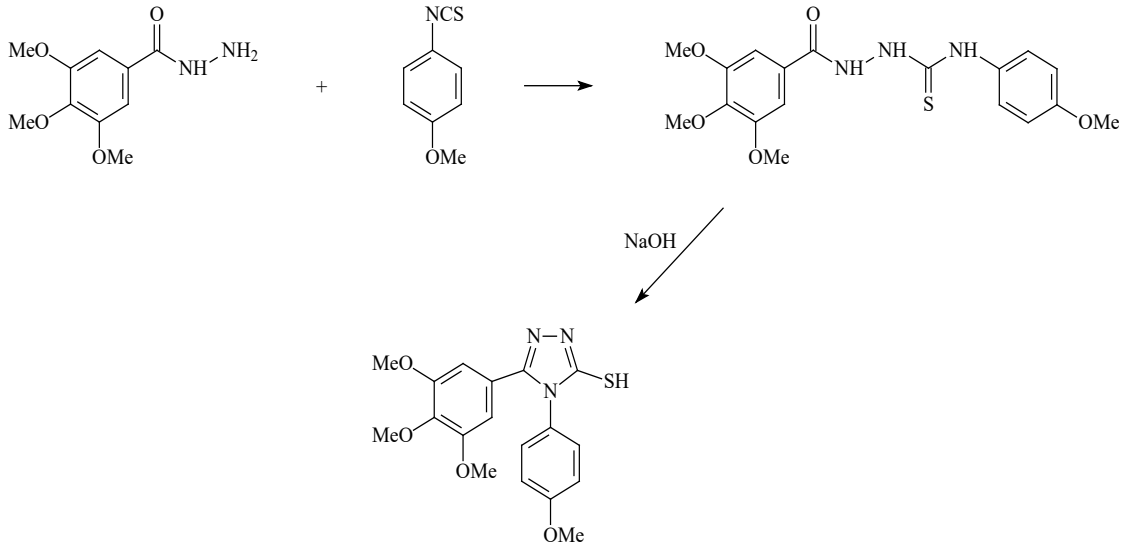
Benzoyl chloride, ammonium thiocyanate, and isatin react to form the thiourea-derived compound. As a result of the reaction of this compound with hydrazine hydrate, an indole-derived 1,2,4-triazole compound is obtained (Afshar et al., 2020).



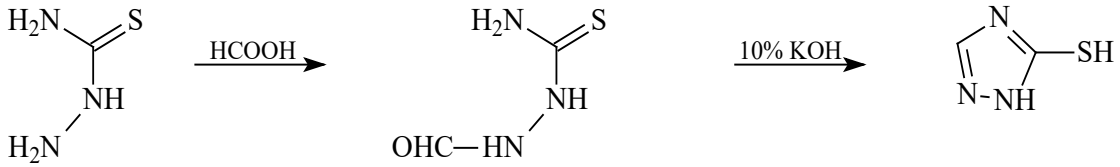
The following procedure was followed for the synthesis of the 1,2,4-triazole-derived compound: Furoic acid hydrazide and 4-bromophenyl isothiocyanate react to form *N*-(4-bromophenyl)-2-(furan-2-carbonyl)hydrazinecarbothioamide. This compound is reacted with NaOH. Then, the reaction mixture is acidified with HCl to give 4-(4-bromophenyl)-5-(furan-2-yl)-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (Dincel et al., 2021)



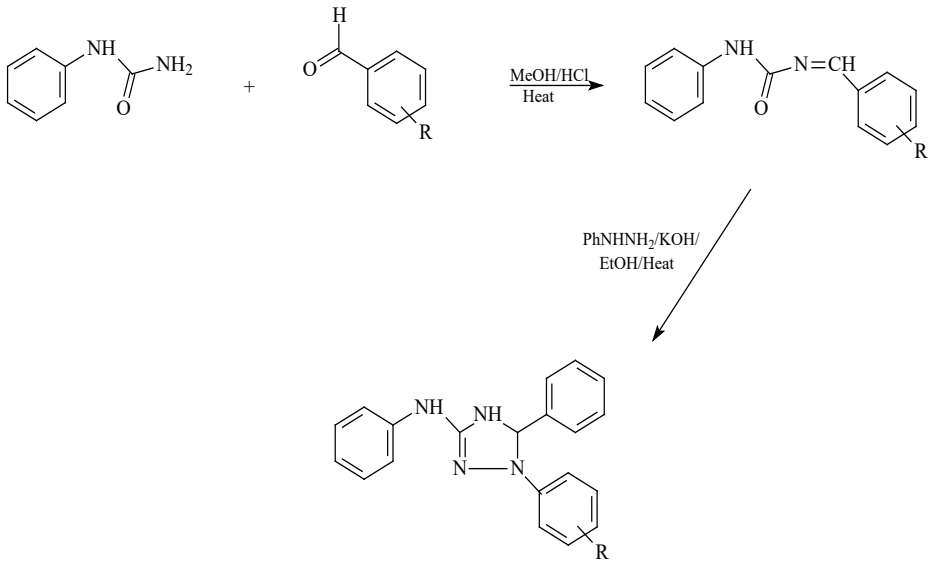
The intermediate product formed by the reaction of 3,4,5-trimethoxybenzohydrazide and 4-methoxyphenyl isothiocyanate is treated with NaOH to obtain 1,2,4-triazole derivative (Al-Mansury et al., 2019).



