

## 4-Chlorophenyl and 2,4,6-tribromophenyl chlorothionoformates: new dealkylating agents for tertiary amines

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### Abstract

4-Chlorophenyl and 2,4,6-tribromophenyl chlorothionoformates react rapidly with tertiary amines at 20°C to give a thiocarbamate and alkyl chloride. The thiocarbamates are converted to the secondary amine salts by treatment with dimethyl sulfate, followed by hydrolysis with water. Rates of reaction, and alkyl group cleavage selectivity in amines were found to be comparable or superior to those previously reported with chloroformates.

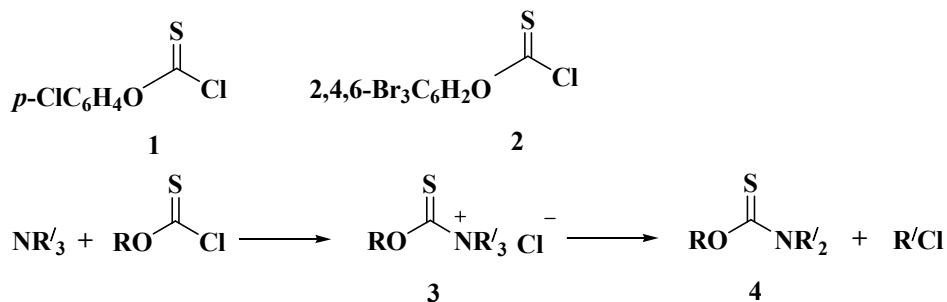
**Keywords:** 4-Chlorophenyl chlorothionoformate, 2,4,6-tribromophenyl chloro thiono- formate

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### Introduction

We have previously reported the epimerization of phthalideisoquinoline alkaloid<sup>1</sup> with thiophosgene and the dealkylation of tertiary aliphatic amines with thiophosgene and 1-chloroethyl chlorothionoformate<sup>2</sup>. The reactivity of these reagents were found to be comparable to that of a number of previously used methods, such as the Von Braun<sup>3</sup> reaction or the use of ethyl chloroformate<sup>4</sup> and phenyl chloroformate<sup>5</sup>. The latter reagents produce products which are difficult to hydrolysis, and accordingly were replaced by 1-chloroethyl chloroformate<sup>6</sup>, 2,2,2-trichloroethyl chloroformate<sup>7</sup> and vinyl chloroformate<sup>8</sup>.

We have found that 4-chlorophenyl chlorothionoformate and 2,4,6-tribromophenyl chlorothionoformate are even more reactive towards amines than chloroformate and thiophosgene, but the ease and selectivity of the analogous second dealkylation step required elaboration. ( Scheme 1 )



### Scheme 1

In this paper we aim to ascertain the relative rates of cleavage of alkyl groups with 4-chlorophenyl chlorothionoformate and 2,4,6-tribromophenyl chlorothionoformate to determine the scope of their effectiveness as a dealkylating agents for tertiary aliphatic amines.

