C–H Activation with Elemental Sulfur: Synthesis of Cyclic Thioureas from Formaldehyde Aminals and S_8

Michael K. Denk,*[a] Shilpi Gupta,[a] John Brownie,[a] Sabiha Tajammul,[a] and Alan J. Lough[b]

Abstract: The C–H activation of cyclic formaldehyde aminals LCH_2 (L = RN-$CH_2CH_2CH_2$-NR and $RNCH_2CH_2$-NR, R = Me, Et, *i*Pr, *t*Bu, or Ph) with S_8 proceeds at unusually low temperatures ($T < 160\,^{\circ}C$) and results in the formation of the respective thioureas LC=S and H_2S. The reaction constitutes a new, solvent-free method for the synthesis of thioureas that eliminates the toxic and highly flammable CS_2. For R = *t*Bu, the ionic carbenium thiocyanates $[LCH]^+$ SCN^- dominate the product spectrum and the respective thioureas are obtained in low yield. The reactivity of the analogous sulfur and oxygen ring systems towards S_8 was investigated. 1,3-Dithiolane is cleanly converted into 1,3-dithiolane-2-thione (S_8, 14 d, 190 °C) and resembles the cyclic formaldehyde aminals in this respect. 1,3-Dioxolane (L = OCH_2CH_2O) is completely inert towards sulfur even under forceful reaction conditions (190 °C, 14 d). The formation of thioureas from aminals was investigated at the CBS-4 and B3LYP/6-31G(d) levels of theory.

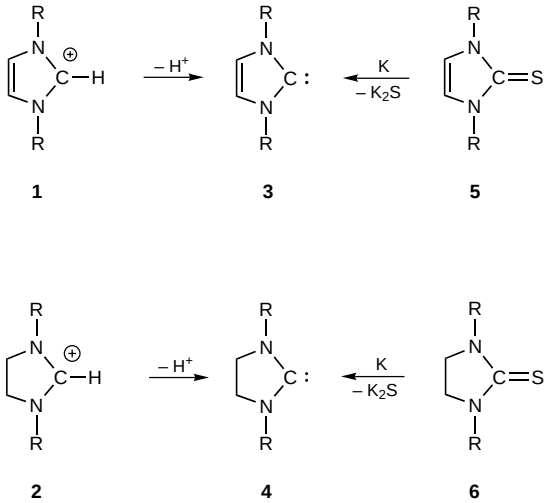
Keywords: ab initio calculations · C–H activation · dehydrogenation · sulfur · thioureas

Introduction

Thioureas[1, 2] are specialty chemicals with a wide range of applications. They are used as vulcanization accelerators,[1, 2b] as bath additives in electroplating processes,[3] and as analytical reagents.[4] Many thiourea derivatives show in vivo and in vitro activity against bacteria, fungi, parasitic worms, and viruses such as the HIV virus.[5] An impressive number of currently used drugs can be regarded as thiourea derivatives.[6] Thioureas can show considerable toxicity towards higher organisms as well, and some thiourea derivatives have been use as insecticides[7] or rodenticides.[8]

Thiourea and its derivatives find widespread use in the mining industry where they are employed as flotation aids for sulfidic ores[9] and as complexing agents for the enrichment of metals through solid–liquid and liquid–liquid extraction processes.[9] The high affinity of thioureas towards noble metals is underlined by the fact that thioureas are capable of dissolving gold or silver in the presence of oxygen. The leaching of gold and silver by thiourea from a variety of mineral sources has accordingly been the subject of numerous studies[10] but, although technically feasible, has so far failed to replace the environmentally notorious cyanide process that is still the standard process for the extraction of gold.[10a,b]

Our interest in thioureas arose from our study of the stable carbenes **4** (Scheme 1) which we obtained in good yields by the reductive desulfurization of the respective thioureas **6** with potassium.[16, 17]



Scheme 1. Synthesis of diaminocarbenes **3** and **4** by deprotonation or reductive desulfurization.

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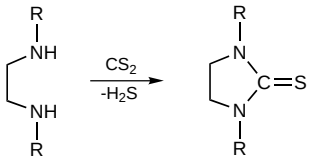
The corresponding carbenes **3** are more readily obtained through deprotonation of imidazolium salts **1**,[11] which are easily accessible through the one-pot condensation reaction of glyoxal, formaldehyde, and primary amines.[11, 12] Other diamino carbenium salts such as **2** are less readily accessible[13] and also tend to give lower yields in the deprotonation step.[14, 15] Due to these shortcomings, the reduction of thioureas is an important alternative for the synthesis of the diaminocarbenes.[16, 17]

Thioureas are typically obtained from the reaction of amines with CS_2 but the approach is not without shortcomings. For example, the synthesis of the cyclic thioureas **6** from the respective ethylenediamines and CS_2 gives yields that decrease with increasing bulk of the substituents on nitrogen (Scheme 2). For *N,N′*-di-*tert*-butylethylenediamine, the yields are inconsistent and often below 10%.



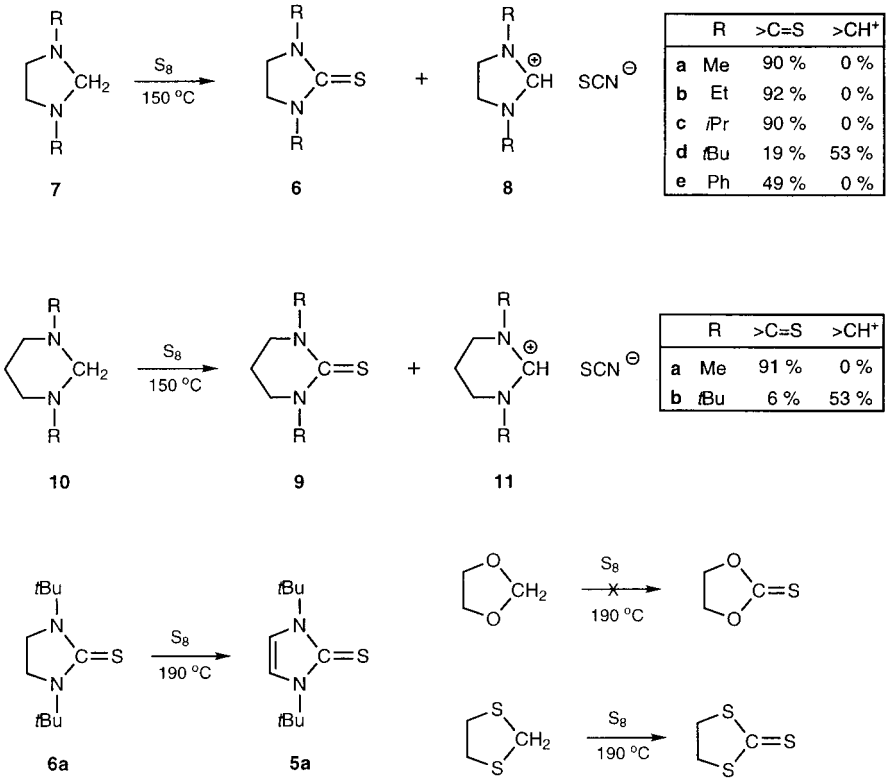
	R	Yield
6a	Me	80 %
6b	Et	74 %
6c	*i*Pr	50 %
6d	*t*Bu	19 %
6e	Ph	49 %

Scheme 2. Synthesis of cyclic thioureas **6** from *N,N′*-disubstituted ethylenediamines and CS_2.

Reasons for the often disappointing yields of the CS_2 route are not well documented in the literature but the issue of low yields has led to the development of improved synthetic procedures that use the addition of oxidizing agents, particularly iodine.[18] For the synthesis of the thioureas investigated in this study, the addition of iodine increases the crude yields (by a factor of 1.1 to 1.2) but tends to give products of lower purity. The additional purification steps required more than offset the increased crude yields.

A promising one-pot reaction, the synthesis of 1,3-diphenylimidazoline-2-thione (**6e**) from *N,N′*-diphenylethylenediamine, triethyl orthoformate, and elemental sulfur, was reported by Wanzlick et al.[19] The method works well as described, but we were unsuccessful in extending the approach to alkyl-substituted diamines.

