International Scholars Journals

African Journal of Chemistry ISSN 4391-3199 Vol. 5 (2), pp. 308-312, February, 2018. Available online at www.internationalscholarsjournals.org © International Scholars Journals

Full Length Research Paper

The study of reactivity and selectivity of tertiary amines with aryl chlorothionoformates

Masomeh Aghazadeh, Arash Afghan and Mehdi M. Baradarani*

Department of Chemistry, Faculty of Science, University of Urmia, Urmia 57135, Iran.

Accepted 23 October, 2017

***o*-Nitrophenyl chlorothionoformate reacts readily with unhindered tertiary aliphatic amines in only 10 min at room temperature, and gives the dialkylamine salts after treatment of initial thiocarbamate with dimethyl sulfate followed by hydrolysis with water. The ease of cleavage of alkyl groups from tertiary amines with 4-chlorophenyl chlorothionoformate is benzyl > *t* -butyl > allyl > methyl and using 2, 4, 6-tribromophenyl chlorothionoformate it is benzyl > allyl > *t*-butyl > methyl.**

Keywords: *o*-Nitrophenyl chlorothionoformate, benzylic and allylic cleavage of tertiary amines, secondary aliphatic amines from tertiary amines.

INTRODUCTION

The use of cyanogen bromide (Hageman, 1953) to achieve the dealkylation of tertiary amines and thus their conversion into secondary amines has largely been replaced in recent years by the use of chloroformate esters (Cooley and Evian, 1989). Initially there were difficulties in the hydrolysis of the first-formed carbamates (Figure 1) but there were overcome to a significant extent by the use of vinyl, (Olofson et al., 1977) or 2,2,2-trichloroethyl chloroformates (Montzka et al., 1974), phenyl chlorothionoformate (Millan and Prager, 1998), Thiophosgene (Baradarani and Prager, 1999), 1-chloroethyl chlorothionoformate (Baradarani and Prager, 2002), and more recently 4-chlorophenyl and 2,4,6-tribromophenyl chlorothionoformates (Heidari and Baradarani, 2006).

During our study of the reaction of 4-chlorophenyl and 2, 4, 6-tribromophenyl chlorothionoformates with various tertiary amines (Heidari and Baradarani, 2006), it became clear that chlorothionoformates are more reactive than chloroformates and appeared to form the intermediate salts 1 and 2 rapidly. The resulting thiocarbamates 3 can be converted into the secondary amine salts by treatment with dimethyl sulfate, followed by hydrolysis with water.

In this paper we introduce *o*-nitrophenyl chlorothionoformate as a powerful dealkylating agent for tertiary aliphatic amines. The selectivity of the cleavage of benzylic, allylic and alkyl groups by aryl chlorothionoformate derivatives has also been investigated in greater detail.

EXPERIMENTAL SECTION

General procedure

^{1}H and ^{13}C NMR spectra were recorded with a Bruker spectrometer in $CDCl_3$ at 300 and 75 MHz unless otherwise indicated and chemical shifts are in ppm (reference TMS). Infrared spectra were recorded on a Thermonicolet-Nexus 670 FT-IR spectrometer, with samples measured as a neat film (oil) or KBr disk (solid). Mass spectra were recorded on an Agilent 6890-N-Network-GC-system. Melting points were determined on a Philips Harris C4954718 apparatus and are not corrected.

Analytical thin-layer chromatography (TLC) was carried out with Merck silica gel 60 F_{254} aluminum 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, NMR 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 (Armarego and Perrin, 1997). All organic extracts were dried with anhydrous sodium sulfate.

***o*-Nitrophenyl chlorothionoformate (4):** Using the reported procedure (Barton et al., 1993) for synthesis of phenyl chlorothionoformate, gave *o*-nitrophenyl chlorothionoformate as yellow crystals in 89% yield, m.p. 46°C. ^{1}H NMR ($CDCl_3$) (ppm) 7.33 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H, Ar), 7.55 (td, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H, Ar), 7.77 (td, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H, Ar), 8.20 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$) (ppm) 124.88, 126.37, 128.30, 135.38, 146.79, 184.84. FT-IR $_{max}$ (KBr disk): 3098, 1589, 1530,

