The Role of Elimination Processes in the Reaction of Substituted Ureas and Thioureas with Chlorides of Mono- and Bifunctional Acids

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Dedicated to Prof. Josef Grobe on the occasion of his 60th birthday

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Reactive Halides, Substituted Ureas, Elimination Reactions, X-Ray

The reaction of phthaloyl chloride with 1,3-dimethylurea in dichloromethane at room temperature leads to the formation of N,N-1,1'-phthaloyl-bis(1,3-dimethylurea) whereas in refluxing solvent N-methyl-phthalimide is the principal product. The reaction of 1,3-bis(trimethylsilyl)-1,3-dimethylurea separately with phthaloyl chloride, 4-nitrobenzoyl chloride and 5-chlorothiophene-2-carbonyl chloride results in the formation of 1,3-phthaloyl-1,3-dimethylurea, 1,3-bis(4-nitrobenzoyl)-1,3-dimethylurea, and N,N-bis(5-chlorothiophene-2-carbonyl)-N-methylamine, respectively. The reaction of N,N-bis(trimethylsilyl)acetamide with furnished N,N-bis(5-chlorothiophene-2-carbonyl)-acetamide while the reaction of with 1,3-dimethylthiourea afforded 1,3-dimethyl-1,3-bis(5-chlorothiophene-2-carbonyl)thiourea. The structures of and were confirmed by low temperature X-ray crystallography. Both display crystallographic twofold symmetry.

The products obtained from the reaction of 1,3-dimethylurea with phosphorus pentachloride, oxalyl chloride and acetyl chloride have been characterized previously. The present study describes the reactions of the bis(trimethyl)silylated 1,3-dimethylurea with phthaloyl chloride, 4-nitrobenzoyl chloride and 5-chlorothiophene carbonyl chloride taking advantage of the leaving group properties of the silyl group. Interesting comparisons may be made with the sulphur-containing analogues of oxygen-containing compounds; the reaction of with 1,3-dimethylthiourea, whose silyl derivative cannot be prepared, has been studied.

The reaction of phthaloyl chloride with 1,3-dimethylurea was studied first. A solution of 1 and 2 in methylene chloride was allowed to stand at room temperature for one week. After filtration and removal of solvent, the product was recrystallized from methanol, and characterized by an X-ray crystallographic study as N-phthaloyl-bis(1,3-dimethylurea) (Fig. 1, Table I).

The molecule displays crystallographic twofold symmetry; the twofold axis 0,1/4 bisects the bonds C(1)–C(1') and C(3)–C(3'). The side chain exhibits an extended conformation, with torsion angles C(2)–C(1)–C(4)–N(1) 60°, C(1)–C(4)–N(1)–C(6) –161°, C(4)–N(1)–C(6)–N(2) 1°, N(1)–C(6)–N(2)–C(7) 179°. The packing diagram of 3 is shown in Fig. 2; it involves layers of phenyl rings parallel to the xy plane.

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The layers are linked by weak hydrogen bonding from the N(2)H group to the carbonyl oxygen [N(2)...O(2) 322 pm].

The principal product obtained from the reaction of 2 with 1,3-dimethylurea in refluxing acetonitrile is N-methylphthalimide 4, which was also the main product obtained when triethylamine was added to the reaction mixture.

Phthaloyl chloride 2, reacts smoothly with 1,3-bis(trimethylsilyl)-1,3-dimethylurea 5 in refluxing methylene chloride to form 1,3-phthaloyl-1,3-dimethylurea 7. Other cyclic derivatives of 1,3-di-

| Symmetry operator (i): -x, y, 0.5-z. |

**Table 1. Bond lengths (pm) and angles (°) for compound 3.**

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methylurea have been described [5–8]. Under similar conditions, the reaction of 4-nitrobenzoyl chloride 6 with 5 was shown to lead to the formation of 1,3-bis(4-nitrobenzoyl)-1,3-dimethylurea 8.

\[ R - \begin{array}{c} C=O \end{array} \]

\[ R - \begin{array}{c} C=O \end{array} \]

R = (CH₃)₃Si

The reaction of 5-chlorothiophene-2-carbonyl chloride 9 with 5 in refluxing methylene chloride leads to the formation of N,N-bis(5-chlorothiophene-2-carbonyl)-N-methylamine 12, which was also characterized by X-ray methods. The molecule of 12 (Fig. 3) possesses crystallographic twofold symmetry, with the atoms N and C(6) lying on the twofold axis 1/2, y, 1/4 (the packing diagram, Fig. 4, makes clear the alignment of the molecules with the N–Me bonds parallel to the b axis).

