Digest paper

Progress in intermolecular and intramolecular reactions of thioamides with diazo compounds and azides

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**ABSTRACT**

Reactions of thioamides with nitrogen-rich 1,3-dipoles, diazo compounds and azides, have been known for long time already. However in recent years introduction of catalysts of different types (rhodium-, ruthenium- and copper-containing and Lewis acids) as well as highly electrophilic sulfonyl azides, allowed the development of new methods for the synthesis of heterocycles, enamines and N-sulfonyl amidines. Moreover, a new methodology in organic synthesis, based on generation and subsequent transformations of α-diazocarbonyl compounds was created. Reactions of sulfonyl azides with thioamides undergo readily in mild conditions to produce different sorts of N-sulfonyl amidines and represent a new type of click-type processes. Most of the cited works were published in the current decade. Earlier seminal papers are also reviewed when they constitute the background for new synthetic methods which were developed further.

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**Introduction**

Thioamides exhibit wide range of biological properties such as antifungal [1], antioxidant [2,3] and anticonvulsant [4] activities. Some of them strongly inhibit phosphoglycerate dehydrogenase [5]. Furthermore they also have found wide applications as intermediates in organic synthesis for the preparation of heterocycles and many valuable organic building-blocks [6–9]. The chemical properties of thioamides are considered in a review from Jagodziński [6] in 2003 and by Dyachenko et al. [7] in 2018. We have turned our attention to data on catalytic and thermal reactions of thioamides with diazo compounds and with sulfonyle azides, information, that these reviews did not contain, apart of a few examples. At the same time these reactions represent new and effective methods for the synthesis of various heterocyclic compounds, new types of amidines and their vinyllogs, enamines [10,11], exhibiting various types of biological activity [10], and can be used in synthetic organic chemistry as valuable chemical reagents [8,9]. In this digest, we have summarized the literature reports on the progress in synthetic methods and in reactions of thioamides with diazo compounds and azides including thermal and catalytic processes.

**Synthesis of thioamides**

The main methods of the synthesis of thioamides include: (i) Thionation of amides with P₄S₁₀ [11a], with complex of P₄S₁₀...
with pyridine in organic solvents [11b] or in the presence of hexamethyldisiloxane [11c], with the system of PCl₃/H₂O/Et₃N [11d] and with Lawesson's reagent [11e], (ii) reaction of nitriles with H₂S or its precursors in the presence of bases [11f], (iii) Wilgerodt-Kindler reaction, including three-component reactions [11 g,h,i], (iv) reactions of aromatic and heteroaromatic compounds with isothiocyanates in the presence of Lewis acids [8].

Reactions of thioamides with diazo compounds

Thermal reactions. In contrast to the cycloaddition reactions of thioketones [12–15], the analogous reactions of thioamides are scarce [16,17]. Careful study of reaction of 2-thiocarbonylthioamides 1 with diphenyl diazomethane 2 undertaken by the Heimgartner group has shown that the thioamide moiety did not take part in cycloaddition reaction but participated in subsequent 1,5-dipolar electrocyclization of thiocarbamoyl thiocarbonyl ylides 3a formed in reaction of thioketone group with compound 2 to afford dithiole 4 in 33% yield (Scheme 1) [16].

Heimgartner and coworkers have shown that N-methylidene thioamides 5, where the C=S bond is conjugated with N=C, are more reactive than thioamides with an adjacent amino group. This reaction is interesting from a theoretical point of view providing evidence that the disruption of thioamide resonance increases the reactivity of the C=S bond toward a diazo group. Thioamide 5 reacted with diazoalkane via intermediate thiocarbonyl ylide 3b to form a mixture of 2,5- and 4,5-dihydrothiazoles 6 and 7 in moderate yields [17]. The formation of two types of products was explained by competition between 1,5- and 1,3-electrocyclic reactions of thiocarbonyl ylide 3 leading to 6 and 7 respectively (Scheme 2).

Alkyl and aryl carbothioamides 8 have been shown to react with ethyl diazopyruvate in the presence of boron trifluoride etherate affording 2-substituted 4-carbethoxythiazoles 9 in good yields (Scheme 3) [18].