---

*Corresponding author. E-mail: m.baradarani@mail.urmia.ac.ir

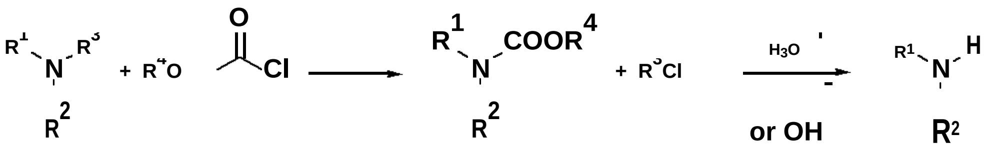
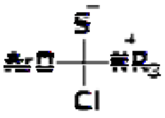


Figure 1. Reaction of tertiary amines with chloroformate esters and then hydrolysis.



1

Z

3

1475, 1347, 1222, 1040, 859, 785, 469 cm^{-1}. MS: *m/z*: 217 (M^+), 139(100), 122.

Typical reaction of tertiary amines with (4): *o*-Nitrophenyl chlorothionoformate (4) (0.54 g, 2.47 mmol) was added to a solution of tertiary amine (2.47 mmol) in dichloromethane (25 ml) and the solution stirred at 20°C for 10 min. The solvent was evaporated affording a crude product which was purified by chromatography (pet. ether: dichloromethane 10:1) on silica gel.

***o*-Nitrophenyl *N,N*-diethylthiocarbamate (5):** Brown oil, 90 yield. ^1H NMR ($CDCl_3$) (ppm) 1.26 (t, J = 7.2 Hz, 3H, CH_3), 1.33 (t, J = 7.2 Hz, 3H, CH_3), 3.72 (q, J = 7.2 Hz, 2H, CH_2), 3.83 (q, J = 7.2 Hz, 2H, CH_2), 7.22 (d, J = 8.1 Hz, 1H, Ar), 7.36 (t, J = 8.1 Hz, 1H, Ar), 7.62 (t, J = 8.1 Hz, 1H, Ar), 8.05 (d, J = 8.1 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$) (ppm) 11.57, 13.21, 44.61, 48.57, 125.52, 126.45, 126.48, 134.48, 142.23, 147.07, 184.82. FT-IR $_{max}$ (KBr disk): 2981, 1722, 1603, 1521, 1461, 1430, 1340, 1211, 1156, 908, 786 cm^{-1}. MS: *m/z*: 253(M^+), 208, 139, 122, 100(100), 72.

***o*-Nitrophenyl *N,N*-dimethylthiocarbamate (6).** Orange crystals, 92 yield, m.p. 112-113 °C. ^1H NMR ($CDCl_3$) (ppm) 3.42 (s, 3H, CH_3), 3.47 (s, 3H, CH_3), 7.28 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H, Ar), 7.41 (td, J_1 = 8.4 Hz, J_2 = 1.5 Hz, 1H, Ar), 7.69 (td, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H, Ar), 8.13 (dd, J_1 = 8.4 Hz, J_2 = 1.5 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$) (ppm) 39.13, 43.54, 125.72, 126.53, 126.59, 134.46, 147.23, 185.93. FT-IR $_{max}$ (KBr disk): 3073, 2940, 1552, 1521, 1477, 1345, 1286, 1212, 1119, 785 cm^{-1}. MS: *m/z*: 226(M^+), 180, 138, 122, 72(100).

***o*-Nitrophenyl piperidine-1-thiocarbamate (7):** Light yellow crystals, 87 yield, m.p. 96-98 °C. ^1H NMR ($CDCl_3$) (ppm) 1.75 (bs, 6H, $3CH_2$), 3.95 (t, J = 5.4 Hz, 2H, CH_2-N), 4.09 (t, J = 5.4 Hz, 2H, CH_2-N), 7.25 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H, Ar), 7.40 (td, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H, Ar), 7.65 (td, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H, Ar), 8.12 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$) (ppm) 24.12, 25.30, 25.84, 48.04, 52.22, 125.68, 126.40, 126.67, 134.39, 142.00, 147.27, 184.15. FT-IR $_{max}$ (KBr disk): 2938, 2853, 1714, 1603, 1514, 1439, 1340, 1267, 1210, 1143, 785, 693 cm^{-1}. MS: *m/z*: 266(M^+), 220, 182, 138, 116(100), 72.