The conformation of the central moiety is specified by the torsion angles C(3)–C(4)–C(5)–N -31°, C(4)–C(5)–N–C(5') -33°. The molecular dimensions (see Table II) of the thiophene ring in 12 are similar to those found in thiophene-3,4-trithioanhydride [9] and 2,5-bis-N-chlorothioimino-3,4-dicyanothiophene [10]. However, it is clear from comparisons of the relevant bond lengths and bond angles that the molecular shape of the

![Fig. 3. The molecule of compound 12 in the crystal, showing the numbering scheme of the asymmetric unit. Radii are arbitrary.](image-url)

![Fig. 4. Stereographic packing diagram of compound 12, viewed parallel to the z axis. Radii are arbitrary; H atoms omitted for clarity.](image-url)
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S-C(1) 171.1(2) S-C(4) 171.6(2)
Cl-C(1) 171.4(2) O-C(5) 121.5(2)
N-C(5) 139.8(2) N-C(6) 146.3(3)
C(1)-C(2) 135.2(2) C(2)-C(3) 140.4(3)
C(3)-C(4) 136.5(2) C(4)-C(5) 146.9(2)
C(1)-S-C(4) 90.7(1) C(5)-N-C(6) 117.7(1)
C(5)-N-C(5i) 124.7(2) C(6)-N-C(5i) 117.7(1)
S-C(1)-C(2) 119.8(1) S-C(1)-C(2) 113.2(1)
Cl-C(1)-C(2) 126.9(1) C(1)-C(2)-C(3) 111.4(2)
C(2)-C(3)-C(4) 113.4(1) S-C(4)-C(3) 111.4(1)
S-C(4)-C(5) 118.8(1) C(3)-C(4)-C(5) 129.6(1)
O-C(5)-N 121.4(2) O-C(5)-C(4) 122.0(1)
N-C(5)-C(4) 116.5(1)

Table II. Bond lengths (pm) and angles (°) for compound 12.

Symmetry operator (i): 1-x, y, 0.5-z.

The thiophene ring is influenced by its substituent groups; in particular, the C(1)–S–C(4) angle of 90.7° in 12 increases to 91.3° in the thiophene anhydride [9] and 94.5° in the dicyanothiophene [10], while the bond lengths S(1)–C(1) and C(1)–C(2) increase from 171.2, 135.2 pm respectively in 12 to 177.5, 143.9 pm [9] and 173.1, 137.8 pm [10].

The formation of 12, which is structurally related to 4, may involve an intermediate similar in structure to 7 but forming 2 on elimination of methyl isocyanate. It is of interest to note that the loss of methyl isocyanate is involved in the mass spectrometric fragmentation pattern of 7, 8, and 12. The substituent in the 5-position of the thiophene ring exerts an electronic influence similar to that experienced on para-substitution in the benzene ring [11]. Other studies have shown that there is no conjugation between the thiophene ring and substituent carbonyl groups [12] and that different proximity effects exist in thiophene and benzene derivatives [13]. The present investigation highlights the ease of methyl isocyanate removal from the bridging 1,3-dimethylurea group by the 5-chlorothiophene carbonyl, in contrast to the 4-nitrobenzoyl groups.

The silyl leaving group properties of N,N-bis(trimethylsilyl)-acetamide 11 allow the formation of N,N-bis(5-chlorothiophene-2-carbonyl)-acetamide 13 in the reaction of 11 with 9 in methylene chloride. The mass spectral fragmentation pattern of 13 shows the profound changes in the breakdown of the bridging group compared with that of 12, as a result of the insertion of the carbonyl group into its structure.

The reaction of 1,3-dimethylthiourea 10 with 9 was investigated to establish the effect on the stability of the urea bridging group with respect to elimination reactions of replacing the oxygen atom by sulphur. The product obtained from this facile reaction was 1,3-dimethyl-1,3-bis(5-chlorothiophene-2-carbonyl)thiourea 14 whose mass spectral fragmentation pattern illustrates the enhanced stability of the thiourea bridging group.

