

Review

Recent Advances in the Synthesis of Isothiocyanates Using Elemental Sulfur

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Abstract: Isothiocyanates (ITCs) are biologically active molecules found in several natural products and pharmaceutical ingredients. Moreover, due to their high and versatile reactivity, they are widely used as intermediates in organic synthesis. This review considers the best practices for the synthesis of ITCs using elemental sulfur, highlighting recent developments. First, we summarize the in situ generation of thiocarbonyl surrogates followed by their transformation in the presence of primary amines leading to ITCs. Second, carbenes and amines afford isocyanides, and the further reaction of this species with sulfur readily generates ITCs under thermal, catalytic or basic conditions. Additionally, we also reveal that in the catalyst-free reaction of isocyanides and sulfur, two—until this time overlooked and not investigated—different mechanistic pathways exist.

Keywords: isothiocyanates; elemental sulfur; carbenes; isocyanides



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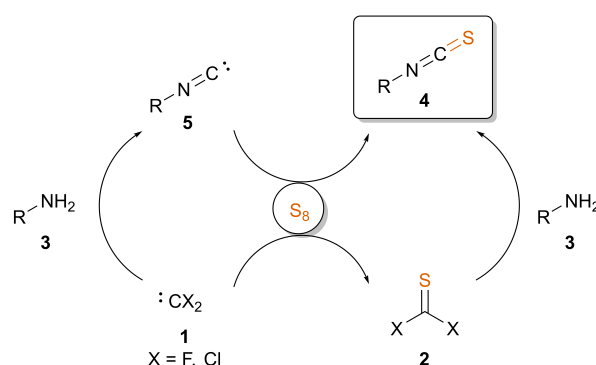
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1. Introduction

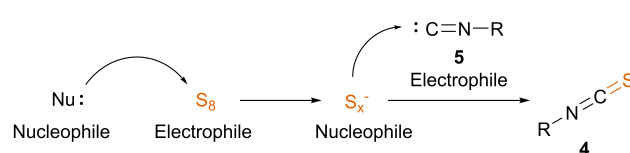
Isothiocyanates (ITCs) are biologically active molecules occurring in cruciferous vegetables such as broccoli, watercress, cabbage and cauliflower suggested to have anti-tumour activity [1–3]. They are represented among natural products and pharmaceutical ingredients by the biologically relevant welwitindolinone and hapalindole alkaloids isolated from various algae species [4]. Notably, glucosinolates, found as secondary metabolites in almost all plants, contain the $-S-C=N-$ functional group and act as a precursor for various ITCs [5,6]. Tissue damage of the plant promotes myrosinase enzyme activity as a defence mechanism, triggering the degradation of glucosinolates, and releasing, e.g., allyl, benzyl or phenethyl ITC or sulforaphane [7]. Sulforaphane, in particular, showed neuroprotective activity in the treatment of the neurodegenerative Alzheimer's and Parkinson's diseases [2,8]. Moreover, ITCs express significant antiproliferative activity as well [3,9], and the anti-microbial nature of certain ITCs makes them useful in food preservation [10]. Recently, they have also been applied as covalent warheads for labelling cysteine or lysine residues in medicinal chemistry and chemical biology applications [11–14]. Notably, due to their high and versatile reactivity, they are widely used as intermediates in organic synthesis [15,16]. ITCs readily react with nucleophiles, participate in cycloadditions leading to diverse heterocycles or are used in polymer chemistry [17].

The synthesis of ITCs generally relies on the reaction between thiophosgene or CS_2 and amines and thus involves the use of highly toxic reagents with narrow functional group compatibility [18–22]. Various thiocarbonyl transfer reagents appeared in recent decades to overcome these drawbacks, such as thiocarbonyl-diimidazole or dipyrindin-2-ylloxymethanethione [23,24]. Decomposition of thiocarbamates or dithiocarbamate salts with various reagents offers a good alternative as well; however, this approach first requires the synthesis of the appropriate precursors [25–30]. Nitrile oxides react with thiourea to afford ITCs and harmless urea, but one should note that the instability of nitrile oxides leads to many by-products, rendering this approach less attractive [31]. The reaction of isocyanides with disulfides in the presence of thallium (I)-salts as catalysts also leads to

the formation of ITCs [32]. This area has been reviewed recently [33]; thus, in this review, we focus solely on sulfur-based synthetic methods, which greatly emerged in recent years (Scheme 1). Elemental sulfur acts as the most atom-efficient surrogate to integrate the sulfur atom into the product [34–36]. The process is based on the nucleophilic attack of in situ generated carbene functionalities (1) on sulfur that behaves as an electrophile due to its empty *d*-orbitals [37]. This approach leads to thiocarbonyl surrogates (2), usually dihalogenides, reacting with primary amines (3) to provide ITCs (4). Otherwise, isocyanides (5), where the terminal carbon atom is able to act as a carbene, also undergo reaction with sulfur under thermal conditions or in the presence of external additives to yield ITCs. Notably, the addition of sulfur to formaldimines was also reported to generate ITCs, but this method is barely used nowadays [38,39]. The convenient activation of sulfur by nucleophilic additives, such as aliphatic amines and hydroxyl, sulfide and cyanide anions [40], and the corresponding significantly milder conditions compared to thermal activation support the notion that a switched mechanism also exists, involving a nucleophilic sulfur anion (S_x^-) and the carbene of the isocyanide (5) acting as an electrophile (Scheme 2). The experimental findings from the research of Al-Mourabit et al. and Meier et al. and those found by our research group also support this latter presumption [41–46]. The exact number or the distribution of sulfur atoms in the forming anions was investigated experimentally and theoretically as well, suggesting that it depends on the reaction conditions and reactants [47].



