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Metal-mediated reactions towards the synthesis of a novel deaminolysed bisurea, dicarbamolyamine

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Abstract: A new selective cobalt acetate tetrahydrate or cerium nitrate hexahydrate mediated cleavage of the C–N bond of a benzoyl isothiocyanate derivative to give (carbamoylamino)methanethioamide is presented. The cleavage of the C–N could not be achieved in the absence of thione. The novel silver-mediated conversion of a thione to the carbonyl was achieved on 1-((benzamido)formyl)urea and replicated on (carbamoylamino)methanethioamide to give the deaminolyzed bisurea (dicarbamolyamine). The compounds were characterized by IR, NMR, microanalysis and GC–MS. The single crystal X–ray diffraction studies of the crystal structures of compounds **I**, **II**, **III** and **V** is discussed.

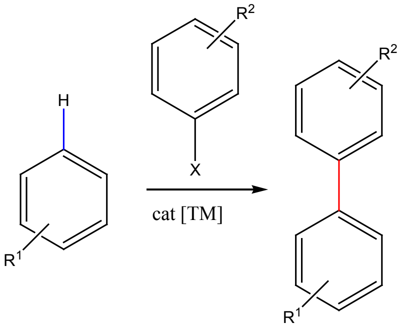
Keywords: benzoyl isothiocyanates, metal-mediated, bisurea, dicarbamolyamine.

1 Introduction

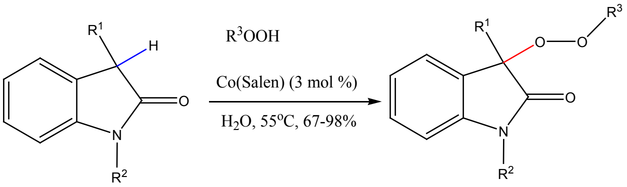
Benzoyl isothiocyanates have been reported extensively [1-2], as was their transformation to other classes of compounds [3-4]. Some transformations of benzoyl isothiocyanates and their analogs allow the simple access to certain compounds [5-9]. The isothiocyanates typically have an electrophillic carbon of the thiocyanate moiety which can be attacked by nucleophiles such as nitrogen and oxygen atoms. A reaction with amines typically leads to thiourea derivatives [10]. Metal-catalyzed reactions have been a subject of much interest for many decades and new metal catalysts are currently being invented. Ackermann et al. [11] have reported a method for the activation and cleavage of a C–H in the synthesis of biaryls using palladium and ruthenium catalysts. The method has been extensively applied in the synthesis of some bioactive compounds.

Cobalt has been used to catalyze the cross-dehydrogenative coupling of benzoxazoles and ethers [12].

Cyclopentanone-2-carboxylates have been converted to δ-lactones by cerium catalysis with α-arylvinylacetate [13]. The synthesis of a molecular cobalt complex that generates super stoichiometric yields of NH_3 *via* the direct reduction of N_2 with protons and electrons has been reported [14]. The cobalt(II) diacetonitrilo has been used to catalyze the activation of weak C–H bonds by either iodosobenzene or *m*-chloroperbenzoic acid [15]. Another impactful bond activation metal-catalyzed reaction is the ruthenium-catalyzed bond-shifting methathesis reactions by Grubbs [16,17]. The cleavage of C–N bonds has been reported to be carried out using transition metals [18].



Scheme 1: Transition-metal-catalyzed direct arylation of arenes by C–H bond cleavage [11].



Scheme 2: Cobalt-catalyzed peroxidation of 2-oxindoles with hydroperoxides [12].

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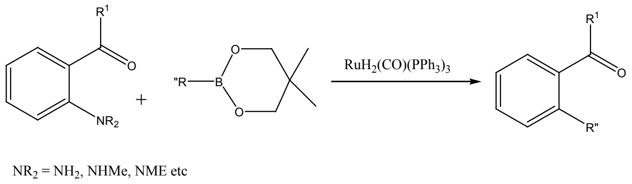
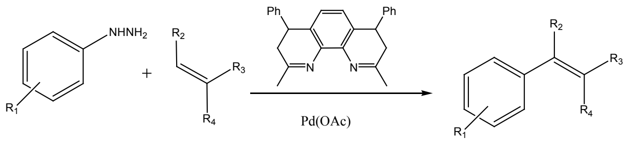


Scheme 3: Cleavage of C–N bonds in aniline derivatives on a ruthenium center [19,20].



Scheme 4: Palladium catalyzed C–N bond cleavage resulting in C-C coupling [21].

Carbon–carbon bond formation has been achieved through the cleavage of aromatic C–N bonds from aniline derivatives [19, 20]. Palladium catalyzed C–C bond formation *via* olefin carbon nitrogen bond cleavage has been reported by Zhu et al. [21].