## Result and Discussion

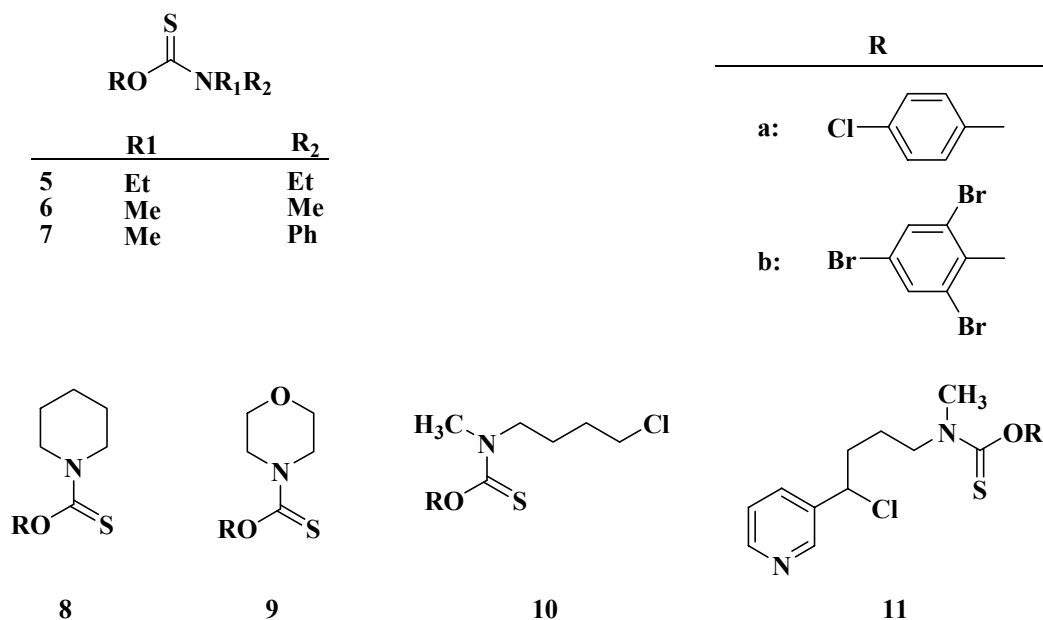
The accepted pathway<sup>9</sup> for dealkylation of tertiary amines with chloroformates involves the rate determining decomposition of the salt (**3**) by chloride, forming the carbamate (**4**) and an alkyl chloride. In a general way this appears also to be the case with chlorothionoformates. The reaction of unhindered tertiary amine with 4-chlorophenyl chlorothionoformates was very rapid at 20°C in dichloromethane as a solvent. When the reaction of triethylamine with an equivalent of (**1**) was followed by <sup>1</sup>H n.m.r analysis, the ammonium salt appeared to form instantly ( $\delta$  CH<sub>2</sub> 4.35 ppm), and chloroethane formation could be followed to completion over the next 40 min. As shown in table 1 and table 2, the reaction of various tertiary amines were complete within 40 minutes by the use of 4-chlorophenyl chlorothionoformate (**1**) and two hours when 2,4,6-tribromophenyl chlorothionoformate was used.

**Table 1.** Dealkylation of tertiary amines with (**1**)

Amine	Condition	Product	% Yield
1. Triethylamine	CH <sub>2</sub> Cl <sub>2</sub> , 40 min, 20 °C	<b>5a</b>	95
2. N,N-Dimethyl benzyl amine	CH <sub>2</sub> Cl <sub>2</sub> , 40 min, 20 °C	<b>6a</b>	97
3. 1-Methylpiperidine	CH <sub>2</sub> Cl <sub>2</sub> , 40 min, 20 °C	<b>8a</b>	96
4. 4-Methylmorpholine	CH <sub>2</sub> Cl <sub>2</sub> , 40 min, 20 °C	<b>9a</b>	96
5. 1-Methylpyrrolidine	CH <sub>2</sub> Cl <sub>2</sub> , 40 min, 20 °C	<b>10a</b>	96
6. (-)-Nicotine	CH <sub>2</sub> Cl <sub>2</sub> , 40 min, 20 °C	<b>11a</b>	95
7. N,N-Dimethylaniline	neat, 24 h, 130 °C	<b>7a</b>	75

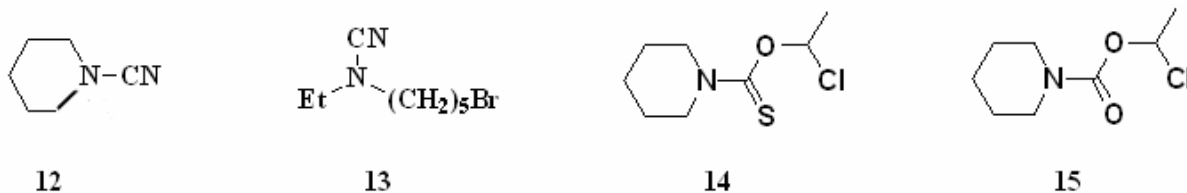
**Table 2.** Dealkylation of tertiary amines with (2)

