Studies on Silyl Furans. II [1]. Halodesilylation of 2-Trimethylsilyl-3,4-bis(methoxycarbonyl)furans

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Reactions of 2-trimethylsilyl-3,4-bis(methoxycarbonyl)furans **1a,b** with sulfuryl chloride, bromine, and iodine monochloride in acetonitrile afforded the corresponding 2-halo-3,4-bis(methoxycarbonyl)furans **2a-f** *via* chloro-, bromo-, and iododesilylation in good yields, respectively. However, the reaction of **1a** with bromine in carbon tetrachloride mainly gave 2-bromo- **2b** and 2-bromo-5-trimethylsilyl-3,4-bis(methoxycarbonyl)furan (**3**) in 37% and 45% yields. Similarly, the reaction of **1a** with iodine monochloride afforded **1a**, 2-chloro- **2a** and 2-iodo-3,4-bis(methoxycarbonyl)furan (**2c**) in 50%, 27%, and 23% yield.

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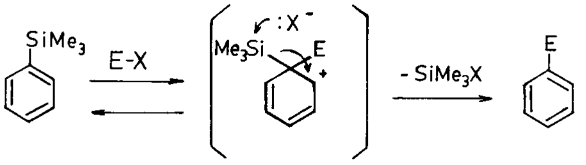
In the electrophilic substitutions of furans, it is difficult to control the reaction products since the furan ring is very susceptible to electrophiles, and cleavage and polymerization of the furan ring often occur under certain reaction conditions. Since the furan ring has dienic character, nitration [2] and bromination [3] of furan afford the 2-nitro and 2-bromofuran *via* the corresponding adducts in most cases. Also, Friedel-Crafts alkylation and acylation of furans [4] have given 2-alkyl and 2-acylfurans, but Friedel-Crafts acylation of alkyl 2-furoate which possesses an electron withdrawing group only afford the expected methyl 5-acyl-2-furoates in small quantity and/or other products [5-7]. On the other hand, it has been well known that the reactions of *C*-trimethylsilylated aromatic and heteroaromatic compounds [8] with various electrophiles occur, in general, at the ring carbon carrying the trimethylsilyl group to give ipso substituted products [9-21].

Scheme 1



[E⁺= acyl, alkyl, halogen, nitro, etc]

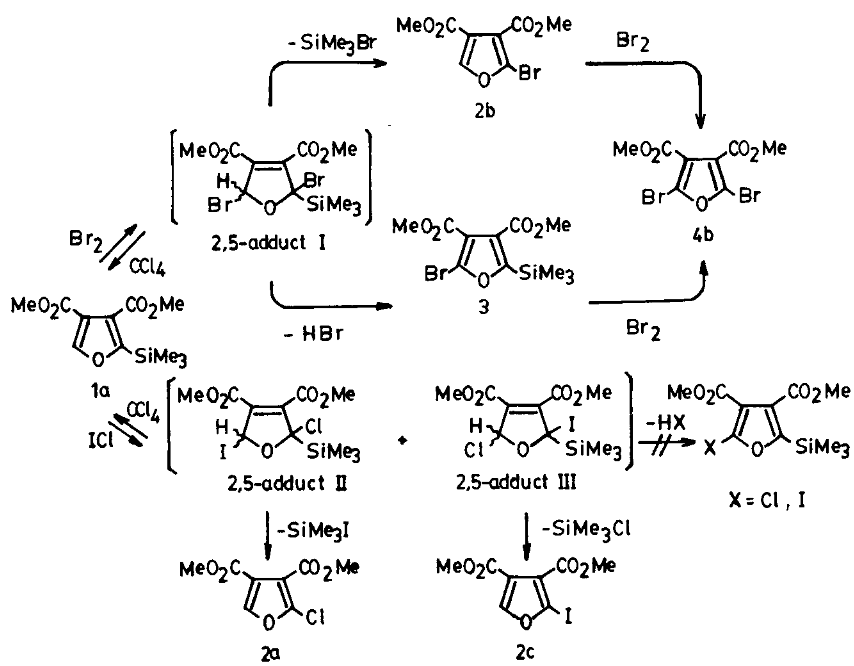
Thus, when the trimethylsilyl group is used as the leaving group of the electrophilic substitutions, it is expected that acidification of the reaction medium by protic acids (HX) can be avoided which are generated by the usual aromatic electrophilic substitution. It seemed feasible that the reactions of silylfurans with appropriate electrophiles would afford the expected substituted furans by depressing cleavage and polymerization of the furan ring and further reaction of the products, thus the authors were interested in investigating electrophilic substitutions of 2-trimethylsilylfurans.