The above-mentioned difficulties have encouraged us to investigate the reaction of formaldehyde aminals[20] with elemental sulfur.[21] We now report the facile conversion of *cyclic* formaldehyde aminals,[22] the imidazolidines **7** and the hexahydropyrimidines **10**, into the respective cyclic thioureas **6** and **9** (see Scheme 3).



	R	>C=S	>CH$^+$
a	Me	90 %	0 %
b	Et	92 %	0 %
c	*i*Pr	90 %	0 %
d	*t*Bu	19 %	53 %
e	Ph	49 %	0 %

	R	>C=S	>CH$^+$
a	Me	91 %	0 %
b	*t*Bu	6 %	53 %

Scheme 3. Reaction of cyclic aminals (**6a**, **7**, **10**), 1,3-dithiolane and 1,3-dioxolane with S_8. For yields based on amines, see Table 2.

Results and Discussion

Synthesis and purification: The cyclic formaldehyde aminals **7** and **10** are readily obtained from the respective 1,ω-diamines[20] and are used without further purification. The onset of the reaction with S_8 (150 °C) is indicated by the evolution of H_2S. Sulfur and most of the aminals are noticeably volatile under these conditions and, to avoid the loss of sulfur or aminal, the reactions are best carried out in closed systems. Standard reflux procedures tend to give lower yields and impure products. The best yields of thioureas are obtained by heating the aminal (0.1 mol) and S_8 (stoichiometric amount) to 150 °C for 12 h in a 50 mL stainless steel cylinder (Swagelock). Much shorter reaction times are sufficient in most cases, but a reaction time of 12 h leads to complete conversion even for aminals with bulky substituents, and does not decrease the yield for aminals that require shorter reaction times.

The thioureas **6** and **9** are conveniently extracted from the crude reaction mixtures with methanol. Evaporation of the solvent gives products that are already pure enough for the reduction to carbenes.[16, 17] Analytically pure samples are obtained following a workup procedure outlined in Scheme 4.

The procedure leads to only minimal losses, and can be applied to large amounts of crude product (>200 g). Irrespective of the substituent R, the thioureas are very soluble in methanol or dichloromethane. Methanol has a very low solubility for S_8 and is therefore the solvent of choice for the extraction of the crude reaction mixtures. The absence of S_8 in the crude methanol filtrates was verified by the GC/MS analysis. Analytically pure samples are obtained by filtration

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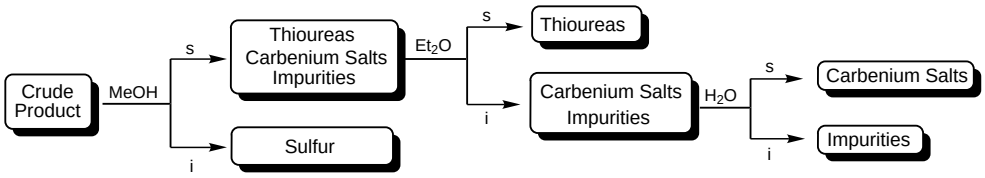

Scheme 4. Purification of the thioureas (**6**, **9**) and carbenium salts (**8**, **11**) from the crude product obtained from the oxidation of cyclic aminals with S_8:. s = soluble, i = insoluble.

Table 1. Solubilities (in gL^{-1} of pure solvent) of selected thioureas (**6**, **9**) and carbenium salts (**8**, **11**) at 25 °C.[a]

	Hexane	Et_2O	CH_3OH	Toluene
6a	5	**17**	90	119
6b	**5**	240	500	432
6c	**40**	300	450	520
6d	11	**86**	58	194
6e	**18**	84	25	138
8	insol.	insol.	250	0.2
9a	6	**44**	242	370
11	insol.	insol.	355	**0.3**

[a] The values for the solvent used for recrystallization are given in boldface.

of the diethyl ether solutions through a short (10 cm) column of neutral Al_2O_3, and recrystallization of the evaporated filtrates from hexanes or diethyl ether (Table 2).

The pure thiocyanate salts **8** and **11** are obtained by dissolving the crude thiocyanate salt fraction in distilled water (5 mL per 1 g of crude material) which removes dark brown impurities as an insoluble fraction. The orange-colored aqueous solutions are extracted with toluene (5 mL portions) until the organic layer remains colorless. Slow evaporation of the aqueous solution gives the pure thiocyanate salts in the form of large colorless prisms.

Scope of reaction: To test the generality of the reaction, the analogous oxygen and sulfur ring systems, 1,3-dioxolane and 1,3-dithiolane, were allowed to react with sulfur (see Scheme 3). 1,3-Dithiolane is cleanly transformed into the 1,3-dithiolane-2-thione and thus reacts analogously to the aminals, but longer reaction times (2 weeks) and higher reaction temperatures (180 °C) are required to achieve a complete conversion.[28] 1,3-Dioxolane is completely inert, even under more forcing reaction conditions (190 °C, 14 days).

Formation of side products: The lower yields of thioureas obtained from the aminals **7d** and **10b** are caused by the formation of the carbenium salts **8** and **11** which are the unexpected main products in these cases. They are obtained in spectroscopically pure form (^1H NMR spectroscopy) from the sublimation residues of the crude reaction mixtures and characterized through their single-crystal X-ray structures (see below).

Carbenium salts like **8**/**11** are not formed (IR, NMR) in the other reactions. Their formation from **7d** and **10b** must be attributed to the presence of the sterically demanding *t*Bu substituent.

Variation of the ring size of the aminals is without influence on the yield or product distribution: the two *tert*-butyl substituted aminals **10b** (six-membered ring) and **7d** (five-membered ring) gave a mixture of the respective carbenium salts and the thioureas in similar ratios, while the methyl-substituted **7a** (five-membered ring) and **10a** (six-membered ring) gave the respective thioureas in similar yields.

GC-MS analysis led to the identification of CS_2 and R–N=C=S which are present as minor (< 1 %) side products in all crude reaction mixtures. Due to their high volatility, they are removed during the evaporation steps outlined in Scheme 4. Substantial amounts of the diamine, *N,N′*-di-*tert*-butyl-1,3-diaminopropane (**12**), were isolated from the dehydrosulfurization reaction of **10b**, but only traces of the corresponding diamines were detected (GC-MS) in the other reactions.

Table 2. Synthesis of cyclic thioureas from diamines: melting points, yields and analytical data.

	M. p. [°C]		Yield [%][a]	Formula		Elemental analysis [%]		
						C	H	N
6a	110–111	111–112[b]	86 (80)	$C_5H_{10}N_2S$	found:	46.33	7.96	21.50
					calcd:	46.12	7.74	21.51
6b	66–67	62–63[b]	87 (74)	$C_7H_{14}N_2S$	found:	53.19	8.75	17.80
		62.2[c]			calcd:	53.12	8.91	17.70
6c	88	86.4[c]	86 (50)	$C_9H_{18}N_2S$	found:	58.22	9.58	14.93
					calcd:	58.01	9.73	15.03
6d	133	–	18 (19)	$C_{11}H_{22}N_2S$	found:	62.73	10.24	13.22
					calcd:	61.63	10.34	13.06
6e	187–188	187–188[d]	47 (49)	$C_{15}H_{14}N_2S$	found:	70.60	5.43	11.07
					calcd:	70.83	5.54	11.01
9a	78–79	79[b]	91 (80)	$C_6H_{12}N_2S$	found:	50.02	8.92	19.38
					calcd:	49.96	8.38	19.42
9b	101	-	6 (0)	$C_{12}H_{24}N_2S$	found:	63.22	10.73	12.31
					calcd:	63.10	10.59	12.26

[a] S_8 route, calculated on diamine; for yields based on aminals see Scheme 3. In parentheses: best yields obtained with the CS_2 or CS_2/I_2 route. [b] Ref. [18b]. [c] Ref. [18a]. [d] Ref. [19].