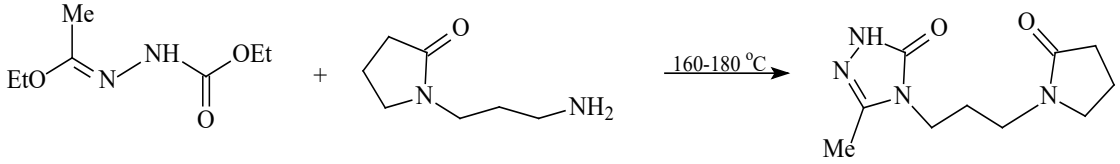
1-formylthiosemicarbazide is formed as a result of the reaction of thiosemicarbazide and formic acid. As a result of the reaction of this compound with 10% KOH, 2*H*-1,2,4-triazole-3-thiol compound is obtained (Khan et al., 2021).



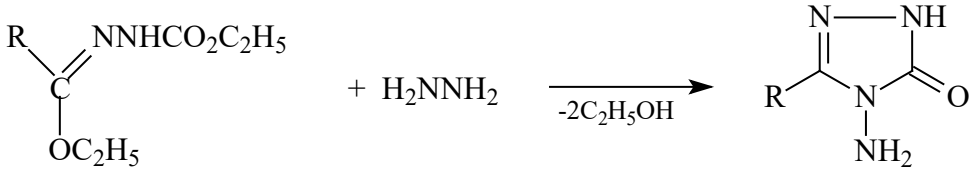
Dihydrotriazoles are synthesized from the cyclization reaction of 3-phenylurea-derived Schiff bases with phenylhydrazine under KOH/EtOH medium (Yusuf & Thakur, 2019).



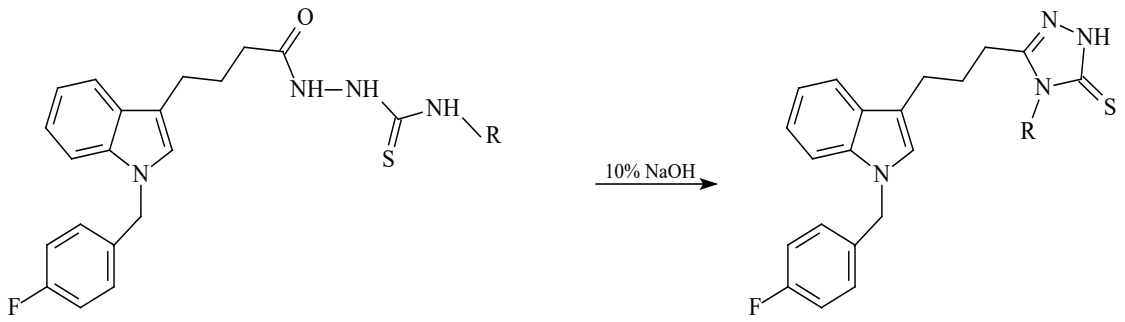
5-methyl-4-[3-(2-oxopyrrolidin-1-yl)propyl]-2,4-dihydro-3*H*-1,2,4-triazol-3-one are obtained by condensation of ethyl 2-(1-ethoxyethylidene)hydrazine-1-carboxylate with 1-(3-aminopropyl)pyrrolidin-2-one under solvent-free conditions at 160-180°C (Suleymanoglu et al., 2019).



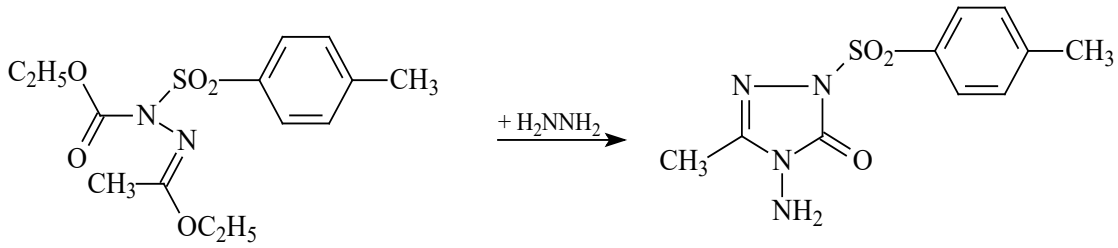
The compound 3-alkyl(aryl)-4-amino-4,5-dihydro-1*H*-1,2,4-triazol-5-one is obtained from the reaction of the corresponding ester ethoxycarbonylhydrazone with an aqueous solution of hydrazine hydrate (Ikizler & Yuksek, 1993).