Regarding the substitutions of trimethylsilylfurans, in 1948 Benkeser and Currie first reported that the reaction of 2-trimethylsilylfuran with acetic anhydride afforded 2-acetyl-5-trimethylsilylfuran (yield = *ca.* 25%) in the presence of a catalytic amount of iodine [22]. More recently, Lukevics *et al* have reported that 2-trimethylsilylfuran was treated with nitronium tetrafluoroborate to give 2-nitro- and 2-nitro-5-trimethylsilylfuran in 10% and 3% yields and with chloramine T in the presence of sodium picrate as the catalyst afforded 3-chloro- and 5-chloro-2-trimethylsilylfuran in 1.4% and 5.6% yields [23].

The authors first attempted to carry out the reaction of 2-trimethylsilylfuran with some electrophiles (X^+, NO_2^+, RCO^+, R^+, and *etc.*), but only decomposed products were obtained. Next, 2-trimethylsilylfurans, which are stabilized to acidic media by introducing an electron withdrawing group to the furan ring, were taken up. On the other hand, the authors have recently prepared 2-trimethylsilyl-3,4-bis(methoxycarbonyl)furan (**1a**) [1] as 2-trimethylsilylfurans and found that this compound easily underwent protodesilylation in basic aqueous media [24].

Thus, the trimethylsilyl group in compounds **1a,b** is expected to react with various electrophiles. In this paper, the authors were interested in the reactions of **1a,b** with various electrophiles excluding protons. The electrophilic substitutions of **1a** with each halogenating reagent (sulfuryl chloride, bromine, and iodine monochloride) were examined. In the first place, treatment of **1a** with sulfuryl chloride in carbon tetrachloride gave no reaction product and **1a** was recovered in near quantitative yield. Next, **1a** was treated with bromine at ambient temperature for 10 hours to give an oily product. The oily product was chromatographed over silica gel using dichloromethane as eluent to give of **3** (bp 130-135°/3 Torr, $C_{11}H_{15}O_5BrSi$), in small amount as a colorless liquid. Compound **3** showed the trimethylsilyl group (850 cm^{-1}) and the ester group (1730 cm^{-1}) absorption bands in the ir spectrum. Also, the ^{1}H nmr of **3** showed the trimethylsilyl group (9H, s, 0.33) and the methyl ester groups (each 3H, each s, 3.77 and

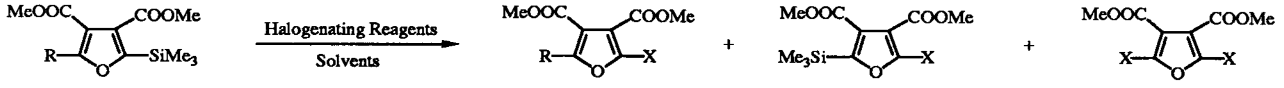
Scheme 2



3.79). In the aromatic region of the spectrum, the signal of the furan ring was not observed. The mass spectrum of **3** showed the molecular ion m/z 336 and 334 (relative intensity 1:1) indicating the presence of one bromine atom and the base peak m/z 321 and 319 (loss of methyl group from the molecular ion) which showed the presence of the trimethylsilyl group in the structure of **3**. From the above spectral data and elemental analysis, **3** was assigned the structure of 2-bromo-5-trimethylsilyl-3,4-bis(methoxycarbonyl)furan which was brominated at the five position of

Table 1

Reaction of 2-Trimethylsilyl-3,4-bis(methoxycarbonyl)furans 1a,b with Sulfuryl Chloride, Bromine, and Iodine Monochloride in Carbon tetrachloride and Acetonitrile



1 2 3 4

a: R = H
b: R = Me

a, R = H, X = Cl, d, R = Me, X = Cl
b, R = H, X = Br, e, R = Me, X = Br
c, R = H, X = I, f, R = Me, X = I

a, X = Cl
b, X = Br

Entry [a]	Substrate	Reagent/Solvent	Products
1	**1a**	SO_2Cl_2/CCl_4	**1a** [c]
2	**1a**	Br_2/CCl_4	**1a** [10], **2a** [45], **3** [37] (+) [d] **4b** [8]
3	**1a**	ICl/CCl_4	**1a** [50], **2a** [27], **2c** [23]
4	**1a**	SO_2Cl_2/CH_3CN	**2b** [90] (68), 4a [10] (+) [d]
5	**1a**	Br_2/CH_3CN	**2b** (76)
6	**1a**	ICl/CH_3CN	**2c** (64)
7	**1b**	SO_2Cl_2/CH_3CN	**2d** (73)
8	**1b**	Br_2/CH_3CN	**2e** (68)
9	**1b**	ICl/CH_3CN	**2f** (74)