Extended reaction times or elevated reaction temperatures do not affect the yield or purity of the products, except for **7d**, for which traces of the aromatic dehydrogenation product **5a** were detected after 72 h at 150–160 °C by GC-MS analysis. The formation of **5a** is due to the dehydrogenation of **6d** under the reaction conditions and **5a** could in fact be obtained on a preparative scale by heating mixtures of **6d** and S_8 to 190 °C for 100 h (yield > 80 %). Increasing the amount of sulfur beyond the stoichiometrically required 0.25 equivalents of S_8 does not lead to any significant changes in the yields or the product distribution.

The compounds **5a**, **6d**, **8**, **11**, and **12** were characterized by single-crystal X-ray diffraction[22–26] and their structures are given in Figures 1 – 5.

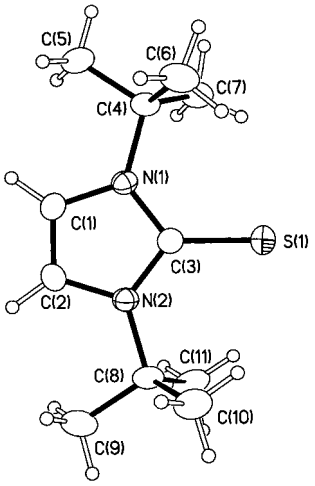

Figure 1. Molecular structure of (*t*BuNCH=CHN*t*Bu)C=S (**5a**) in the solid state (ORTEP view, thermal ellipsoids are at the 50% probability level). Selected bond lengths [pm] and angles [°]: S(1)–C(3) 168.8(3), C(3)–N(1) 136.4(4), N(1)–C(4), 150.3(4), N(1)–C(1), 138.2(5), C(1)–C(2) 132.1(5), C(2)–N(2) 137.6(4), N(2)–C(3) 136.4(4), N(2)–C(8) 151.3(4); S(1)-C(3)-N(1) 127.0(2), S(1)-C(3)-N(2) 127.0(2), N(1)-C(3)-N(2) 105.9(3), C(3)-N(2)-C(2) 109.3(2), N(2)-C(2)-C(1) 105.9(3), C(2)-C(1)-N(1) 108.6(3).

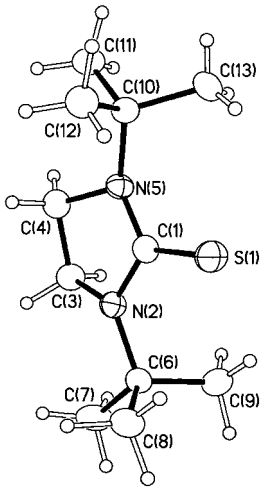

Figure 2. Molecular structure of (*t*BuNCH$_2$–CH$_2$N*t*Bu)C=S (**6d**) in the solid state (ORTEP view, thermal ellipsoids are at the 50% probability level). Selected bond lengths [pm] and angles [°]: C(1)–S(1) 167.4(4), C(1)–N(2) 135.4(5),C(1)–N(5) 135.8(4), N(2)–C(6) 148.6(4), N(2)–C(3) 145.4(4), C(3)–C(4) 148.6(5); S(1)-C(1)-N(2) 125.3(3), S(1)-C(1)-N(5) 125.5(3), N(2)-C(1)-N(5) 109.2(3), C(1)-N(2)-C(6) 126.7(3), C(1)-N(2)-C(3) 109.5(3), C(3)-N(2)-C(6) 119.4(3).

The short C–N bond lengths observed for the thioureas (135 – 138 pm) and carbenium salts (130 – 131 pm) imply a substantial double-bond character. The closest contacts between the thiocyanate anion and the carbenium cation observed for **8** and **11** are in excess of 400 pm and rule out covalent interactions. The disorder observed for **11** was successfully modeled through a superposition of two envelope geometries. The nitrogen atoms in the thioureas and the

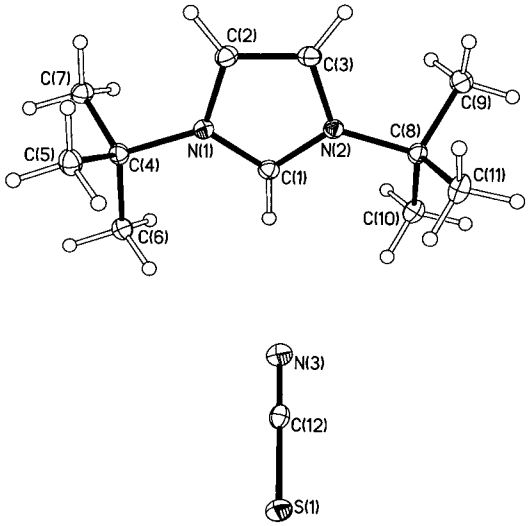

Figure 3. Molecular structure of [(*t*BuNCH$_2$–CH$_2$N*t*Bu)C–H]$^+$ [SCN]$^-$ (**8**) in the solid state (ORTEP view, thermal ellipsoids are at the 50% probability level). Selected bond lengths [pm] and angles [°]: C(1)–N(1) 131.3(2), C(1)–N(2) 131.4(2), N(1)–C(2) 147.3(2), C(2)–C(3) 151.7(3), N(2)–C(4) 149.2(2), N(3)–C(12) 157.8, N(3)···H(1A) 414.6, C(12)-N(3)-H(1A) 141.43(05), N(1)-C(1)-N(2) 113.80(16), C(1)-N(1)-C(2) 108.83(15), N(1)-C(2)-C(3) 102.47(16).

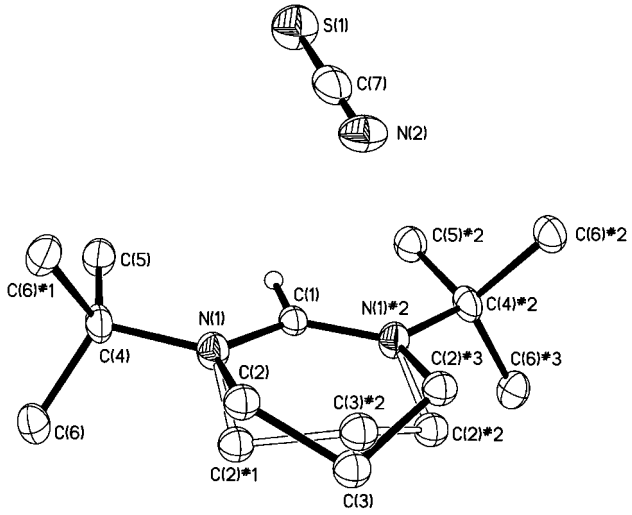

Figure 4. Molecular structure of [(*t*BuNCH$_2$–CH$_2$CH$_2$N*t*Bu)C–H]$^+$ [SCN]$^-$ (**11**) in the solid state (ORTEP view, thermal ellipsoids are at the 50% probability level). Selected bond lengths [pm] and angles [°]: C(1)–N(1) 130.2(6), N(1)–C(2) 149.9(6), N(1)–C(4) 146.66(7); C(1)-N(1)-C(4) 125.1(6), C(1)-N(1)-C(2) 116.0(5), N(1)-C(1)-N(1′) 129.5(10), C(4)-N(1)-C(2) 117.5(4).

carbenium salts are in planar or close to planar environments, except for **6d** which has slightly pyramidal nitrogen atoms (sum of nitrogen bond angles = 353°). An interpretation of the bond lengths in the context of aromatic delocalization in 2-(3*H*)-imidazole – thiones (**5a**) and related systems has been discussed recently.[27]

Mechanism and thermochemistry: In principle, C–H activation reactions can occur through the insertion of sextet species into the C–H bond or through multistep processes that are initiated by the breaking of the C–H bond in homolytic

