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REACTION OF METHYL 2-ARYLETHYLCARBAMATES WITH THIONYL CHLORIDE: FORMATION OF BENZOTHIAZINE AND BENZO[*b*]THIOPHENE RING SYSTEMS

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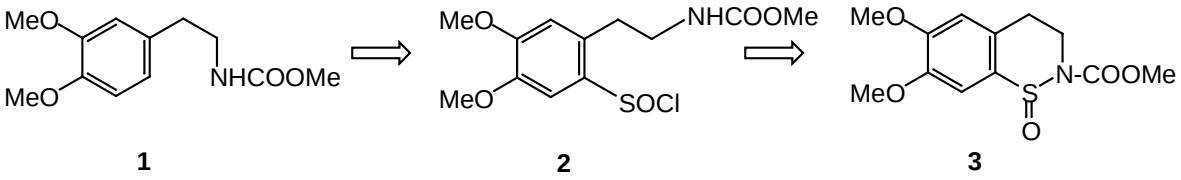
Abstract - The reaction of methyl 2-arylethylcarbamates with thionyl chloride induced a sulfur mediated ring closure to form benzothiazine and benzo[*b*]-thiophene ring systems with concomitant chlorination of the aromatic ring.

Thionyl chloride ($SOCl_2$) is well known to be an excellent dehydration reagent. For example, primary amides form nitriles,[1] and *N*,*N*-dimethylformamide yield Vilsmeier reagent which is useful for synthesis.[2] Bell *et al*. reported that chlorosulfination of aromatic methyl ethers with $SOCl_2$.[3] We tried chlorosulfination of methyl 2-(3,4-dimethoxyphenyl)ethylcarbamate (**1**) aiming to obtain sulfinyl chloride derivative (**2**), which would cyclize to give dihydrobenzothiazine (**3**), an analogue of biologically active benzisothiazolone. However, we found that reaction of **1** with $SOCl_2$ directly gave heterocyclic compound such as benzothiazine and benzo[*b*]thiophene. This is entirely different from the report of Krubsack *et al*.[4] who obtained 3-chloro-2-chlorocarbonylbenzo[*b*]thiophene by the reaction of cinnamic acid with $SOCl_2$, and suggested the intermediacy of α-chloro-α-sulfenyl derivative. Here we describe the reaction of

methyl 2-arylethylcarbamates with $SOCl_2$, which revealed sulfur mediated cyclization together with chlorination reaction.