In this work, we report new preliminary findings of a selective cobalt or cerium mediated cleavage of the C–N bond of a benzoyl isothiocyanate derivative to give (carbamoylamino) methanethioamide. The cleavage of the C–N could not be achieved in the absence of the thione group. The novel silver-catalyzed conversion of the thione to the carbonyl has been achieved on (carbamoylamino) methanethioamide to produce bisurea, dicarbamolyamine. These researchers cannot claim that the cleavage reactions are metal-catalyzed since stoichiometric quantities of the metal ions were used, but more work needs to be done to ascertain the mechanism of the reaction; the first step would be to decode the intermediate species of the metal ions. Hence, the activation of the C–N bonds presented here is termed metal-mediated and not metal-catalyzed reactions.

2 Experimental methods

2.1 Reagent and instrumentation

Analytical grade reagents and solvents for synthesis such as ammonium thiocyanate, dimethyl sulfoxide, cerium nitrate hexahydrate, cobalt acetate tetrahydrate and toluene were obtained from Sigma Aldrich (USA) while silver nitrate, tetrahydrofuran, methanol, diethyl ether, ethyl acetate, benzoyl chloride, acetone, celite, ethanol and hexane were obtained from Merck Chemicals (SA). The chemicals were used as received (i.e. without further purification). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance AV 400 MHz Spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C using DMSO-d$_6$ as solvent and tetramethylsilane as internal standard. Chemical shifts are expressed in ppm. FT–IR spectra were recorded on a Bruker Platinum ATR Spectrophotometer Tensor 27. Elemental analyses were performed using a Vario Elementar Microcube ELIII. Melting points were obtained using a Stuart Lasec SMP30. Masses were determined using an Agilent 7890A GC system connected to a 5975C VL–MSC with an electron impact as the ionization mode and detection by a triple-axis detector. The GC was fitted with a 30 m x 0.25 mm x 0.25 µm DB-5 capillary column. Helium was used as the carrier gas at a flow rate of 1.6 mL.min^{-1} with an average velocity of 30.2 cm s^{-1} and a pressure of 63.7 KPa.

2.2 Preparation

2.2.1 1-((Benzamido)sulfanylenemethyl)urea (I)

1-((Benzamido)sulfanylenemethyl) urea was accessed by dissolving ammonium thiocyanate (0.04 mol, 3.05 g) in 80 mL of acetone; benzoyl chloride (0.04 mol, 5.62 g) was then added and heated under reflux for 2 h. The benzoyl isothiocyanate solution was filtered to remove ammonium chloride, and the urea (0.04 mol, 2.40 g) was then added to the resulting benzoyl isothiocyanate solution and refluxed for 6 h. The initial liquid stood overnight in a fume hood. The obtained product was filtered and recrystallized from DMSO:Toluene (1:1) as a yellow solid. Melting point = 124–126°C. Yield = 88%. ^{1}H NMR (ppm): 11.23 (s, 1H, N–H), 9.86 (s, 1H, N–H), 9.56 (s, 1H, N–H), 7.94 (d, 2H, *J* = 7.6 Hz), 7.64 (t, 1H, *J* = 7.6 Hz), 7.51 (t, 2H, *J* = 7.6 Hz). ^{13}C NMR (ppm): 182.4 (C=S), 168.4 (C=O), 133.3, 132.3, 129.0, IR (ν_{max}, cm^{-1}): 3343 (N–H), 3197 (N–H), 1691 (C=O), 1651 (C=O), 1615 (C=C), 1577 (C=C), 1528 (C–N), 1489 (C–N), 1449 (C–N). Anal. Calcd for $C_9H_9N_3O_2S$: C, 48.42; H, 4.06; N, 18.82; S, 14.36. Found: C, 48.53; H, 4.01; N, 18.34; S, 14.45. LRMS (*m/z*, M$^+$): Found for $C_9H_9N_3O_2S$ = 223.10, expected mass = 223.25.

2.2.2 1-((Benzamido)formyl)urea (II)

1-((Benzamido) sulfanylenemethyl)urea (0.009 mol, 2.03 g) was dissolved in tetrahydrofuran in the presence of silver nitrate (0.009 mol, 1.55 g) and heated under reflux in tetrahydrofuran (20 mL) for 24 h. The reaction mixture was then extracted with diethyl ether:methanol (1:1) (100 mL) and filtered over celite. The solvent was removed by rotary evaporation. The product was recrystallized from DMSO:Toluene (1:1) as a white puffy solid with a melting point of 204–206°C. Yield = 33.0%. ^{1}H NMR (ppm): 11.42 (s, 1H, N–H,), 10.33 (s, 1H, N–H), 8.02 (d, 2H, *J* = 8.0 Hz), 7.72 (t, 1H, *J* = 8.0 Hz), 7.60 (t, 2H, *J* = 7.6 Hz), 7.47 (s, 1H, N–H). ^{13}C NMR (ppm): 169.6 (C=O), 132.1, 128.9, 127.8. IR (ν_{max}, cm^{-1}): 3345 (N–H), 3225 (N–H), 1711 (C=O), 1664 (C=O), 1598 (C=C), 1578 (C=C), 1466 (C–N). Anal. Calcd for $C_9H_9N_3O_3$: C 52.17; H, 4.38; N, 20.28. Found: C 52.37; H, 4.45; N, 20.40. LRMS (*m/z*, M$^+$): Found for $C_9H_9N_3O_3$ = 207.06, expected mass = 207.19.