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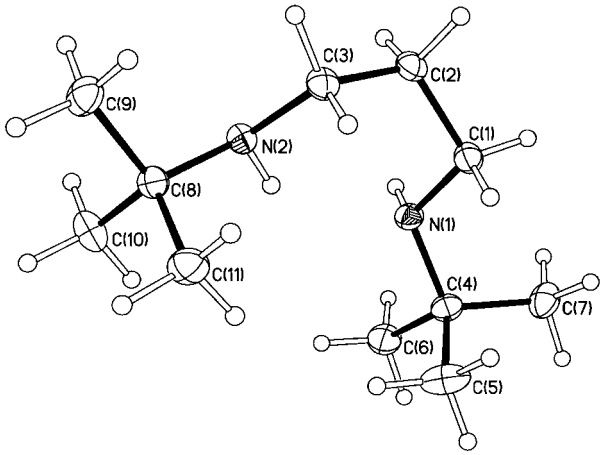
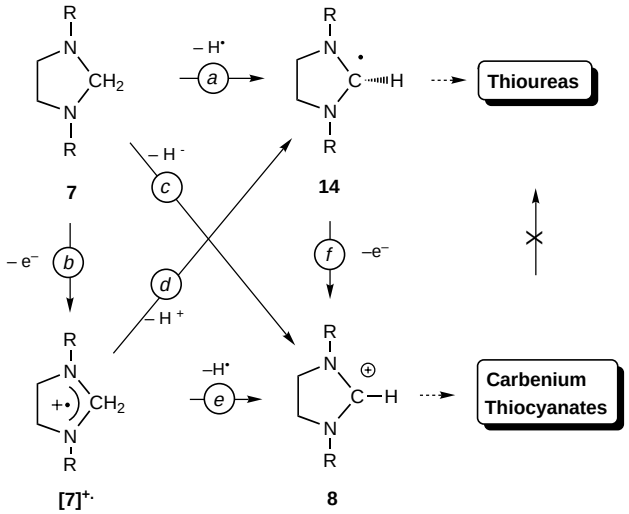


Figure 5. Molecular structure of *t*BuNHCH$_2$–CH$_2$CH$_2$NH*t*Bu (**12**) in the solid state (ORTEP view, thermal ellipsoids are at the 50% probability level). Selected bond lengths [pm] and angles [°]: N(1)–C(1) 146.40(13), C(1)–C(2) 152.34(14), C(2)–C(3) 152.23(15), N(1)–C(4) 147.88(13); N(1)-C(1)-C(2) 111.76(9), C(3)-C(2)-C(1) 114.54(9), H(1N)-N(1)-C(1) 111.3(12).



Scheme 5. Elementary steps (*a*–*f*) of the C–H activation of imidazolidines by S_8.

fashion (formation of H$^{\bullet}$) or in heterolytic fashion (formation of H$^+$ or H$^-$).

The 1,1-elimination of hydrogen from animals to give stable diaminocarbenes was examined by ab initio methods (see below) and is endothermic by +25 kcal mol^{-1} (formation of H_2) or +14 kcal mol^{-1} (formation of H_2S) and can be ruled out as the primary step of the reaction. Future mechanistic studies will focus on the reactions *a*–*c* (Scheme 5) as the most likely initial steps of the observed C–H activation reactions.

An important experimental result for future mechanistic investigations is the fact that the thioureas **6**, **9** and the carbenium salts **8**, **11** cannot be interconverted under the reaction conditions that lead to their formation. This implies that the direct hydride abstraction step *c* (see Scheme 5), which would explain the formation of the carbenium salts, cannot be the only operating pathway. Radical cations of imidazolidines such as **[7]**$^{+\bullet}$ have been previously studied by photoelectron spectroscopy. Their intermediacy would provide a branching step leading to carbenium salts (through hydrogen abstraction) or thioureas (step *d*). The operation of route *a* or route *b* is not mutually exclusive and it is difficult to distinguish between the two pathways if one relies on arguments derived from product distributions alone.

The observed sequence of reactivities for imidazolidines, dioxolanes, and dithiolanes towards S_8 correlates well with the lone pair energies of the respective heteroelements (N > S ≫ O), which is in good agreement with the operation of the single-electron transfter (SET) oxidation step b as the rate-determining step of the reaction.

The thermochemistry of the formation of the thioureas from S_8 and aminals was investigated by computational methods[31, 32] at the B3LYP/6-31G(d)//B3LYP/6-31G(d)[31, 33] and CBS-4[31, 34] levels of theory (Table 3 and 4, respectively). Even more accurate thermochemical data can be obtained from CBS-Q[34] or G2[31, 35] calculations but the use of these methods is typically restricted to systems with six heavy atoms.[31] The CBS-4 approach allows the inclusion S_8 in the calculations and was chosen as a good compromise between high accuracy (mean absolute deviation better than 2 kcal mol^{-1}) and speed. B3LYP/6-31G(d)//B3LYP/6-31G(d) energies have mean absolute deviations of about 8 kcal mol^{-1} and were included for comparison only.

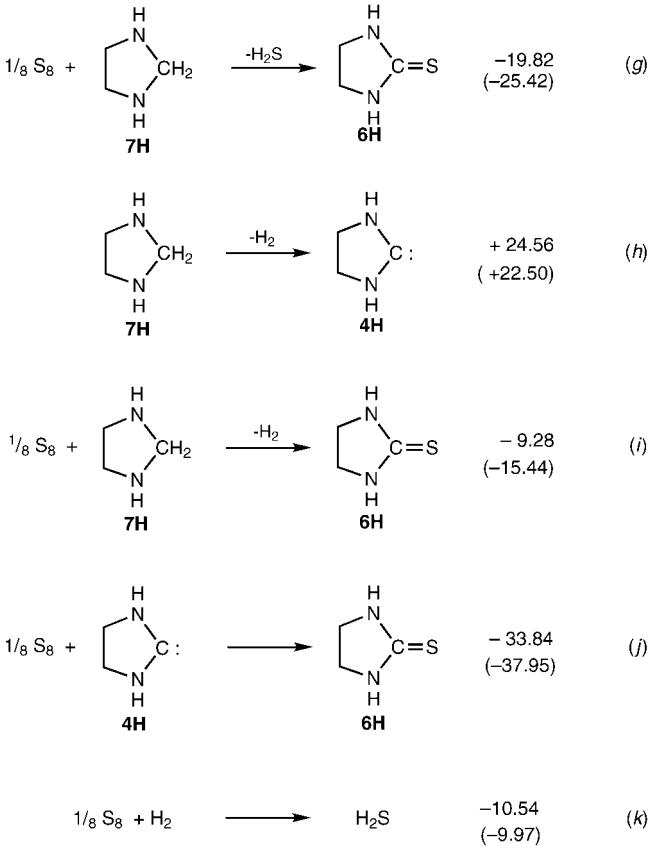
The imidazolidine **7H** (Scheme 6) was chosen as model compound for the aminals **7a**–**7b**. The pyramidal geometry of the nitrogen atoms in **7H** leads to two different isomers

Table 3. Oxidation of aminals with S_8. Selected energies (in Hartrees) at the B3LYP/6–31G(d) level.

	ZPE	E_o	$E_{298.15}$	$H_{298.15}$	$G_{298.15}$
S_8	0.011762	–3185.538724	–3185.527535	–3185.526590	–3185.576877
H_2	0.010145	–1.165337	–1.162976	–1.162032	–1.1768
H_2S	0.015172	–399.370264	–399.367417	–399.366473	–399.389832
anti-**7H**	0.119250	–228.489610	–228.484819	–228.483875	–228.517424
syn-**7H**	0.119409	–228.490046	–228.485331	–228.484387	–228.517766
4H	0.094104	–227.277607	–227.272870	–227.271925	–227.305075
6H	0.098281	–625.533207	–625.527679	–625.526735	–625.562662

Table 4. Oxidation of aminals with S_8. Selected energies (in Hartrees) at the CBS-4 level.