Amine	Condition	Product	%Yield
1. Triethylamine	CH <sub>2</sub> Cl <sub>2</sub> , 2 h, 20 °C	<b>5b</b>	91
2. N,N-Dimethyl benzyl amine	CH <sub>2</sub> Cl <sub>2</sub> , 2 h, 20 °C	<b>6b</b>	96
3. 1-Methylpiperidine	CH <sub>2</sub> Cl <sub>2</sub> , 2 h, 20 °C	<b>8b</b>	93
4. 4-Methylmorpholine	CH <sub>2</sub> Cl <sub>2</sub> , 2 h, 20 °C	<b>9b</b>	83
5. 1-Methylpyrrolidine	CH <sub>2</sub> Cl <sub>2</sub> , 2 h, 20 °C	<b>10b</b>	89
6. N,N-Dimethylaniline	neat, 24 h, 130 °C	<b>7b</b>	71



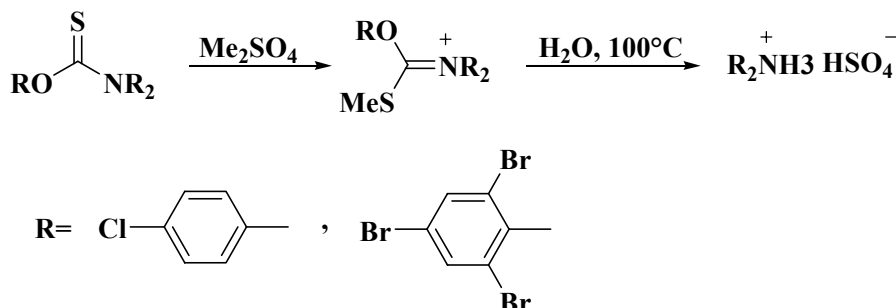
Olofson<sup>8</sup> has used *N*-methylpiperidine as the benchmark for the determination of rate and selectivity of the dealkylation of tertiary amines by vinyl chloroformate, cyanogen bromide, phenylchloroformate, ethyl chloroformate, 2,2,2-trichloroethyl chloroformate and benzyl chloroformate. The use of vinyl chloroformate give the demethylated product in 90% yield but a period at 80°C was required to effect decomposition of the intermediate salt.

The use of 4-chlorophenyl chlorothionoformate and even a hindered derivative like 2,4,6-tribromophenyl chlorothionoformate resulted in dealkylation at 20°C, while the other chloroformates effected the conversion in, at best, 10% yield, under similar conditions. Cyanogen bromide showed low selectivity, giving cyanamide (**12**) (54%), accompanied by the ring opened (**13**) (28%). We reported<sup>2</sup> that the reaction of 1-chloroethyl chlorothionoformate with *N*-methylpiperidine afforded the carbamate (**14**) in 75% yield at reflux for 12 hours in dichloromethane. Similarly, the reaction of 1-chloroethyl-chloroformate with *N*-methylpiperidine gave the carbamate (**15**) at 80°C.