2.2.3 (Carbamoylamino)methanethioamide (III)

Compound **I** (0.01 mol, 2.23 g) was dissolved in 30 mL of solvent (methanol or tetrahydrofuran) 0.01 mol of cerium nitrate hexahydrate (in tetrahydrofuran) or cobalt acetate tetrahydrate (in methanol) and heated under reflux at 100-120°C for 24 h. The solvent was removed at the pump, and the product was purified on the column using ethyl acetate: hexane (1:1). The product recrystallized from ethanol: acetone (1:1) as a colorless solid with a melting point of 113–115°C. Yield = 76%. ^{1}H NMR (ppm): 9.69 (s, N–H, 1H), 9.49 (s, N–H, 1H), 8.95 (s, N–H, 1H), 6.95 (br, N–H, 1H), 6.33 (br, N–H, 1H), ^{13}C NMR (ppm): 181.7 (C=S), 155.0 (C=O). IR (ν_{max}, cm^{-1}): 3438 (N–H), 3367 (N–H), 3167(N–H), 1716 (C=S), 1699 (C=O), 1438 (C–N). Anal. Calcd for $C_2H_5N_3OS{\cdot}H_2O$: C, 17.51; H, 5.14; N, 30.64; S, 23.37. Found: C, 17.42; H, 4.98; N, 30.95; S, 23.62. LRMS (*m/z*, M$^+$): Found for $C_2H_5N_3OS$ = 119.36, expected mass = 119.15.

2.2.4 Dicarbamolyamine (IV)

Compound **III** (0.0003 mol, 0.036 g) and silver nitrate (0.0003 mol, 0.051 g) were heated under reflux in tetrahydrofuran (20 mL) for 24 h. The reaction mixture was then extracted with diethyl ether:methanol (1:1) (100 mL) and filtered over celite. The solvent was removed by rotary evaporation. The product was recrystallized from DMSO:Toluene (1:1) as a light brown solid with a melting point of 98–101°C. Yield = 35%. ^{1}H NMR (ppm): 10.20 (s, N–H, 1H), 9.87 (s, N–H, 1H), 9.74 (s, N–H, 1H), 9.49 (s, N–H, 1H). ^{13}C NMR (ppm): 155.3 (C=O). IR (ν_{max}, cm^{-1}): 3377 (N–H), 3334 (N–H), 3234 (N–H), 1654 (C=O), 1470 (C–N). Anal. Calc for $C_2H_5N_3O_2$: C, 23.30; H, 4.89; N, 40.76. Found: C, 23.42; H, 4.82; N, 40.83. LRMS (*m/z*, M^{2+}): Found for $C_2H_5N_5O_2$ = 105.1, expected mass = 105.08.

2.2.5 Benzamide (V)

1-((Benzamido)sulfanylenemethyl)urea (0.01 mol, 2.23g) was dissolved in tetrahydrofuran. Cobalt acetate tetrahydrate (0.01 mol) was then added and heated under reflux for 24 h. The product was filtered through celite, and the solvent was removed by slow evaporation. The product recrystallized from ethanol as a colorless solid with a melting point of 172–174°C. Yield = 55.0%. ^{1}H NMR (ppm): 7.97 (s, N–H, 1H), 7.85 (d, 2H, *J* = 8.0 Hz), 7.52 (t, 1H, *J* = 8.0 Hz), 7.47 (t, 2H, *J* = 7.6 Hz). ^{13}C NMR (ppm): 168.4 (C=O), 134.9 (C), 131.8 (C–H), 128.7 (C–H), 127.9 (C–H). IR (ν_{max}, cm^{-1}): 3323 (N–H), 3120 (N–H), 1670 (C=O), 1596 (C=C), 1523 (C=C), 1448 (C–N). Anal. Calcd for C_7H_7NO: C 69.41; H, 5.82; N, 11.56. Found: C 69.35; H, 5.76; N, 11.48. LRMS (*m/z*, M$^+$): Found for C_7H_7NO = 121.06, expected mass = 121.14.