Cyanothioformanilide has been shown to exhibit very high reactivity towards diphenyl diazo methane 2 to form α-cyano-β, β’-diphenylenamine 10, in the absence of any catalyst and additives, in 40% yield. It is the first and single example of the synthesis of enamines by reaction of thioamides and diazo compounds. The reaction takes place under very mild conditions and is completed in 25 min at room temperature. A plausible mechanism includes the formation of thiazoline 11 and thiirane 12 intermediates similar to those in reactions of thioketones with diazoalkanes (Scheme 4) [19].

Metal-catalyzed reactions.

Thermal reactions of thioamides with diazo compounds are limited to a few examples of the synthesis of thiazoles, thioisomunchone, benzothiazine, thiophenes and enamines by reactions of thioamides with diazo compounds in the presence of rhodium-, ruthenium- and copper-containing catalysts.

Thiazoles. Villagordo et al. have found that diazoketesters 13 react readily with primary thioamides 14 under reflux in toluene in the presence of copper bromide to afford 2,4,5-trisubstituted thiazoles 15 in 60–80% yields (Scheme 5) [20]. The fact that the
catalyst was used in equimolar amount was the reason to propose a mechanism where thioimidate was the key intermediate of the process. Notably, thioamides of aliphatic acids also react in these conditions to form similar products but in lower yields.

Moody and coworkers demonstrated the use of \( \text{Rh}_2(\text{NHCOC}_3\text{F}_7)_4 \) to prepare a series of thiazoles \( \text{17} \), bearing various aryl substituents in position 2, and carboxylate, phosphonate or tosyl groups in position 5 of the ring, in 35–88% yield \( \text{[21]} \). The authors considered two alternative mechanisms \( A \) and \( B \) for this reaction. The first is similar to work of Villagordo et al. \( \text{[20]} \) and involves the insertion of a carbene into the SH bond of the thioamide – imino tautomer to give thioimidate \( A \). The second one more likely includes the formation of a thiocarbonyl ylide \( B \) as a key intermediate (Scheme 6) \( \text{[21,22]} \). No arguments in favor of the mechanism \( B \) were given.

Intramolecular interaction of diazo and thiocarbonyl functions was observed in rhodium tetraacetate-assisted cyclization of diazo-thione \( \text{19} \) generated from indoline-2-thione \( \text{20} \) and diazo compound \( \text{21} \) to form thioisomunchnone \( \text{22} \). The latter is a masked thiocarbonyl ylide which can react with \( N \)-methylmaleimide and maleic anhydride to afford cycloadducts \( \text{23} \) (Scheme 7) \( \text{[23]} \).

**Benzothiazines.** The Reddy group has discovered the formation of a thiazine ring as a result of the copper-catalyzed reaction of thioamides bearing the diazoester moiety \( \text{24} \) in the molecule. This furnished a small series of benzof[d][1,3]-thiazines \( \text{25} \) in 75–80% yields. A plausible mechanism involves the insertion of a copper carbenoid into the thiocarbonyl group, leading to the formation of a thiocarbonyl ylide followed by an H-shift which finalizes the process (Scheme 8) \( \text{[24]} \).

**Thiophenes.** Jointly with the Nikolaev group we have developed a method for the synthesis of 2,3,5-trisubstituted thiophenes \( \text{26, 27} \) and \( \text{28} \) based on Rh(II)-catalyzed reactions of 2-diazo-2-cyanoacetic \( \text{29} \) and 2-diazo-malic esters \( \text{30} \) with tertiary 2-cyanothioacetamides \( \text{31} \) in 52–97% yields (Scheme 9). A possible mechanism involves the formation of thiocarbonyl ylide \( \text{32} \), intramolecular cyclization of the negatively charged carbon atom of the latter onto the cyano group followed by H and ester shifts to give thiophenes \( \text{27} \) [\( \text{28} \) (Scheme 9)] \( \text{[14]} \). The formation of unexpected products \( \text{28} \), occurring only in the reaction of 2-diazomalic esters, was explained by saponification of ester group followed by decarboxylation to form 4-aminothiophene \( \text{27} \) (\( R = \text{H} \)) and insertion of a carbene derived from diazomalonic esters \( \text{30} \) into the amino group of aminothiophene \( \text{[25]} \).

**Enaminones.** In their earlier publications, the Padwa and Dangshefsky groups used the rhodium-catalyzed reaction of thioamides with diazocarbonyl compounds in the synthesis of indolizomycin \( \text{[26]} \) and thioisomunchnones \( \text{[27]} \). Subsequently, Nakano and co-workers \( \text{[28]} \) have reported the formation of a
mixture of thioimidates and enaminones as a result of the reaction of diazoesters with thiobenzamides.