***o*-Nitrophenyl morpholine-4-thiocarbamate (8):** Yellow crystals, 90 yield, m.p. 135 °C. ^1H NMR ($CDCl_3$) (ppm) 3.84 (t, J = 4.2 Hz, 2H, CH_2 -N), 3.87 (t, J = 4.2 Hz, 2H, CH_2-N), 4.05 (t, J = 4.2 Hz, 2H, CH_2-O), 4.16 (t, J = 4.2 Hz, 2H, CH_2-O),7.29 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H, Ar), 7.43 (td, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H, Ar), 7.70 (td, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H, Ar), 8.14 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H, Ar) . ^{13}C NMR ($CDCl_3$) (ppm) 47.44, 50.65, 66.13, 66.32, 125.86, 126.59, 126.72, 134.61, 141.75, 147.05 185.13. FT-IR $_{max}$ (KBr disk): 2972, 2860, 1601, 1521, 1340, 1245, 1113, 866, 786, 699 cm^{-1}. MS: *m/z*: 268(M^+), 222, 138, 116, 72.

***o*-Nitrophenyl *N*-(4-chlorobutyl)-*N*-methylthiocarbamate (9).** Yellow oil, 90 yield. ^1H NMR ($CDCl_3$) (ppm) 1.84-1.99 (m, 4H, $2CH_2$), 3.37 (s, 3H, CH_3), 3.43 (s, 3H, CH_3), 3.61 (t, J = 6.0 Hz, 2H, CH_2-Cl), 3.64 (t, J = 6.0 Hz, 2H, CH_2-Cl), 3.81 (t, J = 7.2 Hz, 2H, CH_2 -N), 3.94 (t, J = 7.2 Hz, 2H, CH_2-N), 7.25- 8.15 (m, 4H, Ar) for two rotamers. ^{13}C NMR ($CDCl_3$) (ppm) 23.73, 25.06, 29.36, 29.62, 37.09, 41.88, 44.38, 44.64, 51.22, 54.72, 125.57, 125.71, 125.78, 126.19, 126.44, 126.57, 126.62, 134.50, 134.55, 147.02, 147.21, 186.01 for two rotamers. FT-IR $_{max}$ (KBr disk): 2947, 2870, 1604, 1518, 1480, 1348, 1285, 1219, 1120, 781, 699 cm^{-1}. MS: *m/z*: 303(M^+), 256, 148, 91(100), 55.

***o*-Nitrophenyl *N*-(4- chloro- 4-(pyridin-3-yl)butyl)-*N*-methylthiocarbamate (10):** Light brown oil, 68 yield. ^1H NMR ($CDCl_3$) (ppm) 1.94-2.36 (m, 4H, $2CH_2$), 3.32 (s, 3H, CH_3), 3.38(s, 3H, CH_3), 3.82-4.18 (m, 2H, CH_2N), 4.95 (t, J = 7.8 Hz, 1H, CHCl), 5.07 (t, J = 7.8 Hz, 1H, CHCl), 7.13-8.66 (m, 8H, Ar). ^{13}C NMR ($CDCl_3$) (ppm) 23.89, 25.13, 36.03, 36.76, 36.88, 41.95, 51.09, 59.43, 59.65, 126.67, 127.79, 126.38, 126.64, 134.51, 134.67, 137.52, 138.12, 146.07, 146.67, 147.10, 185.73, 186.27 for two rotamers. FT-IR $_{max}$ (KBr disk): 2930, 1604, 1527, 1479, 1348, 1218, 1122, 782, 752, 712 cm^{-1}. MS: *m/z*: 379(M^+), 327, 222, 139(100), 122, 39.

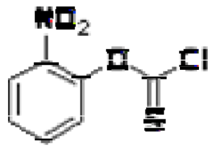
Dealkylation of tertiary amines with other aryl chlorothionoformates. To a solution of tertiary amine (3 mmol) in dichloromethane (30 ml) was added the aryl chlorothionoformate (3 mmol). After 1 h stirring at 20°C, the solvent was evaporated to give a crude product which was purified by chromatography (pet. ether: dichloromethane 10:1) on silica gel.