2.2.6 X-ray crystallography

X-ray diffraction analysis of 1-((benzamido) sulfanylenemethyl) urea (**I**), 1-([benzamido]formyl) urea (**II**), carbamoylamino)methanethioamide (**III**) and benzamide (**V**) were performed at 200 K using a Bruker Kappa Apex II diffractometer with monochromated Mo Kα radiation (λ = 0.71073 Å). APEXII [22], was used for data collection and SAINT [22], for cell refinement and data reduction. The structures were solved using direct methods such as SHELXS–2013 [22] and refined by least-squares procedures using SHELXL-2013 [23], with SHELXLE [24], as a graphical interface. All non-hydrogen atoms were refined anisotropically. Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å for aromatic carbon atoms and C–H 0.99 Å for methylene groups) and were included in the refinement in the model approximation, with *U*iso (H) set to 1.2*U*eq (C). The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C–C bond to best fit the experimental electron density (HFIX 137 in the SHELX program suite [23]), with *U*iso (H) set to 1.5*U*eq (C). Nitrogen-bound H atoms were located on a different Fourier map and refined freely. Data were corrected for absorption effects using the numerical method implemented in SADABS [24].

Ethical approval: The conducted research is not related to either human or animals use.

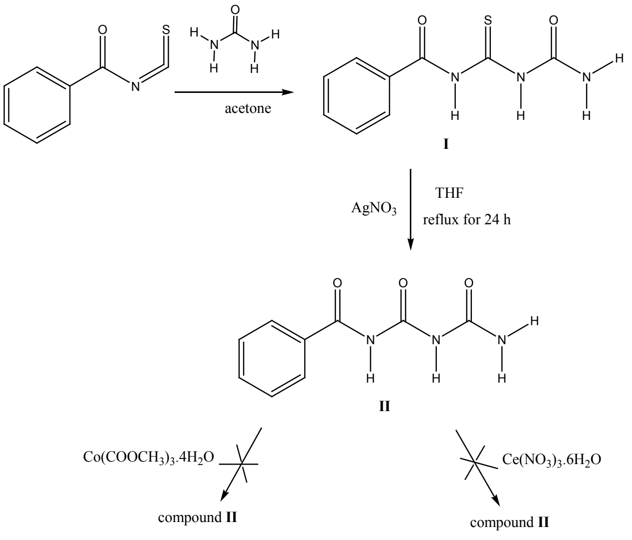
3 Results and discussion

3.1 Synthesis and spectroscopic characterization of compounds

In the synthesis of compound **I**, urea attacks the benzoyl isothiocyanate on the electrophilic carbon of the thiocyanate moiety. Potassium thiocyanate in acetone has been reported to react with benzoyl chloride [25] to form isothiocyanate. Urea was added and heated at 55°C for 5 h, and this gave a yield of 30% while heating under a reflux of acetone for 6 h gave a yield of 88%. The IR spectrum showed bands at 3343 and 3197 cm^{-1} for N–H intervals. Signals were observed at 1691 and 1651 cm^{-1}for the C=O stretch. While signals for the C=C intervals were observed at 1615 and 1577 cm^{-1}, signals for C–N intervals were observed at 1528, 1489 and 1449 cm^{-1}. The ^{1}H NMR spectrum of compound **I** showed singlet signals at 11.23, 9.86 and 9.56 ppm for the N–H protons which were consistent with signals of protons attached to a nitrogen atom making them occur downfield. A doublet signal for an aromatic proton was observed at 7.94 ppm for two protons, while a triplet signal for one proton was observed at 7.64 ppm, also a signal for two aromatic protons resonated at 7.51 ppm. The ^{13}C NMR spectrum showed signals at 182.4 and 168.4 ppm for the C=S and the C=O of a carbonyl respectively. Signals for aromatic carbons occurred between 133.3 and 129.0 ppm.

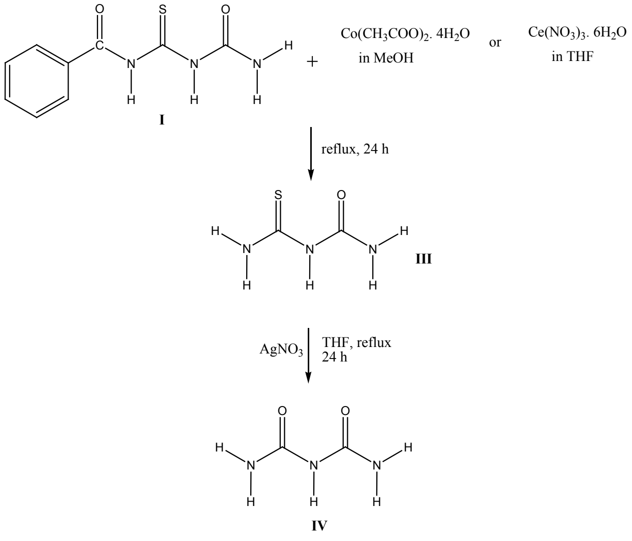
Compound **II** was formed by the silver mediated substitution of sulfur with oxygen in compound **I**; the source of oxygen was presumably water, and the silver by-product was also presumably an allotrope of silver sulfide. The IR spectrum showed bands for the N–H intervals at 3345 and 3225 cm^{-1}. The band for the C=O interval was observed at 1710 cm^{-1} [26]. A band for the C=N and the aromatic C=C were observed at 1663 and 1598 cm^{-1}, respectively [27], suggesting that the C–N were not distinct single bonds. The ^{1}H NMR spectrum gave three single signals at 11.42, 10.33 and 7.47 ppm for the N–H protons, a double signal was observed for two protons at 8.02 ppm while a triple signal for a proton was observed at 7.72 ppm; another triple signal was observed at 7.60 ppm for two protons. The ^{13}C NMR spectrum gave a signal at 169.6 ppm for the carbonyl. Signals between 132.1 and 127.8 ppm were observed for aromatic carbons.

