

C–H Activation with Elemental Sulfur: Synthesis of Cyclic Thioureas from Formaldehyde Aminals and S₈

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 LCH₂ (L = RN-CH₂CH₂CH₂-NR and RNCH₂CH₂-NR, R = Me, Et, *i*Pr, *t*Bu, or Ph) with S₈ proceeds at unusually low temperatures (*T* < 160 °C) and results in the formation of the respective thioureas LC=S and H₂S. The reaction constitutes a new, solvent-free method for the synthesis of thioureas that eliminates the toxic and highly flammable CS₂. 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 S₈ was investigated. 1,3-

Dithiolane is cleanly converted into 1,3-dithiolane-2-thione (S₈, 14 d, 190 °C) and resembles the cyclic formaldehyde aminals in this respect. 1,3-Dioxolane (L = OCH₂CH₂O) 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

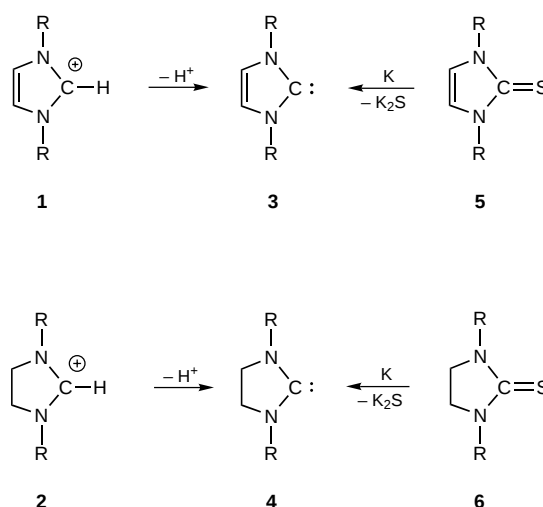
Introduction

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 used 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]



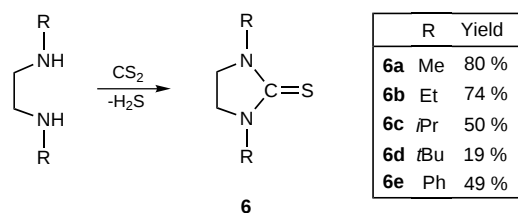
Scheme 1. Synthesis of diaminocarbenes **3** and **4** by deprotonation or reductive desulfurization.

[a] Prof. Dr. M. K. Denk, S. Gupta, J. Brownie, Dr. S. Tajammul
Department of Chemistry, Erindale College
University of Toronto, Mississauga, 3359 Mississauga Road North
ON, L5L 1C6 (Canada)
Fax: (+1) 905-828-5425
E-mail: mdenk@credit.erin.utoronto.ca

[b] Dr. A. J. Lough
X-ray Laboratory, Department of Chemistry
University of Toronto, Toronto, 80 St. George Street
ON, M5S 3H6 (Canada)

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 CS₂ but the approach is not without shortcomings. For example, the synthesis of the cyclic thioureas **6** from the respective ethylenediamines and CS₂ 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 %.

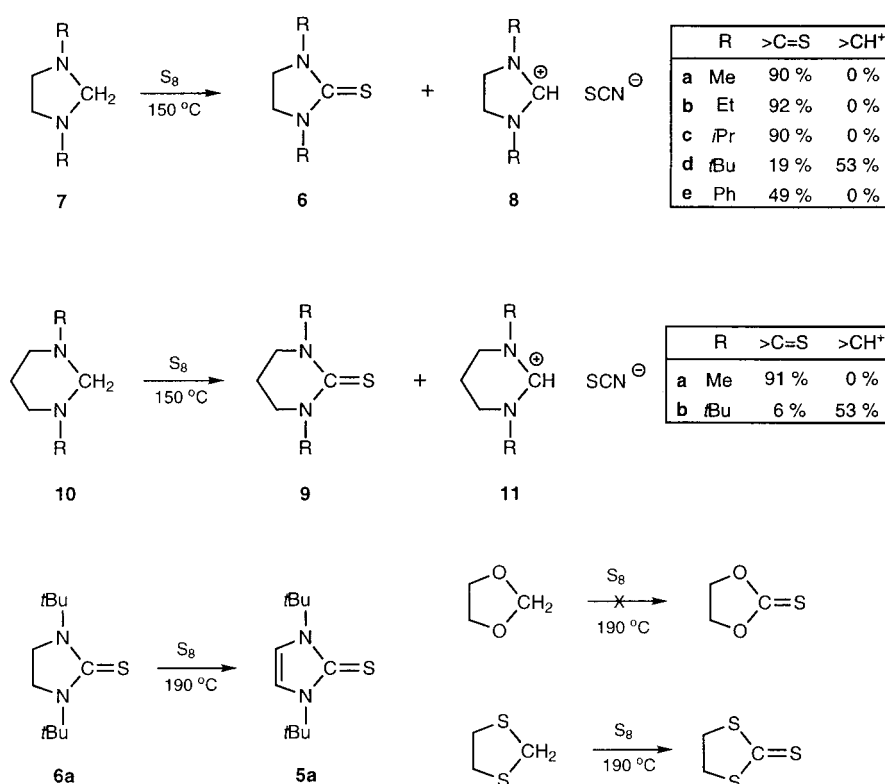


Scheme 2. Synthesis of cyclic thioureas **6** from *N,N'*-disubstituted ethylenediamines and CS₂.

Reasons for the often disappointing yields of the CS₂ 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).



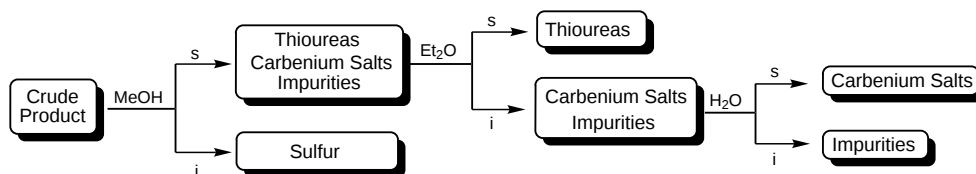
Scheme 3. Reaction of cyclic aminals (**6a**, **7**, **10**), 1,3-dithiolane and 1,3-dioxolane with S₈. For yields based on amines, see Table 2.

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 S₈ (150 °C) is indicated by the evolution of H₂S. 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 S₈ (stoichiometric amount) to 150 °C for 12 h in a 50 mL stainless steel cylinder (Swagelok). 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 S₈ and is therefore the solvent of choice for the extraction of the crude reaction mixtures. The absence of S₈ in the crude methanol filtrates was verified by the GC/MS analysis. Analytically pure samples are obtained by filtration



Scheme 4. Purification of the thioureas (**6**, **9**) and carbenium salts (**8**, **11**) from the crude product obtained from the oxidation of cyclic amins with S₈: s = soluble, i = insoluble.

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

	Hexane	Et ₂ O	CH ₃ OH	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 Al₂O₃, 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 amins, 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 amins **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 amins is without influence on the yield or product distribution: the two *tert*-butyl substituted amins **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 CS₂ 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.