Scheme 1. The most popular reaction pathways to ITCs (4) involving elemental sulfur.

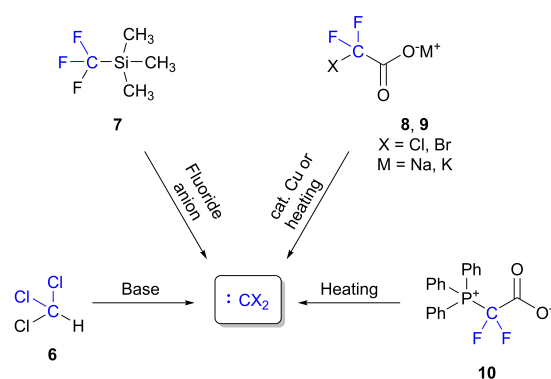


Scheme 2. Nucleophilic activation of sulfur, inducing the transformation of isocyanide (5) to ITC (4).

2. Synthesis of ITCs through Thiocarbonyl Surrogates

Thiocarbonyls such as thiophosgene or thiocarbonyl fluoride are typical precursors for the synthesis of ITCs [33,48]. However, due to their extremely reactive, volatile and toxic nature (bp. 70–75 °C and $\sim(-60)$ °C, respectively), they are inconvenient to store and handle. The in situ preparation of thiocarbonyl surrogates from carbenes and sulfur is the most significant approach considering the focus of this review on sulfur-based ITC synthesis. Besides the well-known trapping of (hetero)cyclic carbenes with sulfur, the transformation of di- or trihalogenated compounds to halocarbenes and the following reaction with sulfur are considered as a convenient process [49–51]. Common halogenated reagents are chloroform (6), trimethyl(trifluoromethyl)silane (F_3CSiMe_3 , 7) and the sodium and potassium salts of chlorodifluoroacetic acid (e.g., ClF_2CCO_2Na , 8) and bromodifluoroacetic acid (e.g., BrF_2CCO_2K , 9, Scheme 3) [52]. Notably, (triphenylphosphonio)difluoroacetate (PDFA, 10), prepared from BrF_2CCO_2K with triphenylphosphine, is a more efficient precursor of difluorocarbene based on the research work of Xiao and co-workers [53,54]. In EtOAc

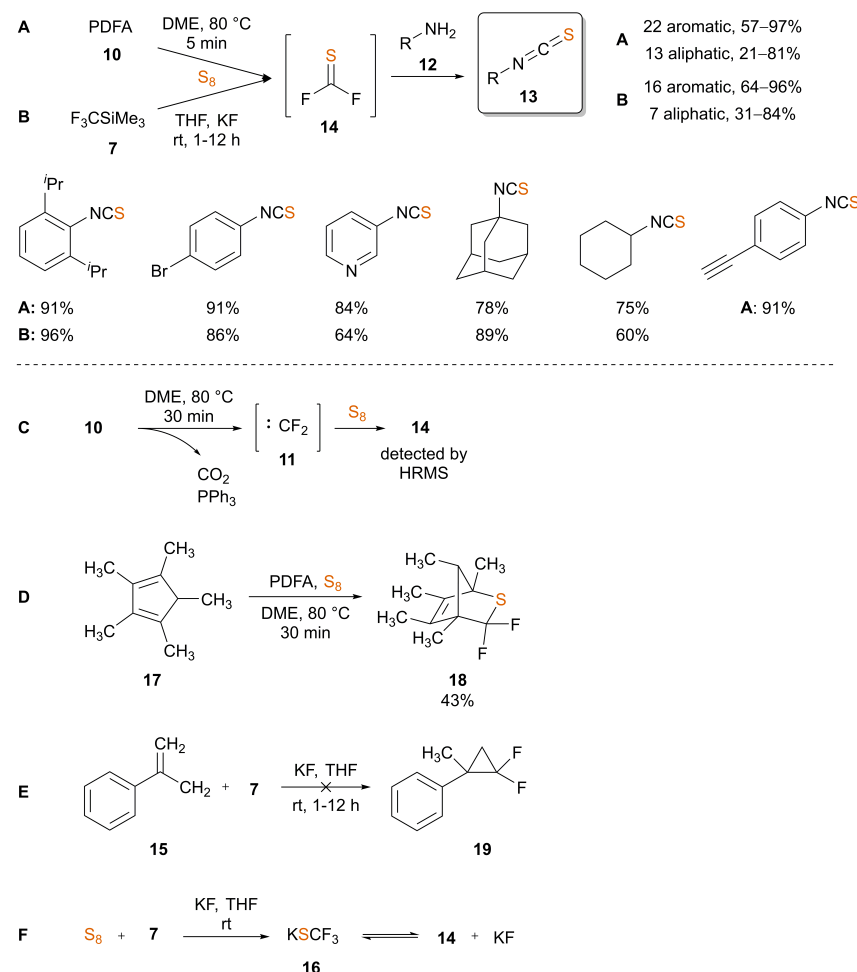
or nitromethane at reflux temperature, PDFA (**10**) decomposes to difluorocarbene (**11**), which is rapidly consumed by sulfur [55]. DFT calculations revealed that the reaction of sulfur and difluorocarbene is exothermic, with a high thermodynamic driving force ($\Delta G = -207.1 \text{ kJ mol}^{-1}$) and low activation energy barriers ($\Delta G^\ddagger = 33 - 42 \text{ kJ mol}^{-1}$). Eventually, Xiao and co-workers discovered the three-component reaction of **10**, sulfur and primary amines (**12**) resulting in ITCs (**13**) in 5 min at 80°C in DME (Scheme 4A) [56]. The reaction tolerated a wide range of functional groups, including nitrile groups, halogens and heteroaromatic nitrogen atoms. In particular, unsaturated C=C double and C $\equiv$ C triple bonds remained intact, which demonstrates the preferable reaction of difluorocarbene (**11**) with sulfur over other optional scavengers under the applied reaction conditions [52]. They proved the formation of thiocarbonyl fluoride (**14**) directly using HRMS and indirectly by trapping it in a Diels–Alder cycloaddition (Scheme 4C,D). In their three-component ITC synthesis, Jiang and co-authors introduced F_3CSiMe_3 (**7**) as a difluorocarbene source (Scheme 4B) [57]. Here, KF is responsible for the initiation of the reaction under ambient conditions in THF. Although they failed to capture difluorocarbene (**11**) in control experiments with prop-1-en-2-ylbenzene (**15**) under standard reaction conditions (Scheme 4E), the F_3CS^- anion (**16**) could be detected by HRMS. Based on literature data, they suspected the formation of thiocarbonyl fluoride (**14**) by the reversible decomposition of **16** (Scheme 4F) [58–61].