An attempt to cleave the C–N bond, in the α position to the benzoyl group of compound **II** using cobalt acetate tetrahydrate or cerium nitrate hexahydrate was not successful as only the initial material was obtained (**Scheme 5**). But the cleavage was successful when compound **I** was used as the initial material (**Scheme 6**). This showed that the cobalt and cerium catalyzed cleavage reaction required the presence of the thione group for the cleavage to occur, possibly due to the weakening of the C–N bond by the polarizing effect of the sulfur. Compound **III** was formed by the cerium nitrate hexahydrate or cobalt acetate tetrahydrate mediated cleavage of compound **I** in THF and methanol, respectively. The IR spectrum showed bands at 3438, 3367 and 3167 cm^{-1} for the N–H interval, a band was observed at 1716 cm^{-1} for the C=S interval [28], while the C=O interval was observed at 1699 cm^{-1}. The ^{1}H NMR spectrum of compound III showed single resonances for protons at 9.69, 9.49 and 8.95 ppm, while broad signals for protons were also observed at 6.95 and 6.33 ppm. The ^{13}C NMR spectrum gave resonances at 181.7 for the (C=S) of a thione and 155.0 for the C=O of a carbonyl.

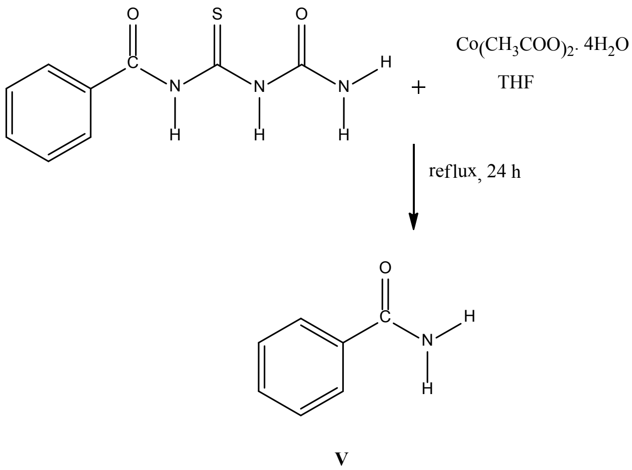


Scheme 5: Synthesis of compounds **I** and **II**.

The cobalt acetate mediated cleavage of compound **I** in THF gave a benzamide (**V**) as the only isolable product (**Scheme 7**). The reaction of cobalt acetate tetrahydrate with benzoyl iosthiocyanate derivatives yielded a benzamide (**V**) as one of the side products regardless of the initial material. This reaction was confirmed using three different benzoyl isothiocyanate derivatives. But with methanol as a solvent, (carbamoylamino) methanethioamide (**III**) was obtained. Cobalt cleaves benzamide from 1-((benzamido) sulfanylenemethyl)urea (**I**) in a non-specific way resulting in a mixture of products. But cobalt acetate tetrahydrate in methanol yields (carbamoylamino) methanethioamide and possibly benzoic acid. Scheme **6** gives the synthesis scheme for the synthesis of compounds **III** and **IV** with the last step being the silver reaction. The IR spectrum of compound **IV**, dicarbamolyamine, showed bands at 3377, 3334 and 3234 cm^{-1} for the N–H interval, and a band was



Scheme 6: Synthesis of compounds **III** and **IV**.



Scheme 7: Synthesis of compound **V**.

observed at 1654 cm^{-1} for the C=O interval. The ^{1}H NMR spectrum of compound **IV** showed single resonances for protons at 10.20, 9.87, 9.74 and 9.49 ppm due to the amine protons. To our knowledge, this is the first presentation of dicarbamolyamine in the literature, the closest derivatives being diacyl ureas which were recently published by Hernandez et al. [29].