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 S₈ to 190 °C for 100 h (yield > 80 %). Increasing the amount of sulfur beyond the stoichiometrically required 0.25 equivalents of S₈ does not lead to any significant changes in the yields or the product distribution.

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 ₃ H ₁₀ N ₂ S	found:	46.33	7.96	21.50
					calcd:	46.12	7.74	21.51
6b	66–67	62–63 ^[b]	87 (74)	C ₇ H ₁₄ N ₂ S	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 ₉ H ₁₈ N ₂ S	found:	58.22	9.58	14.93
					calcd:	58.01	9.73	15.03
6d	133	–	18 (19)	C ₁₁ H ₂₂ N ₂ S	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 ₂ S	found:	70.60	5.43	11.07
					calcd:	70.83	5.54	11.01
9a	78–79	79 ^[b]	91 (80)	C ₆ H ₁₂ N ₂ S	found:	50.02	8.92	19.38
					calcd:	49.96	8.38	19.42
9b	101	–	6 (0)	C ₁₂ H ₂₄ N ₂ S	found:	63.22	10.73	12.31
					calcd:	63.10	10.59	12.26

[a] S₈ route, calculated on diamine; for yields based on amins see Scheme 3. In parentheses: best yields obtained with the CS₂ or CS₂/I₂ route. [b] Ref. [18b]. [c] Ref. [18a]. [d] Ref. [19].

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.

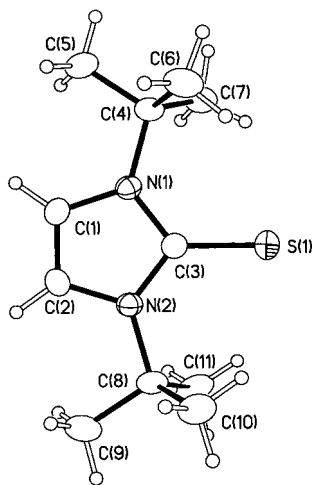


Figure 1. Molecular structure of $(t\text{BuNCH=CHN}t\text{Bu})\text{C=S}$ (**5a**) in the solid state (ORTEP view, thermal ellipsoids are at the 50% probability level). Selected bond lengths [pm] and angles [°]: S(1)–C(3) 168.8(3), C(3)–N(1) 136.4(4), N(1)–C(4), 150.3(4), N(1)–C(1), 138.2(5), C(1)–C(2) 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).

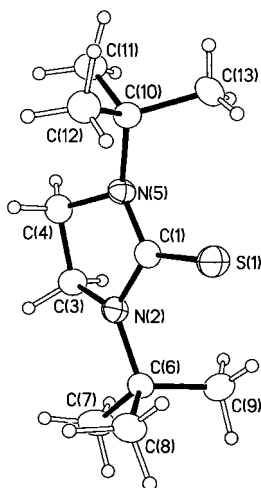


Figure 2. Molecular structure of $(t\text{BuNCH}_2\text{--CH}_2\text{N}t\text{Bu})\text{C=S}$ (**6d**) in the solid state (ORTEP view, thermal ellipsoids are at the 50% probability level). Selected bond lengths [pm] and angles [°]: C(1)–S(1) 167.4(4), C(1)–N(2) 135.4(5), C(1)–N(5) 135.8(4), N(2)–C(6) 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

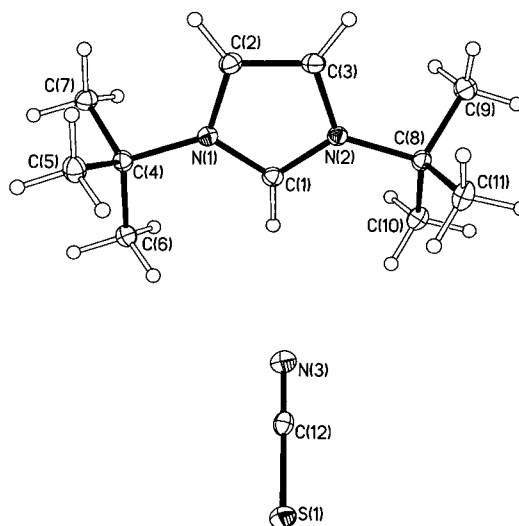


Figure 3. Molecular structure of $[(t\text{BuNCH}_2\text{--CH}_2\text{N}t\text{Bu})\text{C-H}]^+ [\text{SCN}]^-$ (**8**) in the solid state (ORTEP view, thermal ellipsoids are at the 50% probability level). Selected bond lengths [pm] and angles [°]: C(1)–N(1) 131.3(2), C(1)–N(2) 131.4(2), N(1)–C(2) 147.3(2), 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).

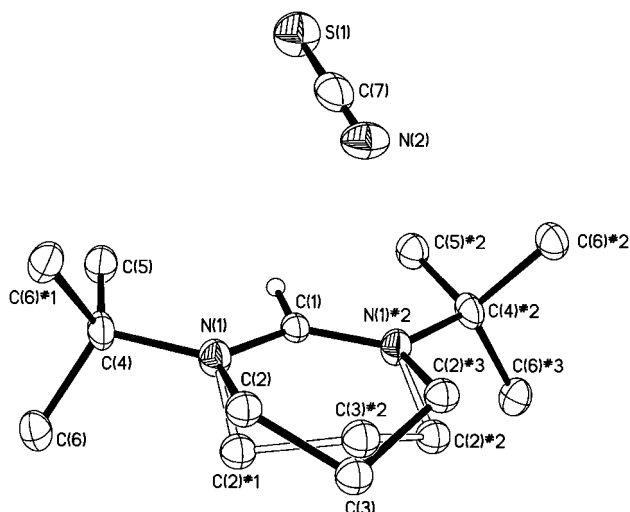


Figure 4. Molecular structure of $[(t\text{BuNCH}_2\text{--CH}_2\text{CH}_2\text{N}t\text{Bu})\text{C-H}]^+ [\text{SCN}]^-$ (**11**) in the solid state (ORTEP view, thermal ellipsoids are at the 50% probability level). Selected bond lengths [pm] and angles [°]: C(1)–N(1) 130.2(6), N(1)–C(2) 149.9(6), 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