Phenyl *N*-allyl-*N*-methylthiocarbamate (12): Yellow oil , 90 yield. ^1H NMR ($CDCl_3$) (ppm) 3.28 (s, 3H, CH_3), 3.43 (s, 3H, CH_3), 4.33 (d, J = 5.4 Hz, 2H, CH_2), 4.56 (d, J = 6.0 Hz, 2H, CH_2), 5.21-5.35 (m, 2H, CH_2), 5.87-5.98 (m, 1H, CH), 7.07-7.12 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$) (ppm) 36.17, 41.30, 53.84, 57.77, 117.73, 118.58, 122.78, 122.82, 125.94, 129.18, 129.19, 131.13, 131.55, 154.07, 154.20, 187.81. FT-IR $_{max}$ (KBr disk): 3065, 2933, 1591, 1512, 1489, 1398, 1245, 1201, 1137, 769, 690 cm^{-1}. MS: *m/z*: 207(M^+), 180, 114, 91(100), 41.

4-chlorophenyl *N*-allyl-*N*-methylthiocarbamate (14): Light yellow oil, 87 yield. ^1H NMR ($CDCl_3$) (ppm) 3.26 (s, 3H, CH_3), 3.41 (s, 3H, CH_3), 4.31 (d, J = 5.4 Hz, 2H, CH_2), 4.53 (d, J = 6.0 Hz, 2H, CH_2), 5.22-5.34 (m, 2H, CH_2), 5.83-5.97 (m, 1H, CH), 6.97-7.38 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$) (ppm) 36.20, 41.38, 53.88, 57.87,

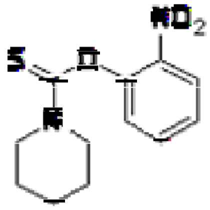
Table 1. Dealkylation of tertiary amines using *o*-nitrophenyl chlorothionoformate (4)

	Amine	Conditions	Product	Yield
1	Triethylamine	CH_2Cl_2,10 min, 20 °C	5 + EtCl	90
2	*N*,*N*-Dimethylbenzylamine	CH_2Cl_2, 10 min, 20 °C	6+ BzCl	92
3	1-Methylpiperidine	CH_2Cl_2, 7 min, 20 °C	7 + MeCl	87
4	4-Methylmorpholine	CH_2Cl_2, 10 min, 20 °C	8 + MeCl	90
5	1-Methylpyrrolidine	CH_2Cl_2, 30 min, 20 °C	9	90
6	(-)-Nicotine	CH_2Cl_2, 30 min, 20 °C	10	68
7	*N*-allyl-*N*-methylbenzylamine	CH_2Cl_2, 10 min, 20 °C	11	87

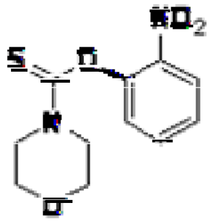


4

	R1	R2
5	Et	Et
6	Bz	Bz



7



8

117.83, 118.75, 124.19, 124.24, 129.23, 129.26, 130.89, 131.35, 152.43, 152.45, 187.39, 187.75. FT-IR $_{max}$ (KBr disk): 3048, 2931, 1652, 1513, 1485, 1398, 1246, 1206, 1085, 1013, 832, 712 cm^{-1}. MS: *m/z*: 241(M^+), 180, 114, 91(100), 41.

2,4,6-Tribromophenyl *N*-allyl-*N*-methylthiocarbamate. White crystals, 78 yield, m.p. 83-86 °C. ^1H NMR ($CDCl_3$) (ppm) 3.37 (s, 3H, CH_3), 3.42 (s, 3H, CH_3), 4.37 (d, *J* = 5.1 Hz, 2H, CH_2), 4.53(d, *J* = 5.4 Hz, 2H, CH_2), 5.30-5.36 (m, 2H, CH_2), 5.87-6.01 (m, 1H, CH), 7.74 (s, 2H, Ar). ^{13}C NMR ($CDCl_3$) (ppm) 36.65, 41.45, 54.25, 58.01, 118.64, 118.32, 119.65, 119.74, 130.45, 131.07, 134.72, 134.74, 147.93, 183.54, 184.12. FT-IR $_{max}$ (KBr disk): 3058, 2921, 1550, 1518, 1439, 1399, 1224, 1106, 925, 860,741 cm^{-1}. MS: *m/z*: 447, 445(M^+), 443, 266, 148, 91(100), 41.