Until 2012, there were only two publications where the rhodium-catalyzed variants were used in intermolecular reactions [26,28]. Recent trends in the progress of reaction of this type dealt with the use of ruthenium-[29–31] and copper-containing catalysts [32,33]. A systematic study was made by Hussaini and co-workers, who have discovered and carefully studied intermolecular reactions of primary, secondary and tertiary thioamides with diazo ketones and diazoesters in the presence of seven types of ruthenium catalysts [29–31]. They have found that the reaction of thioamides with diazo dicarbonyl compounds such as diazoesters, diazoketoesters and diazoketones takes place readily in a sealed tube at 120 °C in the presence of ruthenium catalysts, Grubbs-1 or [P(Ph)₃]RuCl₂ to furnish enaminones in good yields. Because of dimerization of diazo compounds, two equivalents of diazo compounds are required to complete their reactions with N-benzylthiopyrrolidine (Scheme 10).

In optimal conditions, the reaction of diazoacetophenone with thioamide follows another course to give iminothioether as the main product. It is worth mentioning that the direction of the reaction of thioamides with diazoketones depends on whether primary or secondary thioamides were used leading to 3-hydroxy-thiazolines or thioimidates, respectively. The use of triphenylphosphine as an additive in the reaction of secondary thioamides allows to convert to Z-enamine in 83% yield (Scheme 11) [29].

The proposed mechanism of enaminone formation includes the formation of ruthenium carbene, followed by the attack of the latter onto the sulfur atom of thioamides to form ruthenium complex and, after release of the catalyst, the formation of thiocarbonyl ylide (Scheme 12) [29]. The latter, via 1,3-electrocyclic reaction, forms thirane and elimination of sulfur gives rise to the final product, enaminone.

The Hussaini group has improved the synthesis of enaminones from thioamides based on the copper-catalyzed reactions of diazo carbonyl compounds [20]. They have found that the use of (CuOTf)₂Tol in dichloroethane at 90 °C is the method of choice for the synthesis of enaminones by reactions of thioamides with various types of diazo compounds (Schemes 13) [31].
The reaction has broad scope and tolerates variations of structures of both starting reagents, diazo compounds and thioamides. Thus, 2-diazomalonic ester, 2-diazo-2-acetyl(benzoyl)acetic ester, 2-diazoketones, 2-diazo-2-phenylsulphonylacetone, diazo compounds bearing various amide groups and diazo acetophenone were used in reactions with primary, secondary and tertiary thioamides to afford a variety of enaminones, predominantly in very good yields. Contrary to the reactions in the presence of Rh and Ru catalysts, no dimers of diazo compounds or thioimidates were observed. The authors have shown that reaction of thioamide 34 with diazo compounds 34 bearing different R1 and R2 occurs in most cases diastereoselectively with d.e. from 1:1 to 17:1. This selectivity was explained by the higher stability of Z-isomer. The formation of the products of insertion in NH and CH bonds does not occur. A plausible mechanism for formation of enamines proposed by the authors is similar to that proposed by Hussani et al. for the reaction catalyzed by a ruthenium catalyst [30]. Further improvement of the approach to enaminones by copper-catalyzed reaction of diazo compounds with thioamide was made by the Hussaini group by the use of a copper(I)-complexed magnetic nanoparticle catalyst. The catalyst reduces the time of reaction, decreases its temperature and provides high yields of a series of enaminones [32].