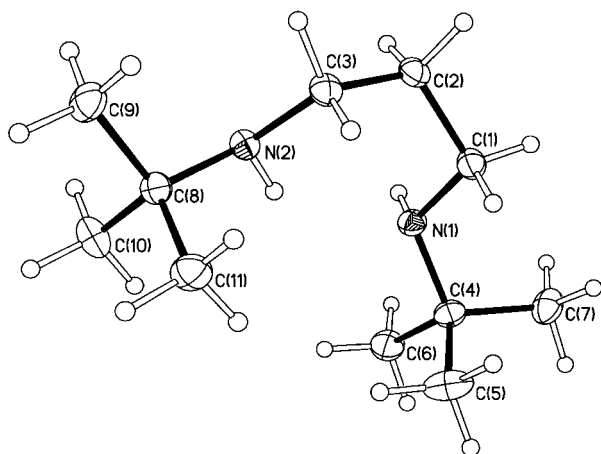


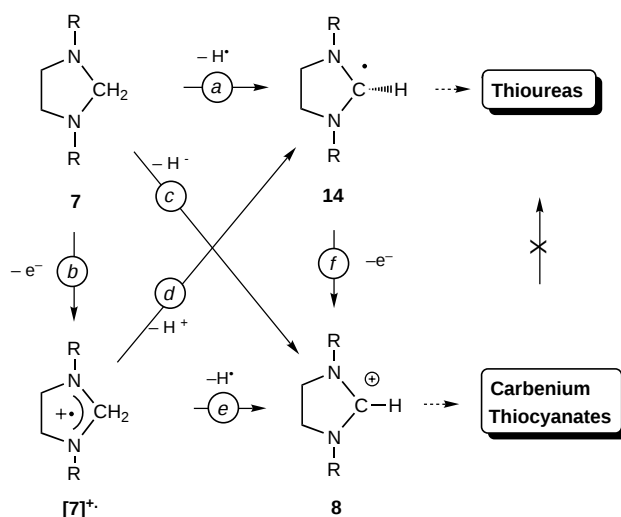
Figure 5. Molecular structure of *t*BuNHCH₂–CH₂CH₂NH*t*Bu (**12**) in the solid state (ORTEP view, thermal ellipsoids are at the 50% probability level). Selected bond lengths [pm] and angles [°]: N(1)–C(1) 146.40(13), C(1)–C(2) 152.34(14), C(2)–C(3) 152.23(15), N(1)–C(4) 147.88(13); N(1)–C(1)–C(2) 111.76(9), C(3)–C(2)–C(1) 114.54(9), H(1N)–N(1)–C(1) 111.3(12).

fashion (formation of H[•]) 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 H₂) or +14 kcal mol^{–1} (formation of H₂S) 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]^{•+} 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 S₈ 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 transfer



Scheme 5. Elementary steps (*a*–*f*) of the C–H activation of imidazolidines by S₈.

(SET) oxidation step *b* as the rate-determining step of the reaction.

The thermochemistry of the formation of the thioureas from S₈ and animals 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 S₈ 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.

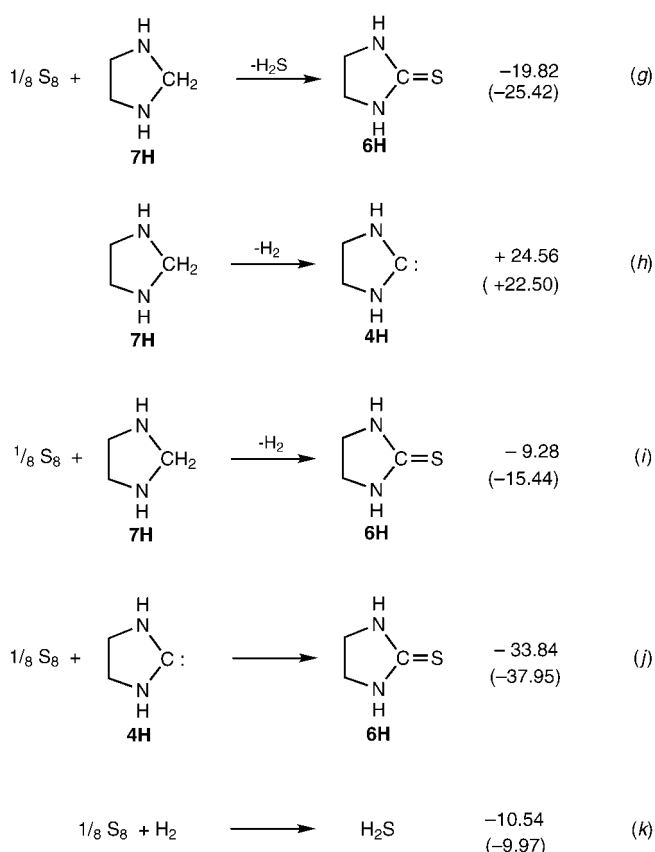
The imidazolidine **7H** (Scheme 6) was chosen as model compound for the animals **7a**–**7b**. The pyramidal geometry of the nitrogen atoms in **7H** leads to two different isomers

Table 3. Oxidation of animals with S₈. Selected energies (in Hartrees) at the B3LYP/6–31G(d) level.

	ZPE	<i>E</i> ₀	<i>E</i> _{298,15}	<i>H</i> _{298,15}	<i>G</i> _{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 ₂ S	0.015172	–399.370264	–399.367417	–399.366473	–399.389832
<i>anti</i> - 7H	0.119250	–228.489610	–228.484819	–228.483875	–228.517424
<i>syn</i> - 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 animals with S₈. Selected energies (in Hartrees) at the CBS-4 level.

	ZPE	<i>E</i> ₀	<i>E</i> _{298,15}	<i>H</i> _{298,15}	<i>G</i> _{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 ₂ S	0.016379	–398.936720	–398.933875	–398.932930	–398.956239
<i>anti</i> - 7H	0.126308	–228.243185	–228.238072	–228.237128	–228.271617
<i>syn</i> - 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 , $\Delta G = -19.82 \text{ kcal mol}^{-1}$) and reaction i, (by-product H_2 , $\Delta G = -9.28 \text{ kcal mol}^{-1}$).

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 amina. The abundance of easily accessible starting materials makes reaction h, the 1,1-elimination of H_2 from formaldehyde amins to give carbenes, a worthwhile target of synthetic studies. The ΔG value of $+24.6 \text{ kcal mol}^{-1}$ 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_0		$\Delta E_{298.15}$		$\Delta H_{298.15}$		$\Delta G_{298.15}$	
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 amina oxidation seems unlikely. Even if the endothermic elimination of hydrogen from the amina ($\Delta G = +24.6 \text{ kcal mol}^{-1}$) is combined with the formation of H_2S ($\Delta G = -10.5 \text{ kcal mol}^{-1}$) the overall reaction still has a positive ΔG value of $+14.1 \text{ kcal mol}^{-1}$. 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] ($\Delta H = -35 \pm 2 \text{ kcal mol}^{-1}$) is in very good agreement with the CBS-4 value that we obtain for the reaction k ($\Delta H = -35.03 \text{ kcal mol}^{-1}$).

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

Conclusion

A novel method for the synthesis of tetrasubstituted thioureas consists of heating cyclic formaldehyde amins 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 $>\text{CH}_2 \rightarrow >\text{C}=\text{S}$ 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 amins (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 (^1H), Bruker 500 MHz (^{13}C), or Varian 400 MHz spectrometers (^{13}C) at normal spectrometer temperature. The spectra are referenced against tetramethylsilane (TMS) (^1H 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 amins 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 ($3 \times 20 \text{ g}$) of NaOH were added to the cold mixture. The upper layer was separated and the aqueous layer was extracted with diethyl ether ($3 \times 100 \text{ mL}$). 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 amins 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

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 CS₂: CS₂ (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 S₈: Sulfur (1.22 g, 4.75 mmol) was added to the amina (19.0 mmol) in a Swagelok 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 Al₂O₃. 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 of 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 Swagelok stainless steel cylinder. The cylinder was sealed and placed in an oil bath (150 °C) for 72 h. The ¹H 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 Swagelok stainless steel cylinder. The cylinder was sealed and placed in an oil bath (150 °C). After 20 h, a ¹H 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. ¹H NMR (CDCl₃): δ = 3.97 (s, 4H; SCH₂).