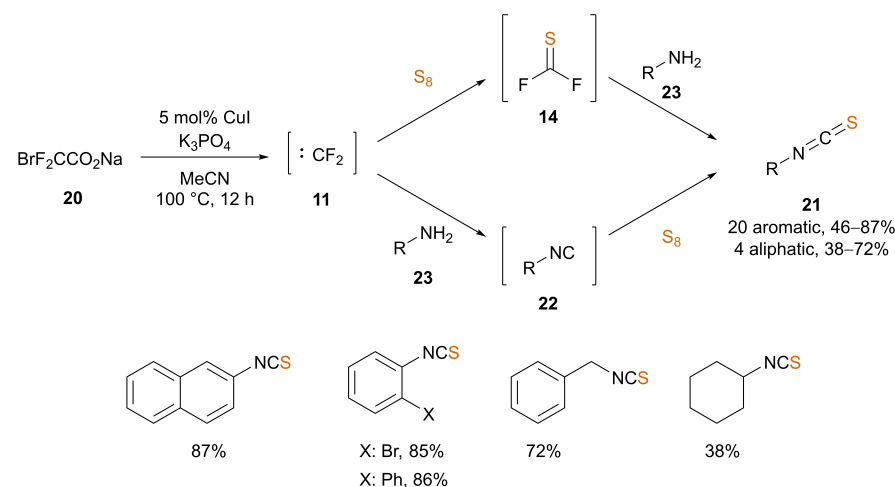
Scheme 3. Methods for dihalocarbene generation.

Zhang and Feng carried out the synthesis of ITCs starting from $\text{BrF}_2\text{CCO}_2\text{Na}$ (**20**, Scheme 5) [62]. The reaction conditions were harsh compared to the PDFA- and F_3CSiMe_3 -based methods, resulting in the formation of ITCs (**21**) after 12 h at 100°C in the presence of a copper catalyst and an excess of the base. Presumably, the role of the base is to promote the HBr elimination from **20** and to react with the acid, while the copper catalyst is assumed to play a role in the formation of difluorocarbene (**11**), and it might also stabilize the reactive intermediate [63,64]. The authors suggested two mechanistic pathways: through thiocarbonyl fluoride **14** or through the formation of an isocyanide Under standard reaction conditions, in the absence of sulfur, they isolated naphthalene-2-isocyanide (**24**) in 55% yield, which they transformed to **25** with sulfur in 83% yield (Scheme 6A). On the other hand, *ortho*-phenylenediamine (**26**) did not provide the expected cyclic thiourea (**27**) but rather 1-difluoromethyl benzimidazole (**28**) under standard reaction conditions, suggesting a fast attack on the carbene by the neighbouring amine. Similarly, the incorporation of sulfur was unsuccessful in the case of *ortho*-hydroxy aniline (**29**), where the standard conditions led to the formation of benzoxazole **30** (Scheme 6B). Interestingly, contrary to the latter result, Weng and co-workers showed that *ortho*-hydroxy anilines provide *N*-substituted benzoxazole-2-thiones (**31**) if difluorocarbene is generated in the reaction (Scheme 6C) under different conditions [59]. Consequently, in the case of the preparation of ITCs **21** (Scheme 5), the relatively harsh conditions, long reaction times and the control experiments do not support the in situ generation of thiocarbonyl fluoride. In fact, the generation of difluorocarbene from bromodifluoroacetate or the less reactive chlorodifluoroacetate readily

