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ELECTROPHILIC REACTIONS OF TRIHALOGENOMETHANESULFENYL ACETATES AND TRIFLUOROACETATES

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SUMMARY

The stable trihalogenomethanesulfenyl acetates, $AcoscF_nCl_{3-n}$ (2) were prepared by the reaction of the corresponding trihalogenomethanesulfenyl chlorides with sodium acetate. These and fluorochloromethanesulfenyl trifluoracetates $CF_3CooscF_nCl_{3-n}$ (1) added rapidly in trans manner to cyclohexene to yield B-acetoxy and B-trifluoroacetoxy sulfides (3). The trifluoroacetates (1) also reacted with some aromatics containing electron-donating substituents, such as anisole, toluene, p-xylene, mesitylene and pentamethylbenzene, or with electron-rich heteroaromatics, such as thiophene, to give trihalogenomethylmercapto derivatives.

INTRODUCTION

Since Havlik and Kharasch [1] had reported the first sulfenyl acetate, 2,4-dinitrobenzenesulfenyl acetate, Putnam and Sharkey [2] synthesized a number of other sulfenyl carboxylates and found that most of them were quite unstable. It was deduced that the stability of sulfenyl carboxylates correlates to the elec-

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tron-withdrawing ability of the functional group attached to the sulfur. Based on this, Haas and Oh [3] synthesized perfluorochloromethanesulfenyl trifluoroacetates (1), by the reaction of the corresponding sulfenyl chloride with silver trifluoroacetate, which could be distilled without decomposition:

$$CF_{3}COOAg + CF_{n}Cl_{3-n}SCl \longrightarrow AgCl + CF_{3}COOSCF_{n}Cl_{3-n}$$

$$\frac{1}{n} \begin{vmatrix} a & b & c \\ 3 & 2 & 1 \end{vmatrix} (1)$$

RESULTS

In this most recent investigation, we found that trihalogenomethanesulfenyl chlorides also reacted smoothly with sodium acetate to give the corresponding sulfenyl acetates (2):

$$CH_{3}COONa + CF_{n}Cl_{3-n}SC1 \longrightarrow NaCl + CH_{3}COOSCF_{n}Cl_{3-n}$$

$$\frac{2 | a | b | c | d}{n | 3 | 2 | 1 | 0} (2)$$

The reactivity of the sulfenyl chlorides towards acetylation depended on their degree of fluorination. Trifluoromethylsulfenylchloride reacted readily at -20 to 0°C without solvent; however, the reaction with CF_2CISCI and $CFCl_2SCI$ in methylene chloride at room temperature required 5 - 8 h for completion. Under the same conditions, the reaction with CCl_3SCI took more than 24 h. The yield of $CH_3COOSCF_3$ was rather low (ca. 50 %) due to formation of the by-products CF_3SSCF_3 , $CF_3SO_2SCF_3$ and acetic anhydride. Their formation can be explained as follows:

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 $\begin{array}{rcl} \mathrm{CH}_{3}\mathrm{COOSCF}_{3} &+ & \mathrm{CH}_{3}\mathrm{COONa} &\longrightarrow & (\mathrm{CH}_{3}\mathrm{CO})_{2}\mathrm{O} &+ & \langle \mathrm{NaOSCF}_{3} \rangle \\ \mathrm{CF}_{3}\mathrm{SC1} &+ & \langle \mathrm{NaOSCF}_{3} \rangle &\longrightarrow & \mathrm{CF}_{3}\mathrm{SOSCF}_{3} &+ & \underline{\mathrm{NaC1}} \\ \mathrm{2CF}_{3}\mathrm{SOSCF}_{3} &\longrightarrow & \underline{\mathrm{CF}}_{3}\mathrm{SSCF}_{3} &+ & \underline{\mathrm{CF}}_{3}\mathrm{SO}_{2}\mathrm{SCF}_{3} \end{array}$