***o*-Nitrophenyl *N*-allyl -*N*-methylthiocarbamate. White crystals , 87** yield, m.p. 56-58 °C. ^1H NMR ($CDCl_3$) (ppm) 3.34 (s, 3H, CH_3), 3.41(s, 3H, CH_3), 4.34 (d, *J* = 5.1 Hz, 2H, CH_2), 4.54 (d, *J* = 5.4 Hz, 2H, CH_2), 5.25-5.42 (m, 2H, CH_2), 5.87-6.04 (m, 1H, CH), 7.23-8.18 (m, 4H, Ar) . ^{13}C NMR ($CDCl_3$) (ppm) 36.63, 41.25, 54.23, 58.05, 118.47, 118.51, 125.69, 125.77, 126.53, 126.59, 130.48, 131.29, 134.45, 134.52, 147.07, 147.26, 185.76, 186.35. FT-IR $_{max}$ (KBr disk): 3081, 2920, 1603, 1521, 1479, 1405, 1347, 1246, 1215, 1136, 1087, 922, 790, 707 cm^{-1}. MS: *m/z*: 252(M^+), 180, 138, 122, 91(100), 41.

2,4,6-Tribromophenyl *N-t*-butyl-*N*-methylthiocarbamate (13): Yellow oil, 40 yield. ^1H NMR ($CDCl_3$) (ppm) 1.68 (s, 9H, $3CH_3$), 3.60 (s, 3H, CH_3), 7.71 (s, 2H, Ar). ^{13}C NMR ($CDCl_3$) (ppm) 29.36, 30.22, 61.77, 134.23, 134.81, 135.30, 148.26, 185.52. FT-IR $_{max}$ (KBr disk): 2923, 2852, 1486, 1438, 1383, 1234, 1164, 1120, 855, 742 cm^{-1}. MS: *m/z*: 463, 461(M^+), 459, 330(100), 141, 114, 57.

Hydrolysis of (5): The Thiocarbamate (5) (0.2 g, 0.78 mmol) and dimethyl sulfate (0.24 g, 0.18 ml, 1.91 mmol) were refluxed under nitrogen for 2 h in dichloromethane (10 ml). The solvent was evaporated affording green oil which was washed twice with ether (20 ml) to give the minimum salt as a pale green oil (0.32 g). The salt (0.1 g,0.26 mmol) was dissolved in water (5 ml) and refluxed for 2 h. Excess water was evaporated under reduced pressure to afford dimethylamine hydrogen sulfate as a spectroscpically pure orange oil (0.04 g, > 95%).

RESULTS AND DISCUSSION

The procedure used by Barton and co-workers (Barton et al., 1993) for the synthesis of phenyl chlorothionoformate was directly applicable to the synthesis of *o*-nitrophenyl chloro-thionoformate (4). The reaction of tertiary amines with *o*-nitrophenyl chloro-thionoformate was even more rapid than with 4-chlorophenyl or 2,4,6-tribromophenyl chlorothionoformates (Heidari and. Baradarani, 2006). Thus, when triethylamine, *N* -methylpiperidine, or *N*-methylmorpholine were treated with an equivalent of 4 in dichloromethane as a solvent, the de-ethylated 5, and the demethylated products 7, 8 were obtained within 10 min in excellent yields. As shown in Table 1, the reaction of most unhindered tertiary amines also went to completion within 10 min.

When *N*-methylpyrrolidine as a representative of a five-membered ring amine was treated with *o*-nitrophenyl chlorothionoformate in dichloromethane, the reaction proceeded to completion rapidly at 20°C and ring opening was achieved leading to 9 in 90% yield. This product gave ^1H and ^{13}C NMR signals indicating that it exists as two slowly interchanging rotamers at ambient temperature. Similarly (-)-nicotine was treated with 4 and the