By contrast, 4-chlorophenyl and even 2,4,6-tribromophenyl chlorothionoformates cleanly converted triethylamine and *N*-methylpiperidine to the corresponding thiocarbamate (**8**) at room temperature within 40 min (**1**) or two hours (**2**). Thus demonstrating agent the reactivity of **1** and **2** with tertiary amines is superior to that of vinylchloroformate, 1-chloroethyl chloroformate and the 1-chloroethyl chlorothiono-formate. Selectivity of the cleavage of alkyl group by chlorothionoformates were also investigated. Reaction of *N,N*-dimethylbenzylamine with (**1**) and (**2**) resulted only in debenzylation, at room temperature in almost quantitative yield. While *N*-methyl-morpholine undergoes considerable ring opening on reaction with either cyanogen bromide<sup>10</sup> or chlorothionoformate, only the demethylation was observed. Demethylation of *N,N*-dimethyl-aniline with (**1**) and (**2**) were very slow, but the demethylated product (**7**) were isolated in 75% and 71% yields after reaction at 130°C for 24 h; a similar reaction, with phenyl chloroformate<sup>5</sup> gave 80% yield at 100°C after 60 h. When *N*-methylpyrrolidine as a five membered ring amine was treated with (**1**) in dichloromethan the reaction proceeded to completion rapidly at 20°C, but ring opening was achieved leading to (**10a**) in 96% yield, as two rotamers by <sup>1</sup>H and <sup>13</sup>C nmr spectroscopy. Similarly ring opening product (**10b**) as two rotamers was produced in 89% yield from the reaction of *N*-methylpyrrolidine with (**2**) at 20°C for two hours. When (-)-nicotine was treated with (**1**) and (**2**) at 20°C, the ring opened products **11a** and **11b** were formed in 89 and 86% yields, respectively.

In conclusion 4-chlorophenyl chlorothionoformate (**1**) and 2,4,6-tribromophenyl chlorothionoformate (**2**) are shown to be useful dealkylating agents for tertiary amine. The dialkylthiocarbamates could be readily converted to the corresponding amines by sequential treatment with dimethylsulfate followed by their hydrolysis in water. (Scheme 2)



Scheme 2

## Experimental Section

**General Procedures.**  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r spectra were recorded with a Bruker spectrometer in  $\text{CDCl}_3$  at 300MHz unless otherwise indicated and chemical shifts are in ppm. Infrared spectra were recorded on a Thermo Nicolet-Nexus 670 FT-IR spectrometer, with samples measured as a neat film (oil) or KBr disk (solid). Mass spectra were recorded on a Agilent 6890-N-Network-GC-system. Melting points were determined on a Philip Harris C4954718 apparatus and remain uncorrected.

Analytical thin-layer chromatography (TLC) was carried out with Merck silica gel 60 F<sub>254</sub> aluminium sheets. The identity of previously prepared compounds was confirmed by comparison of spectra data with that of published. In all cases isolation of only a single thiocarbamate is reported, n.m.r analysis of the crude product mixture confirmed that no other thiocarbamate was produced.

The routine purification of reagents and solutions was carried out by standard laboratory procedures. All organic extracts were dried with anhydrous sodium sulfate.

**Typical reaction of tertiary amine with 1.** 4-Chlorophenyl chlorothionoformate<sup>12</sup> (**1**) (1.02g, 4.94mmol) was added to a solution of tertiary amine (4.94mmol) in dichloromethane (20ml) and the solution stirred under nitrogen at 20°C for 40 minutes. The solvent was evaporated affording a crude oily product which was purified by chromatography (pet. ether:dichloromethane 20:1) on silica.

**O-4-Chlorophenyl diethylthiocarbamate (5a).** White crystals, 95% yield, m.p. 76-79°C.  $^1\text{H}$  NMR  $\delta$  1.33(t,  $J=7.2$ , 6H, 2CH<sub>3</sub>), 3.69(q,  $J=7.2$ , 2H, CH<sub>2</sub>), 3.90(q,  $J=7.2$ , 2H, CH<sub>2</sub>), 7.02(d,  $J=9$ , 2H, Ar), 7.36(d,  $J=9$ , 2H, Ar);  $^{13}\text{C}$  NMR  $\delta$  11.79, 13.55, 44.33, 48.49, 124.22, 129.22, 131.24, 152.38, 186.48; FT-IR  $\nu_{\text{max}}$ : 2975, 1514, 1484, 1428, 1312, 1284, 1213, 1160, 1128, 1081, 832, 692  $\text{cm}^{-1}$ ; MS : m/z : 242(M<sup>+</sup>), 116, 100(100), 88, 72, 60.