Spectroscopic data

1,3-Dimethylimidazolidine-2-thione (6a): Colorless hexagons, m. p. 110–111 °C (lit.: 111–112 °C^[18b]); ¹H NMR (200 MHz, C₆D₆, 25 °C): δ = 2.35 (s; CH₂CH₂), 2.82 (s; NCH₃); ¹H NMR (CDCl₃): δ = 3.13 (s; NCH₃), 3.54 (s; CH₂CH₂); ¹³C NMR (400 MHz, C₆D₆, 25 °C): δ = 34.95 (¹J(C,H) = 138 Hz; NCH₃), 46.78 (¹J(C,H) = 145 Hz; CH₂CH₂), 184.52 (C=S); ¹³C NMR (400 MHz, CDCl₃, 25 °C): δ = 35.11 (¹J(C,H) = 139 Hz; NCH₃), 48.33 (¹J(C,H) = 145 Hz; CH₂CH₂), 184.0 (C=S); MS (70 eV) *m/z* (%): 130 (100) [*M*]⁺, 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 (CCl₄, CaF₂): $\tilde{\nu}$ = 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]); ¹H NMR (200 MHz, C₆D₆, 25 °C): δ = 0.87 (t, ³J(H,H) = 7.2 Hz, 6H; NCH₂CH₃), 2.56 (s, 4H; CH₂CH₂), 3.51 (q, ³J(H,H) = 7.2 Hz, 4H; NCH₂CH₃); ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 1.17 (t, ³J(H,H) = 7.3 Hz, 6H; NCH₂CH₃), 3.54 (s, 4H; CH₂CH₂), 3.67 (q, ³J(H,H) = 7.3 Hz, 4H; NCH₂CH₃); ¹³C NMR (400 MHz, C₆D₆, 25 °C): δ = 12.90 (CH₃), 45.48 (CH₂CH₂), 49.05 (NCH₂CH₃), 183.05 (C=S); ¹³C NMR (400 MHz, CDCl₃, 25 °C): δ = 12.00 (CH₃), 41.98 (CH₂CH₂), 45.36 (NCH₂CH₃), 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, 1194 w, 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]); ¹H NMR (200 MHz, C₆D₆, CDCl₃, 25 °C): δ = 0.91 (d, ³J(H,H) = 6.9 Hz, 12H; (CH₃)₂CH), 2.73 (s, 4H; NCH₂), 5.17 (sept, ³J(H,H) = 6.9 Hz, 2H; CH(CH₃)₂); ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 1.17 (d, ³J(H,H) = 6.6 Hz, 6H; (CH₃)₂CH), 3.45 (s, 4H; NCH₂), 4.93 (sept, ³J(H,H) = 6.6 Hz, 2H; CH(CH₃)₂); ¹³C NMR (400 MHz, C₆D₆, 25 °C): δ = 19.12 ((CH₃)₂CH), 40.38 (CH₂CH₂), 46.78 (CH(CH₃)₂), 182.28 (C=S); MS (70 eV) *m/z* (%): 186 (100) [*M*]⁺, 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; ¹H NMR (C₆D₆): δ = 1.55 (s, 18H; C(CH₃)₃), 2.75 (s, 4H; NCH₂); ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 1.58 (s, 18H; C(CH₃)₃), 3.42 (s, 4H; NCH₂); ¹³C NMR (400 MHz, C₆D₆, 25 °C): δ = 28.09 (C(CH₃)₃), 44.22 (NCH₂), 56.41 (C(CH₃)₃), 184.43 (C=S); ¹³C NMR (400 MHz, CDCl₃, 25 °C): δ = 27.93 (C(CH₃)₃), 44.31 (NCH₂), 56.42 (C(CH₃)₃), 183.13 (C=S); MS (70 eV) *m/z* (%): 214 (76) [*M*]⁺, 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; ¹H NMR (200 MHz, C₆D₆, 25 °C): δ = 3.05 (s, 4H; CH₂CH₂), 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); ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 4.14 (s; CH₂CH₂), 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); ¹³C NMR (400 MHz, CDCl₃, 25 °C): δ = 42.29 (CH₂CH₂), 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; ¹H NMR (200 MHz, C₆D₆, 25 °C): δ = 2.20 (s, 6H; NCH₃), 2.56 (s, 4H; CH₂CH₂), 3.18 (s, 2H; NCH₂N); ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 2.36 (s, 6H; NCH₃), 2.76 (s, 4H; CH₂CH₂), 3.28 (s, 2H; NCH₂N); ¹³C NMR (400 MHz, CDCl₃, 25 °C): δ = 41.60 (NCH₃), 54.67 (CH₂CH₂), 79.85 (NCH₂N); MS (70 eV) *m/z* (%): 100 (4) [*M*]⁺, 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; ¹H NMR (200 MHz, C₆D₆, 25 °C): δ = 1.01 (t, ³J(H,H) = 7.4 Hz, 6H; CH₃CH₂), 2.41 (q, ³J(H,H) = 7.4 Hz, 4H; CH₃CH₂), 2.61 (s, 4H; CH₂CH₂), 3.35 (s, 2H; NCH₂N); ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 1.10 (t, ³J(H,H) = 7.2 Hz, 6H; CH₃CH₂), 2.56 (q, ³J(H,H) = 7.2 Hz, 4H; CH₃CH₂), 2.80 (s, 4H; CH₂CH₂), 3.42 (s, 2H; NCH₂N); ¹³C NMR (400 MHz, C₆D₆, 25 °C): δ = 14.47 (CH₃CH₂), 49.60 (CH₃CH₂), 52.55 (CH₂CH₂), 76.78 (NCH₂N); 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; ¹H NMR (200 MHz, C₆D₆, 25 °C): δ = 0.98 (d, ³J(H,H) = 6.3 Hz, 12H; CH(CH₃)₂), 2.37 (sept, ³J(H,H) = 6.3 Hz, 2H; CH(CH₃)₂), 2.64 (s, 4H; CH₂CH₂), 3.48 (s, 2H; NCH₂N); ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 1.08 (d, ³J(H,H) = 6.0 Hz, 12H; CH(CH₃)₂), 2.51 (sept, ³J(H,H) = 6.0 Hz, 2H; CH(CH₃)₂), 2.84 (s, 4H; CH₂CH₂), 3.52 (s, NCH₂N); ¹³C NMR (400 MHz, C₆D₆, 25 °C): δ = 22.04 (CH(CH₃)₂), 50.73 (CH₂CH₂), 53.99 (CH(CH₃)₂), 73.36 (NCH₂N); MS (70 eV) *m/z* (%): 156 (3) [*M*]⁺, 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, 1371 m, 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, C₆D₆, 25 °C): δ = 1.09 (s, 18H; C(CH₃)₃), 2.75 (s, 4H; NCH₂CH₂), 3.67 (s, 2H; N₂CH₂); ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 1.07 (s, 18H; C(CH₃)₃), 2.83 (s, 4H; CH₂CH₂), 3.56 (s, 2H; N₂CH₂); ¹³C NMR (400 MHz, C₆D₆, 25 °C): δ = 26.1 (C(CH₃)₃), 46.0 (CH₂CH₂), 52.0 (C(CH₃)₃), 63.3 (N₂CH₂); MS (70 eV): *m/z* (%): 184 (15) [M]⁺, 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, 861 w, 820 m, 743 w cm⁻¹.