Reactions of sulfenyl acetates and trifluoroacetates reported in literature [2,3] indicate that compounds of this type can formally be regarded as peroxides and disulfides, which can undergo radical reactions. Accordingly, Putnam and Sharkey [2] and Haas and Oh [3] have studied the decomposition of sulfenyl carboxylates by heating or under UV radiation. Due to the difference in electronegativity between sulfur and oxygen, the O-S bond may be polarized such that sulfenyl carboxylates should undergo some electrophilic reactions. Thus, Havlick and Kharasch [1] found that 2,4-dinitrobenzenesulfenvl acetate added readily to cyclohexene while the addition to ethylene chloride at 60°C required 16 days. Recently, Trost et al. [4] and Morishta [5] reported that the sulfenyl trifluoroacetates CF3COOSC6H5 and CF3COOSCH3, which they postulated to be reactive transient intermediates. added to olefins rapidly under mild conditions. This lead to the conclusion that sulfenyl trifluoroacetates were much more reactive than the corresponding acetates. Therefore, trihalogenomethanesulfenyl trifluoroacetates 1 should also be reactive electrophiles. Indeed, 1 added spontaneously and exothermally to cyclohexene to give the following trans adducts:

+
$$CF_3COOSCF_nCl_{3-n}$$

 $3 | \underline{a} | \underline{b} | \underline{c}$
 $3 | \underline{c} | \underline{c} | \underline{c} | \underline{c}$
 $3 | \underline{c} | \underline{c}$

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Sulfenyl acetates (2) also reacted with cyclohexene, but the reaction proceeded relatively moderately according to:



The reactivity of (2) increased with the number of fluorine atoms, such that ($\underline{4}\underline{d}$) did not react with cyclohexene even after 20 h at 80 - 90°C, although the reaction proceeded smoothly in acetic acid. The strong electrophilic reagent (1) reacted with aromatics containing electron-donating substituents:

ArH + $CF_3COOSCF_nCl_{3-n} \rightarrow CF_3COOH$ ArSC F_nCl_{3-n}



The reaction rate depended both on the electrophilicity of (1) and on the nature of the aromatic compounds.

Anisole, with the strongly electron-donating methoxy group, and the electron rich pentamethylbenzene and mesitylene reacted rapidly with $(\underline{1a})$ at room temperature; however, with (1c) all substitution reactions occured only upon heating or adding catalytic amounts of CF₃COOH. Selectivity of substitution was observed with both enisole and toluene. With (1) the substitution of anisole yielded only para products, while toluene afforded a mixture of both ortho and para isomers (ortho:para = 3:4).

The reaction was carried out <u>in situ</u>, <u>i.e.</u> by addition of the sulfenyl chloride to a suspension of CF_3COOAg in the appropriate aromatic compound.

Thiophene, a heteroaromatic with excess $\tilde{\mu}$ -electrons, was sulfenylated by (<u>1</u>) under mild conditions giving the 2-substituted thiophene (10)



The acetates (2) reacted with thiophene only in the presence of CF $_{\rm 3}{\rm COOH}$.

All previously unreported compounds were characterized by IR, NMR, and mass spectroscopy and by elemental analysis. Known compounds were characterized by comparison of spectroscopic data with those reported in the literature.

The ¹H-NMR spectra of the cyclohexene derivatives showed ABXpatterns and were consistent with those previously reported [5, 6], especially with Morishta's [5] results. Trans configuration was identified from the typical coupling constants (8 - 10 Hz) of the vicinal methine protons. ¹H-NMR spectra of para-trihalogenomethylmercapto anisols showed typical AB-patterns with coupling constants of <u>ca</u>. 9 Hz. The $2-CF_nCl_{3-n}S$ -substituted thiophenes were confirmed by comparison of their IR spectra with those of authentic samples [7].

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 325 infrared spectrophotometer. Liquids were measured as capillary films between KBr plates. Weak bonds and shoulders are not reported.