**O-4-Chlorophenyl dimethylthiocarbamate (6a).** White crystals, 97% yield, m.p. 50-51°C.  $^1\text{H}$  NMR  $\delta$  3.29(s, 3H, CH<sub>3</sub>), 3.40(s, 3H, CH<sub>3</sub>), 7.00(d,  $J=8.7$ , 2H, Ar), 7.33(d,  $J=8.7$ , 2H, Ar);  $^{13}\text{C}$  NMR  $\delta$  38.84, 43.34, 124.31, 129.20, 131.15, 152.53, 187.25; FT-IR  $\nu_{\text{max}}$ : 2934, 1536, 1483, 1395, 1287, 1211, 1140, 1081, 1010, 836, 700  $\text{cm}^{-1}$ ; MS : m/z : 215(M<sup>+</sup>), 88, 72(100), 44.

**O-4-Chlorophenyl piperidine-1-carbothioate (8a).** Milky crystals, 96% yield, m.p. 54-55°C.  $^1\text{H}$  NMR  $\delta$  1.72(bs, 6H, 3CH<sub>2</sub>), 3.90(bs, 2H, CH<sub>2</sub>), 4.10(bs, 2H, CH<sub>2</sub>), 7.00(d,  $J=7.8$ , 2H, Ar), 7.34(d,  $J=7.8$ , 2H, Ar);  $^{13}\text{C}$  NMR  $\delta$  24.16, 25.26, 26.09, 47.56, 51.84, 124.26, 129.17, 131.16, 152.47, 185.76; FT-IR  $\nu_{\text{max}}$ : 2937, 2853, 1499, 1443, 1283, 1206, 1165, 1146, 1011, 836, 694  $\text{cm}^{-1}$ ; MS : m/z : 255(M<sup>+</sup>), 128, 112(100), 69, 41.

**O-4-chlorophenyl morpholine-4-carbothioate (9a).** White crystals, 96% yield, m.p. 96-98°C.  $^1\text{H}$  NMR  $\delta$  3.78(t,  $J=4.8$ , 2H, CH<sub>2</sub>-N), 3.84(t,  $J=4.5$ , 2H, CH<sub>2</sub>-N), 3.97(t,  $J=4.8$ , 2H, CH<sub>2</sub>-O), 4.15(t,  $J=4.8$ , 2H, CH<sub>2</sub>-O), 7.14(d,  $J=8.7$ , 2H, Ar), 7.37(d,  $J=8.7$ , 2H, Ar);  $^{13}\text{C}$  NMR  $\delta$  46.82, 50.24, 66.09, 66.32, 124.16, 129.33, 131.54, 152.18, 186.85; FT-IR  $\nu_{\text{max}}$ : 2869, 1487, 1443, 1283, 1244, 1205, 1114, 1082, 1037, 836  $\text{cm}^{-1}$ ; MS : m/z : 257(M<sup>+</sup>), 130, 114(100), 86, 70.

**O-4-Chlorophenyl 4-chlorobutyl(methyl)carbamothioate (10a).** Yellow oil, 96% yield,  $^1\text{H}$  NMR  $\delta$  (rotamer 1) 1.83(m, 4H, 2CH<sub>2</sub>), 3.26(s, 3H, CH<sub>3</sub>), 3.54-3.62(m, 2H, CH<sub>2</sub>-N), 3.72(t,  $J=7.2$ , 2H, CH<sub>2</sub>-Cl), 6.99(d,  $J=7.2$ , 2H, Ar), 7.33(d,  $J=6.9$ , 2H, Ar);  $^1\text{H}$  NMR  $\delta$  (rotamer 2) 1.83(m, 4H, 2CH<sub>2</sub>), 3.38(s, 3H, CH<sub>3</sub>), 3.54-3.62(m, 2H, CH<sub>2</sub>-N), 3.89(t,  $J=7.2$ , 2H, CH<sub>2</sub>-Cl), 6.99(d,  $J=7.2$ , 2H, Ar), 7.33(d,  $J=6.9$ , 2H, Ar);