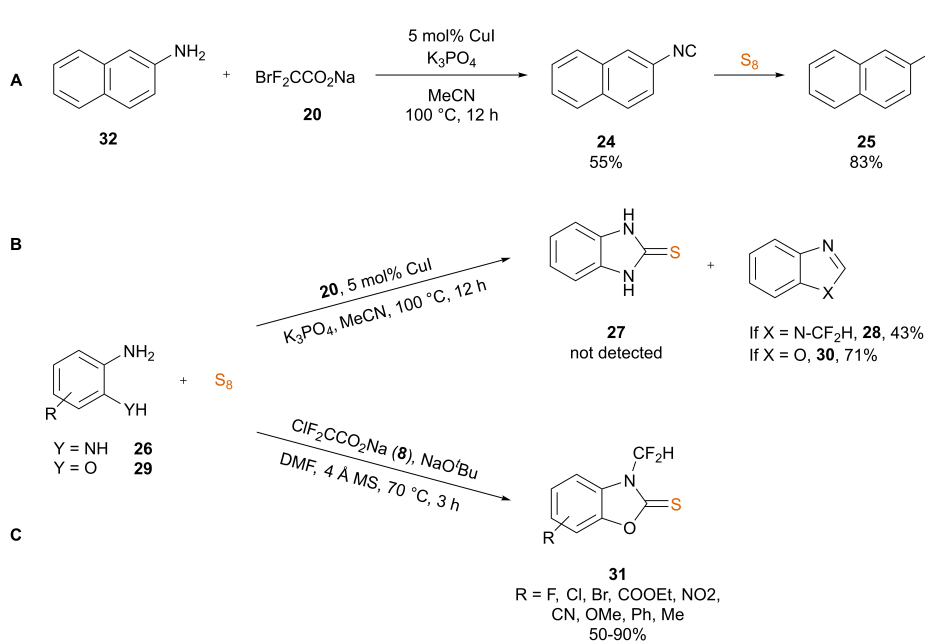
happens under 100 °C [63–65]. In conclusion, a more likely mechanism for the copper-catalysed ITC formation might rather be the transformation of the primary amine (**23**) into an isocyanide (**22**), which directly reacts with sulfur, resulting in ITC (**21**, Scheme 5).



Scheme 4. Approaches for ITC formation through thiocarbonyl difluoride by Xiao ([56], (A)) and Jiang ([57], (B)) with selected examples. Experiments to prove mechanistic assumptions (C–F). The scheme is based on Scheme 4 from [56] and Scheme 4 from [57].

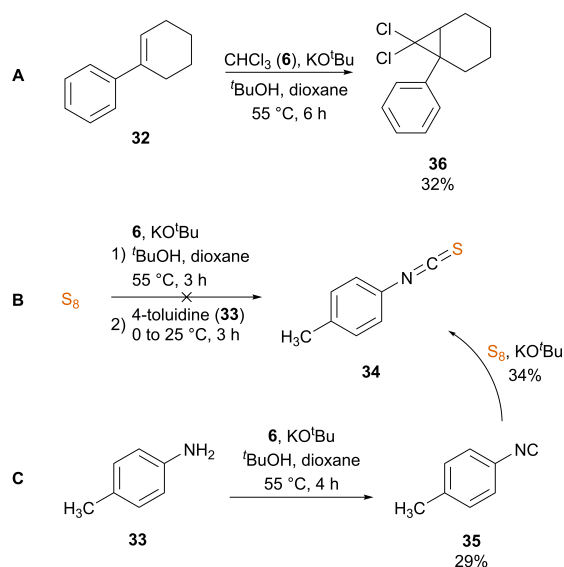


Scheme 5. Method and proposed mechanistic pathways for the copper-catalyzed synthesis of ITCs (**21**) through difluorocarbene (**11**, [62]) with selected examples.



Scheme 6. Control reactions for the proposed mechanistic pathways of the Zhang and Feng ([62]) synthesis (**A,B**). Reaction of *ortho*-hydroxy anilines with sulfur and difluorocarbene by Weng ([52], (**C**)). (**A,B**) are based on Schemes 2 and 4 from [62].

Interestingly, dichlorocarbene is less prone to react with sulfur, forming thiophosgene as Tan and co-workers suggested in their study in the multicomponent synthesis of thioureas [66]. Starting from chloroform (**6**) and KO^tBu at 55 °C, they trapped dichlorocarbene with the activated cyclohexene **32** (Scheme 7A). Nonetheless, the combination of sulfur with dichlorocarbene and sequentially with 4-toluidine (**33**) did not result in the formation of the corresponding ITC (**34**, Scheme 7B). On the contrary, in a sequential approach used on **33**, they generated the isocyanide **35** with dichlorocarbene, which was further transformed to **34** with sulfur under standard reaction conditions (Scheme 7C). This latter experiment suggests that isocyanide may be the key intermediate in the reaction.