3.2 Crystal structures of compounds I, II, III and V

X-ray crystal structures of the compounds **I**, **II**, **III** and **V** were obtained using single crystals grown by crystallization. **Table 1** and **2** shows the crystallographic data, selected bond lengths and bond angles for the crystal structures of compounds **I**, **II**, **III** and **V**.

Compound **I** was recrystallized from DMSO:Toluene (1:1) and obtained as a yellow solid. It recrystallized in the monoclinic space group *C2/c* while compound **II** was recrystallized from DMSO:Toluene (1:1) as a white solid. It was crystallized in the monoclinic space group *P21/c*. The ORTEP diagram for compound **I** is presented in **Figure 2** while the ORTEP diagram for compound **II** is presented in **Figure 3**. Compound **III** was recrystallized from ethanol:acetone (1:1) and obtained as a colorless solid. It recrystallized in the monoclinic space group *P21/m*. **Figure 4** shows the ORTEP diagram for compound **III**, while **Figure 5** displays the ORTEP diagram for **c**ompound **V.** Compound **V** was recrystallized from ethanol as a colorless solid in the monoclinic space group *P21/c*.

The bond distance of O1-C1 in compound **I** which was 1.215(2) Å, is consistent with a carbonyl while the N1-C1, N1-C2, and N2-C3 bond distances in compound **I** were 1.386(2), 1.367(2) and 1.402(2) Å respectively which were consistent with the C–N single bond [30]. The bond distance of S1-C2, which was 1.648 (2) Å, is consistent with a bond length of a thione [31]. The bond angles of O2-C3-N2 and S1-C2-N1 are 121.8(1) and 127.6(1) respectively showed that the carbon atom is sp^2 hybridized.

In the crystal structure of compound **II**, the carbonyl group (O2-C2) is in an opposite position from the benzoyl carbonyl while the thione group in compound **I** is aligned. The oxygen and sulfur atoms are as far removed from each other as possible to reduce repulsion between their respective electron densities. The bond distances of O1-C1, O2-C2, O3-C3 which were 1.220(1), 1.218(1) and 1.229(1) Å, respectively, were consistent with a carbonyl while the N1-C1, N1-C2, N2-C2 and N2-C3 bond distances in compound **II** were 1.377(1), 1.396(1), 1.359(1) and 1.410(1) Å respectively and consistent with the C–N single bond [31]. The bond angles of O1-C1-N1, N1-C2-N2 and O2-C2-N2 were 121.7(1), 116.6(1) and 124.9(1) respectively.

In compound **III**, the bond distances of O1-C12 and O2-C22 in compound **III** were 1.240(2) and 1.234(2) Å respectively, and were consistent with a carbonyl, while the N21-C21, N11-C11 and N12-C11 bond distances in compound **III** were 1.307(3), 1.312(2), and 1.366(2)Å respectively which were also consistent with the C–N single bond. However, these were stronger C–N bonds. The S1-C11 and S2-C21 were also found to be 1.697(2) and 1.708(2) respectively. The bond angles of S2-C21-N21, S1-C11-N11 and S2-C21-N22, O2-C2-N2 were 122.0(1), 121.8(1) and 118.5(1) respectively, while the N11-C11-N12, N22-C22-N23, N12-C12-N13 were 119.4(2), 113.2(2), and 113.2(2) respectively. These were comparable to reported values [32].

Table 1: Crystallographic data and structure refinement summary for compounds **I**, **II**, **III**, and **V**.

Property	Compound I	Compound II	Compound III	Compound V
Formula	$C_9H_9N_3O_2S$	$C_9H_9N_3O_3$	$C_2H_5N_3OS$, H_2O	C_7H_7NO
CCDC Numbers	1549036	1549037	1836320	1549034
Formula Weight	223.26	207.19	137.17	121.14
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	P21/c	P21/m	P21/c
a [Å]	10.2528(5)	7.8993(4)	9.2101(7)	5.5666(3)
b [Å]	12.8418(6)	22.3734(10)	6.2485(5)	5.0317(3)
c [Å]	16.0986(7)	5.1861(2)	10.2174(8)	21.7543(15)
α [°]	90	90	90	90
β [°]	106.159(2)	99.912(2)	103.340(4)	90.184(3)
γ [°]	90	90	90	90
V [Å^3]	2035.87(16)	902.88(7)	572.14(8)	609.32(6)
Z	8	4	4	4
D(calc) [g/cm^3]	1.457	1.524	1.592	1.321
Mu(MoKa) [/mm]	0.301	0.118	0.478	0.090
F(000)	928	432	288	256
Crystal Size [mm]	0.24 x 0.41 x 0.47	0.04 x0.32 x 0.62	0.40 x 0.47 x 0.55	0.08 x 0.13 x 0.34
Temperature	200	200	200	200
Radiation MoKa, [Å]	0.71073	0.71073	0.71073	0.71073
Theta Min-Max [°]	2.6, 28.3	1.8, 28.3	2.0, 28.4	3.7, 28.4
Dataset	-9: 13 ; -13: 17 ; -21: 21	-9: 10 ; -29: 29 ; -6: 6	-12: 12 ; -8: 8 ; -5: 13	-7: 7 ; -6: 6 ; -29: 29
Tot., Uniq. Data, R(int)	9431, 2514, 0.013	12790, 2244, 0.022	1550, 1550, 0.000	5655, 1514, 0.015
Observed Data [I > 2.0 sigma(I)]	2215	1939	1478	1267
Nref	2514	2244	1550	1514
Npar	152	152	136	90
R	0.0351	0.0354	0.0292	0.0367
$_wR_2$	0.1000	0.0948	0.0812	0.1050
S	1.06	1.06	1.09	1.03
Max. and Av. Shift/Error	0.00, 0.00	0.00, 0.00	0.00, 0.00	0.00, 0.00
Min. and Max. Resd. Dens. [e/Å^3]	-0.58	-0.22	-0.26	-0.17
Min. and Max. Resd. Dens. [e/Å^3]	0.47	0.30	0.44	0.35