 $\frac{1}{H-NMR}$ spectra were obtained on a Bruker WP 80 SY. $^{19}F-$ and $^{13}C-$ NMR spectra were obtained on a Bruker WM 250 PFT-spectrometer. All spectra were recorded in CDCl₃ solution, using TMS (^{1}H , ^{13}C) or C₆F₆ (^{19}F)^{*} as internal standards.

<u>Mass spectra</u> were recorded on a Varian MAT-spectrometer CH 7 at an ionization potential of 70 eV and 100 μ Å.

Starting materials: Sulfenyl trifluoroacetates were prepared via literature method [3].

Preparation of Trihalomethanesulfenyl Acetates

A) $2\underline{a}$: CF₃SCl was condensed into a vessel containing sodium acetate at -80°C. The vessel was allowed to stand for 12 h at 0°C. The product was isolated in a -80°C trap via distillation in a conventional Pyrex vacuum apparatus. For further purification, $2\underline{a}$ was redistilled, b.p. 85 - 87°C.

B) $\frac{2}{2}$, $\frac{1}{2}$, $\frac{1}{2}$: a mixture of $CF_nCl_{3-n}SCl$ (n = 2, 1, 0) and sodium acetate in ethylene chloride was stirred at ambient temperature

^{*}All values calibrated against CFCl3.

until completion as indicated by the disappearance of the initial yellow-green colour. The reaction mixture was filtered and the solvent was removed in vacuo. The residue was redistilled under reduced pressure to yield the analytically pure substances 2b-d. Reaction conditions, boiling points and analytical data are given in Table 1.

Addition of 1 and 2 to Cyclohexene

A) Upon addition of 2a - g to cyclohexene, an exothermic reaction occurred yielding the desired products, which were isolated via vacuum distillation. The reaction of 2d with cyclohexene was carried out in acetic acid at 20°C (42 h). The product was purified by distillation.

B) For better temperature control, $\underline{1a} - \underline{c}$ were added dropwise into cyclohexene at -20 - 0°C after which the reaction mixture was warmed to 20°C. Products were isolated by vacuum distillation. Reaction conditions, results and characteristic data are given in Tables 3, 4 and 5.

Reaction of (1) with aromatics

A) As in previously described reactions, $1 \pm - \pm$ were mixed with aromatics at 0 - 20°C and heated to the temperature indicated in Table 6. The products were isolated by vacuum distillation.

B) The compounds 5a, b were also made in-situ via condensation of CF_3SCl at -40°C or dropwise addition of $CF_nCl_{3-n}SCl$ (n = 2, 1) at 0 - 20°C into a suspension of CF_3COOAg and the corresponding aromatic reagent. For CF_2ClSCl and $CFCl_2SCl$, the reaction mixtures were heated to the temperature indicated in Table 6 until the mixture became colourless. Methylene chloride

Reagents		Solvent	Reaction-	Time	Product	Yield
CH ₃ COONa g(mmol)	CF _n Cl _{3-n} SCl g(mmol)	CH ₂ Cl ₂ [ml]	temperature [°c]	[h]	โก]	
12.75 (155)	CF ₃ SC1 13.11 (96) CF ₂ ClSC1		0	12	≧a	52
20 (244)	30.6 (200) CFC1 ₂ SC1	50	20	5	<u>2</u> ₽	97
60 (732)	48 (283) CCl ₃ SCl	200	20	8	<u>2</u> ⊆	89
41 (500)	33 (177)	150	20	42	<u>2</u> ₫	81