$^{13}\text{C}$  NMR  $\delta$  (rotamer 1) 23.81, 29.59, 36.85, 44.42, 50.81, 124.24, 129.17, 131.17, 152.42, 187.16.  $^{13}\text{C}$  NMR  $\delta$  (rotamer 2) 25.27, 29.59, 41.65, 44.70, 54.53, 124.39, 129.26, 131.22, 152.42, 187.31; FT-IR  $\nu_{\text{max}}$ : 2943, 1517, 1485, 1401, 1208, 1132, 1085, 1014, 833  $\text{cm}^{-1}$ ; MS :  $m/z$  : 291(M<sup>+</sup>), 148, 91(100), 74, 55.

**O-4-Chlorophenyl 4-chloro-4-(pyridin-3-yl)butyl(methyl)carbamothioate (11a).** Yellowish orange oil, 95% yield,  $^1\text{H}$  NMR (rotamer 1) (CDCl<sub>3</sub>)  $\delta$  (ppm) 1.70-2.20(m, 4H, 2CH<sub>2</sub>), 3.22(s, 3H, CH<sub>3</sub>), 3.70(t,  $J=7.2$ , 2H, CH<sub>2</sub>-N), 4.88-4.98(m, 1H, CH-Cl), 6.89-6.98(m, 2H, Ar), 7.20-7.33(m, 3H, Ar), 7.67-7.75(m, 1H, Ar), 8.53-8.61(m, 2H, Ar);  $^1\text{H}$  NMR (rotamer 2) (CDCl<sub>3</sub>)  $\delta$  (ppm) 1.70-2.20(m, 4H, 2CH<sub>2</sub>), 3.34(s, 3H, CH<sub>3</sub>), 3.78-4.09(m, 2H, CH<sub>2</sub>-N), 4.88-4.98(m, 1H, CH-Cl), 6.89-6.98(m, 2H, Ar), 7.20-7.33(m, 3H, Ar), 7.67-7.75(m, 1H, Ar), 8.53-8.61(m, 2H, Ar);  $^{13}\text{C}$  NMR (rotamer1) (CDCl<sub>3</sub>)  $\delta$  (ppm) 23.88, 36.62, 36.78, 50.69, 59.96, 123.75, 124.13, 129.20, 131.27, 134.43, 136.85, 148.24, 149.70, 152.27, 187.20;  $^{13}\text{C}$  NMR (rotamer 2) (CDCl<sub>3</sub>)  $\delta$  (ppm) 25.31, 36.74, 41.69, 54.26, 60.21, 123.75, 124.25, 129.29, 131.34, 134.55, 137.14, 148.34, 149.87, 152.30, 187.46; FT-IR  $\nu_{\text{max}}$  (KBr disk): 2938, 1518, 1485, 1402, 1208, 1136, 1085, 834, 713  $\text{cm}^{-1}$ ; MS :  $m/z$  : 369(M<sup>+</sup>), 225(100), 197, 168.

**Reaction of *N,N*-dimethylaniline with (1).** The mixture of *N,N*-dimethylaniline (0.5g, 0.52ml, 4.12mmol) and 4-chlorophenyl chlorothionoformate (**1**) (0.854g, 4.12mmol) were heated under nitrogen at 130°C for 24 hours to give a blue oil. The resulted oily product was purified by chromatography (pet. ether:ethyl acetate 20:1) and *O*-4-chloro-phenyl methyl(phenyl)thiocarbamate (**7a**) was separated as a yellow crystals (0.86g, 75%), m.p. 107-110°C.

$^1\text{H}$  NMR  $\delta$  3.71(s, 3H, CH<sub>3</sub>), 7.04-7.77(m, 9H, Ar-H);  $^{13}\text{C}$  NMR  $\delta$  44.94, 124.12, 125.64, 127.94, 129.29, 129.60, 131.30, 143.41, 152.53, 187.53; FT-IR  $\nu_{\text{max}}$ : 1495, 1484, 1390, 1212, 1162, 1083, 700, 693  $\text{cm}^{-1}$ ; MS :  $m/z$  : 277(M<sup>+</sup>), 150, 134(100), 109, 77.