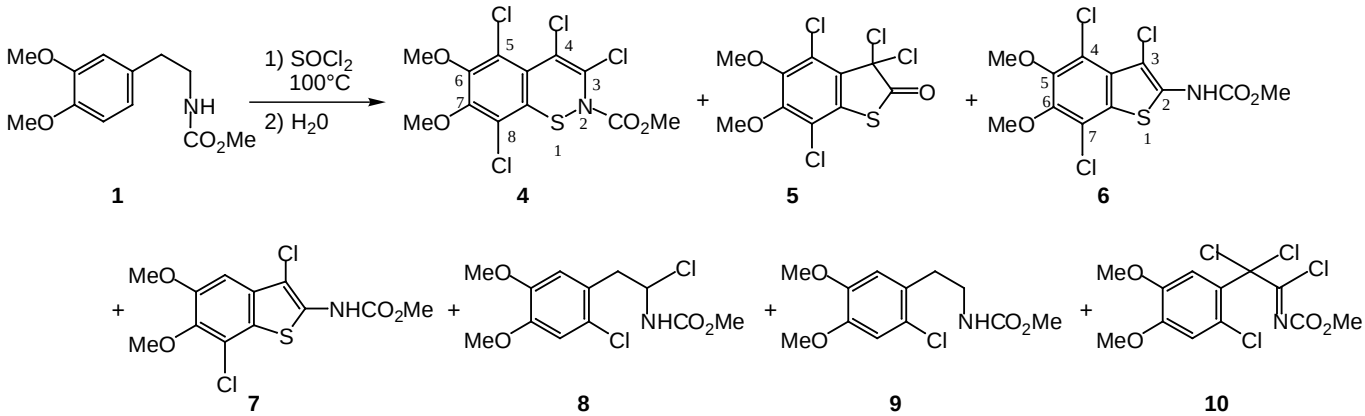


1 **2** **3**

Scheme 1

Results and Discussion

Reaction of **1** with $SOCl_2$ was carried out in a sealed tube without a solvent at 100°C for 1 h. It was interesting that thioheterocyclic compounds were obtained though expected **2** or **3** were not formed. Chromatography of the reaction mixture gave three cyclized products, a benzothiazine (**4**) (17%), a 3*H*-benzo[*b*]thiophen-2-one (**5**) (3%), a benzo[*b*]thiophene (**6**) (38%), and two uncyclized chloro derivatives (**8**) (9%) and (**9**) (14%) (Table 1, Entry 1). The structures of the products were elucidated by ^{1}H- and ^{13}C-NMR spectra and elementary analyses. When the reaction time was elongated to 5 h, the major product was the benzothiazine (**4**) (55%) and a new non-cyclized chlorinated derivative (**10**) (18%) was produced. The other by-products were the benzo[*b*]thiophen-2(3*H*)-one (**5**) (4%) and benzo[*b*]thiophene (**6**) (7%) (Entry 2).



1 **4** **5** **6** **7** **8** **9** **10**

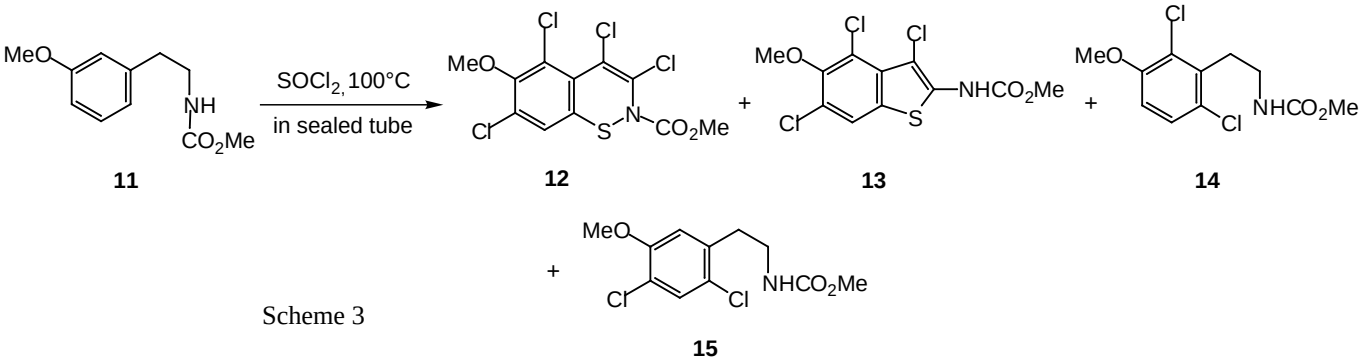
Scheme 2

Next we carried out the reaction in octane. The reaction at 100°C for 1 h gave a new benzo[*b*]thiophene derivative (**7**) (28%) along with **6** (9%) and **9** (20%) (Entry 3). When the reaction time was elongated to 5 h, the same compounds as in Entry 2 were produced though the ratio of the products was different.

Table 1. Reaction of methyl 2-(3,4-dimethoxyphenyl)ethylcarbamate (**1**) with $SOCl_2$

Entry	Conditions		Products (Yield, %)						
	Solvent	Time	**4**	**5**	**6**	**7**	**8**	**9**	**10**
1	neat	1 h	17	3	38	-	9	14	-
2	neat	5 h	55	4	7	-	-	-	18
3	octane	1 h	-	-	9	28	-	20	-
4	octane	5 h	30	5	23	-	-	-	5