[a] Reactions were carried out at ambient temperature for 10 hours (Entries 1,2), 20 hours (Entry 3), and one-half hour (Entries 4-9). [b] Isolated yields were shown in parenthesis and relative yields by means of glc were shown in square brackets. [c] Compound **1a** was recovered in quantitative yield. [d] Plus sign means less than 1% yield.

Table 2

Reactions of Dimethyl Furan-3,4-Dicarboxylate (5) with Sulfuryl Chloride, Bromine, and Iodine Monochloride in Acetonitrile

5 2 4b

a, X = Cl
b, X = Br

Entry	Reagent	Reaction Temeperature (°C)	Conditions Time hours	Products [a] (%)
1	SO_2Cl_2	20	19	5 (90) [b]
2	Br_2	20	46	5 [50], **2b** [37], **4b** [13]
3	ICl	20	10	5 [79], **2a** [21]

[a] Relative yields were determined by glc. [b] Isolated yield are shown.

1a. Because other elutions were difficult to further fractionate, the eluant was subjected to gc-ms to carry out separation and identification. The gc-ms spectrum of the eluant showed the molecular ions **A** m/z 256, **B** m/z 264 and 262 (relative intensity 1:1), **C** m/z 344, 342, and 340 (relative intensity 1:2:1), and **3** m/z 336 and 334 (relative intensity 1:1), respectively. The component of peak **A** was identified with **1a** by comparison with the mass spectrum of **1a**. The component of peak **B** was assumed to be the mono-bromo compound because the abundances of the two isotopic molecular ions are almost equal in intensity. Thus, the component of peak **B** was proposed to be 2-bromo-3,4-bis(methoxycarbonyl)furan (**2b**) (mp 53-55°, Table 1, entry 5, experimental) by comparison with the mass spectral fragmentation pattern of **2b** which was prepared by bromodesilylation of **1a** as described hereafter. In addition, the component of peak **C** was assumed to be a dibromo compound as the isotopic abundance of three molecular ions showed the intensity of 1:2:1. Thus, the component of peak **C** was identified as 2,5-dibromo-3,4-bis(methoxycarbonyl)furan (**4b**) (mp 110-111°, experimental) as the mass spectral fragmentation pattern of **4b** equals that of peak **C**. The results of this reaction are as follows: When a solution of bromine in carbon tetrachloride was added dropwise to a solution of **1a** in carbon tetrachloride, the reddish brown color of bromine immediately faded, a white precipitate deposited after a few minutes but the precipitate disappeared after ten minutes. Although the detailed mechanism of formation of these compounds, **2b**, **3**, and **4b**, are not clear, one might assume the reaction pathway is that shown in Scheme 2. Bromine adds at the 2-and 5-positions of **1a** to form the 2,5-adduct **I** (white precipitate from which **2b** and **3** might be produced by loss of hydrogen bromide and/or trimethylsilyl bromide). Treatment of **1a** with iodine monochloride in carbon tetrachloride at ambient temperature for 20 hours gave an oily product. Because the oily product were difficult to fractionate into each component, they were subjected to gc-ms to carry out the separation and identification. The gc-ms showed the molecular ions **A** m/z 220 and 218 (relative intensity 1:2.8), **B** m/z 256, and **C** m/z 310. The component of peak **A** was assumed to be a monochloro compound by the isotopic abundance of the molecular ion. Thus, the component of peak **A** was assigned the structure 2-chloro-3,4-bis-(methoxycarbonyl)furan (**2a**) (bp 101-103°/3 Torr, Table 1 entry 4, experimental) by comparison with the mass fragmentation of **2a** which was prepared by chlorodesilylation of **1a** as described hereafter. The component of peak **B** was identified as **1a** by comparison with mass spectrum of **1a**. In addition, the component of peak **C** was assumed to be a monoiodo compound (iodine atom is monoisotopic) by not quite showing the isotopic abundance of the molecular ion. Thus, the component of peak **C** was identified as 2-iodo-3,4-bis-(methoxycarbonyl)furan (**2c**) (mp 63-65°, Table 1, entry 6, experimental) by comparison with mass spectral fragmentation pattern of **2c** which was prepared by iododesilylation of **1a** as described below. Thus, the iodination of **1a** resulted in **2a** besides **2c**, differing from the usual manner in iodination of aromatic compounds or trimethylsilyl aromatic compounds by iodine monochloride in carbon tetrachloride [25-31]. Although the detailed mechanisms for formation of **2a** is not clear, it might be regarded that iodine monochloride was initially added to the 2- and 5-positions of **1a** to give two types of 2,5-adducts **II** and **III**, followed by **II** and **III** furnishing **2a** and **2c** presumably through elimination of trimethylsilyl iodide or trimethylsilyl chloride, respectively (Scheme 2).