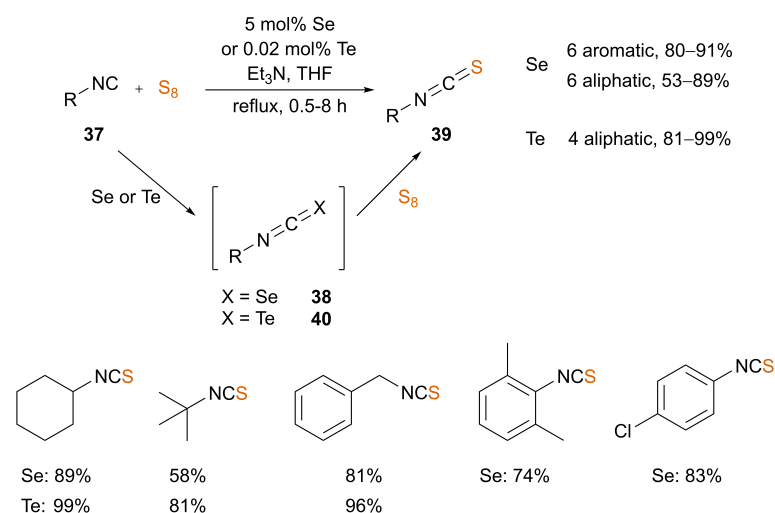
Scheme 7. Control reaction for the generation of dichlorocarbene (**A**). Method for the synthesis of ITC **34** using chloroform (**6**) by Tan and co-workers ([66], (**B,C**)). The scheme is based on Scheme 3 from [66].

3. Synthesis of ITCs from Isocyanides

The sulfuration of isocyanides directly leads to ITCs (Scheme 1). Aromatic isocyanides and sulfur afford ITCs refluxing in benzene for 3 days, resulting in moderate yields [34]. On the other hand, aliphatic isocyanides practically do not undergo any reaction at all [32]. This led researchers to the revelation that catalysis or other types of activation, particularly nucleophilic additives, are necessary for an efficient, useful and comprehensive methodology.

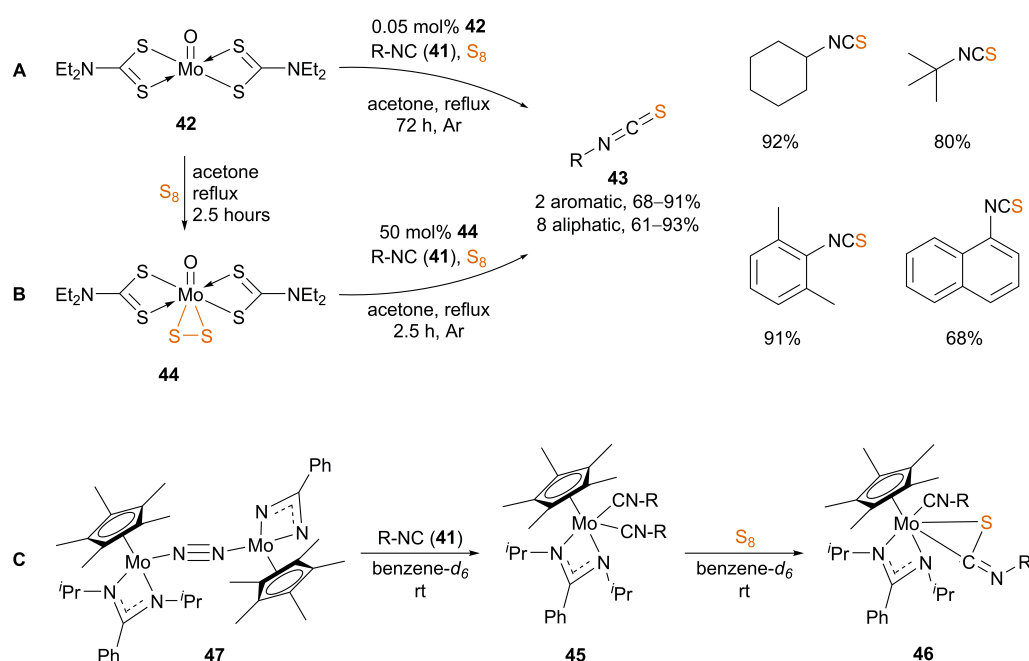
3.1. Catalysis

The application of chalcogens or transition metal catalysts, such as selenium [67], tellurium [68], molybdenum [69,70] or rhodium [71], greatly facilitates the generation of ITCs offering excellent yields. These results have already been discussed in previous excellent reviews; thus, we provide only a focused overview of this field [72,73]. In contrast to sulfur, in the presence of a base, selenium readily reacts with isocyanides (37) in refluxing THF, resulting in isoselenocyanates (38), which may turn into ITCs (39) with sulfur in only a few hours (Scheme 8) [67]. Fujiwara and co-workers showed that selenium is, indeed, a necessary additive in the reaction, but only in a catalytic amount of 5 mol%. Later, they revealed the enhanced catalytic activity of the analogous tellurium on aliphatic derivatives, providing better yields using a significantly lower catalyst loading of 0.02 mol% [68].