1,3-Diphenylimidazolidine (7e): Colorless plates, m. p. 127 °C; ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 3.66 (s, 4H; CH₂CH₂), 4.67 (s, 2H; N₂CH₂), 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); ¹³C NMR (400 MHz, C₆D₆, 25 °C): δ = 46.47 (CH₂CH₂), 65.85 (N₂CH₂), 112.44 (*ortho*-CH), 117.64 (*para*-CH), 129.36 (*meta*-CH), 146.41 (*ipso*-C); MS (70 eV): *m/z* (%): 224 (60) [M]⁺, 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, CDCl₃, 25 °C): δ = 1.52 (s, 18H; C(CH₃)₃), 4.11 (s, 4H; NCH₂), 8.09 (s, 1H; CH⁺); ¹³C NMR (400 MHz, CDCl₃, 25 °C): δ = 27.92 (C(CH₃)₃), 45.37 (NCH₂), 56.86 (C(CH₃)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, C₆D₆, 25 °C): δ = 1.03 (q, ³J = 6.2 Hz, 4H; CH₂CH₂CH₂), 2.43 (t, ³J(H,H) = 6.2 Hz, 4H; CH₂CH₂CH₂), 3.25 (s, 6H; NCH₃); ¹H NMR (CDCl₃): δ = 2.04 (quin, ³J(H,H) = 6.2 Hz, 2H; CH₂CH₂CH₂), 3.38 (t, ³J(H,H) = 6.2 Hz, 4H; CH₂CH₂CH₂), 3.43 (s, 6H; NCH₃); ¹³C NMR (400 MHz, C₆D₆, 25 °C): δ = 21.21 (CH₂CH₂CH₂), 43.20 (NCH₃), 48.41 (CH₂CH₂CH₂), 180.59 (C=S); MS (40 eV): *m/z* (%): 144 [M]⁺ (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, CDCl₃, 25 °C): δ = 1.64 (s, C(CH₃)₃), 2.07 (quin, ³J(H,H) = 7.1 Hz, CH₂CH₂CH₂), 3.16 (t, ³J(H,H) = 7.1 Hz, CH₂N); ¹³C NMR (400 MHz, CDCl₃, 25 °C): δ = 28.10 (q, ¹J(C,H) = 124.2 Hz, C(CH₃)₃), 29.36 (CH₂CH₂CH₂), 42.39 (t, ¹J(C,H) = 137.6 Hz, NCH₃), 52.09 (C(CH₃)₃), 185.32 (C=S); ¹⁵N NMR (500 MHz, CDCl₃, 25 °C): δ = -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, C₆D₆, 25 °C): δ = 1.54 (quin, ³J(H,H) = 4.8 Hz, 2H; CH₂CH₂CH₂), 2.11 (s, 6H; NCH₃), 2.25 (t, ³J(H,H) = 4.8 Hz, 4H; CH₂CH₂CH₂), 2.90 (s, 2H; NCH₂N); ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 1.70 (quin, ³J(H,H) = 5.6 Hz, 2H; CH₂CH₂CH₂), 2.24 (s, 6H; NCH₃), 2.41 (t, ³J(H,H) = 5.6 Hz, 4H; CH₂CH₂CH₂), 2.98 (s; NCH₂N); ¹³C NMR (400 MHz, C₆D₆, 25 °C): δ = 23.43 (CH₂CH₂CH₂), 42.86 (NCH₃), 54.22 (CH₂CH₂CH₂), 79.61 (NCH₂N); 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, C₆D₆, 25 °C): δ = 1.04 (s, 18H; C(CH₃)₃), 1.61 (quin, ³J(H,H) = 5.4 Hz, 2H; CH₂CH₂CH₂), 2.52 (t, ³J(H,H) = 5.4 Hz, 4H; CH₂CH₂CH₂), 3.44 (s, 4H; NCH₂N); ¹³C NMR (400 MHz, C₆D₆, 25 °C): δ = 26.83 (C(CH₃)₃), 29.31 (CH₂CH₂CH₂), 45.99 (NCH₂), 53.24 (C(CH₃)₃), 65.31 (NCH₂N); 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, CDCl₃, 25 °C): δ = 1.52 (s,

18H; C(CH₃)₃), 2.15 (m, 2H; CH₂CH₂CH₂), 3.56 (m, 4H; NCH₂), 8.07 (s, CH⁺); ¹³C NMR (400 MHz, CDCl₃, 25 °C): δ = 19.78 (t, ¹J(C,H) = 133.4 Hz, CH₂CH₂CH₂), 27.49 (q, ¹J(C,H) = 127.6 Hz, C(CH₃)₃), 39.77 (t, ¹J(C,H) = 144.0 Hz; NCH₂), 61.16 (s; C(CH₃)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, C₆D₆, 25 °C): δ = 0.59 (s, 2H; NH), 1.03 (s, 18H; C(CH₃)₃), 1.52 (quin, 2H; ³J(H,H) = 6.4 Hz, CH₂CH₂CH₂), 2.58 (t, ³J(H,H) = 6.4 Hz, 4H; NCH₂); ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 1.10 (s, 18H; C(CH₃)₃), 1.75 (quin, ³J(H,H) = 6.4 Hz, 2H; CH₂CH₂CH₂), 2.71 (t, ³J(H,H) = 6.4 Hz, 4H; NCH₂); ¹³C NMR (400 MHz, C₆D₆, 25 °C): δ = 29.42 (C(CH₃)₃), 32.87 (CH₂CH₂CH₂), 41.52 (NCH₂), 50.04 (C(CH₃)₃).

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for support of this work through an operating grant. The comments of Prof. Ian Still on parts of the manuscript are gratefully acknowledged. We thank one of the referees for drawing our attention to the work on amination radical cations by Nelsen and Buschek (ref. [29]).