Next, in order to examine the solvent effect on this reaction, **1a**, was allowed to react with sulfuryl chloride in an aprotic polar solvent such as acetonitrile at ambient temperature for one half hour to give expected 2-chloro-3,4-bis(methoxycarbonyl)furan (**2a**) in 68% yields. In the same manner, **1a** was allowed to react with bromine and iodine monochloride to afford the corresponding 2-bromo-**2b** and 2-iodo-3,4-bis(methoxycarbonyl)furan (**2c**) in 76% and 64% yields. Also, the reactions of **1b** with sulfuryl chloride, bromine, and iodine monochloride proceeded smoothly, in acetonitrile to afford the corresponding 2-chloro- **2d**, 2-bromo- **2e**, and 2-iodo-5-methyl-3,4-bis(methoxycarbonyl)furan (**2f**) in 73%, 68%, and 74% yields, respectively. As described above, it was demonstrated that the halodesilylations of these 2-trimethylsilylfurans **1** with various halogenating reagents in a nonpolar solvent such as carbon tetrachloride nonselectively proceeded to give many products, whereas in an aprotic polar solvent such as acetonitrile the similar reactions predominantly afford 2-halodesilylated products **2** in good yields. These results are summarized in Table 1.

Finally, the halogenation of 3,4-bis(methoxycarbonyl)furan (**5**) was investigated to find how the trimethylsilyl group behaves as a potential leaving group. That is, the treatment of **5** with sulfuryl chloride, bromine, and iodine monochloride in carbon tetrachloride gave only unchanged **5** yield = *ca.* 80%) in all cases. Also, the acetonitrile, no chlorination at the 2-position of the furan ring was observed. In the bromination, in spite of prolonged reaction times, **2b** was obtained in 37% yield together with unchanged **5** and 2,5-dibromo-3,4-bis(methoxycarbonyl)furan (**4b**) in 50% and 13% yields. Reaction of **5** with iodine monochloride in acetonitrile afforded **2a** and unchanged **5** in 21% and 79% yields. The formation of **2a** suggests that **5** reacts with chloride, presumably generated by dissociation of iodine monochloride [32]. These results (in Table 2) clearly show that the halodesilylation of these furans is potentially useful for the synthesis of halofurans. The halodesilylation of **1a,b** appears to be very attractive in the following respects, in comparison with the methods [33] hitherto used, a) the procedure is simple, b) the reaction conditions are mild, c) the yields were moderate in most cases. The application of this methodology for the electrophilic substitution of **1a,b** and other trimethylsilylated furans with various electrophiles is currently under study. These results will be reported in due course.

EXPERIMENTAL

All melting points (open capillaries) and boiling points were uncorrected. The ^{1}H nmr spectra were determined at 60 MHz with Nippon Denshi JNM PMX-60SI NMR spectrometer with TMS as the internal reference, and the ir spectra were measured in a JASCO IR-810 spectrometer. Mass spectra were obtained on Nippon Denshi DX-300 spectrometer at 70 eV using a direct inlet system. All the extracts were dried over the anhydrous sodium sulfate or magnesium sulfate.

General Method for Halodesilylation of 2-Trimethylsilyl-3,4-bis(methoxycarbonyl)furan (**1a**) in Carbon Tetrachloride (Entries 1-3).

A solution of 10 mmoles of the halogenating reagent (sulfuryl chloride, bromine and iodine monochloride) in 3 ml of carbon tetrachloride was added dropwise within 10 minutes to a solution of 10 mmoles of 2-trimethylsilyl-3,4-bis(methoxycarbonyl)furan (**1a**) in 10 ml of carbon tetrachloride with stirring at ambient temperature. After the solution was stirred for the prescribed time (as shown in Table 1, entries 1-3), the reaction mixture was poured into ice-water and was extracted with dichloromethane. The extract was washed with 10% sodium thiosulfate solution, water, and brine, and evaporated in vacuum to leave the products as shown Table 1.