Transformations of α-diazothioacetamides. The cyclization of α-diazothiocarbonyl compounds 47 occur as a very fast 1,5-electrocyclic reaction to form relatively stable 1,2,3-thiadiazoles 48 (Scheme 14) [34,35]. The theoretical and experimental study of this and similar electrocyclic reactions have shown them to proceed with very low barriers which led to the concept of heteroelectrocyclic [36] or pseudopericyclic [37] reactions. Because the cyclization of diazothiocarbonyl compounds is straightforward to 1,2,3-thiadiazoles, the methods of the synthesis of the latter are based on the syntheses involving unstable diazothiones [34,35]. The three general methods leading to compounds 48 include the diazo group transfer [34,35,38] onto active methylene thioamides with sulfonyl azides, diazotization of amines bearing thiocarbamoyl group and rearrangements of 1,2,3-triazole-4-carbothioamides [35]. 1,2,3-Thiadiazoles are prone to transformations and rearrangements taking place via α-diazothiones as shown in Scheme 15. Thus thiadiazoles 48 undergo Dimroth-type rearrangement to form 1H-1,2,3-triazol-3-ium-5-thiolates 49, in good yields [34]. 4-Carbimino-1,2,3-thiadiazoles 48 (R3 = HC = NR) formed by reaction of 4-formyl-1,2,3-thiadiazole with amines, are labile and rearrange to 1,2,3-triazol-4-carbothioamides 50 under the conditions used for their generation [39,40]. It was found that interaction of 1,2,3-thiadiazolylhydrazones of acetophenones with phosphorus pentachloride in benzene or toluene leads to 5H-[1,2,3]triazolo[5,1-b][1,3,4]thiadiazines 51. The reaction most likely involves Dimroth-type rearrangement of the thiadiazole ring into a triazole followed by intramolecular cyclization of Me and SH groups after treatment with PCl₅ [41].
Recently, we have prepared a series of 5-sulfonylamido-1,2,3-triazoles as sodium salts by reaction of tertiary 2-cyanothioacetamides with various arylsulfonyl azides in very good yields (Schemes 14 and 15) \[42,43\]. The proposed mechanism involves the cyclization of diazo compounds bearing thiocarbonyl and imidamide groups to triazoles. Careful studies have shown that the reaction occurs via three pathways to furnish generally a mixture of 5-amino-4-cyano-1,2,3-thiadiazoles of type \(48\) (\(R^3 = \text{CN}\)), 5-sulfonylamido-1,2,3-triazole-4-carbothioamides \(52\) and 5-amino-1,2,3-thiadiazole-4-carboximidamides \(53\) (Scheme 15). Optimizing the reaction, we managed to find conditions for the synthesis of each compound as a single product. Amidino-thiadiazoles \(53\) were prepared by rearrangement of triazole \(52\) occurring in dilute hydrochloric acid \[42\]. Interestingly, reactions of tertiary cyanothioacetamides \(56\) with highly electrophilic 5-azido-1-methyl-4-nitroimidazole led to thiadiazole of type \(53\) (\(R = 1\)-methyl-4-nitroimidazol-5-yl) \[44\].

The first example of transformation of 1,2,3-thiadiazoles via carbene intermediate was observed in 2006 by the Morzherin group when a 1,2,3-thiadiazole bearing an ethoxycarbonylvinyl group in position \(48\) was refluxed in \(n\)-butanol causing the loss of \(N_2\) from the intermediate diazo compound \(47\) to afford 5-ethoxyfurans \(54\) via carbene \(55\) (Scheme 14) \[45\]. Ten years later, Gevorgyan and Kurandina \[46\] and subsequently the Lee group \[47–49\] have undertaken rhodium-catalyzed reactions of 1,2,3-thiadiazoles with alkenes, alkynes and nitriles, including the intramolecular mode, that confirms the existence of an equilibrium between 1,2,3-thiadiazole \(48\) and its open chain isomer, diazo thioacetamide \(47\) (Scheme 14).

### Reactions of thioamides with azides

This section is organized according to the type of product obtained.
1,2,3-Triazoles. Primary thioamide 57 was first found to undergo cyclization upon action of aryl azides 58 in ethanolic sodium ethoxide into ethyl 5-amino-1-phenyl-1,2,3-triazole-4-carboxylates 59 via a Dimroth reaction mechanism (Scheme 16) [43].

Tetrazoles. In recent years, the synthesis of tetrazoles from thioamides and azides was much improved by introducing new azidation systems that include catalysts and additives. Thus, primary aliphatic and aromatic, secondary acyclic, cyclic, and heterocyclic thioamides 60 undergo 'unprecedented high-yield simple and mild conversion' into 5-substituted, 1,5-disubstituted, or annulated tetrazoles 61, on treatment with a SiCl₄/NaN₃ reagent system in refluxing acetonitrile (Scheme 17). The authors evidenced the mechanism of activation of C=S bond by its interaction with SiCl₄ to form thioimidate 62 by isolating N-silyl triazoles 64 (when primary thioamides are put into the reaction). The cyclization of azidoimine 63 formed in reaction of thioimidate 62 with sodium azide to intermediate tetrazole 64 followed by hydrolysis of the latter are final steps in the synthesis of tetrazoles 61 [50].