The bond distances of O1-C7 in compound **V** which were 1.240(1) unit were consistent with a carbonyl while the N1-C7 bond distances in compound **V** were 1.330(2) unit, consistent with the C-N single bond [33]. The bond distances of C3-C4, C4-C5 and C1-C2, were 1.375(2), 1.384(2) and 1.389(2) unit respectively. The bond angles of C2-C1-C6, C1-C2-C3, and O1-C7-C1 were 119.5(1), 120.0(1) unit and 120.3(1) respectively.

Because of the strength of the C–N bonds, it is not easy to justify the observed reactions. The benzamide formation is probably the only one that fits the justification for its formation as the C–N bonds in the β position to the benzoyl group were weaker than the rest found in compounds **1** and **II**. It is clear therefore, that the metals play a significant role in these reactions to activate the C–N bond cleavage. A further study will be the detailed mechanisms of these reactions as well as the formation of 3,5-diamino- 1,2,4-triazole by a reaction with hydrazine and synthesis of a new urea-formaldehyde resin which will

Table 2: Selected bond lengths (Å) and bond angles (°) for compounds **I, II, III** and **V**.

Bond lengths (Å)

I		**II**		**III**		**V**	
S1-C2	1.648(1)	O1-C1	1.220(1)	S1-C11	1.697(2)	O1-C7	1.240(1)
O1-C1	1.215(2)	O2-C2	1.218(1)	N21-C21	1.307(3)	C3-C4	1.375(2)
O2-C3	1.239(2)	O3-C3	1.229(1)	S2-C21	1.708(2)	N1-C7	1.330(2)
N1-C1	1.386(2)	N1-C1	1.377(1)	N22-C21	1.365(2)	C4-C5	1.384(2)
N1-C2	1.367(2)	N1-C2	1.396(1)	O1-C12	1.240(2)	C1-C2	1.389(2)
N2-C3	1.402(2)	N2-C2	1.359(1)	N22-C22	1.396(2)	C5-C6	1.388(2)
N3-C3	1.325(2)	N2-C3	1.410(1)	N11-C11	1.312(2)	C1-C6	1.386(2)
N2-C2	1.374(2)	N3-C3	1.327(1)	N23-C22	1.327(2)	C1-C7	1.499(2)

Bond angles (°)

I		**II**		**III**		**V**	
C1-N1-C2	128.8(1)	C1-N1-C2	129.1(1)	C11-N12-C12	127.8(2)	C2-C1-C6	119.5(1)
C2-N2-C3	128.6(1)	O1-C1-N1	121.7(1)	S2-C21-N21	122.0(1)	O1-C7-C1	120.3(1)
N2-C3-N3	113.9(1)	N1-C2-N2	116.6(1)	S1-C11-N11	121.8(1)	C2-C1-C7	122.0(1)
O2-C3-N3	124.4(1)	O2-C2-N2	124.9(1)	S2-C21-N22	118.5(1)	C6-C1-C7	118.5(1)
S1-C2-N2	118.2(1)	O2-C2-N1	118.6(1)	S1-C11-N12	118.7(1)	C1-C2-C3	120.0(1)
N1-C2-N2	114.2(1)	O3-C3-N3	124.9(1)	N21-C21-N22	119.5(2)	C2-C3-C4	120.2(1)
O2-C3-N2	121.8(1)	N2-C3-N3	117.9(1)	N11-C11-N12	119.4(2)	C3-C4-C5	120.3(1)
S1-C2-N1	127.6(1)	O3-C3-N2	117.2(1)	O2-C22-N22	123.0(2)	C4-C5-C6	119.8(1)