**Experimental**

The solvents were freshly distilled and dried before use. The chemicals used were available commercially. 1,3-Dimethylthiourea was dried over phosphorus pentoxide. 1,3-Bis(trimethylsilyl)-1,3-dimethylurea was synthesized by the literature method [14]. 5-Chlorothiophene-2-carbonyl chloride was kindly made available by Dr. Meidert of Hoechst AG. Elemental analyses were performed by the National Analytical Laboratory, Mel-
bourne. The melting points are uncorrected. Mass spectra were obtained using an AEI MS9 spectrometer.

\[ N.N{-1',1''{-Phthaloyl-bis(1,3-dimethylurea)} 3 \]

A solution containing 1,3-dimethylurea 1 (8.80 g, 0.10 mol) and phthaloyl chloride 2 (10.1 g, 0.05 mol) in methylene chloride (20 ml) was allowed to stand at room temperature (20 °C) for one week. The solid material (5.86 g) that separated was filtered off. Methylene chloride was removed, leaving a crystalline product that was washed with toluene (50 ml) and oven dried (120 °C). Recrystallization from hot methanol (50 ml) gave (3) (4.28 g, 28.3%), m.p. 162-163 °C. The recrystallized product was dissolved in methanol/methylene chloride. A final recrystallization treatment the product was recovered by removal of methylene chloride. A final recrystallization from hot methanol (20 ml) gave 12 (1.48 g, 46.7%), m.p. 125-126 °C. MS: m/e (%) 391 (7) [M-1]+; 284 (4.8) [M-CI]+; 262 (3.3) [M-CH3NCO]+; 227 (2.5) [M-CI-CH3NCO]+; 199 (1.6) [M-CI-CH3NCO-CH2]+; 145 (100) [M-CH3NCO-C4H4(SCl)-CO]+; 117 (12) [M-CH3NCO-C4H4(SCl)-CO].

\[ C_{17}H_{14}N_2O_5 (386.28) \]

Caled C 52.86 H 3.65 N 14.50, Found C 52.77 H 3.60 N 14.41.

\[ N.N{-Bis(5-chloro-thiophene-2-carbonyl)-N-methylamine} 12 \]

A solution of 5 (2.32 g, 0.01 mol) and 9 (3.28 g, 0.02 mol) in methylene chloride (20 ml) was refluxed for 30 min. After removal of most of the methylene chloride under reduced pressure, a crude product (3.35 g) was obtained, which was washed with cold methanol (50 ml) and oven dried (80 °C), then recrystallized from hot methanol (50 ml). The recrystallized product was dissolved in methylene chloride (25 ml) and the solution treated with activated charcoal for 20 min. After filtration the product was recovered by removal of methylene chloride. A final recrystallization from hot methanol (20 ml) gave 13 (2.40 g, 31.0%), m.p. 127-128 °C. MS: m/e (%) 319 (7) [M-1]+; 284 (4.8) [M-CI]+; 262 (3.3) [M-CH3NCO]+; 227 (2.5) [M-CI-CH3NCO]+; 199 (1.6) [M-CI-CH3NCO-CH2]+; 145 (100) [M-CH3NCO-C4H4(SCl)-CO]+; 117 (12) [M-CH3NCO-C4H4(SCl)-CO].

\[ C_{17}H_{14}N_2O_5 (386.28) \]

Caled C 52.86 H 3.65 N 14.50, Found C 52.77 H 3.60 N 14.41.

\[ N,N{-Bis(5-chlorothiophene-2-carbonyl)-acetamide} 13 \]

A solution of 11 (4.06 g, 0.02 mol) and 9 (6.56 g, 0.04 mol) was refluxed in methylene chloride for 3 h. After cooling, the solution was treated with activated charcoal (2 g), filtered and the methylene chloride removed. The solid product was washed with acetonitrile (50 ml) and recrystallized twice from hot toluene (2×20 ml) to give 13 (2.40 g, 38.6%).

\[ C_{17}H_{14}N_2O_5 (386.28) \]

Caled C 52.86 H 3.65 N 14.50, Found C 52.77 H 3.60 N 14.41.

\[ N,N{-Bis(5-chlorothiophene-2-carbonyl)-acetamide} 13 \]

A solution of 11 (4.06 g, 0.02 mol) and 9 (6.56 g, 0.04 mol) was refluxed in methylene chloride for 20 min, after which the charcoal was removed by filtration. Most of the methylene chloride was removed and the product recrystallized again from methanol/methylene chloride to give 8 (3.15 g, 81.6%), m.p. 182-183 °C. MS: m/e (%) 386 (0.3) [M]+; 329 (1.25) [M-CH3NCO]+; 301 (1.2) [M-CH3NCO-CH2]+; 150 (100) [M-CH2NCO-CH2-N(CH3)2]+; 104 (24) [M-CH2NCO-CH2-N(CH3)2-N-].

\[ C_{17}H_{14}N_2O_5 (386.28) \]