Another azidation system, trimethylsilylacetylene (TMSA)/triphenylphosphine (TPP)/diisopropyl azodicarboxylate (DIAD), was also used to prepare several tetrazoles 65 including bis tetrazoles, from linear N₄,N₆-ditritylated polyamino mono- or bithioamides 66 (Scheme 18) [51].

The same azidation system was applied to prepare 5-(4-(1,2-dithiolan-3-yl)butyl)-1-(3,4-dimethoxyphenethyl)-1H-tetrazole 67a in good yield from thioamide 68a (Scheme 19) [52]. The synthesis of tetrazoles 67a-e was carried out in order to explore the influence of the bioisosteric replacement of the amide group on the neuroprotective activity of the lipoic acid/dopamine conjugate (Scheme 19). Thioamides with similar structures 68b and 68c in the same reaction conditions afforded tetrazoles 67b and 67c in drastically different yields (100% and 47%, resp.) while the starting and resulting compounds differ only in the number of methylene chains in the linker between NH and 3,4-dihydro-benzopyran [53]. No rationale is given to the observed phenomenon. Tetrazoles 67d,e, comprising both 5-(4-(1,2-dithiolan-3-yl)butyl) (as in [52]) and 1-(3,4-dihydro-6-methoxy-2,2,7,8-tetramethyl-2H-1-benzopyran-5-yl-methyl) (as in [53]) moieties were reported in the paper [54]. Here again, the same correlation between the length of the linker in starting thioamides 68d,e and the yield of tetrazoles 67d,e was observed and left undiscussed.

In the search for new P2X7 antagonists among tetrazole derivatives, the investigators [55,56] have synthesized tetrazoles 69 from thioamides 70 with TMSA in the presence of mercury(II) salts (Scheme 20). A small variations of the method involves addition of a base and triethylamine, to the reaction mixture [55]. Neither the data within the paper [55] nor comparison with reactions described in the other sources [57,58] could be used to deduce the role of triethylamine in the process. The yield of a representative tetrazole 69 (R¹, R² = Cl, H) prepared by the researchers from Abbott Laboratories [55] was unusually high (95%). The use of mercury(II) acetate was advantageous in one more synthesis from thioamide 70 (R¹ = 6-methoxycarbonyl-imidazo[1,2-a]pyridin-8-yl, R² = CHF2) [57]: the yield of the corresponding tetrazole 69 was as high as 97% (Scheme 20). Catalysis with mercury(II) acetate

\[
\text{Scheme 16. Synthesis of triazoles from primary thioamides 57 and aryl azides 58.}
\]

\[
\text{Scheme 17. Synthesis of tetrazoles 61.}
\]

\[
\text{Scheme 18. Synthesis of tetrazoles 65.}
\]
is not a guarantee of success: the yield of tetrazole 69 (R1 = (2-thiophene)methyl, R2 = 1-[4-(benzo[d]thiazole-2-yl)phenyl]prop-1-yl) was disappointingly low (13%) (Scheme 20) [58]. Anyway, there remains a concern that the use of toxic mercury-containing compounds conflicts with the current trend of applying more eco-friendly techniques.

TMSA/DCM/FeCl3 [59] and the metal scavenger Smopex®-301 (styril diphenylphosphine grafted polyolefin fiber) [60] were applied for the synthesis of a sterically rich tetrazole and 1-benzyl-5-(hex-5-enyl)-1H-tetrazole respectively.

Dihydroimidazole. A unique reaction, where the reacting center in the thioamide counterpart is neither C=S nor C-NH2 bond but a central C atom, is the cyclization of 3,6-diazidopyridazine 71 with diethyl (2-amino-2-thioxoethyl)phosphonate (72) in the presence of EtONa (Scheme 21) [61]. The authors postulate the intermediacy of the tetrazolopyrazine 73 resulting from the attack of the nitrene that could be formed from the azide 71, onto the CH2 in phosphonate 72. However, the structure of the resulting 7,8-dihydroimidazo[1,2-f]tetrazolo[1,5-b]pyridazine 74 has not been 100% reliably proved.

Amidines. Cyanothioformamides 75 were combined with phenyl azide 76 to afford amidines 77 as the final products; the process is postulated to be accompanied with elimination of N2 and S from
thiatriazole 78 and thiaziridine 79 intermediates (Scheme 22) [62]. Presumably, as in the reaction with diazo compounds (cf. Scheme 4), the cyano group attached to the thioamide group activates the C=S bond for the cycloaddition with 1,3-dipoles.