	ZPE	E_o	$E_{298.15}$	$H_{298.15}$	$G_{298.15}$
S_8	0.013977	–3182.008354	–3181.997607	–3181.996663	–3182.046130
H_2	0.010610	–1.172206	–1.169845	–1.168901	–1.183673
H_2S	0.016379	–398.936720	–398.933875	–398.932930	–398.956239
anti-**7H**	0.126308	–228.243185	–228.238072	–228.237128	–228.271617
syn-**7H**	0.126496	–228.243956	–228.238951	–228.238007	–228.272219
4H	0.101020	–227.021839	–227.017201	–227.016257	–227.049401
6H	0.105082	–624.828427	–624.822610	–624.821666	–624.859111



Scheme 6. Oxidation of imidazolidines by S_8 (reactions $g-k$). Reaction energies $\Delta G_{298.15}$ at the CBS-4 level and at the B3LYP/6–31G(d) level (in parentheses).

with *syn* or *anti* orientation of the N–H bonds. The *syn* isomer is slightly more stable and was the one used for the determination of the thermodynamic parameters. The computationally derived free energies indicate that there are in fact two different reactions that can account for the formation of thioureas, reaction *g*, (by-product H_2S, $\Delta G = -19.82$ kcal mol^{-1}) and reaction *i*, (by-product H_2, $\Delta G = -9.28$ kcal mol^{-1}).

Reaction *i* is characterized by a lower stoichiometry in sulfur and was ruled out experimentally: lowering the amount of sulfur to the amount required by reaction *i* leads to 50% conversion of the aminal. The abundance of easily accessible starting materials makes reaction *h*, the 1,1-elimination of H_2 from formaldehyde aminals to give carbenes, a worthwhile target of synthetic studies. The ΔG value of $+24.6$ kcal mol^{-1} obtained at the CBS-4 level rules out a direct conversion but the process could well become feasible by coupling reaction *h* with a sufficiently exothermic hydrogenation reaction (Table 5).

Table 5. Reaction energies (in kcal mol^{-1}) at the CBS-4 level and at the B3LYP/6–31G(d) level (in italics).

	ΔE_o		$\Delta E_{298.15}$		$\Delta H_{298.15}$		$\Delta G_{298.15}$	
g	−11.99	*−18.04*	−11.34	*−17.50*	−10.93	*−17.05*	−19.82	*−25.42*
h	+31.32	*+29.56*	+32.57	*+30.74*	+33.16	*+31.64*	+24.56	*+22.50*
i	−3.54	*−10.14*	−2.39	*−9.03*	−1.87	*−8.51*	−9.28	*−15.44*
j	−34.85	*−39.70*	−34.95	*−40.08*	−35.03	*−40.15*	−33.84	*−37.95*
k	−8.45	*−7.90*	−8.99	*−8.47*	−9.07	*−8.55*	−10.54	*−9.97*

Carbenes are known to react with sulfur to give thioureas[36] but, based on the CBS-4 data, their intermediacy in the aminal oxidation seems unlikely. Even if the endothermic elimination of hydrogen from the aminal ($\Delta G = +24.6$ kcal mol^{-1}) is combined with the formation of H_2S ($\Delta G = -10.5$ kcal mol^{-1}) the overall reaction still has a positive ΔG value of $+14.1$ kcal mol^{-1}. The reaction of diaminocarbenes with S_8 has recently been the subject of thermochemical experiments.[36] The experimental value obtained for the reaction of the analogous *N,N′*-dimesitylcarbene with S_8[36] ($\Delta H = -35 \pm 2$ kcal mol^{-1}) is in very good agreement with the CBS-4 value that we obtain for the reaction *k* ($\Delta H = -35.03$ kcal mol^{-1}).

The B3LYP/6-31G(d) value ($\Delta H = -40.15$ kcal mol^{-1}) significantly deviates from this experimental value.

Conclusion

A novel method for the synthesis of tetrasubstituted thioureas consists of heating cyclic formaldehyde aminals and with S_8 to 150 °C. The reaction is simple to perform, does not require solvents, and gives thioureas in good to excellent yields and purities. The transformation $>CH_2 \rightarrow >C{=}S$ amounts to a C–H activation by S_8. The transformation can be carried out in a similar fashion for the thia analogues of the investigated aminals (1,3-dithiolanes), while the oxa analogues (1,3-dioxolanes) were found to be inert towards S_8.

Experimental Section

General: Melting points were recorded in sealed capillaries and are uncorrected. Mass spectra were determined at an ionizing voltage of 40 eV or 70 eV as indicated. NMR spectra were recorded on Varian Gemini 200 (^{1}H), Bruker 500 MHz (^{13}C), or Varian 400 MHz spectrometers (^{13}C) at normal spectrometer temperature. The spectra are referenced against tetramethylsilane (TMS) (^{1}H and ^{13}C, internal). IR spectra were recorded as nujol mulls on a Nicolet FT Spectrometer. All starting materials were obtained from Aldrich and used as received. The synthesis of the aminals and their oxidation with S_8 were conducted under an atmosphere of nitrogen or argon (purity 99.994 or better).[30] Elemental analyses were performed at Guelph Chemical Laboratories Ltd. (Canada).

Reactions and procedures

Synthesis of *N,N′*-di-*tert*-butyl-1,3-propanediamine (12): 1,3-Dibromopropane (100.00 g, 495.3 mmol), *tert*-butylamine (260 mL, 181.13 g, 2.47 mol), and distilled water (20 mL) were added together in a 1 L two-necked round-bottom flask with stirrer and reflux condenser. The clear two-phase system slowly turned turbid and reached boiling temperature. The reaction was completed by boiling under reflux overnight. Three portions (3×20 g) of NaOH were added to the cold mixture. The upper layer was separated and the aqueous layer was extracted with diethyl ether (3×100 mL). The combined organic extracts were dried by stirring with NaOH (10 g) overnight. Evaporation of the diethyl ether left shiny white flakes of pure *N,N′*-di-*tert*-butyl-1,3-propylenediamine. Yield 78.3 g (85%).

1,3-Diphenylimidazolidine (7e): Unlike the other aminals obtained in this study, the formation of **7e** required acid catalysis. Following the procedure of Wanzlick et al.,[19] *N,N′*-diphenylethylenediamine (3.50 g, 16.5 mmol) was dissolved in MeOH (100 mL). To this solution was added paraformaldehyde (0.50 g, 16.6 mmol) and a solution of acetic acid (1.5 mL) in MeOH (10 mL). The reaction was stirred until

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the paraformaldehyde had dissolved. Methanol was removed in vacuo and the resulting crude material was sublimed at 125 °C/1 Torr (oil bath). Yield 3.00 g (81 %).

Synthesis of imidazolidines 7 and hexahydropyrimidines 10: In a 100 mL Schlenk flask, paraformaldehyde (5.00 g, 16.60 mmol) and diethyl ether (20 mL) were added to the diamine (16.90 mmol). The mixture was stirred until all of the paraformaldehyde was consumed. The upper layer was separated and dried over NaOH (1.0 g) for 24 h. Yields 90–100 %.

Synthesis of thioureas from 1,ω-diamines and CS_2: CS_2 (11.7 mL, 14.8 g, 195 mmol) was added dropwise under external water cooling to a mixture of the diamine (195 mmol) and pyridine (50 mL). After the strongly exothermic reaction has ceased, the mixture was boiled to reflux for 24 h (oil bath 150 °C, gas evolution). Iodine (4.40 g, 17.3 mmol) was added to the cold reaction mixture and the solution boiled to reflux for an additional 20 h. The pyridine was removed in vacuo, and the resulting brown solid was extracted with dichloromethane. The dichloromethane solution was washed with deionized water (3 × 20 mL), the dichloromethane evaporated in vacuo, and the residue sublimed at 1 Torr. Spectroscopic data see below. Yields: **6a** (80 %), **6b** (74 %), **6c** (50 %), **6d** (19 %), **9a** (80 %), **9b** (< 1 %).