Heating of methyl 2-(3-methoxyphenyl)ethylcarbamate (**11**) with $SOCl_2$ at 100°C for 6 h gave **12**, **13**, **14**, and **15** in 5, 12, 8 and 7% yields, respectively (see Scheme 3, Table 2). The structures of **12**, **13**, and **14** were deduced on the basis of ^{1}H-, ^{13}C-NMR, and MS spectral analyses. The position of chlorine atoms on the aromatic ring in the products (**12**, **13,** and **14**) was determined by the NOE correlation spectroscopy (NOESY). The product (**14**) showed a cross peak between 4-H (δ6.77, d, *J*=8.9 Hz) and OMe (δ 3.88, s), thus confirming that chlorine atoms were introduced at *ortho* and *para* position to the OMe group. However, in **12** and **13**, the cross peaks between the aromatic proton (**12**: δ 7.33, s; **13**: δ 7.62, s) and methoxyl protons (**12**: δ 3.99, s; **13**: δ 3.92, s) were not observed implying that the two chlorine atoms were introduced at the *ortho* positions of the OMe group.



11 **12** **13** **14**

15

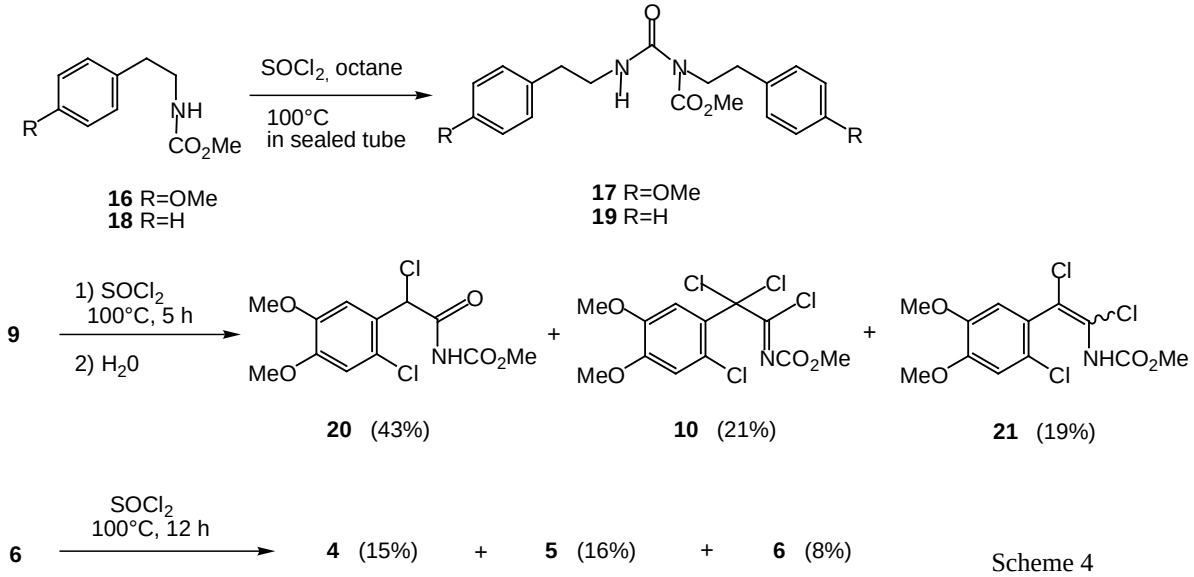
Scheme 3

In order to clarify the pathway of constructing the benzothiophene and benzothiazine rings we carried out several experiments. Similar reactions of methyl 2-(4-methoxyphenyl)ethylcarbamate (**16**) and methyl 2-phenylethylcarbamate (**18**), the both of which do not have OMe group which is activated on the *ortho* position of the ethylcarbamate side chain, gave neither benzothiophene nor benzothiazine derivatives,

Table 2. Reaction of methyl 2-(3-methoxyphenyl)ethylcarbamate (**11**) with $SOCl_2$

Entry	Conditions		Products (Yield, %)				
	Solvent	Time	**12**	**13**	**14**	**15**	**11**
1	neat	6 h	5	12	8	7	-
2	neat	21h	14	-	-	-	-
3	octane	9 h	16	6	-	-	41
4	octane	20 h	19	8	-	-	-