Caled C 52.86 H 3.65 N 14.50, Found C 52.77 H 3.60 N 14.41.
34.5%), m.p. 188–189 °C. MS: m/e (%) 347 (0.03) [M-1]+; 306 (122) [M-CH(CN)]+;
203 (13) [M-C\textsubscript{4}H\textsubscript{6}SCl(CO)+H]+; 162 (59) [M-CH\textsubscript{3}CN-C-H\textsubscript{3}Cl(CO)+H]+;
145 (100) [M-C\textsubscript{4}H\textsubscript{8}SCl(CO)-CH\textsubscript{3}NCO]+.

\[C\textsubscript{4}H\textsubscript{2}Cl\textsubscript{2}N\textsubscript{2}O\textsubscript{5}S\textsubscript{2} (348.21)\]
Calcd C 39.58 H 2.51 N 7.06 S 24.28 Cl 18.11.
Found C 39.70 H 2.56 N 7.12 S 24.46 Cl 18.03.

**X-ray crystal structure determination of compound 3**

Crystal data: \(C_{14}H_{18}N_{2}O_{4}\), \(M_r = 306.3\), monoclinic, C2/c, \(a = 1748.9(5)\), \(b = 818.4(2)\), \(c = 1082.2(3)\) pm, \(\beta = 102.88(2)^\circ\), \(U = 1.5099\) nm\(^3\), \(Z = 4\), \(D_x\) = 1.348 Mg m\(^{-3}\), \(F(000) = 648\), \(\lambda\)(MoK\(\alpha\)) = 71.069 pm, \(\mu = 0.09\) mm\(^{-1}\), \(\tau = -95\) °C.

**Data collection and reduction**: A colourless parallelepiped 0.5 x 0.4 x 0.4 mm was mounted on a glass fibre and transferred to the cold gas stream of the diffractometer (Siemens R3 with LT-2 low temperature attachment). Of 2163 intensities registered with monochromated MoK\(\alpha\) radiation (2\(\theta_{\text{max}} = 55^\circ\)), 1740 were unique (\(R_{\text{int}} = 0.017\) and 1409 > 4\(\sigma(F)\) considered observed. Cell constants were refined from setting angles of 48 reflections in the 2\(\theta\) range 20–25°.

**Structure solution and refinement**: (Program system “Siemens SHELXTL PLUS”). The structure was solved by routine direct methods and subjected to anisotropic full-matrix least-squares refinement on \(F\). H atoms were included using a riding model. The weighting scheme was \(w^{-1} = \sigma^2(F) + gF^2\), with \(g = 0.0002\); the final \(R\) was 0.040, with \(wR = 0.049\). 100 parameters; S 2.1; max. \(\Delta/\sigma\) 0.001; max. \(\Delta/\sigma\) 0.2 x 10\(^{-6}\) pm\(^{-3}\). Final atomic coordinates are presented in Table III.

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**X-ray crystal structure determination of compound 12**

Crystal data: \(C_{10}H_{19}Cl_{2}N_{2}O_{5}S_{2}\), \(M_r = 320.2\), monoclinic, C2/c, \(a = 973.6(3)\), \(b = 1595.2(5)\), \(c = 867.0(3)\) pm, \(\beta = 98.59(3)^\circ\), \(U = 1.3315\) nm\(^3\), \(Z = 4\), \(D_x\) = 1.597 Mg m\(^{-3}\), \(F(000) = 648\), \(\lambda\)(MoK\(\alpha\)) = 71.069 pm, \(\mu = 0.78\) mm\(^{-1}\), \(T = -15\) °C.

Data collection and refinement: A colourless block 0.7 x 0.35 x 0.4 mm was used. Other details as for 3, with the following differences: 3170 reflections, 1531 unique \(R_{\text{int}} = 0.019\), 1315 observed. The H atoms of the methyl group at C(6) are disordered over two positions. An extinction correction of the form \(F_{\text{corr}} = F/[1 + xF^2/\sin 2\theta]^{0.25}\) was applied; \(x\) refined to 4.6(6) x 10\(^{-6}\). 84 parameters, \(R = 0.032\), \(wR = 0.042\), g 0.00015, S 2.1, max. \(\Delta/\sigma\) 0.002; max. \(\Delta/\sigma\) 0.24 x 10\(^{-6}\) pm\(^{-3}\). Final atomic coordinates are presented in Table IV.

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Table III. Atom coordinates (x 10\(^4\)) and equivalent isotropic temperature factors (pm\(^2\)) for compound 3.

Table IV. Atom coordinates (x 10\(^4\)) and equivalent isotropic temperature factors (pm\(^2\)) for compound 12.
Further details of the structure determinations (H atom coordinates, structure factors, temperature factors) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote a full literature citation and the reference number CSD 55811.

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