Reaction of imidazolidines and hexahydropyrimidines with S_8: Sulfur (1.22 g, 4.75 mmol) was added to the aminal (19.0 mmol) in a Swagelock 50 mL stainless steel cylinder. The vessel was sealed and placed in an oil bath (150 °C) for 12 h. The cold reaction mixture was extracted with methanol (3 × 10 mL). The combined methanol extracts were filtered and the methanol was evaporated in vacuo. The thioureas were obtained by extraction of the solid residue with toluene (2 × 10 mL). The toluene extract was filtered through a short column (length 10 cm , diameter 1 cm) of neutral Al_2O_3. Analytically pure samples of the thioureas were obtained by recrystallization from the solvent indicated in Table 1. The carbenium salts were isolated by dissolving the toluene-insoluble fraction in water (5 mL). The resulting orange solution was decanted or filtered from the brown, insoluble impurities, and extracted with toluene (5 mL portions) until the organic phase remained colorless. The carbenium thiocyanates were obtained by slow evaporation of the aqueous phase in the form or large colorless crystals. Yields of thioureas (**6**, **9**) and carbenium salts (**8**, **11**): **6a** (90 %), **6b** (92 %), **6c** (90 %), **6d** (19 %) + **8** (80 %), **6e** (49 %), **9a** (91 %), **9b** (6 %) + **11** (86 %). For the synthesis of 1,3-diphenylimidazolidine-2-thione (**6e**), the crude reaction mixture was extracted with chloroform (3 × 10 mL) because **6e** was practically insoluble in MeOH. The solvent was removed in vacuo and the remaining brown-yellow solid sublimed at 105 °C/1 Torr. The sublimate consisted of pure *N,N′*-diphenylethylenediamine (43 %), the brown sublimation residue consisted of spectroscopically pure **6e** (49 %).

Attempted dehydrosulfurization of 1,3-dioxolane: Sulfur (0.68 g, 2.65 mmol) and 1,3-dioxolane (0.79 g, 11.0 mmol) were added together in a 50 mL Swagelock stainless steel cylinder. The cylinder was sealed and placed in an oil bath (150 °C) for 72 h. The ^{1}H NMR spectrum of the crude reaction mixture showed only signals for the starting material (1,3-dioxolane).

Dehydrosulfurization of 1,3-dithiolane: Sulfur (0.87 g, 3.39 mmol) and 1,3-dithiolane (1.44 g, 13.6 mmol) were added together in a 50 mL Swagelock stainless steel cylinder. The cylinder was sealed and placed in an oil bath (150 °C). After 20 h, a ^{1}H NMR spectrum of the crude reaction mixture showed only signals of the starting material (90 %) and of 1,3-dithiolane-2-thione (10 %). Complete conversion was achieved after 100 h at 190 °C. ^{1}H NMR ($CDCl_3$): $\delta = 3.97$ (s, 4H; SCH_2).

Spectroscopic data

1,3-Dimethylimidazolidine-2-thione (6a): Colorless hexagons, m. p. 110–111 °C (lit.: 111–112 °C[18b]); ^{1}H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 2.35$ (s; CH_2CH_2), 2.82 (s; NCH_3); ^{1}H NMR ($CDCl_3$): $\delta = 3.13$ (s; NCH_3), 3.54 (s; CH_2CH_2); ^{13}C NMR (400 MHz, C_6D_6, 25 °C): $\delta = 34.95$ (^1J(C,H) = 138 Hz; NCH_3), 46.78 (^1J(C,H) = 145 Hz; CH_2CH_2), 184.52 (C=S); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 35.11$ (^1J(C,H) = 139 Hz; NCH_3), 48.33 (^1J(C,H) = 145 Hz; CH_2CH_2), 184.0 (C=S); MS (70 eV) *m/z* (%): 130 (100) $[M]^{+\bullet}$, 115 (7), 97 (7), 88 (10), 76 (57), 69 (25), 57 (33); HR-MS: *m/z*: 130.0564, calcd: 130.0565; fit: 0.3 ppm; IR (NaCl, Nujol): $\tilde{\nu} = 1619$ w, 1507 s, 1499 s, 1459 vs, 1451 vs, 1430 s, 1398 m, 1383 s, 1327 vs, 1286 vs, 1223 s, 1202 m, 1134 w, 1116 s, 1068 m, 1017 vw, 959 m, 641 m, 634 m, 626 m, 509 s cm^{-1}; IR (CCl_4, CaF_2): $\tilde{\nu} = 2931$ w, 2868 w, 1504 s, 1469 w, 1441 w, 1398 m, 1342 vs, 1293 m, 1117 s cm^{-1}.

1,3-Diethylimidazolidine-2-thione (6b): Long, colorless needles, m. p. 62–63 °C (lit.: 62–63 °C[18b]); ^{1}H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 0.87$ (t, ^3J(H,H) = 7.2 Hz, 6H; NCH_2CH_3), 2.56 (s, 4H; CH_2CH_2), 3.51 (q, ^3J(H,H) = 7.2 Hz, 4H; NCH_2CH_3); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.17$ (t, ^3J(H,H) = 7.3 Hz, 6H; NCH_2CH_3), 3.54 (s, 4H; CH_2CH_2), 3.67 (q, ^3J(H,H) = 7.3 Hz, 4H; NCH_2CH_3); ^{13}C NMR (400 MHz, C_6D_6, 25 °C): $\delta = 12.90$ (CH_3), 45.48 (CH_2CH_2), 49.05 (NCH_2CH_3), 183.05 (C=S); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 12.00$ (CH_3), 41.98 (CH_2CH_2), 45.36 (NCH_2CH_3), 181.42 (C=S); IR (NaCl, Nujol): $\tilde{\nu} = 1502$ vs, 1446 vs, 1431 s, 1352 m, 1334 s, 1278 vs, 1253 m, 1202 w, 1194w, 1129 m, 1111 w, 1073 w, 1067 w, 994 vw, 893 vw, 783 m, 631 m cm^{-1}.

1,3-Diisopropylimidazolidine-2-thione (6c): Colorless needles, m. p. 86–87 °C (lit.: 86.4 °C[18a]); ^{1}H NMR (200 MHz, C_6D_6, $CDCl_3$, 25 °C): $\delta = 0.91$ (d, ^3J(H,H) = 6.9 Hz, 12H; $(CH_3)_2CH$), 2.73 (s, 4H; NCH_2), 5.17 (sept, ^3J(H,H) = 6.9 Hz, 2H; $CH(CH_3)_2$); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.17$ (d, ^3J(H,H) = 6.6 Hz, 6H; $(CH_3)_2CH$), 3.45 (s, 4H; NCH_2), 4.93 (sept, ^3J(H,H) = 6.6 Hz, 2H; $CH(CH_3)_2$); ^{13}C NMR (400 MHz, C_6D_6, 25 °C): $\delta = 19.12$ ($(CH_3)_2CH$) 40.38 (CH_2CH_2), 46.78 ($CH(CH_3)_2$), 182.28 (C=S); MS (70 eV): *m/z* (%): 186 (100) $[M]^{+\bullet}$, 171 (40), 143 (30), 129 (68), 111 (13), 101 (13), 83 (33), 70 (21); HR-MS: 186.118530, calcd: 186.1191; fit = 2.9 ppm; IR (KBr, Nujol): $\tilde{\nu} = 1486$ s, 1426 s, 1364 m, 1326 s, 1274 s, 1161 m, 1126 m, 1083 m, 1039 m, 985 w, 955 w, 920 w, 872 w, 803 w, 710 w, 674 w, 639 s, 605 m, 502 m, 456 m, 422 s cm^{-1}.

1,3-Di-*tert*-butylimidazolidine-2-thione (6d): Colorless octahedra, m. p. 130–131 °C; ^{1}H NMR (C_6D_6): $\delta = 1.55$ (s, 18H; $C(CH_3)_3$), 2.75 (s, 4H; NCH_2); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.58$ (s, 18H; $C(CH_3)_3$), 3.42 (s, 4H; NCH_2); ^{13}C NMR (400 MHz, C_6D_6, 25 °C): $\delta = 28.09$ ($C(CH_3)_3$), 44.22 (NCH_2), 56.41 ($C(CH_3)_3$), 184.43 (C=S); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 27.93$ ($C(CH_3)_3$), 44.31 (NCH_2), 56.42 ($C(CH_3)_3$), 183.13 (C=S); MS (70 eV): *m/z* (%): 214 (76) $[M]^{+\bullet}$, 157 (35), 143 (56), 115 (10), 102 (100), 84 (12), 74 (16), 70 (12), 57 (49); IR (NaCl, Nujol): $\tilde{\nu} = 1655$ w, 1630 m, 1365 m, 1315 s, 1264 m, 1199 w, 1119 w, 1033 m, 940 w, 885 vw, 841 vw, 745 w, 722 w, 651 m cm^{-1}.