Isolation of **3** from The Reaction Mixture of Entry 2 in Table 1.

The mixture of **1a**, **2b**, **3**, and **4b** (Table 1, Entry 2) was separated by column chromatography (silica gel: wako gel C-300) with dichloromethane as the eluant to give **3** in a small amount as a colorless liquid, bp 130-135°; ir (sodium chloride): 2950 cm^{-1} (SiMe$_3$), 1730 cm^{-1} (C=O); ^{1}H nmr (carbon tetrachloride): δ 0.33 (9H, s, SiMe$_3$), 3.77 and 3.79 (each 3H, each s, 2 x CH$_2$Me) ppm; ms: m/z 336/334 (M$^+$ 10.34/9.80%), 321/319 (M$^+$-15, 100/96.15%).

Anal. Calcd. for $C_{11}H_{15}O_5BrSi$: C, 39.41; H, 4.51. Found: C, 39.45; H, 4.37.

Preparation of Diethyl 2,5-Dibromofuran-3,4-dicarboxylate (**4b**).

To a solution of **1a** (2.0 g, 7.8 mmoles) in carbon tetrachloride (30 ml) was added a solution of bromine (2.5 g, 15.6 mmoles) in carbon tetrachloride (10 ml). After refluxing for 4 hours, the reaction mixture was poured into ice-water, and was extracted with dichloromethane. The extract was washed with 10% sodium thiosulfate solution, water and brine, and evaporated in vacuum to leave a residue that was recrystallized from hexane to give **4b** 1.5 g (56%) as colorless prisms, mp 110-111°; ir (potassium bromide): 1720 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 3.81 (6H, s, 2 x CO$_2$Me) ppm; ms: m/z 344/342/340 (M$^+$, 24.12/47.24/24.62%), 311 (M$^+$-31, 100%).

Anal. Calcd. for $C_8H_6O_5Br_2$: C, 28.10; H, 1.77. Found: C, 27.80; H, 1.75.

Halodesilylation of 2-Trimethylsilyl-3,4-bis(methoxycarbonyl)furans **1a,b** in Acetonitrile (Entries 4-9 in Table 1). General Method.

A solution of 10 mmoles of the halogenating reagent (sulfuryl chloride, bromine, and iodine monochloride) in 3 ml of acetonitrile was added dropwise within 10 minutes to a solution of 2-trimethylsilyl-3,4-bis(methoxycarbonyl)furans **1a,b** in 10 ml of acetonitrile at ambient temperature. After stirring for one half hour, the reaction mixture was poured into ice-water and extracted with dichloromethane. The extract was washed with 10% sodium thiosulfate solution, water, and evaporated in vaccum to leave a residue that was recrystallized from cyclohexane to give in 64-76% yields of the corresponding 2-halo-3,4-bis(methoxycarbonyl)furans **2a-f**, respectively.

2-Chloro-3,4-bis(methoxycarbonyl)furan (**2a**).

This compound had the following physical properties, bp 101-103°/3 Torr, colorless liquid; ir (sodium chloride): 1740 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 3.69 and 3.73 (each 3H, each s, 2 x CO$_2$Me), 7.66 (1H, s, furyl 5-H) ppm; ms: m/z 220/218 (M$^+$, 10.56/29.29%), 187 (M$^+$-31, 100%).

Anal. Calcd. for $C_8H_7O_5Cl$: C, 43.96; H, 3.23. Found: C, 43.92; H, 3.19.

2-Bromo-3,4-bis(methoxycarbonyl)furan (**2b**).

This compound had the following physical properties, mp 53-55°, colorless prisms (from cyclohexane); ir (potassium bromide): 1730 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 3.77 and 3.80 (each 3H, each s, 2 x CO_2Me), 7.85 (1H, s, furyl 5-H) ppm; ms: m/z 264/262 (M^+, 39.96/38.48%), 233 (M^+-31, 100%).

Anal. Calcd. for $C_8H_7O_5Br$: C, 36.53; H, 2.68. Found: C, 36.38; H, 2.64.

2-Iodo-3,4-bis(methoxycarbonyl)furan (**2c**).