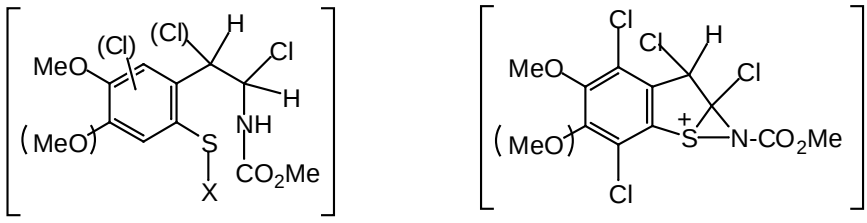
instead produced urea derivatives (**17** and **19**) in low yields, with considerable recovery of the starting materials, respectively. Methyl 2-(6-chloro-3,4-dimethoxyphenyl)ethylcarbamate (**9**), on further reaction with $SOCl_2$, did not yield any cyclized product and merely produced further chlorinated compounds (**20** (43%), **10** (21%), and **21** (19%)). Treatment of the benzothiophene (**6**) with $SOCl_2$ at 100°C caused a hydrolytic elimination of the carbamate group to yield **5** (16%) and, at the same time, the ring expansion reaction to **4** was observed (15%). It is confirmed that the thioheterocyclization requires OMe group which is attached at the *meta* position of the ethylcarbamate side chain.



Scheme 4

Tables 1 and 2 suggested that the first step of the reaction leading to heterocycles from **1** and **11** should be formation of the thio intermediate (**i**) by the attack of $SOCl_2$ to the *para* position of OMe group. The intermediate (**i**) cyclizes to the benzo[*b*]thiophene (**6** and **13**), which would give the benzothiazine (**4** and

12) by the ring expansion *via* the thioaziridine intermediate (**ii**) (Scheme 5). Chlorination of aromatic ring could be subsequent step of sulfenylation, because none of the chlorinated products was obtained from **16** and **18**.



i (X=Cl or other)[5] **ii**

Scheme 5

EXPERIMENTAL

Unless otherwise stated, the following procedure was adopted. Melting points were determined on a Yanaco micro-melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO IR-810 spectrophotometer and data are given in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra were taken with a JEOL JNM-EX90 (90 MHz for ^{1}H and 22.5 MHz for ^{13}C), JEOL JNM-AL300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) or JNM-α500 (500 MHz for ^{1}H) spectrometer in $CDCl_3$ solutions with TMS as an internal standard and the chemical shifts are given in δ values. MS and HRMS were taken with a JEOL JMS D-300 and JEOL JMS-HX110A spectrometer and given in *m*/*z*. Column chromatography (CC) and medium pressure column chromatography (MPLC) were done on silica gel. Elemental analyses were performed with a YANACO MT-3.

Reaction of Methyl 2-(3,4-dimethoxyphenyl)ethylcarbamate (1) with $SOCl_2$ i) A mixture of $SOCl_2$ (3 mL, 41 mmol) and **1** (200 mg, 0.83 mmol) was heated in a sealed tube at 100°C for 1 h. After cooling, the reaction mixture was poured into water (50 mL), and extracted with $CHCl_3$. The extract was dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed with AcOEt-hexane (1:2), the solvent of the fraction was evaporated. The crude product was purified by MPLC with AcOEt-hexane (1:4, 1:1) to give **4** (58 mg, 17%), **5** (9 mg, 3%), **6** (118 mg, 38%), **8** (23 mg, 9%) and **9** (32 mg, 14%). 3,4,5,8-Tetrachloro-6,7-dimethoxy-2-methoxycarbonyl-2*H*-1,2-benzothiazine (**4**): Yellow