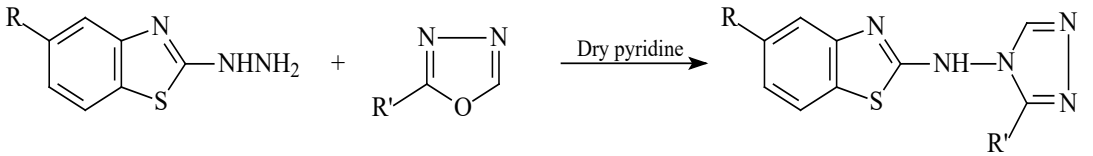
1,2,4-triazole-derived compounds are made by heating with 10% NaOH solution of corresponding thiosemicarbazides via cyclodehydration reaction (Ali et al., 2019).



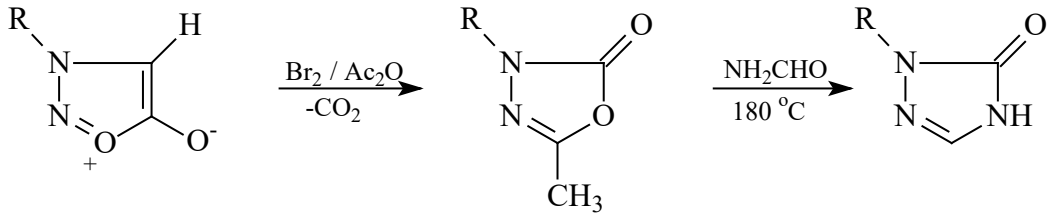
The compound 4-Amino-5-methyl-3-oxo-2-tosyl-1,2,4-triazol-3-one is obtained by the reaction of *N*^{1}-ethoxylcarbonyles *N*^{1}-tosylhydrazonates and hydrazine hydrate in ethanol containing a catalytic amount of glacial acetic acid (Saadaoui et al., 2019).



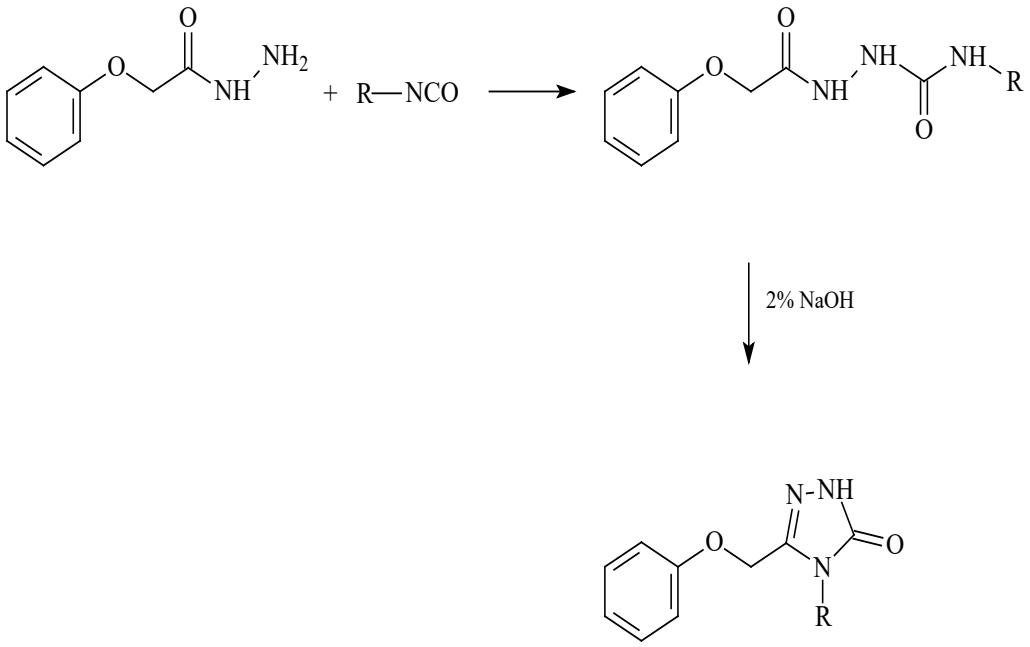
N-[3-(substituted-4*H*-1,2,4-triazol-4-yl)]benzo[d]thiazol-2-amines are formed as a result of condensation of oxadiazoles with hydrazinylbenzothiazoles (Tariq et al., 2018).



N-arylsydnone is converted to 3-aryl-5-methyl-1,3,4-oxadiazol-2(3*H*)-one by the [3 + 2] cycloaddition reaction with bromine in acetic anhydride followed by the release of CO_2. Then, this compound reacts with formamide at 180°C to synthesize 2-aryl-2*H*-1,2,4-triazol-3(4*H*)-one as a result of nitrogen addition to the ring and demethylation at C_5 (Somagond et al., 2018).



Semicarbazide derivatives are synthesized by the reaction of phenoxyacetic acid hydrazide with suitable isocyanates at room temperature. Heating the semicarbazide derivatives in 2% aqueous sodium hydroxide solution provides 5-phenoxymethyl-4-substituted-1,2,4-triazol-3-one (Pachuta-Stec et al., 2017).



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