**Typical reaction of tertiary amine with (2).** 2,4,6-Tribromophenyl chlorothionoformate<sup>13</sup> (**2**) (0.809g, 1.97mmol) was added to a solution of tertiary amine (0.2g, 0.273ml, 1.97mmol) in dichloromethane (20ml) and the solution stirred under nitrogen at 20°C for 2 hours. The solvent was evaporated affording a crude oily product which was purified by chromatography (pet. ether:ethyl acetate 20:1) on silica.

**O-2,4,6-Tribromophenyl diethylthiocarbamate (5b).** White crystals, 91% yield, m.p. 76-78°C.  $^1\text{H}$  NMR  $\delta$  1.34(t,  $J=7.2$ , 3H, CH<sub>3</sub>), 1.41(t,  $J=7.2$ , 3H, CH<sub>3</sub>), 3.75(q,  $J=7.2$ , 2H, CH<sub>2</sub>), 3.89(q,  $J=7.2$ , 2H, CH<sub>2</sub>), 7.17(s, 2H, Ar);  $^{13}\text{C}$  NMR  $\delta$  11.63, 13.57, 44.72, 48.81, 119.46, 119.84, 134.66, 148.05, 182.76; FT-IR  $\nu_{\text{max}}$ : 2973, 1547, 1516, 1433, 1361, 1214, 1158, 1089, 859, 709  $\text{cm}^{-1}$ ; MS :  $m/z$  : 446(M<sup>+</sup>), 366, 266, 100(100), 72.

**O-2,4,6-Tribromophenyl dimethylthiocarbamate (6b).** White crystals, 96% yield, m.p. 125-127°C.  $^1\text{H NMR}$   $\delta$  3.42(s, 3H, CH<sub>3</sub>), 3.49(s, 3H, CH<sub>3</sub>), 7.72(s, 2H, Ar);  $^{13}\text{C NMR}$   $\delta$  39.14, 43.71, 119.59, 119.68, 134.72, 148.10, 183.75; FT-IR  $\nu_{\text{max}}$ : 3069, 1541, 1441, 1389, 1280, 1229, 1107, 855, 745, 728  $\text{cm}^{-1}$ ; MS : m/z : 417(M<sup>+</sup>), 266, 187, 88, 72(100).

**O-2,4,6-Tribromophenyl piperidine-1-carbothioate (8b).** white crystals, 93% yield, m.p. 128-130°C (decomposed).  $^1\text{H NMR}$   $\delta$  1.76(bs, 6H, 3CH<sub>2</sub>), 3.97(bs, 2H, CH<sub>2</sub>), 4.10(bs, 2H, CH<sub>2</sub>), 7.71(s, 2H, Ar);  $^{13}\text{C NMR}$   $\delta$  24.17, 25.37, 26.19, 48.10, 52.40, 119.43, 119.81, 134.67, 148.01, 182.03; FT-IR  $\nu_{\text{max}}$ : 2937, 1515, 1439, 1290, 1226, 1129, 1087, 852, 741, 713  $\text{cm}^{-1}$ ; MS : m/z : 458(M<sup>+</sup>), 378, 266, 187, 112(100), 69, 41.

**O-2,4,6-Tribromophenyl morpholine-4-carbothioate (9b).** white crystals, 83% yield, m.p. 176-179°C (decomposed).  $^1\text{H NMR}$   $\delta$  3.81(t,  $J= 4.8$ , 2H, CH<sub>2</sub>-N), 3.86(t,  $J= 4.8$ , 2H, CH<sub>2</sub>-N), 4.05(t,  $J= 4.8$ , 2H, CH<sub>2</sub>-O), 4.17(t,  $J= 4.8$ , 2H, CH<sub>2</sub>-O), 7.72(s, 2H, Ar);  $^{13}\text{C NMR}$   $\delta$  47.44, 50.75, 66.30, 66.38, 119.60, 119.77, 134.77, 147.79, 182.94; FT-IR  $\nu_{\text{max}}$ : 2859, 1515, 1434, 1282, 1246, 1220, 1194, 1113, 1032, 848, 739  $\text{cm}^{-1}$ ; MS : m/z : 459(M<sup>+</sup>), 380, 347, 266, 187, 114(100), 70, 42.