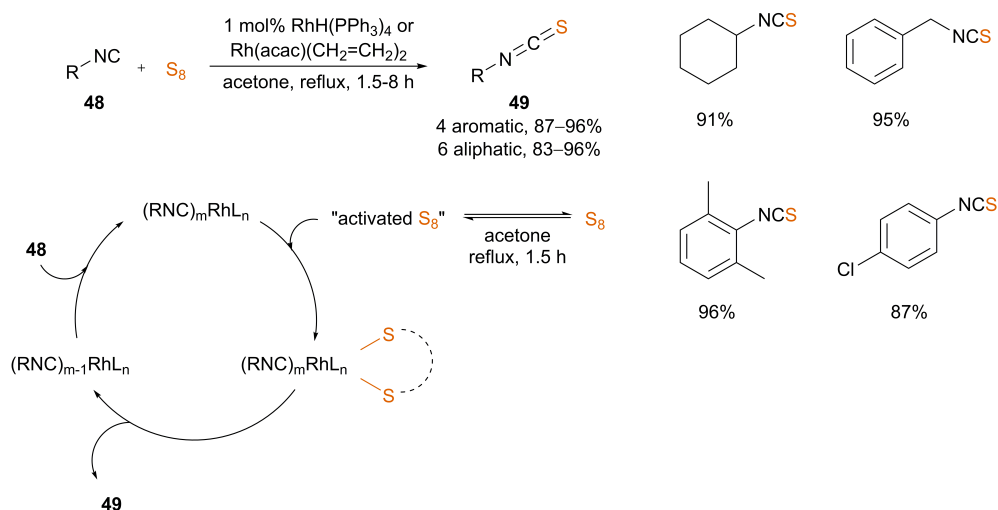
Scheme 8. Selenium- and tellurium-catalyzed transformation of isocyanides (37) leading to ITCs (39, [67,68]) and selected examples.

To circumvent the toxicity of chalcogens, Stalke and co-workers introduced a base-free approach using a molybdenum catalyst, which they already applied in the episulfidation of alkenes and allenes with sulfur [69,74,75]. The reaction of isocyanides (41) and sulfur in the presence of catalyst 42 required 3 days in refluxing acetone, resulting in ITCs (43) in good to excellent yields (Scheme 9A) [69]. The first step of the reaction might be the sulfuration of 42 providing the molybdenum disulfur complex 44, which acts as the active sulfur-transferring agent. The application of 44 in stoichiometric amounts leads to 43 in only 2.5 h, supporting its involvement in the reaction (Scheme 9B). The work of Sita and co-workers also supports the participation of the catalyst in the sulfur-to-isocyanide addition. They prepared *bis*(isocyanide)-Mo complexes 45 through ligand exchange, which they further transformed to κ -(S,C)-ITC-molybdenum complexes (46) with sulfur (Scheme 9C) [70]. Presumably, 46 is a key intermediate of the reaction, characterized by X-ray crystallography. Starting from 47 in the presence of isocyanide and sulfur afforded ITCs in 16 h of reaction time indicated by ^1H -NMR experiments at 50 °C in benzene- d_6 with a catalyst loading of 5%.



Scheme 9. Molybdenum-catalyzed transformation of isocyanides (**41**) to ITCs (**43**) with selected examples and mechanistic insights ([69,70]). (A,B) are based on Scheme 1 from [71]. (C) is based on Schemes 1 and 2 from [70].

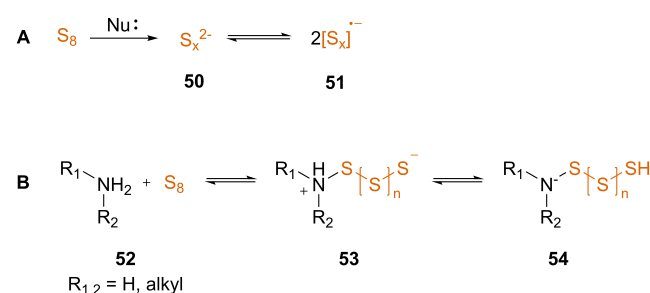
Next to molybdenum, the catalytic activity of rhodium in reactions with sulfur was demonstrated in the synthesis of 1,4-dithiins from cyclic alkenes, in the synthesis of diaryl sulfides and in the episulfidation of alkenes [76–78]. Yamaguchi and co-workers applied 1% RhH(PPh₃)₄ and Rh(acac)(CH₂=CH₂)₂ in the transformation of isocyanides (**48**) to ITCs (**49**) in refluxing acetone (Scheme 10) [71]. Notably, they observed shorter reaction times if they refluxed sulfur in acetone for 1.5 h prior to use. The activation period for sulfur probably involves the thermal generation of polysulfides, followed by sulfur atom exchange promoted by the catalyst [79]. In particular, the application of organic tri- and tetrasulfides in the reaction with the isocyanide also led to the formation of ITC.



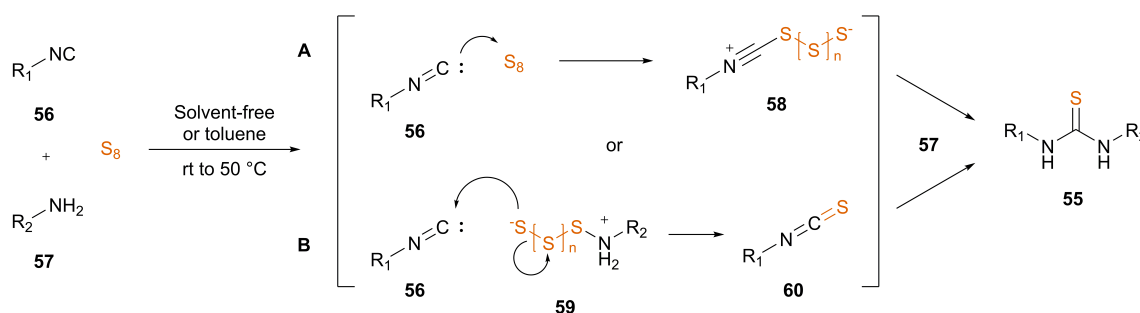
Scheme 10. Rhodium-catalyzed transformation of isocyanides (**48**) to ITCs (**49**) with selected examples and mechanistic insights ([71]). Scheme is based on Scheme 1 from [71].