amorphous. IR ($CHCl_3$): 1720. ^{1}H-NMR: 4.00 (s, 6H), 3.95 (s, 3H). ^{13}C-NMR: 183.8, 162.3, 153.3, 150.7, 129.7, 127.9, 127.5, 121.1, 86.6, 61.4x2, 54.6. MS: *m/z* 403 (M^+ for ^{35}Cl), 405 (M^++2), 407 (M^++4). HRMS: Calcd for $C_{12}H_9NO_4Cl_4S$: 402.9004. Found: 402.8997. 3,3,4,7-Tetrachloro-5,6-dimethoxybenzo-[*b*]thiophen-2(3*H*)-one (**5**): Pale yellow gum. IR (KBr): 1730. ^{1}H-NMR: 4.02 (s, 3H), 3.96 (s, 3H). ^{13}C-NMR: 190.3, 153.3, 150.3, 128.2, 127.6, 127.4, 121.4, 82.7, 61.4x2. MS: *m/z* 346 (M^+ for ^{35}Cl), 348 (M^++2), 350 (M^++4). HRMS: Calcd for $C_{10}H_6O_3Cl_4S$: 345.8789. Found: 345.8733. Methyl (3,4,7-trichloro-5,6-dimethoxybenzo[*b*]thienyl)carbamate (**6**)**:** Pale yellow prisms. mp 170-172°C (Et_2O-hexane). IR (KBr): 3400, 1740. ^{1}H-NMR: 7.53 (br s, 1H), 3.96 (s, 3H), 3.94 (s, 3H), 3.90 (s, 3H). ^{13}C-NMR: 153.1, 149.5, 147.1, 136.2, 128.8, 126.6, 119.8, 105.1, 102.0, 61.6, 61.2, 53.5. MS: *m/z* 369 (M^+ for ^{35}Cl), 371 (M^++2), 373 (M^++4). HRMS: Calcd for $C_{12}H_{10}NO_4Cl_3S$: 368.9393. Found: 368.9392. *Anal. Calcd* for $C_{12}H_{10}NO_4Cl_3S$: C, 38.89; H, 2.72; N, 3.78. Found: C, 38.61; H, 2.76; N, 3.75. Methyl 1-chloro-2-(6-chloro-3,4-dimethoxyphenyl)ethylcarbamate (**8**): Reddish purple gum. IR ($CHCl_3$): 3450, 1725. ^{1}H-NMR: 7.02 (s, 1H), 6.84 (s, 1H), 5.68-5.35 (m, 1H), 5.10 (br s, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.81-3.58 (m, 2H), 3.67 (s, 3H). ^{13}C -NMR: 156.7, 149.7, 148.3, 127.5, 124.4, 112.2, 110.7, 58.3, 56.2x2, 52.4, 47.6. MS: *m/z* 307 (M^+ for ^{35}Cl), 309 (M^++2), 311 (M^++4). Methyl 2-(6-chloro-3,4-dimethoxyphenyl)-ethylcarbamate (**9**): Light yellow prisms. mp 76-78°C (Et_2O-hexane). IR (KBr): 3340, 1695. ^{1}H-NMR: 6.84 (s, 1H), 6.70 (s, 1H), 4.89 (br s, 1H), 3.85 (s, 6H), 3.67 (s, 3H), 3.59-3.21 (m, 2H), 3.05-2.72 (m, 2H). ^{13}C -NMR: 156.9, 148.1, 147.7, 128.0, 124.8, 113.3, 112.5, 66.0x2, 51.9, 40.8, 33.4. MS: *m/z* 273 (M^+ for ^{35}Cl), 275 (M^++2). HRMS: Calcd for $C_{12}H_{16}NO_4Cl$: 273.0767. Found: 273.0772.

ii) A mixture of $SOCl_2$ (3 mL, 41 mmol) and **1** (200 mg, 0.83 mmol) was heated in a sealed tube at 100°C for 5 h and worked up as described above to give **4** (186 mg, 55%), **5** (12 mg, 4%), **6** (22 mg, 7%) and **10** (56 mg, 18%). 1,2,2-Trichloro-*N*-methoxycarbonyl-2-(6-chloro-3,4-dimethoxyphenyl)ethylimine (**10**): Pale yellow gum. IR ($CHCl_3$): 1750. ^{1}H-NMR: 7.62 (s, 1H), 6.93 (s, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 3.91 (s, 3H). ^{13}C -NMR: 157.1, 152.6, 149.8, 148.5, 128.2, 124.5, 114.2, 113.1, 88.1, 56.2x2, 55.4. MS: *m/z*