Preparative Conditions and Yields of Perhalogenomethanesulfenyl Acetates

TABLE 2

Physical and Characteristic Data for the Sulfenyl Acetates 2

Com-	Formula	в.р.	IR	1 _H -	19 _{F-}	C %		H %	
pound	(Mol-weight)	°C (mm)	cm ⁻¹	ppm	ppm	calc.	found	calc.	found
2 <u>a</u>	C ₃ H ₃ F ₃ O ₂ S 160.1	85-87	1800	2.52	51.9	22.50	22.1	1.88	1.9
<u>2</u> ₽	176.6	53 (35)	1790- 1800	2.50	34.5	20.40	20.4	1.71	1.7
2₽	C ₃ H ₃ Cl ₂ FO ₂ S 193.1	68-70 (20)	1780- 1800	2.46	26.7	18.66	18.4	1.57	1.6
2d ==	C ₃ H ₃ Cl ₃ O ₂ S 209.6	75-77 (10)	1760- 1800	2.37		17.18	16.9	1.43	1.5

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Addition of Perhalogenomethanesulfenyl Acetates and Trifluoroacetates to Cyclohexene (Reaction Conditions)

Reagents		Sol-	Tempera-	Time	Prod-	Yield	
Cyclohexene	RCOOSCF _n Cl _{3-n}	vent ml	ture	h	uct	8	
g (mmol)	g (mmol)						
3 (36.6)	CF ₃ COOSCF ₃ 5.5 (25.7)		-20 - 0	(directly)	3 <u>a</u>	66	
2 (24.4)	CF ₃ COOSCF ₂ C1 4 (17.4)		0 - 20	11	₹Ē	92	
2 (24.4)	CF ₃ COOSCFCl ₂ 3.4 (13.8)		20	u	<u>3</u> ⊆	66	
10 (122)	CH ₃ COOSCF ₃ 12.5 (78.1)		20	5	4 <u>a</u>	55	
5 (61.0)	CH ₃ COOSCF ₂ C1 4.56 (25.8)		20	12	<u>4</u> ₽	52	
10 (122)	CH ₃ COOSCFC1 ₂ 13 (67.4)		20	24	<u>4</u> ⊆	70	
20 (244)	CH ₃ COOSCC1 ₃ 28.2 (35)	сн ₃ соон 20	80	3	4 ₫	71	

TABLE 4

Physical and Characteristic Data for the Cyclohexene Adducts $\underline{3}$ and $\underline{4}$

Adducts	B.P.	Formula	C %		Н %		IR (C=O)
	°C_(mm)	(Mol-weight)	calc.	found	calc.	found	
<u>3</u> a_	74-76 (10)	C ₉ H ₁₀ F ₆ O ₂ S (296.1)	36.47	35.6	3.38	4.3	1790
≩₽	46-47 (0.1)	C ₉ H ₁₀ ClF ₅ O ₂ S (312.6)	34.54	34.5	3.20	3.3	1790
<u>3</u> ⊆	130 (15)	C ₉ H ₁₀ C1 ₂ F ₄ O ₂ S (329.1)	32.81	32.9	3.04	3.1	1785
4 ₫	87 (8)	C ₉ H ₁₃ F ₃ O ₂ S (242.1)	44.61	44.2	5.37	5.5	1745
<u>4</u> ₽	52-53 (0.1)	C ₉ H ₁₃ ClF ₂ O ₂ S (258.6)	41.76	40.8	5.03	5.1	1745
4 ⊆	69-71 (0.1)	C ₉ H ₁₃ Cl ₂ FO ₂ S (275.1)	39.25	28.6	4.73	4.8	1740
4 ₫	88-89 (0.1)	C ₉ H ₁₃ Cl ₃ O ₂ S (291.6)	37.04	36.1	4.39	4.5	1740