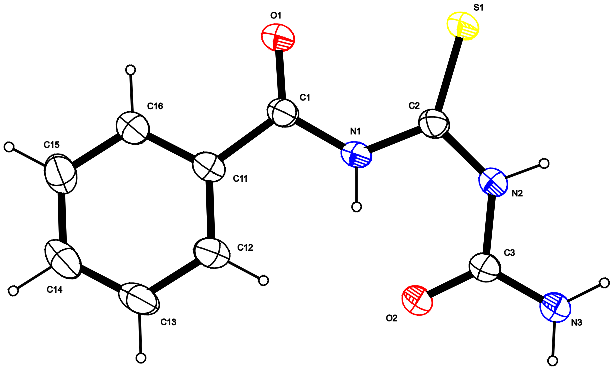


Figure 2: An ORTEP view of 1-((benzamido) sulfanylenemethyl) urea **(I)** shows 50% probability displacement ellipsoids and the atom labeling.

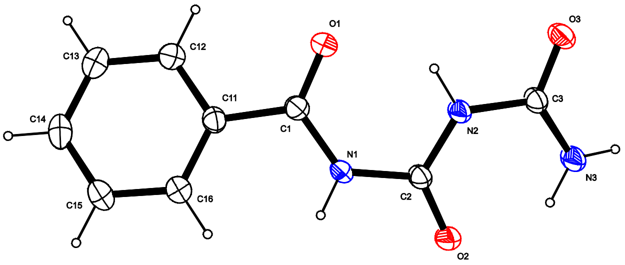


Figure 3: An ORTEP view of 1-((benzamido)formyl) urea (**II**) shows 50% probability displacement ellipsoids and the atom labeling.

be compared with the current standard using monomeric urea.

4 Conclusions

A novel selective C–N bond cleavage of a benzoyl isothiocyanate derivative to give (carbamoylamino) methanethioamide has been achieved using cobalt acetate tetrahydrate in methanol. The product has also been accessed using cerium nitrate hexahydrate as a catalyst in THF. The cleavage of the C–N bond does not occur in the absence of the thione group in compound **II.** A novel silver catalyzed conversion of a thione to the carbonyl has been achieved on 1-([benzamido]formyl)urea (**I**) and replicated on (carbamoylamino) methanethioamide (**III**) to give bisurea (dicarbamolyamine). The structures of the compounds have been confirmed using IR, NMR, microanalysis and GC-MS. Single crystal X-ray diffraction studies of the crystal structures of compounds **I, II, III** and **V** have been presented. These show evidence of the formation of the new molecules *via* metal mediation, and a further study is to investigate the detailed mechanisms of these reactions.

Supplementary Material: Supplementary material CCDC-

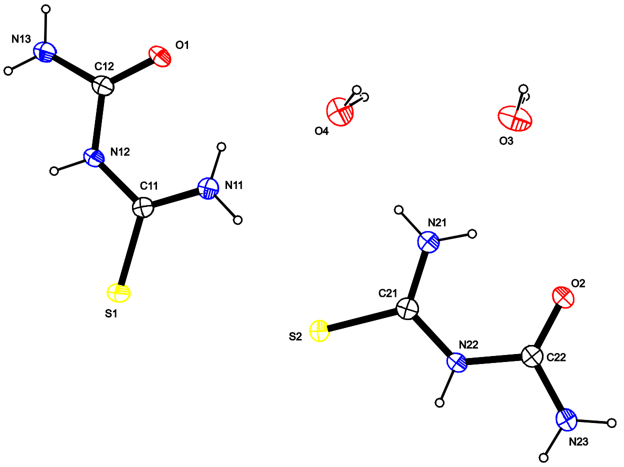


Figure 4: An ORTEP view of (carbamoylamino) methanethioamide (**III**) shows 50% probability displacement ellipsoids and the atom labeling.

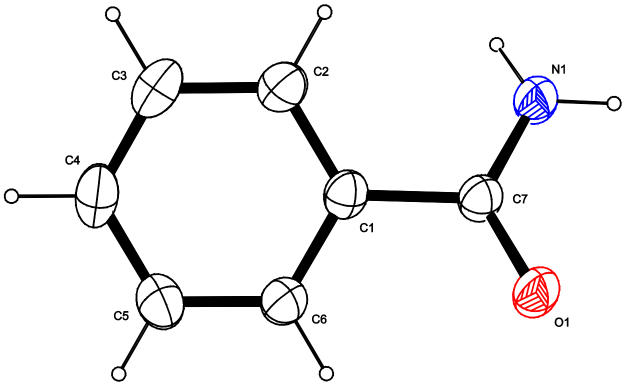


Figure 5: An ORTEP view of benzamide (**V**) shows 50% probability displacement ellipsoids and the atom labeling.

1549036 for **1**, CCDC-1549037 for **II**, CCDC- 1836320 for **III** and CCDC-1549034 for **V** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac. uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

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