373 (M^+ for ^{35}Cl), 375 (M^++2), 377 (M^++4).

iii) A solution of **1** (200 mg, 0.83 mmol) and $SOCl_2$ (1.5 mL, 21 mmol) in octane (1.5 mL) was heated in a sealed tube at 100°C for 1 h. After cooling, the reaction mixture was poured into water (50 mL) and extracted with $CHCl_3$. The extract was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was chromatographed with AcOEt-hexane (1:2), the solvent of the fraction was evaporated. The crude product was purified by MPLC with AcOEt-hexane (1:4, 1:1) to give **6** (28 mg, 9%), **7** (79 mg, 28%) and **9** (46 mg, 20%). Methyl (3,7-dichloro-5,6-dimethoxybenzo[*b*]thienyl)carbamate (**7**): Pale yellow gum. IR ($CHCl_3$): 3450, 1730. ^{1}H-NMR: 7.37 (br s, 1H), 7.00 (s, 1H), 3.95 (s, 3H), 3.91 (s, 3H), 3.89 (s, 3H). ^{13}C -NMR: 153.1, 152.9, 143.5, 134.5, 130.5, 124.0, 121.5, 102.4, 101.1, 61.2, 56.3, 53.5. MS: *m/z* 335 (M^+ for ^{35}Cl), 337 (M^++2), 339 (M^++4). HRMS: Calcd for $C_{12}H_{11}NO_4Cl_2S$: 334.9783. Found: 334.9756.

iv) A solution of **1** (200 mg, 0.83 mmol) and $SOCl_2$ (1.5 mL, 21 mmol) in octane (1.5 mL) was heated in a sealed tube at 100°C for 5 h and worked up as described above to give **4** (102 mg, 30%), **5** (15 mg, 5%), **6** (71 mg, 23%) and **10** (16 mg, 5%).

Reaction of Methyl 2-(3-methoxyphenyl)ethylcarbamate (11) with $SOCl_2$ i) A mixture of **11** (300 mg, 1.44 mmol) and $SOCl_2$ (3.1 mL, 42 mmol) was stirred in a sealed tube at 100°C for 6 h. The mixture was concentrated *in vacuo* and purified by CC with AcOEt-hexane (1:8) to give **12** (29 mg, 5%), **13** (60 mg, 12%), **14** (32 mg, 8%) and **15** (26 mg, 7%). 3,4,5,7-Tetrachloro-6-methoxy-2-methoxy-carbonyl-2*H*-1,2-benzothiazine (**12**): Yellow gum. IR ($CHCl_3$): 1690. ^{1}H-NMR: 7.33 (s, 1H), 3.99 (s, 3H), 3.96 (s, 3H). ^{13}C-NMR: 184.5, 162.3, 152.9, 133.4, 131.7, 130.0, 129.7, 122.4, 85.5, 61.1, 60.3. MS: m/z 373 (M^+ for ^{35}Cl), 375 (M^++2), 377 (M^++4). HRMS: Calcd for $C_{11}H_7NO_3Cl_4S$: 372.8900. Found: 372.8950. Methyl (3,4,6-trichloro-5-methoxybenzo[*b*]thienyl)carbamate (**13**): Light yellow prisms. mp 179-181°C (Et_2O-hexane). IR (KBr): 1730. ^{1}H-NMR: 7.62 (s, 1H), 7.55 (br s, 1H), 3.92 (s, 3H), 3.89 (s, 3H). ^{13}C-NMR: 153.1, 150.7, 136.6, 129.8, 129.7, 125.1, 121.8, 121.7, 101.3, 60.9, 53.6. HRMS: Calcd for $C_{11}H_8NO_3Cl_3S$: 338.9288. Found: 338.9278. Methyl 2-(2,6-dichloro-3-methoxyphenyl)ethylcarbamate