However, this novel reaction remains the only example of formation of amidines from the reaction of thioamides with aryl azides. In contrast to aromatic azides, the highly electrophilic sulfonyl azides were shown by Zelenskaya et al. [63] and other groups following up on this report [64–69] to be more prone to react with thioamides to form N-sulfonyl amidines. Thus Zelenskaya et al. discovered that thioamides of acetic and benzoic acid 80 reacted with tosyl azide 81 in pyridine to form N-tosylamidines 82 in 73–86% yields (Scheme 23) [63].

The Chiba group has found that the reaction proceeds also in water, alcohols and other polar solvents [65,66]. Protic solvents, ethanol and water gave the best results. The reaction has a wide scope; primary, secondary and tertiary thioamides 83 including cyclic ones react with mesyl- and benzenesulfonyl azides 84 to afford a variety of different N-sulfonyl amidines 85 in good to excellent yields (Scheme 24). It was shown that the reaction of thioamides of acetic acid (83, R^3 = Me) occurs faster than thiobenzamides (83, R^3 = Ph). Based on the fact that the reaction goes faster in polar than in apolar solvent and on calculation data for the energy and population of frontier orbitals, the author proposed a two-step mechanism for the formation of amidines 85 involving a thiatriazene intermediate.

Further study of the reaction resulted in the development of a solvent-free protocol which was used by the Bakulev group for the successful synthesis of active methylene amidines 86a-d from

![Scheme 22. Reaction of cyanothioamides 75 with azide 76.](image)

![Scheme 23. Synthesis of amidines 82 [63].](image)

![Scheme 24. Synthesis of amidines 85 from reaction of thioamides 83 with sulfonyl azides 84.](image)

![Scheme 25. Synthesis of active methylene amidines 86.](image)
reaction of active methylene thioamides 87 with a variety of sulfonyl azides 88. The absence of a solvent and the use of an equimolar amount of azide makes the protocol more eco-friendly (Scheme 25) [67].

The Bakulev and Lubec groups in cooperation applied this approach to the synthesis of N-sulfonlamidines of modafinic acid 89 which is a very effective inhibitor of dopamine transporter (Scheme 26) [68]. The scope of starting materials included a series of sulfonyl azides 90 and primary and tertiary thioamides of modafinic acid 91. Here again, two general protocols were applied: (i) refluxing ethanol with 5 equivalents of an azide and (ii) neat, in solvent-free conditions with equimolar amount of an azide. The second variant was demonstrated to be more favorable, providing comparable yields in much shorter time and better economy in azide.

The reaction was further adapted to the synthesis of hybrid molecules comprising benzimidazole and N-sulfonlamidine moieties, both known to impart biological activities of various types. In this specific application, the solvent-free protocol and the use of water as a solvent have failed. The reaction of thioamides 92 with azides 93 was found to be successful when a mixture of starting reagents in equimolar ratio was kept for 2–10 h in ethanol at reflux to form amidines 94 (Scheme 27) [69]. It was shown that sulfonlamidines 95 did not react with thioamides 92 (R = CF3) in any of the applied conditions.

In conclusion, contrary to thioketones, thioamides, due to ‘thioamide resonance’, are much less active in reactions with dipoles. Exceptions from this rule are thioamides of cyanoformic acid, which easily react with diazo compounds and azides at room temperature resulting in amidines and their vinyllogs, enamines. Developments in synthetic methods based on the reactions under consideration included the use of sulfonlamides in preparation of N-sulfonlamidines and introduction of ruthenium- and copper-containing catalysts in the synthesis of enamines. The use of rhodium-containing catalysts in the reaction of diazo compounds with thioamides affords various heterocyclic compounds, such as mono- and bicyclic thiophenes, thiosulphonamides, thiazoles, and benzothiazines. Application of another type of catalysts, Lewis acids, in reaction of thioamides with inorganic azides gave impetus to progress in the preparative chemistry of tetrazoles. Further advance in synthetic possibilities of reactions of thioamides with diazo compounds and azides could be achieved after theoretical investigations of the high reactivity of thioamides of cyanoformic acid towards dipolar compounds and the unique capability of sulfonlamidines to react with thioamides to form amidines.

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