1,3-Diphenylimidazolidine-2-thione (6e): Thin plates, m.p. 124–125; ^{1}H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 3.05$ (s, 4H; CH_2CH_2), 7.00 (t, ^3J(H,H) = 7.2 Hz, 2H; *para*-CH), 7.19 (t, ^3J(H,H) = 7.2 Hz; *meta*-CH), 7.59 (d, ^3J(H,H) = 7.8 Hz; *ortho*-CH); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 4.14$ (s; CH_2CH_2), 7.26 (t, ^3J(H,H) = 7.6 Hz; *para*-CH), 7.42 (t, ^3J(H,H) = 7.6 Hz; *meta*-CH), 7.56 (d, ^3J(H,H) = 8.0 Hz; *ortho*-CH); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 42.29$ (CH_2CH_2), 125.36 (*meta*-CH), 126.52 (*ortho*-CH), 128.78 (*para*-CH), 140.76 (*ipso*-C), 181.17 (C=S); IR (KCl, Nujol): $\tilde{\nu} = 1598$ m, 1581 w, 1499 m, 1423 m, 1395 m, 1342 s, 1289 s, 1271 s, 1080 w, 761 s, 692 s, 562 s cm^{-1}.

1,3-Dimethylimidazolidine (7a): Colorless oil; ^{1}H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 2.20$ (s, 6H; NCH_3), 2.56 (s, 4H; CH_2CH_2), 3.18 (s, 2H; NCH_2N); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 2.36$ (s, 6H; NCH_3), 2.76 (s, 4H; CH_2CH_2), 3.28 (s, 2H; NCH_2N); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 41.60$ (NCH_3), 54.67 (CH_2CH_2), 79.85 (NCH_2N); MS (70 eV): *m/z* (%): 100 (4) $[M]^{+\bullet}$, 99 (41), 85 (24), 57 (21), 42 (100), 28 (32), 18 (35); IR (NaCl, neat): $\tilde{\nu} = 1455$ s, 1370 s, 1228 s, 1115 s, 1033 m, 967 w, 921 m, 872 s, 810 s cm^{-1}.

1,3-Diethylimidazolidine (7b): Colorless oil; ^{1}H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 1.01$ (t, ^3J(H,H) = 7.4 Hz, 6H; CH_3CH_2), 2.41 (q, ^3J(H,H) = 7.4 Hz, 4H; CH_3CH_2), 2.61 (s, 4H; CH_2CH_2), 3.35 (s, 2H; NCH_2N); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.10$ (t, ^3J(H,H) = 7.2 Hz, 6H; CH_3CH_2), 2.56 (q, ^3J(H,H) = 7.2 Hz, 4H; CH_3CH_2), 2.80 (s, 4H; CH_2CH_2), 3.42 (s, 2H; NCH_2N); ^{13}C NMR (400 MHz, C_6D_6, 25 °C): $\delta = 14.47$ (CH_3CH_2), 49.60 (CH_3CH_2), 52.55 (CH_2CH_2), 76.78 (NCH_2N); IR (KCl, neat): $\tilde{\nu} = 3338$ w, 2969 s, 2935 s, 2800 s, 1678 s, 1470 m, 1452 m, 1375 m, 1346 m, 1315 w, 1289 m, 1197 m, 1147 m, 1105 m, 1049 w, 961 w, 866 w, 790 w cm^{-1}.

1,3-Diisopropylimidazolidine (7c): Colorless oil; ^{1}H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 0.98$ (d, ^3J(H,H) = 6.3 Hz, 12H; $CH(CH_3)_2$), 2.37 (sept, ^3J(H,H) = 6.3 Hz, 2H; $CH(CH_3)_2$), 2.64 (s, 4H; CH_2CH_2), 3.48 (s, 2H; NCH_2N); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.08$ (d, ^3J(H,H) = 6.0 Hz, 12H; $CH(CH_3)_2$), 2.51 (sept, ^3J(H,H) = 6.0 Hz, 2H; $CH(CH_3)_2$), 2.84 (s, 4H; CH_2CH_2), 3.52 (s, NCH_2N); ^{13}C NMR (400 MHz, C_6D_6, 25 °C): $\delta = 22.04$ ($CH(CH_3)_2$), 50.73 (CH_2CH_2), 53.99 ($CH(CH_3)_2$), 73.36 (NCH_2N); MS (70 eV): *m/z* (%): 156 (3) $[M]^{+\bullet}$, 155 (14), 141 (11), 127 (85), 113 (56), 99 (30), 85 (44), 72 (100), 56 (48); IR (KBr, neat): $\tilde{\nu} = 2969$ vs,

2927 s, 2874 m, 2799 s, 2607 m, 1471 m, 1458 m, 1381, s, 1371m, 1327 s, 1200 s, 1118 w, 1089 w, 1032 m, 779 w cm^{-1}.

1,3-Di-*tert*-butylimidazolidine (7d): Colorless oil; ^1H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 1.09$ (s, 18H; $C(CH_3)_3$), 2.75 (s, 4H; NCH_2CH_2), 3.67 (s, 2H; N_2CH_2); ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.07$ (s, 18H; $C(CH_3)_3$), 2.83 (s, 4H; CH_2CH_2), 3.56 (s, 2H; N_2CH_2); ^{13}C NMR (400 MHz, C_6D_6, 25 °C): $\delta = 26.1$ ($C(CH_3)_3$), 46.0 (CH_2CH_2), 52.0 ($C(CH_3)_3$), 63.3 (N_2CH_2); MS (70 eV): *m/z* (%): 184 (15) $[M]^{+\bullet}$, 183 (97), 127 (30), 113 (100), 98 (8), 84 (30), 71 (89), 57 (28); IR (NaCl, neat): $\tilde{\nu} =$ 2968 s, 2872 s, 2822 s, 1654 w, 1473 m, 1463 m, 1392 s, 1360 s, 1275 s, 1251 s, 1225 s, 1211 s, 1158 m, 1104 w, 1086 w, 1037 m, 922 w, 861w, 820 m, 743 w cm^{-1}.

1,3-Diphenylimidazolidine (7e): Colorless plates, m. p. 127 °C; ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 3.66$ (s, 4H; CH_2CH_2), 4.67 (s, 2H; N_2CH_2), 6.68 (d, $^3J(H,H) = 8.1$ Hz, 4H; *ortho*-CH), 6.80 (t, $^3J(H,H) = 7.3$ Hz, 2H; *para*-CH), 7.30 (t, $^3J(H,H) = 7.7$ Hz, 4H; *meta*-CH); ^{13}C NMR (400 MHz, C_6D_6, 25 °C): $\delta = 46.47$ (CH_2CH_2), 65.85 (N_2CH_2), 112.44 (*ortho*-CH), 117.64 (*para*-CH), 129.36 (*meta*-CH), 146.41 (*ipso*-C); MS (70 eV): *m/z* (%): 224 (60) $[M]^{+\bullet}$, 223 (81), 119 (70), 106 (63), 91 (100), 77 (54), 65 (9), 51 (21); IR (NaCl, Nujol): $\tilde{\nu} =$ 1601 m, 1574 m, 1502 s, 1327 m, 1239 m, 1186 m, 1158 m, 995 m, 868 w, 745 s, 693 s cm^{-1}.

1,3-Di-*tert*-butylimidazolidinium thiocyanate (8): Colorless prisms; ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.52$ (s, 18H; $C(CH_3)_3$), 4.11 (s, 4H; NCH_2), 8.09 (s, 1H; CH^+); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): $\delta =$ 27.92 ($C(CH_3)_3$), 45.37 (NCH_2), 56.86 ($C(CH_3)_3$), 130.81 (SCN), 152.33 (CH^+); IR (NaCl, Nujol): $\tilde{\nu} =$ 2203 w, 2066 m, 1632 m, 1301 m, 1215 w, 1167 w, 1060 w, 907 s, 888 w, 761 m, 736 s cm^{-1}.