(**14**): Orange gum. IR ($CHCl_3$): 3450, 1720. ^{1}H-NMR: 7.25 (d, *J* = 8.9 Hz, 1H), 6.77 (d, *J* = 8.9 Hz, 1H), 4.82 (br s, 1H), 3.88 (s, 3H), 3.66 (s, 3H), 3.55-3.32 (m, 2H), 3.32-3.05 (m, 2H). ^{13}C -NMR: 157.0, 154.2, 135.8, 127.9, 126.6, 124.1, 110.8, 56.4, 52.0, 39.5, 31.8. HRMS: Calcd for $C_{11}H_{13}NO_3Cl_2$: 277.0273. Found: 277.0300. Methyl 2-(4,6-dichloro-3-methoxyphenyl)ethylcarbamate (**15**): Orange gum. IR ($CHCl_3$): 3450, 1720. ^{1}H-NMR: 7.37 (s, 1H), 6.78 (s, 1H), 4.76 (br s, 1H), 3.88 (s, 3H), 3.67 (s, 3H), 3.59-3.19 (m, 2H), 3.19-2.78 (m, 2H). ^{13}C -NMR: 157.1, 153.8, 135.9, 130.5, 125.3, 121.4, 114.1, 56.4, 52.2, 40.5, 34.0. HRMS: Calcd for $C_{11}H_{13}NO_3Cl_2$: 277.0272. Found: 277.0305.

ii) A mixture of **11** (300 mg, 1.44 mmol) and $SOCl_2$ (3.1 mL, 42 mmol) was stirred in a sealed tube at 100°C for 21 h and worked up as described above to give **12** (74 mg, 14%).

iii) A solution of **11** (300 mg, 1.44 mmol) and $SOCl_2$ (3.1 mL, 42 mmol) in octane (3 mL) was heated in a sealed tube at 100°C for 9 h. The mixture was concentrated *in vacuo* and subjected to CC with AcOEt-hexane (1:8) to give **12** (78 mg, 16%), **13** (28 mg, 6%) with recovery of **11** (122 mg, 41%).

iv) A solution of **11** (300 mg, 1.44 mmol) and $SOCl_2$ (3.1 mL, 42 mmol) in octane (3 mL) was heated in a sealed tube at 100°C for 20 h and worked up as described above to give **12** (113 mg, 19%) and **13** (39 mg, 8%).

Reaction of Methyl 2-(4-methoxyphenyl)ethylcarbamate (16) with $SOCl_2$ A solution of **16** (300 mg, 1.44 mmol) and $SOCl_2$ (3.1 mL, 42 mmol) in octane (3 mL) was heated in a sealed tube at 100°C for 29 h. The mixture was concentrated *in vacuo* and the resulting residue was purified by CC with AcOEt-hexane (1:5) to give **17** (18 mg, 7%) with recovery of **16** (246 mg, 82%). *N*,*N*'-Bis(4-methoxy-phenylethyl)-*N*-methoxycarbonylurea (**17**): Colorless gum. IR ($CHCl_3$): 3300, 1730, 1680. ^{1}H-NMR: 8.62 (br t, *J* = 4.0 Hz, 1H), 7.38-6.71 (m, 8H), 4.10-3.31 (m, 4H), 3.78 (s, 6H), 3.69 (s, 3H), 2.98-2.60 (m, 4H). ^{13}C -NMR: 158.2x2, 156.5, 154.1, 131.0, 130.9, 129.9x2, 129.7x2, 113.9x2, 113.8x2, 55.2x2, 53.3, 45.4, 42.2, 35.0, 34.5. MS: m/z 386 (M^+). HRMS: Calcd for $C_{21}H_{26}N_2O_5$: 386.1842. Found: 386.1863.