TABLE 5		
1 _{H- and}	¹⁹ F-NMR Data for the Cyclohexene Adducts $\frac{3}{2}$ and $\frac{4}{2}$	
Adducts	¹ H Chemical Shifts, ppm	19 _{F, ppm}
3₫	1.2 - 2.0 (m, 6H), 2.0 - 2.5 (m, 2H), 3.31 (dt, J 3.5 and 9.5 Hz, 1H), 4.96 (dt, J 4 and 9 Hz, 1H)	75.9, 40.2
₹₽	1.2 - 2.0 (m, 6H), 2.0 - 2.5 (m, 2H), 3.38 (dt, J 4.0 and 9.5 Hz, 1H), 4.98 (dt, J 4 and 8 Hz, 1H)	76.0, 25.7
<u>3</u> ⊑	1.2 - 2.0 (m, 6H), 2.0 - 2.5 (m, 2H), 3.45 (dt, J 4 and 8 Hz, 1H), 5.01 (dt, J 4 and 8 Hz, 1H)	75.3, 16.6
<u>4</u> ≘	1.25 - 1.9 (m, 4H), 2.08 (s, 3H), 2.07 - 2.45 (m, 1H), 3.22 (dt, J 4.2 and 10 Hz, 1H), 4.74 (dt, J 4.5 and 9.0 Hz, 1H)	41.0
<u>4</u> ₽	1.25 - 1.9 (m, 4H), 2.06 (s, 3H), 2.07 - 2.45 (m, 1H), 3.28 (dt, J 4.2 and 9.6 Hz, 1H), 4.75 (dt, J 4.0 and 8.9 Hz), 1H)	26.5
4 ⊆	1.3 - 1.9 (m, 4H), 2.08 (s, 3H), 2.2 - 2.5 (m, 1H), 3.36 (dt, J 3.6 and 9.2 Hz, 1H), 4.80 (dt, J 4.5 and 9.1 Hz, 1H)	15.9
<u>4</u> ₫	1.27 - 2.0 (m, 4H), 2.07 (s, 3H), 2.24 - 2.64 (m, 1H), 3.47 (dt, J 4.2 and 8.5 Hz, 1H), 4.89 (dt, J 3.8 and 8.0 Hz, 1H)	

Reaction of 2 and 3 with Aromatics and Thiophene

Reagents g (mmol)			Tempera- ture (°C) Time (h)	Product (Yield %)
Anisol	CF ₃ COOAg	CF ₃ SCl	50 - 60	<u>≦a</u>
10 (92.5)	5 (22.6)	4.3 (31.5)	(1)	(83)
Anisol	CF ₃ COOAg	CF ₂ CISCl	50 - 60	<u>5</u> ⊉
10 (92.5)	5 (22.6)	3.5 (22.9)	(1)	(50)
Anisol	CF ₃ COOSCFC1 ₂		70 - 80	돌⊆
11 (102)	8 (32.4)		(1)	(83)
Toluene	CF ₃ COOSCF ₃	СF ₃ СООН	50 - 60	<u> 6</u> 2
11.5 (125)	12.5 (58.4)	10 (87.7)	(4)	(8 0)
		(<u>c</u> c	ntinued on f	acing page)