- [1] For a comprehensive review of the technological uses of thiourea and its derivatives see: a) B. Mertschnek, F. Meck in *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A26, **1995**, 803–815; b) D. C. Schröder, *Chem. Rev.* **1955**, 55, 181–221; c) E. E. Reid, *Organic Chemistry of Bivalent Sulfur*, Chem. Publishing Co, New York, **1963**, p. 65.
- [2] For synthetic methods see: *Houben Weyl, Methoden der Organischen Chemie*, Band E3, *Kohlensäure-Derivate*, Thieme, Stuttgart, **1983**, 484–621.
- [3] a) O. Azzaroni, P. L. Schilardi, R. C. Salvarazza, A. J. Arvia, *Langmuir* **1999**, 15, 1508–1514; b) P. Schilardi, S. Méndez, R. C. Salvarazza, A. J. Arvia, *Langmuir* **1998**, 14, 4308–4314; c) S. Méndez, G. Andreasen, P. Schilardi, M. Figueroa, L. Vázquez, R. C. Salvarazza, A. J. Arvia, *Langmuir* **1998**, 14, 2515–2524; d) V. San Martín, S. Sanllorente, S. Palmero, *Electrochim. Acta* **1998**, 44, 579–585; e) V. V. Mozolis, S. P. Iokubaite, *Russ. Chem. Rev.* (Engl. transl.) **1973**, 42, 587–595; f) M. Alodan, W. Smyrl, *Electrochim. Acta* **1998**, 44, 299–309.
- [4] a) G. Hennrich, H. Sonnenschein, U. Resch-Genger, *J. Am. Chem. Soc.* **1999**, 121, 5073–5074; b) V. R. Pediredi, S. Chatterjee, A. Ranganathan, C. N. R. Rao, *J. Am. Chem. Soc.* **1997**, 119, 10867–10868; c) A. D. Burrows, S. Menzer, D. Michael, P. Mingos, A. J. P. White, D. J. Williams, *J. Chem. Soc. Dalton Trans.* **1997**, 4237–4240; d) J. Smith, J. L. Liras, S. E. Schneider, E. V. Anslyn, *J. Org. Chem.* **1996**, 61, 8811–8818; e) S. Singh, S. P. Mathur, R. S. Thakur, M. Katyal, *Acta Cien. Indica Chem.* **1987**, 13, 40; f) P. S. Sidhu, G. H. Penner, K. R. Jeffrey, B. Zhao, Z. L. Wang, I. Goh, *J. Phys. Chem. B* **1997**, 101, 9087–9097.
- [5] a) L. Yépez-Mulia, R. Morales-Hurtado, N. Viveros-Guzmán, R. Cedillo-Rivera, F. Hernández-Luis, R. Castillo, A. Hernández-Campos, O. Muñoz, *Arch. Med. Res.* **1999**, 30, 368–374; b) H. Kogen, K. Tago, M. Arai, E. Minami, K. Masuda, T. Akiyama, *Bioorg. Med. Chem. Lett.* **1999**, 9, 1347–1350; c) S. Liu, C. Tang, B. Ho, M. Ankersen, C. E. Stidsen, A. M. Crider, *J. Med. Chem.* **1998**, 41, 4693–4705; d) C. T. Supuran, A. Scozzafava, B. C. Jurca, M. A. Ilies, *Eur. J. Med. Chem.* **1998**, 33, 83–93; e) E. G. Chalina, L. Chakarova, *Eur. J. Med. Chem.* **1998**, 33, 975–983; f) E. G. Chalina, L. Chakarova, D. Staneva, *Eur. J. Med. Chem.* **1998**, 33, 985–990; g) L. F. Jalandar, J.-E. Lönnqvist, *Heterocycles* **1998**, 48, 743–747; h) K. Prabhakar, F. Jadhav, J. Woerner, H.-W. Man, *Bioorg. Med. Chem. Lett.* **1997**, 7, 2145–2148; i) O. Vajragupta, A. Pathomsakul, C. Matayatsuk, L. Ruangreangyinyod, Y. Wonkrajang, W. O. Foye, *J. Pharm. Sci.* **1985**, 85, 258–260; j) S. N. Pandeya, P. Ram, V. Shankar, *J. Sci. Ind. Res.* **1981**, 40, 458; k) C. Mao, E. A. Sudbeck, T. K. Venkatachalam, F. M. Uckun, *Bioorg. Med. Chem. Lett.* **1999**, 9, 1393–1398; l) F. M. Uckun,