3.2. Nucleophile-Induced Transformation of Isocyanide to ITC

The most common activation of sulfur is the cleavage of the octasulfur ring by nucleophiles [42–45,80–82]. Generally, cyanide, hydroxyl and sulfide ions may homolytically (Scheme 11A) or heterolytically (Scheme 11B) cleave sulfur–sulfur bonds under mild conditions, generating reactive linear polysulfide anion chains of different lengths (50) and radical anions (51) [83,84]. Notably, nucleophilic aliphatic amines (52) are very effective in activating sulfur, while (hetero)aromatic amines are generally not nucleophilic enough [85]. Primary and secondary amines can perform under ambient conditions; however, their use is limited as they necessarily react with in situ generated ITCs. Tertiary amines need harsher conditions to activate sulfur and possibly the presence of a proton source to be able to stabilize the linear polysulfide chains [86]. Al-Mourabit and co-workers established a three-component protocol for the synthesis of thioureas (55) starting from isocyanides (56), aliphatic amines (57) and sulfur [46]. They proposed two mechanistic pathways, with one through an intermediate containing a nitrilium structural element (58) resulting from the nucleophilic attack of 56 on sulfur (Scheme 12A). The electrophilic adduct 58 then reacts with 57, affording the thioureas 55. On the other hand, the aliphatic amines 57 might generate nucleophilic polysulfide anions (59) from sulfur at first (Scheme 12B), thus switching the reactivity, the isocyanide 56 being the electrophile and sulfur the nucleophile. The in situ generated ITCs (60) then might react with 57 in a simple addition, providing 55. The mild conditions support equation B, as in the absence of external additives, the reaction would require significantly higher thermal activation [32,34].



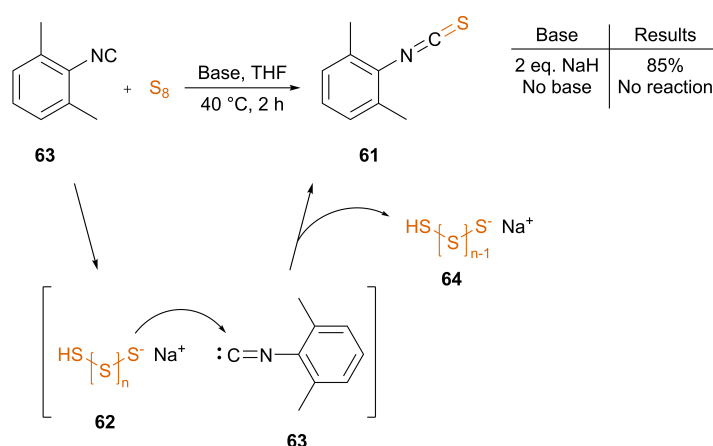
Scheme 11. Nucleophilic activation of sulfur leading to reactive polysulfide anions (50) and radical anions (51, (A)), and the mechanism of sulfur activation by nucleophilic aliphatic amines (52, (B)).



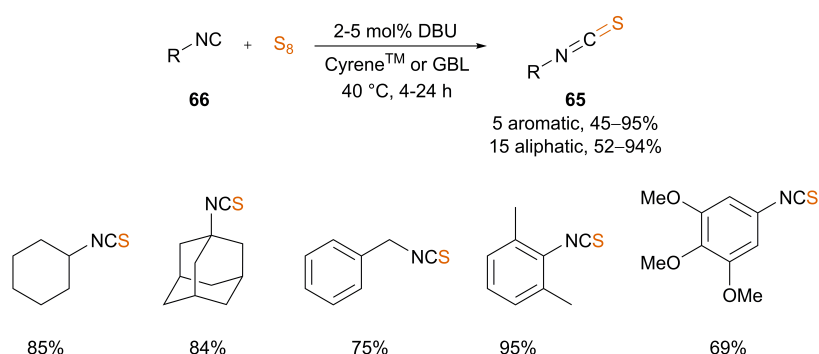
Scheme 12. Proposed mechanistic pathways for the synthesis of thioureas (55) from isocyanides (56) and amines (57). Isocyanides acting as nucleophiles through nitrilium cation pathway (A) or activated sulfur as nucleophile reagent leading to the formation of ITC intermediates ((B), 60, [46]). Scheme is based on Scheme 3 from [46].