**O-2,4,6-Tribromophenyl 4-chlorobutyl(methyl)carbamothioate (10b).** colourless oil, 89% yield,  $^1\text{H NMR}$   $\delta$  (rotamer 1) 1.89(bs, 4H, 2CH<sub>2</sub>), 3.34(s, 3H, CH<sub>3</sub>), 3.58(t,  $J= 5.7$ , 2H, CH<sub>2</sub>-N), 3.77(t,  $J= 7.2$ , 2H, CH<sub>2</sub>-Cl), 7.69(s, 2H, Ar);  $^1\text{H NMR}$   $\delta$  (rotamer 2) 1.89(bs, 4H, 2CH<sub>2</sub>), 3.60(t,  $J= 6.3$ , 2H, CH<sub>2</sub>-N), 3.92(t,  $J= 6.6$ , 2H, CH<sub>2</sub>-Cl), 7.69(s, 2H, Ar);  $^{13}\text{C NMR}$   $\delta$  (rotamer 1) 23.82, 29.44, 37.12, 44.60, 51.31, 119.60, 119.75, 134.65, 147.96, 183.42;  $^{13}\text{C NMR}$   $\delta$  (rotamer 2) 25.31, 29.73, 42.13, 44.75, 54.65, 119.62, 119.82, 134.70, 148.07, 183.69; FT-IR  $\nu_{\text{max}}$ : 2941, 1524, 1440, 1403, 1286, 1226, 1090, 857, 743  $\text{cm}^{-1}$ ; MS : m/z : 444(M<sup>+</sup>), 364, 345, 266, 187, 164, 91(100).

**Reaction of *N,N*-dimethylaniline with 2.** The mixture of 2,4,6-tribromophenyl chlorothionoformate (**2**) (1.68g, 4.12mmol) and *N,N*-dimethylaniline (0.5g, 0.52ml, 4.12mmol) were heated under nitrogen at 130°C for 24 hours to give a blue oil. The oily product was purified by column chromatography (pet. ether:ethyl acetate 20:1) and O-2,4,6-tribromophenyl methyl(phenyl)thiocarbamate (**7b**) was separated as a yellow crystals (1.4g, 71%), m.p. 127-129°C.  $^1\text{H NMR}$   $\delta$  3.77(s, 3H, CH<sub>3</sub>), 7.36-7.51(m, 5H, Ar-N), 7.66(s, 2H, Ar);  $^{13}\text{C NMR}$   $\delta$  45.19, 119.52, 119.64, 125.90, 128.16, 129.53, 134.65, 143.07, 148.03, 183.61; FT-IR  $\nu_{\text{max}}$ : 2922, 1492, 1437, 1386, 1231, 1159, 1085, 718, 693  $\text{cm}^{-1}$ ; MS : m/z : 480(M<sup>+</sup>), 400, 345, 266, 187, 134(100), 106, 77.

**Hydrolysis of 5a.** The thiocarbamate (**5a**) (0.51g, 2 mmol) and dimethylsulfate (0.261g, 2.07 mmol) were refluxed under nitrogen for 3 hours in 1,2-dichloroethane (20ml). The solvent was evaporated affording a green oil which was washed twice with ether (10ml) to give the iminium salt. The salt (0.54g, 2 mmol) was dissolved in water and refluxed for 2 hours. Excess water was evaporated under reduced pressure to afford 4-chloro-*N*-methylbutan-1-amine hydrogensulfate as a spectroscopically pure oil (0.33 g) in 96% yield.

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