- C. Mao, S. Pendergrass, D. Maher, D. Zhu, L. Tuel-Ahlgren, T. K. Venkatachalam, *Bioorg. Med. Chem. Lett.* **1999**, 9, 2721–2726.
- [6] For example: carbimazole (thyreostatic), propylthiouracil (thyreostatic), methylthiouracil (thyreostatic), and thiamylal (ultrashort narcotic).
- [7] a) *The Pesticide Manual*, 9th ed. (Eds.: C. R. Worthing, R. J. Hance), The British Crop Protection Council, Farnham, **1991**; b) K. H. Büchel, *The Chemistry of Pesticides*, Wiley, New York, **1983**, p315; c) J. Drabek, *Spec. Publ. Royal Soc. Chem.* **1990**, 79, 170.
- [8] R. Wegler, *Chemie der Pflanzenschutz- und Schädlingsbekämpfungsmittel*, Springer, Berlin, **1970**, 605–606.
- [9] a) L. Chai, M. Okido, W. Wei, *Hydrometallurgy* **1999**, 53, 255–266; b) F. Z. El Aamrani, A. Kumar, J. L. Cortina, A. M. Sastre, *Anal. Chim. Acta* **1999**, 382, 205–213; c) Y.-Z. Wei, M. Yamaguchi, M. Kumagai, Y. Takashima, T. Hoshikawa, F. Kawamura, *J. Alloys Compd.* **1998**, 271–273, 693–696; d) G. Fairthorne, D. Fornasiero, J. Ralston, *Int. J. Miner. Process.* **1997**, 50, 227–224; e) K. Ennasaf, D. Pareau, M. Z. Benabdallah, G. Durand, *Bull. Soc. Chim. Fr.* **1996**, 133, 151–159; f) K. Ennasaf, D. Pareau, M. Z. Benabdallah, G. Durand, *Bull. Soc. Chim. Fr.* **1995**, 132, 985–994; g) G. L. Yan, J. Alstad, *J. Radioanal. Nucl. Chem. Lett.* **1995**, 201, 191–198; h) K. R. Koch, C. Sacht, S. Bourne, *Inorg. Chim. Acta* **1995**, 232, 109–115; i) S.-G. Kim, H. J. Lee, J.-K. Oh, E.-C. Lee, *Hydrometallurgy* **1995**, 38, 7–13; j) P. A. Distin, G. D. Demopoulos, *J. Met.* **1985**, 46; k) K.-H. König, M. Schuster, G. Schneeweis, B. Steinbrech, *Fresenius' Z. Anal. Chem.* **1985**, 325, 621; l) A. S. Chernyak, M. Knothe, *Hydrometallurgy* **1983**, 11, 265.
- [10] a) F. Korte, *GIT Laborfachzeitschrift* **1999**, 1082–1083; b) F. Korte, *Fresenius Environmental Bulletin* **1998**, 7, 128–141; c) F. Korte, F. Coulston, *Ecotox. Environ. Safe.* **1998**, 41, 119–129; d) S. Ubaldini, P. Fornari, R. Massida, C. Abuzzese, *Hydrometallurgy* **1998**, 48, 113–124; e) L. M. Abrantes, M. C. Costa, *Hydrometallurgy* **1996**, 40, 99–110; f) D. S. R. Murthy, P. M. Prasad, *Hydrometallurgy* **1996**, 42, 27–33; g) L. Tremblay, G. Deschênes, E. Ghali, J. McMullen, M. Lanouette, *Int. J. Miner. Process.* **1996**, 48, 225–244; h) G. Zuo, M. Muhammed, *Reactive Polymers* **1995**, 24, 165–181; i) G. Zuo, M. Muhammed, *React. & Funct. Poly.* **1995**, 27, 187–198; j) P. J. Conradi, M. W. Johns, R. J. Fowles, *Hydrometallurgy* **1995**, 37, 349–366; k) M. F. Almeida, M. A. Amarante, *Minerals Engineering* **1995**, 8, 257–271; l) D.-E. Akretche, S. K. Slimane, H. Kerdjoudj, *Hydrometallurgy* **1995**, 38, 189–204; m) S. Singh, S. P. Mathur, R. S. Thakur, L. Keemti, *Orient. J. Chem.* **1987**, 3, 203; n) Yu. A. Zolotov, O. M. Petrukhn, V. N. Shevchenko, V. V. Dunina, E. G. Rukhadze, *Anal. Chim. Acta* **1978**, 100, 613–618.
- [11] A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, 113, 361.
- [12] a) A. J. Arduengo, (Wilmington, Delaware), US Pat. 5077414, **1991**; b) B. L. Benac, E. M. Burgess, A. J. Arduengo, *Org. Synth.* **1986**, 64, 92.
- [13] a) R. W. Alder, M. E. Blake, *Chem. Commun.* **1998**, 441; b) R. W. Alder, M. E. Blake, *Chem. Commun.* **1997**, 1513–1514; c) R. W. Alder, P. R. Allen, G. Murray, A. G. Orpen, *Angew. Chem.* **1996**, 108, 1211–1213; *Angew. Chem. Int. Ed. Engl.* **1996**, 35, 1121–1123; d) R. W. Alder, P. R. Allen, S. J. Williams, *J. Chem. Soc. Chem. Commun.* **1995**, 1267–1268; e) H. Eilingsfeld, G. Neubauer, M. Seefelder, H. Weidinger, *Chem. Ber.* **1964**, 97, 1232.
- [14] R. W. Alder, C. P. Butts, A. G. Orpen, *J. Am. Chem. Soc.* **1998**, 120, 11526–11527.
- [15] This may be due in part to the formation of complexes between diaminocarbenes and alkali halides a) R. W. Alder, M. E. Blake, C. Bortolotti, S. Bufali, C. P. Butts, E. Linehan, J. M. Oliva, A. G. Orpen, M. J. Quayle, *Chem. Commun.* **1999**, 241–242; b) R. W. Alder, M. E. Blake, J. M. Oliva, *J. Chem. Phys. A* **1999**, 103, 11200–11211.
- [16] a) N. Kuhn, E. Niquet, M. Steimann, I. Walker, *Z. Naturforsch. B* **1999**, 54, 1181–1187; b) N. Kuhn, T. Kratz, *Synthesis* **1993**, 561–562.
- [17] a) M. K. Denk, A. Thadani, K. Hatano, A. J. Lough, *Angew. Chem.* **1997**, 109, 2719–2721; *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 2607–2609; b) M. K. Denk, K. Hatano, M. J. Ma, *Tetrahedron Lett.* **1999**, 40, 2057–2060; c) M. K. Denk, J. Rodezno, S. Gupta, A. J. Lough, *J. Organomet. Chem.* **2001**, 617–618, 737–740; d) M. K. Denk, J. Rodezno, *J. Organomet. Chem.* **2000**, 608, 122–125.
- [18] a) R. A. Donia, J. A. Shotton, L. A. Bentz, G. E. P. Smith, *J. Org. Chem.* **1949**, 14, 946–951; b) C.-D. Li, S. L. Mella, A. C. Sartorelli, *J. Med. Chem.* **1981**, 24, 1089–1092; c) J. Van Alphen, *Rec. Trav. Chim.* **1937**, 36, 343–350.
- [19] H. W. Wanzlick, B. Lachmann, E. Schikora, *Chem. Ber.* **1965**, 98, 3170–3177.
- [20] The reaction of formaldehyde with unsubstituted 1,2-diaminoethane and 1,3-diaminopropane has recently been shown to lead to the formation of complex aza-bicyclic and aza-macrocyclic systems: a) M. R. Suissa, C. Rømming, J. Dale, *Chem. Commun.* **1997**, 113–114; b) J. Dale, T. Sigvartsen, *Acta Chem. Scand.* **1991**, 45, 1064–1070; c) J. Dale, C. Rømming, T. Sigvartsen, *Acta Chem. Scand.* **1991**, 45, 1071–1075.
- [21] For the recent use of sulfur in inorganic and organic synthetic reactions see: a) S. Al-Ahmad, B. Boje, J. Magull, T. Rauchfuss, Y. Zheng, *J. Am. Chem. Soc.* **1995**, 117, 1145–1146; b) D. Jungk, N. Schmidt, J. Hahn, P. Versloot, J. G. Haasnoot, J. Reedijk, *Tetrahedron* **1994**, 50, 11187; c) F. Bigoli, M. A. Pellinghelli, D. Atzei, P. Deplano, E. F. Trogu, *Phosphorus & Sulfur* **1988**, 37, 189–194; d) T. S. Cameron, A. Decken, M. Fang, S. Parsons, J. Passmore, D. J. Wood, *Chem. Commun.* **1999**, 1801–1802.
- [22] The use of noncyclic formaldehyde amins gives lower yields and leads to the formation of *N*-thioformyl derivatives which can become the main products under certain reaction conditions. Details will be published elsewhere.
- [23] X-ray crystallographic data. **5a**: C₁₁H₂₀N₂S, *M_r* = 212.35, crystal size = 0.06 × 0.13 × 0.18 mm, orthorhombic, space group: *Pca*2₁, *a* = 11.573(1), *b* = 9.5648(8), *c* = 11.169(1) Å, *V* = 1236.4(1) Å³, *Z* = 4, $\rho_{\text{calcd}} = 1.141 \text{ g cm}^{-3}$, $\lambda(\text{Cu K}\alpha) = 1.54178 \text{ Å}$, $\mu(\text{Cu K}\alpha) = 0.564 \text{ mm}^{-1}$, *F*(000) = 464, scan type: $2\theta - \theta$, *T* = 293(2) K, $4.62^\circ < \theta < 57.1^\circ$, 993 independent reflections (*R_i* = 0.0342), no. of observations [*F*(*F*) > 4σ(*F*)] = 1253, *R* = 0.033, *R_w* = 0.088, maximum peak in final Fourier difference synthesis = 0.28 e Å⁻³. **6d**: C₁₁H₂₂N₂S, *M_r* = 214.37, crystal size = 0.34 × 0.42 × 0.28 mm, orthorhombic, space group: *Pca*2₁, *a* = 11.615(1), *b* = 9.248(2), *c* = 11.041(1) Å, *V* = 1186.0(3) Å³, *Z* = 4, $\rho_{\text{calcd}} = 1.201 \text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ Å}$, $\mu = 0.564 \text{ mm}^{-1}$, *F*(000) = 472, scan type: $2\theta - \theta$, *T* = 173(2) K, $2.82^\circ < \theta < 29.99^\circ$, 2004 independent reflections (*R_i* = 0.0342), no. of observations [*F*(*F*) > 4σ(*F*)] = 2343, *R* = 0.064, *R_w* = 0.123, maximum peak in final Fourier difference synthesis = 0.93 e Å⁻³. **8**: C₁₂H₂₃N₃S, *M_r* = 241.39, crystal size = 0.32 × 0.30 × 0.15 mm, monoclinic, space group: *P2*(1)/*n*, *a* = 6.9049(2), *b* = 14.7905(5), *c* = 13.6393(5) Å, $\beta = 96.971(5)^\circ$, *V* = 1382.64(8) Å³, *Z* = 4, $\rho_{\text{calcd}} = 1.160 \text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.7103 \text{ Å}$, $\mu = 0.215 \text{ mm}^{-1}$, *F*(000) = 528, scan type $2\theta - \theta$, *T* = 150.0(1) K, $4.08^\circ < \theta < 26.38^\circ$, 2816 independent reflections (*R_i* = 0.0483), *R_w* = 0.059, maximum peak in final Fourier difference synthesis +0.487 e Å⁻³ and -0.355 e Å⁻³. **11**: C₁₃H₂₅N₃S, *M_r* = 255.42, crystal size = 0.25 × 0.18 × 0.12 mm, orthorhombic, space group: *Im*2_m, *a* = 6.9330(12), *b* = 10.1506(10), *c* = 10.5640(17) Å, *V* = 743.43(19) Å³, *Z* = 2, $\rho_{\text{calcd}} = 1.141 \text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.7103 \text{ Å}$, $\mu = 0.203 \text{ mm}^{-1}$, *F*(000) = 280, scan type: $2\theta - \theta$, *T* = 100.0(1) K, $5.25^\circ < \theta < 24.98^\circ$, 716 independent reflections (*R_i* = 0.082), *R* = 0.071, *R_w* = 0.018, maximum peak in final Fourier difference synthesis +0.66 e Å⁻³ and -0.26 e Å⁻³. **12**: C₁₁H₂H₂₄N₂, *M_r* = 186.34, crystal size 0.32 × 0.25 × 0.18 mm³, monoclinic, space group *P2*(1)/*n*, *a* = 9.4791(3), *b* = 8.6096(4), *c* = 16.0961(3) Å, $\beta = 103.054(3)^\circ$, *V* = 1279.68(8) Å³, *Z* = 4, $\rho_{\text{calcd}} = 0.967 \text{ Mg m}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ Å}$, $\mu = 0.057 \text{ mm}^{-1}$, *F*(000) = 424, scan type: $2\theta - \theta$, *T* = 150.0(1) K, $4.41^\circ < \theta < 26.38^\circ$, 2604 independent reflections (*R_i* = 0.036), *R* = 0.0372, *R_w* = 0.0902, maximum peak in final Fourier difference synthesis 0.173 and -0.132 e Å⁻³. Data were collected on a Siemens P4 diffractometer. No absorption correction was applied. Lorentz and polarization corrections were applied. Systematically absent reflections were rejected and equivalent reflections were merged. The heavy-atom positions were determined by direct methods. Subsequent difference Fourier synthesis revealed the positions of all other non-hydrogen atoms: hydrogen atoms were placed in idealized position. The non-hydrogen atoms were refined by the full-matrix least-squares method, with the hydrogen atoms riding on their supporting carbon atoms. A weighting Scheme ($w^{-1} = \sigma^2(F) + 0.001 F^2$) was applied and the data were corrected for the effects of anomalous dispersion and secondary extinction. Crystallographic calculations were carried out using the SHELXTL/PC^[24] program, version 5.1, on a Pentium 133 PC in the Chemical Crystallography Laboratory, University of Toronto, Canada.