1,3-Dimethylhexahydropyrimidine-2-thione (9a): Colorless platelets, m.p. 76 – 77 °C (lit.: 79 °C[18b]); ^1H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 1.03$ (q, $^3J = 6.2$ Hz, 4H; $CH_2CH_2CH_2$), 2.43 (t, $^3J(H,H) = 6.2$ Hz, 4H; $CH_2CH_2CH_2$), 3.25 (s, 6H; NCH_3); ^1H NMR ($CDCl_3$): $\delta = 2.04$ (quin, $^3J(H,H) = 6.2$ Hz, 2H; $CH_2CH_2CH_2$), 3.38 (t, $^3J(H,H) = 6.2$ Hz, 4H; $CH_2CH_2CH_2$), 3.43 (s, 6H; NCH_3); ^{13}C NMR (400 MHz, C_6D_6, 25 °C): $\delta = 21.21$ ($CH_2CH_2CH_2$), 43.20 (NCH_3), 48.41 ($CH_2CH_2CH_2$), 180.59 (C=S); MS (40 eV): *m/z* (%): 144 $[M]^{+\bullet}$ (100), 129 (2), 111 (8), 97 (6), 84 (4), 70 (15), 55 (4), 44 (27), 42 (23), 32 (8), 28 (21); IR (KBr, pellet): $\tilde{\nu} =$ 2956 s, 2933 s, 2863 s, 1528 s, 1487 m, 1450 m, 1399 m, 1348 s, 1315 s, 1220 m, 1099 m, 1037 m, 933 w, 900 vw, 864 w, 847 w, 638 w, 607 w, 572 w, 495 w, 429 w cm^{-1}.

1,3-Di-*tert*-butylhexahydropyrimidine-2-thione (9b): Colorless prisms; ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.64$ (s, $C(CH_3)_3$), 2.07 (quin, $^3J(H,H) = 7.1$ Hz, $CH_2CH_2CH_2$), 3.16 (t, $^3J(H,H) = 7.1$ Hz, CH_2N); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 28.10$ (q, $^1J(C,H) = 124.2$ Hz, $C(CH_3)_3$), 29.36 ($CH_2CH_2CH_2$), 42.39 (t, $^1J(C,H) = 137.6$ Hz, NCH_2), 52.09 ($C(CH_3)_3$), 185.32 (C=S); ^{15}N NMR (500 MHz, $CDCl_3$, 25 °C): $\delta =$ – 325.13; MS (40 eV): *m/z* (%): 228 (30), 227 (40), 197 (7), 171 (100), 157 (15), 125 (15), 116 (85), 98 (10), 72 (12), 57 (40), 41 (45); IR (NaCl, Nujol): $\tilde{\nu} =$ 1527 s, 1489 w, 1460 s, 1398 m, 1348 s, 1315 s, 1220 m, 1097 w, 864 w cm^{-1}.

1,3-Dimethylhexahydropyrimidine (10a): Colorless oil; ^1H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 1.54$ (quin, $^3J(H,H) = 4.8$ Hz, 2H; $CH_2CH_2CH_2$), 2.11 (s, 6H; NCH_3), 2.25 (t, $^3J(H,H) = 4.8$ Hz, 4H; $CH_2CH_2CH_2$), 2.90 (s, 2H; NCH_2N); ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.70$ (quin, $^3J(H,H) = 5.6$ Hz, 2H; $CH_2CH_2CH_2$), 2.24 (s, 6H; NCH_3), 2.41 (t, $^3J(H,H) = 5.6$ Hz, 4H; $CH_2CH_2CH_2$), 2.98 (s; NCH_2N); ^{13}C NMR (400 MHz, C_6D_6, 25 °C): $\delta = 23.43$ ($CH_2CH_2CH_2$), 42.86 (NCH_3), 54.22 ($CH_2CH_2CH_2$), 79.61 (NCH_2N); IR (NaCl, neat): $\tilde{\nu} =$ 3396 br, 2939 s, 2851 s, 2780 s, 2727 s, 2666 m, 2643 m, 2567 w, 2482 vw, 2463 vw, 1655 vw, 1466 s, 1445 s, 1337 w, 1300 m, 1275 s, 1254 w, 1206 m, 1196 m, 1148 s, 1113 s, 1097 m, 1073 s, 1046 s, 987 m, 968 s, 945 m, 915 w, 906 vw, 894 w, 823 m, 783 m cm^{-1}.

1,3-Di-*tert*-butylhexahydropyrimidine (10b): Colorless oil; ^1H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 1.04$ (s, 18H; $C(CH_3)_3$), 1.61 (quin, $^3J(H,H) = 5.4$ Hz, 2H; $CH_2CH_2CH_2$), 2.52 (t, $^3J(H,H) = 5.4$ Hz, 4H; $CH_2CH_2CH_2$), 3.44 (s, 4H; NCH_2N); ^{13}C NMR (400 MHz, C_6D_6, 25 °C): $\delta = 26.83$ ($C(CH_3)_3$), 29.31 ($CH_2CH_2CH_2$), 45.99 (NCH_2), 53.24 ($C(CH_3)_3$), 65.31 (NCH_2N); IR (NaCl, neat): $\tilde{\nu} =$ 3396 w, 2939 s, 2851 s, 2780 s, 2727 s, 2666 m, 2643 m, 2567 w, 2482 vw, 2463 vw, 1655 vw, 1466 s, 1445 s, 1337 w, 1300 m, 1275 s, 1254 w, 1206 m, 1196 m, 1148 s, 1113 s, 1097 m, 1073 s, 1046 s, 987 m, 968 s, 945 m, 915 w, 906 vw, 894 w, 823 m, 783 m cm^{-1}.

1,3-Di-*tert*-butylhexahydropyrimidinium thiocyanate (11): Colorless prisms, m. p. 200 – 204 °C; ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.52$ (s, 18H; $C(CH_3)_3$), 2.15 (m, 2H; $CH_2CH_2CH_2$), 3.56 (m, 4H; NCH_2), 8.07 (s, CH^+); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 19.78$ (t, $^1J(C,H) =$ 133.4 Hz, $CH_2CH_2CH_2$), 27.49 (q, $^1J(C,H) = 127.6$ Hz, $C(CH_3)_3$), 39.77 (t, $^1J(C,H) = 144.0$ Hz; NCH_2), 61.16 (s; $C(CH_3)_3$), 130.96 (s; SCN), 146.34 (d, $^1J(C,H) = 189.1$ Hz; CH^+); IR (NaCl, Nujol): $\tilde{\nu} = 2360$ m, 2057 s, 1672 s, 1461 s, 1411 m, 1395 m, 1369 s, 1331 s, 1236 s, 1192 s, 1092 m, 1009 m, 980 m, 942 w cm^{-1}.

***N,N'*-Di-*tert*-butyl-1,3-propanediamine (12)**: Colorless plates, m. p. 29 °C; ^1H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 0.59$ (s, 2H; NH), 1.03 (s, 18H; $C(CH_3)_3$), 1.52 (quin, 2H; $^3J(H,H) = 6.4$ Hz, $CH_2CH_2CH_2$), 2.58 (t, $^3J(H,H) = 6.4$ Hz, 4H; NCH_2); ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta =$ 1.10 (s, 18H; $C(CH_3)_3$), 1.75 (quin, $^3J(H,H) = 6.4$ Hz, 2H; $CH_2CH_2CH_2$), 2.71 (t, $^3J(H,H) = 6.4$ Hz, 4H; NCH_2); ^{13}C NMR (400 MHz, C_6D_6, 25 °C): $\delta = 29.42$ ($C(CH_3)_3$), 32.87 ($CH_2CH_2CH_2$), 41.52 (NCH_2), 50.04 ($C(CH_3)_3$).

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