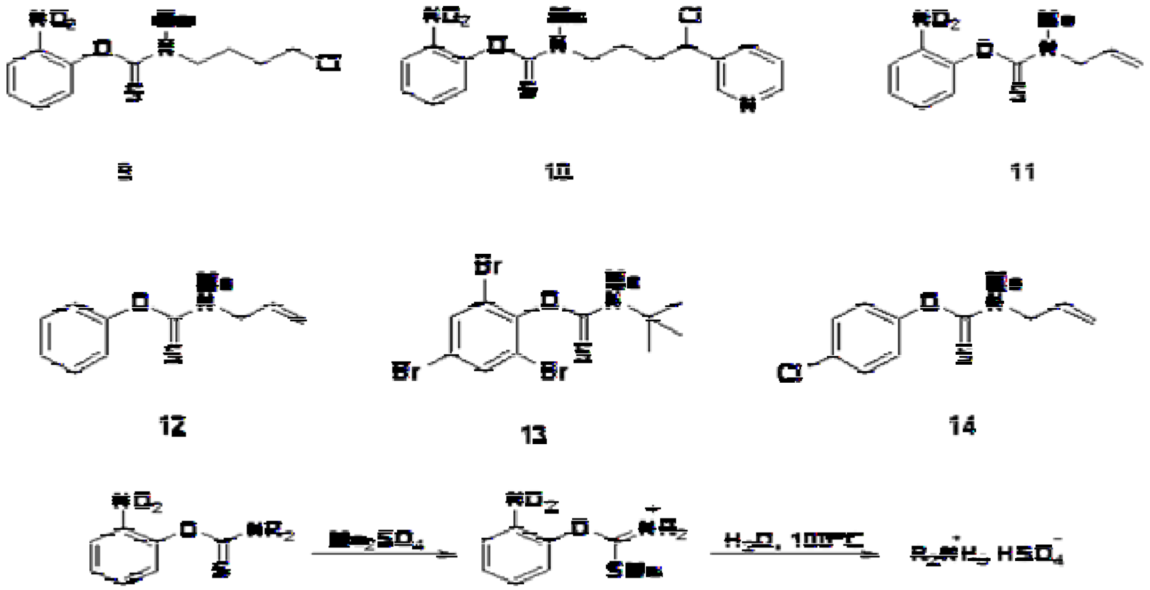


Figure 2. Methylation of Thiocarbamates with Dimethylsulfate and then hydrolysis.

ring opening of pyrrolidine took place, with cleavage of the benzylic C–N bond, at 20°C in 68% yield to produce 10 in 30 min.

Kapnang and Charles (1983) has shown that the ease of cleavage of alkyl groups from tertiary amines with chloroformates is benzyl > allyl > methyl and in our investigation a similar pattern of selectivity was found for the chlorothionoformate-promoted cleavages.

Reaction of *N,N*-dimethylbenzylamine with 4 resulted only in debenzylation, as was expected, in quantitative yield and in only 10 min at room temperature (Montzka et al., 1974; Heidari and Baradarani, 2006) . In order to ascertain the relative ease of cleavage of allyl, benzyl, tertiary alkyl and methyl groups, *N* -allyl-*N*-methylbenzylamine was synthesized from *N*-allylbenzylamine (Carpino, 1960) by reaction with formaldehyde and formic acid in 80% yield (Moore et al., 2005). This amine also reacted readily with phenyl chlorothionoformate giving the debenzylated product 12 at 20°C in 90% yield. Exclusive debenzylation also occurred when *N*-allyl-*N*-methylbenzylamine was reacted with phenyl, 4-chlorophenyl or 2,4,6-tribromophenyl chlorothionoformates. By contrast, we found that *o*-nitrophenyl chlorothionoformate effected debenzylation of *N*-allyl-*N*-methylbenzylamine in essentially quantitative yield, affording *o*-nitrophenyl *N*-allyl-*N*-methylthiocarbamate 11 in only 10 min.

All attempts at dealkylation of *N*-*t*-butyl-*N*-methylbenzylamine using phenyl, 4-chlorophenyl or *o*-nitrophenyl chlorothionoformate were unsuccessful, but when 2,4,6-tribromophenyl chlorothionoformate was reacted with this amine in dichloromethane the debenzylation product 13 was isolated in 35% yield.