- [24] a) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467–473; b) *Bruker Analytical X-ray Systems*, Madison, Wisconsin, USA, **1998**.
- [25] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-158166 (**5a**), CCDC-158167 (**6d**), CCDC-158168 (**8**), CCDC-158169 (**11**), CCDC-158170 (**12**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
- [26] C. K. Johnson, ORTEP, FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, National Laboratories, Oak Ridge/Tennessee, USA, 1965.
- [27] a) R. Cae-Olivares, O. Jiménez-Sandoval, S. Hernández-Ortega, M. Sánchez, R. A. Toscano, I. Haiduc, *Heteroatom Chem.* **1995**, *6*, 89–97; b) G. B. Ansell, D. M. Forkey, D. W. Moore, *J. Chem. Soc. Chem. Commun.* **1970**, 56–57.
- [28] M. K. Denk, J. Brownie, unpublished results.
- [29] J. M. Buschek, *J. Am. Chem. Soc.* **1974**, *96*, 7930–7934.
- [30] The cyclic formaldehyde amins investigated in this study are attacked by O₂. Reaction of neat **7d** with O₂ at 120 °C resulted in the complete consumption of the amins. The main reaction product (40 %) is the *N,N*-di(formyl)-*N,N*-di-*tert*-butylethylenediamine, *t*BuN(CH=O)CH₂CH₂N(CH=O)*t*Bu, which was characterized by single-crystal X-ray crystallography. Details will be reported elsewhere.
- [31] The calculations were carried out with the Gaussian 94 suite of programs: Gaussian 94, Revision D.4, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995. Molecular geometries were fully optimized and vibrational frequencies were calculated as indicated. The absence of virtual frequencies ensures that the calculated structures are minima rather than saddle points.^[32]
- [32] a) J. B. Foresman, A. Frisch, *Exploring Chemistry with Electronic Structure Methods*, 2nd ed., Gaussian Inc., Pittsburgh, PA, **1996**; b) I. Bytheway, M. W. Wong, *Chem. Phys. Lett.* **1998**, *282*, 219–226; c) A. P. Scott, L. Radom, *J. Phys. Chem.* **1996**, *100*, 16502–16513; d) A. P. Scott, B. T. Golding, L. Radom, *New. J. Chem.* **1998**, 1171–1173; e) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257.
- [33] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785; c) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
- [34] The Gaussian keyword CBS-4m^[32a] was used to call up the modified CBS-4 procedure. J. W. Ochterski, G. A. Peterson, J. A. Montgomery Jr., *J. Chem. Phys.* **1996**, *104*, 2598.
- [35] L. A. Curtiss, K. Raghavachari, G. W. Trucks, J. A. Pople, *J. Chem. Phys.* **1991**, *94*, 7221.
- [36] J. K. Huang, H. J. Schanz, E. D. Stevens, S. P. Nolan, *Inorg. Chem.* **2000**, *39*, 1042–1045. The smaller reaction enthalpy of -24.1 ± 1.5 kcal mol⁻¹ reported for R=1-adamantyl is presumably due to steric effects (repulsion between sulfur and the adamantyl substituent in the respective thiourea).

Received: August 24, 2000

Revised: June 13, 2001 [F2692]