This compound had the following physical properties, mp 63-65°, colorless prisms (from cyclohexane); ir (potassium bromide): 1730 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 3.71 and 3.77 (each 3H, each s, 2 x CO_2Me), 7.89 (1H, s, furyl 5-H) ppm; ms: m/z 310 (M^+, 80.1%), 279 (M^+-31, 100%).

Anal. Calcd. for $C_8H_7O_5I$: C, 30.99; H, 2.28. Found: C, 31.23; H, 2.26.

2-Chloro-5-methyl-3,4-bis(methoxycarbonyl)furan (**2d**).

This compound had the following physical properties, mp 56-58°, colorless prisms (from cyclohexane); ir (potassium bromide): 1730 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 2.39 (3H, s, furyl 5-Me), 3.72 and 3.76 (each 3H, each s, 2 x CO_2Me) ppm; ms: m/z 234/232 (M^+, 9.23/29.18%), 200 (M^+-33, 100%).

Anal. Calcd. for $C_9H_9O_5Cl$: C, 46.47; H, 3.90. Found: C, 46.38; H, 3.88.

2-Bromo-5-methyl-3,4-bis(methoxycarbonyl)furan (**2e**).

This compound had the following physical properties, mp 72-73°, colorless prisms (from cyclohexane); ir (potassium bromide): 1720 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 2.43 (3H, s, furyl 5-Me), 3.74 and 3.77 (each 3H, each s, 2 x CO_2Me) ppm; ms: m/z 278/276 (M^+, 27.58/28.33%), 246 (M^+-32, 100%).

Anal. Calcd. for $C_9H_9O_5Br$: C, 39.02; H, 3.27. Found: C, 39.00; H, 3.26.

2-Iodo-5-methyl-3,4-bis(methoxycarbonyl)furan (**2f**).

This compound had the following physical properties, mp 74-76°, colorless prisms (from cyclohexane); ir (potassium bromide): 1710 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 2.47 (3H, s, furyl 5-Me), 3.74 and 3.79 (each 3H, each s, 2 x CO_2Me) ppm; ms: m/z 324 (M^+, 46.78%), 292 (M^+-32, 100%).

Anal. Calcd. for $C_9H_9O_5I$: C, 33.36; H, 2.80. Found: C, 33.35; H, 2.73.

Isolation of 2,5-Dichloro-3,4-bis(methoxycarbonyl)furan (**4a**) from Reaction Mixture of Entry 4 in Table 1.

The reaction mixture of **2a** and **4a** (Entry 4, Table 1) was purified by column chromatography (silica gel: wako gel C-300) with dichloromethane as eluant to give **4a** in a trace amount, colorless prisms, mp 63-68° (from petroleum ether); ir (potassium bromide): 1730 cm^{-1} (C=O); ^{1}H nmr (deuteriochloroform): δ 3.87 (6H, s, 2 x CO_2Me) ppm; ms: m/z 256/254/252 (M^+, 2.16/11.35/-17.56%), 221 (M^+-31, 100%).

Anal. Calcd. for $C_8H_6O_5Cl_2$: C, 37.97; H, 2.39. Found: C, 37.93; H, 2.51.

Preparation of 3,4-Bis(methoxycarbonyl)furan (**5**) by Protodesilylation of **1a** with Potassium Fluoride-Dimethylformamide-Water.

A suspension of potassium fluoride (2 g, 34.4 mmoles) and **1a** (10 g, 39 mmoles) in wet dimethylformamide (100 ml) was stirred for 10 hours at ambient temperature. The reaction mixture was poured into water and was extracted with diethyl ether. The extract was washed with water and brine, and evaporated to leave a residue that was distilled in vacuum to give **5**, 5.0 g (70%) as a colorless liquid, bp 105-108°/2 Torr (lit [25] 102°/6 Torr), which crystallized on standing, colorless prisms, mp 44-46° (lit [25] 45°).

General Method for Halogenation of 3,4-Bis(methoxycarbonylfuran (**5**).

A solution of 2.7 mmoles of the halogenating reagent (sulfuryl chloride, bromine, and iodine monochloride) in 3 ml of acetonitrile was added to a solution of 2.7 mmoles of **5** in 3 ml of acetonitrile with stirring at ambient temperature. After stirring for the appropriate time as shown in Table 2, the reaction mixture was poured into water and was extracted with dichloromethane. The extract was washed with 10% sodium thiosulfate, water and brine, and evaporated in vacuum to leave the mixture of **2**,**4**, unchanged **5** (the relative yields were determined by gc).

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