The question of relative reactivity of *t*-butyl and allyl groups was answered by examining the reactivity of *N*-methyl-*N*-*t*-butylallylamine with two different reagents: 4-chlorophenyl and 2,4,6- tribromophenyl chlorothionoformates. The amine was synthesized by reaction of *t*-butylamine with allyl chloride to form *N*-*t*-butylallylamine (35%), followed by *N*-methylation with formaldehyde and formic acid to give the desired amine in 73% yield. To bring about a reaction of this amine with 4-chlorophenyl chlorothionoformate, reaction at 20°C for one day was required, affording 4-chlorophenyl *N*-allyl-*N*- methylthiocarbamate (14) but with 2,4,6-tribromophenyl chlorothionoformate, reaction at 20°C for one day, only deallylation product 13 was obtained.

We conclude that *o*- nitrophenyl chlorothionoformate is a powerful dealkylating agent for tertiary amines with high reactivity, and 2,4,6-tribromophenyl chlorothionoformate is a useful dealkylating agent for tertiary amines with high selectivity. We can also conclude that the relative rates of cleavage of common alkyl groups from tertiary amines with unhindered reagents such as 4-chlorophenyl chlorothionoformate is benzyl > *t*-butyl > allyl > methyl, and that in the use of a hindered reagent such as 2,4,6- tribromophenyl chlorothionoformate the relative order is: benzyl > allyl > t-butyl > methyl.

Although the dialkyl thionochloroformates resulting from these reactions, are relatively easily hydrolyzed, cleavage is best achieved if the thiocarbamate is first methylated with dimethyl sulfate (Figure 2), thus making the secondary amines readily accessible.

ACKNOWLEDGEMENTS

The authors are grateful to the University of Urmia for support of this work and to professor J. A. Joule (The

School of Chemistry, the University of Manchester, UK) for helpful comments.

REFERENCES

Armarego WLF, Perrin D (1997). Purification of Laboratory Chemicals, fourth edition.

Baradarani MM, Prager RH (1999). The specific epimerisation of phthalideisoquinoline alkaloids, Tetrahedron Lett., 40: 7403.

Baradarani MM, Prager RH (2001). The Dealkylation of tertiary Amines with thiophosgene and 1-chloroethylchlorothienoformate J. Sci. I. R. Iran., 12, 27 (2001). Chem. Abstr. 2002, 136, 262753.

Barton DHR, Jang DO, Jaszberenyi JC (1993). The invention of radical reactions. Part XXXI. Diphenylsilane: a reagent for deoxygenation of alcohols via their thiocarbonyl derivatives, deamination via isonitriles, and dehalogenation of bromo- and iodo- compounds by radical chain chemistry, Tetrahedron, 49: 7193.

Carpino LA, Santilli AA, Murray RW (1960), Oxidative Reactions of Hydrazines. V. Synthesis of Monobenzyl 1,1-Disubstituted Hydrazines and 2-Amino-2,3-dihydro-1H-benz[de]isoquinoline. J. Am. Chem. Soc. 82: 2728.

Cooley JH, Evain EJ (1989). Amine Dealkylations with Acyl Chlorides Synthesis, p.1.

Hageman HA, (1953). The yon Braun cyanogen bromide reaction. Org. React., 7:198.

Heidari M, Baradarani MM (1974) 4-Chlorophenyl and 2,4,6-tribromophenyl chlorothionoformates: new dealkylating agents for tertiary amines, Arkivoc, 11: 167-175.

Kapnang H, Charles G (1983). Reaction des chloroformiates sur les amines tertiaires: competition entre n-demethylation, desamination, n-debenzylation et n-desallylation, Tetrahedron Lett., Tetrahedron Lett., 24: 3233Millan DS, Prager RH, (1998). The dealkylation of tertiary aliphatic amines with phenyl chlorothionoformate,Tetrahedron Lett., 39: 4378.

Montzka TA, Matiskella JD, Partyka RA (1974). 2,2,2-trichloroethyl chloroformate: A general reagent for demethylation of tertiary methylamines, Tetrahedron Lett., 14: 132.

Moore JL, Taylore SM, Soloshonok VA (2005). An efficient and operationally convenient general synthesis of tertiary amines by direct alkylation of secondary amines with alkyl halides in the presence of Huenig's base, Arkivoc, 6: 287-292.

Olofson RA, Schnur RC, Bunes, Pepe JP (1977). Selective N-dealkylation of tertiary amines with vinyl chloroformate: An improved synthesis of naloxone, Tetrahedron Lett.,17: 1567.