Reagents g (mmol)			Tempera- ture (°C) Time (h)	Product (Yield %)
Toluene	CF ₃ COOSCF ₂ Cl	СF ₃ СООН	70 - 80	<u></u>
10 (109)	8 (34.7)	3 (26.3)	(4)	(72)
Toluene	CF ₃ COOSCFCl ₂	CF ₃ COOH	70 - 80	<u>६</u>
12 (130)	10 (41.8)	3 (26.3)	(4)	(58)
p-Xylene	CF ₃ COOAg	CF ₃ SC1	50 - 60	<u>7</u> ª
8 (75.5)	6.2 (28.0)	8 (58.6)	(2)	(64)
p-Xylene	CF ₃ COOAg	ClCF ₂ SCl	60 - 70	<u> 7</u> 늘
10 (94.3)	5.5 (25.0)	5 (32.7)	(2)	(61)
p-Xylenene	CF ₃ COOSCFC1 ₂	СF ₃ СООН	80 - 90	<u>7</u> <u>2</u>
10 (94.3)	5 (20.2)	5 (43.9)	(2)	(58)
Mesitylene	CF ₃ COOSCF ₃		0 - 20	<u> 월</u> 콜
3 (25.0)	5 (23.4)		(1)	(73)
Mesitylene	CF ₃ COOAg	CF ₂ ClSCl	20	<u>월</u> 눹
12 (100)	6 (27.2)	4.7 (30.7)	(2)	(61)
Mesitylene	CF ₃ COOSFC1 ₂	СF ₃ СООН	20	월 <u>⊆</u>
10 (83.3)	7 (28.3)	3 (26.3)	(4)	(65)
Pentamethylbenzene ^{a)}	CF ₃ COOAg	CF ₃ SC1	20 - 40	일 <u>ब</u>
7 (47.2)	15.3 (69.3)	13 (95.2)	(2)	(79)
Pentamethylbenzene ^{a)}	CF ₃ COOAg	CF ₂ CISCl	20 - 40	일 <u></u>
4.5 (37.4)	7 (31.7)	6 (31.2)	(2)	(54)
Pentamethylbenzene ^{a)}	CF ₃ COOAg	CFCl ₂ SCl	20 - 40	9⊆⊆
5.44 (36.7)	8.1 (36.7)	7 (41.3)	(3)	(53)
Thiophene	CF ₃ COOSCF ₃		20 - 50	<u>10a</u>
4.2 (50)	5 (23.4)		(1)	(55)
Thiophene	CF ₃ COOSCFCl ₂		20 - 50	<u>10⊊</u>
10 (119)	5 (20.2)		(1)	(80)
Thiophene	CH ₃ COOSCF ₃	СF ₃ СООН	20 - 50	19ª
4.2 (50)	5 (31.3)	3 (26.3)	(2)	(62)

a) dissolved in CH_2Cl_2

(continued overleaf)

308	3	0	8
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TABLE 6 (cont.)

Reagents g (mmol)			Tempera- ture (°C) Time (h)	Product (Yield %)
Thiophene	CH ₃ COOSCF ₂ Cl	СF ₃ СООН	20 - 50	<u>10</u> ⊵
4.2 (50)	6 (34.1)	3.3 (28.9)	(2)	(53)
Thiophene	сн ₃ сооѕсғсі ₂	сғ _з соон	20 - 50	<u>1</u> 0⊆
8.4 (100)	10 (51.8)	6.6 (57.8)	(2)	(75)

TABLE 7

Physical and Analytical Data for the Trihalogenomethylmercapto Aromatics

Compound	Formula	B.P.	C 8		Н %	
	(Mol-weight)	°C (mm)	Calc. For	und	Calc.	Found
<u>5a</u>	C ₈ H ₇ F ₃ OS (208).3)	83 - 85 (10)	46.13 46	.3	3.36	3.4
<u>5</u> ₽	C ₈ H ₇ ClF ₂ OS (224.8)	49 - 50 (0.1)	42.74 40	.5	3.11	3.4
5 <u>c</u>	C ₈ H ₇ Cl ₂ FOS (241.2)	74 - 75 (0.04)	39.83 39	.9	2.90	3.1
<u>€</u> a, <u>6</u> a'	C ₈ H ₇ F ₃ S (192.3)	162 - 163, 53 - 55 (10)	49.97 50	.1	3.67	3.8
<u>6</u> ₽, 6₽'	C ₈ H ₇ ClF ₂ S (208.8)	82 - 84 (10)	46.02 46	.0	3.38	3.4
<u>6</u> ⊆, <u>6</u> ⊆'	C ₈ H ₇ Cl ₂ FS (225.3)	50 - 52 (0.06)	42.65 43	.5	3.13	3.5
<u>7</u> a	C ₉ H ₉ F ₃ S (206.3)	68 - 69 (10)	52.40 53	.0	4.40	4.9
<u>7</u> ₽	C ₉ H ₉ ClF ₂ S (222.8)	70 - 71 (0.8)	48.52 47	.7	4.07	4.2
<u>7</u> <u></u>	C ₉ H ₁₀ Cl ₂ FS (239.2)	63 - 65 (0.06)	45.19 47	.0	3.79	4.0
§₫	C ₁₀ H ₁₁ F ₃ S (220.2)	89 - 90 (10)	54.55 54	. 4	5.04	5.2
<u>8</u> 5	C ₁₀ H ₁₁ ClF ₂ S (236.7)	110 - 112 (10)	50.74 50	.3	4.68	4.6
§⊊	C ₁₀ H ₁₁ Cl ₂ FS (253.2)	54 - 55 (0.1)				
<u>9</u> ª	C ₁₂ H ₁₅ F ₃ S (248.2)	75 - 76 (0.09)	58.07 59	.5	6.09	6.3
₹₽	C ₁₂ H ₁₅ ClF ₂ S (264.7)	90 - 91 (0.05)	54.45 56	. 2	5.71	6.0
<u></u> 2⊆	C ₁₂ H ₁₅ Cl ₂ FS (281.2)	107 - 109 (0.15)				
<u>10</u> a	C ₅ H ₃ F ₃ S ₂ (184.1)	135 - 137 [7]				
10b	$C_{5}H_{3}ClF_{2}S_{2}$ (200.6)	54 - 55 (10) [7]				
1 <u>9</u> c	C ₅ H ₃ Cl ₂ FS ₂ (217.1)	35 - 36 (0.06)	27.65 27	.5	1.38	1.4