Our research towards the multicomponent synthesis of thio- and dithiocarbamates from isocyanides revealed that a diverse set of nucleophilic additives, such as NaH, NaOEt, Cs₂CO₃, DIPEA or DBU, are able to activate sulfur. In addition, we isolated the ITC intermediate 61 from the reaction in 85% yield at 40 °C, after 2 h (Scheme 13) [42]. The mild conditions and the observation that, in the absence of additives, no reaction occurred also support the need for the activation of sulfur. This suggests the existence of the second

mechanism above (Scheme 12B) involving the formation of a nucleophilic reactive intermediate (62) attacking the electrophilic carbene (63). Benefiting from this new, convenient synthesis of ITCs, we established the improved, chromatography-free multicomponent synthesis of thioureas using tertiary amines as external activators that are resistant to acylation [43,44]. For this purpose, we prepared aqueous solutions of polysulfide anions, generated from sulfur and tertiary amines. We proved the existence of polysulfide anions in the reaction, on one hand, by the preparation of aqueous solutions in high concentrations (up to 0.4 M with respect to sulfur) and, on the other hand, by investigation of the solutions by NMR. Consequently, we proposed a switched mechanism towards the formation of ITCs from isocyanides and sulfur, where the nucleophile-activated sulfur attacks the electrophilic carbene. Most importantly, this transformation has proven to be more efficient, requiring shorter reaction times and milder conditions and featuring excellent functional group tolerance, validated in the synthesis of a diversely substituted set of thioureas, 2-iminothiazolines and 2-aminothiazoles [43–45]. Finally, Meier and co-authors recently published their improved method for the synthesis of ITCs (65) from isocyanides (66) and sulfur in the presence of only a 2–5 mol% base in renewable solvents (Scheme 14) [41]. They probed several tertiary amines, including DMAP, NMI, Et₃N, DABCO, DBU and TBD, in the reaction and found that, generally, higher basicity led to better conversions. Eventually, they applied the developed method in the synthesis of a small library of ITCs, showing the wide applicability of the method. They proposed the same mechanistic suggestions, involving sulfur as a nucleophilic partner in the reaction with the electrophilic isocyanide (66).



Scheme 13. Base-promoted transformation of isocyanides to ITCs with mechanistic insights ([42]).



Scheme 14. Base-promoted transformation of isocyanides (66) to ITCs (65) and selected examples by Meier and co-workers ([41]). Scheme is based on Scheme 3 from [41].

4. Overview and Practical Considerations of the Discussed Methods

Table 1 provides a comparison between the discussed synthetic approaches starting from amines or isocyanides with sulfur. When designing a multistep synthesis plan, depending on the stability of the substrate, one should consider the nature of additives, solvent, temperature and inert conditions if necessary. Generally, reactions involving difluorocarbene or thiocarbonyl fluoride require inert conditions, while isocyanide can be transformed to ITC under less strict conditions. The modification of amines is most effective using PDFA, but in the case of sensible compounds, one may turn to the room temperature approach involving F_3CSiMe_3 as a carbene source (Table 1, entry 2). The presence of potassium fluoride, however, may result in the removal of silyl groups on a complex structure, and a copper catalyst might lead to side coupling reactions and waste containing transition metals. Selenium and tellurium should be handled with care due to toxicity, while Mo or Rh catalysts increase the price and, again, transition metals in the waste. ITC formation from isocyanides, on the other hand, is very effective in the presence of bases. This approach can be performed in a relatively short reaction time compared to the transition metal-catalysed pathways, even under aqueous conditions. Based on the scope of substrates in the reported methods, one may note that all approaches provide ITCs in good to excellent yields. Challenging derivatives might be trityl ITC, generally obtained in lower yields, presumably because of steric hindrance, and low-molecular weight aliphatic ITCs, such as *tert*-butyl ITC due to its volatile nature.

Table 1. Summary of methods for ITC synthesis with the application of elemental sulfur.

Ref.	Starting Material	Additive	Inert Atmosphere	Solvent	T (°C)	T (h)	Yield (%)
[56]	Amine	PDFA	Yes	DME	80	0.083	21–97
[57]		F_3CSiMe_3 + KF	Yes	THF	rt	1–12	31–96
[62]		BrF_2CCOOK + 5 mol% CuI, K_3PO_4	No	MeCN	100	12	38–87
[67,68]	Isocyanide	5 mol% Se or 0.02 mol% Te	No	THF	reflux	0.5–8	53–99
[69,70]		“Mo” (X)	No	acetone	reflux	72	61–93
[71]		“Rh” (X)	Yes	acetone	reflux	1.5–8	83–96
[42]		2 eq. NaH	Yes	THF	40	2	85
[41]		2–5 mol% DBU	No	Cyrene TM or GBL	40	4–24	34–95

5. Conclusions and Outlook

ITCs are a biologically and synthetically relevant functional group, being present in important metabolites, natural products and synthetic intermediates. Their efficient and clean synthesis is of high interest, leading to the appearance of several recent methods. In particular, there are two strategies involving elemental sulfur for the incorporation of the sulfur atom, offering practical and modern approaches. The in situ generation of thiocarbonyl fluoride from difluorocarbene and sulfur provides ITCs with primary amines, or sulfuration of isocyanides may directly lead to ITCs under thermal-, catalytic- or nucleophile-induced conditions. Based on previous literature data and our recent results, we highlighted mechanistic insights into the latter transformation. Besides the conventional nucleophilic carbene and electrophilic sulfur setup, a switched mechanism is also proposed, where the polysulfide anions activated by a nucleophile are able to transform the isocyanide to ITC. This approach offers an efficient, mild and green synthesis of ITCs. We expect that this spotlight on ITC synthesis revealing different mechanistic pathways will inspire further research in the field and open up novel synthetic methodologies due to a deeper understanding.

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