Reaction of Methyl 2-phenylethylcarbamate (18) with $SOCl_2$ A solution of **18** (300 mg, 1.7

mmol) and $SOCl_2$ (3.6 mL, 49 mmol) in octane (3.6 mL) was heated in a sealed tube at 100°C for 140 h. The resulting mixture was concentrated *in vacuo* and the residue was purified by CC with AcOEt-hexane (1:6) to give **19** (39 mg, 14%) with recovery of **18** (149 mg, 50%). *N*-Methoxycarbonyl-*N,N'*-bis-(phenylethyl)urea (**19**): Colorless gum. IR ($CHCl_3$): 3300, 1720, 1680. ^{1}H-NMR: 8.64 (br t, J = 4.0 Hz, 1H), 7.41-7.08 (m, 10H), 4.12-3.80 (m, 2H), 3.65 (s, 3H), 3.70-3.39 (m, 2H), 2.99-2.72 (m, 4H). ^{13}C-NMR: 156.5, 154.1, 139.0, 138.9, 128.9x2, 128.7x2, 128.5x2, 128.3x2, 126.4, 126.3, 53.3, 45.2, 42.0, 35.9, 35.5. HRMS: Calcd for $C_{19}H_{22}N_2O_3$: 326.1631. Found: 326.1641.

Reaction of Methyl 2-(2-chloro-4,5-dimethoxyphenyl)ethylcarbamate (9) with $SOCl_2$ A mixture of **9** (200 mg, 0.73 mmol) and $SOCl_2$ (3 mL, 41 mmol) was stirred in a sealed tube at 100°C for 5 h. The reaction mixture was poured into water (50 mL) and extracted with AcOEt. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was purified by CC with AcOEt-hexane (1:2), the solvent of the fraction was evaporated. The crude product was purified by MPLC with AcOEt-hexane (1:2) to give **20** (101 mg, 43%), **10** (57 mg, 21%) and **21** (47 mg, 19%). Methyl 2-chloro-2-(6-chloro-3,4-dimethoxyphenyl)-1-oxoethylcarbamate (**20**): Light yellow gum. ^{1}H-NMR: 8.19 (br s, 1H), 7.02 (s, 1H), 6.88 (s, 1H), 6.31 (s, 1H), 3.88 (s, 6H), 3.82 (s, 3H). ^{13}C -NMR: 166.3, 151.1, 150.3, 148.3, 125.3, 124.6, 112.3, 111.8, 56.9, 56.2x2, 53.4. MS: *m/z* 321 (M^+ for ^{35}Cl), 323 (M^++2), 325 (M^++4). Methyl 1,2-dichloro-2-(6-chloro-3,4-dimethoxyphenyl)ethenylcarbamate (**21**): Yellow gum. ^{1}H-NMR: 6.85 (s, 2H), 3.88 (s, 3H), 3.85 (s, 3H), 3.66 (s, 3H). ^{13}C -NMR: 153.6, 150.4, 147.9, 129.2, 125.9, 125.7, 124.2, 112.3x2, 56.2x2, 53.1. MS: *m/z* 339 (M^+ for ^{35}Cl), 341 (M^++2), 343 (M^++4).

Reaction of Methyl (3,4,7-trichloro-5,6-dimethoxybenzo[*b*]thienyl)carbamate (6) with $SOCl_2$ A mixture of **6** (60 mg, 0.16 mmol) and $SOCl_2$ (0.35 mL, 5 mmol) was stirred in a sealed tube at 100°C for 12 h. The resulting mixture was concentrated *in vacuo* and the residue was purified by CC with AcOEt-hexane (1:10) to give **4** (10 mg, 15%), **5** (9 mg, 16%), with recovery of **6** (5 mg, 8%).

REFERENCES AND NOTES

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4. T. Higa and A. J. Krubsack, *J. Org. Chem.*, 1975, **40**, 3037.
5. Bell reported that sulfinyl chloride, sulfide, disulfide derivatives were obtained by the reaction of aromatic methyl ether with thionyl chloride. The intermediate in our case is considered that one of these functions, though it is not clear.