NMR Spectral Data for the Aromatic and Heteroaromatic Trihalomethylmercapto Derivatives

Compound	¹ H Chemical Shifts, ppm	19 _F
5 <u>a</u>	3.80 (s, 3H), 7.21 (AB, $J_{AB} = 9 Hz$)	45.0
<u>5</u> b	3.76 (s, 3H), 7.21 (AB, $J_{AB} = 9 Hz$)	29.55
5 <u>⊆</u>	3.72 (s, 3H), 7.22 (AB, $J_{AB} = 9 Hz$)	18.50
<u>6a</u>	2.30 (3H), 7.30 (AB, $J_{AB} = 8.9 \text{ Hz}$)	43.02
<u>§</u> ª'	2.50 (3H), 7.26 (m, 2H), 7.60 (1H)	43.90
ê <u></u> ট	2.35 (s, 3H), 7.33 (AB, $J_{AB} = 9 Hz$)	28.0
<u>é</u> <u>b</u> '	2.51 (s, 3H), 7.62 (d, $J = 9 Hz$, 1H), 7.30	28.84
	m, 3H)	
§⊆	2.35 (3H), 7.31 (AB)	
<u>6</u> <u>2</u> <u>'</u>	2.52 (3H), 7.55 (1H), 7.32 (m, 3H)	
<u>7</u> ª	2.30 (3H), 2.47 (3H), 7.14 (2H), 7.42 (1H)	
<u>7</u> ₽	2.30 (s, 3H), 2,47 (s, 3H), 7.17 (s, 2H),	28.0
	7.45 (s, 1H)	
<u>7</u> g	2.24 (s, 3H), 2,32 (s, 3H), 7.10 (s, 2H),	17.50
	7.20 (s, 1H)	
<u>8</u> a	2.36 (s, 3H), 2.62 (s, 6H), 7.08 (s, 2H)	42.9
<u>8</u> ₽	2.38 (s, 3H), 2.63 (s, 6H), 7.28 (s, 2H)	27.3
§⊆	2.37 (s, 3H), 2.52 (s, 6H), 6.95 (s, 2H)	
<u>9</u> a	2.38 (s, 9H), 2.62 (s, 6H)	43.7
<u>9</u> ৳	2.40 (s, 9H), 2.72 (s, 6H)	28.4
2⊆	2.27 (s, 9H), 2.58 (s, 6H)	17.3
<u>10</u> a [7]		
<u>1</u> <u>0</u> <u>b</u> [7]		
<u>10</u> <u></u>	7.16 (dd, 1H), 7.45 (dd, 1H), 7.68 (dd, 1H)	23.5

was added to the mixture followed by filtration of the suspension. The solvent was evaporated from the filtrate in vacuo and the remaining residue purified by vacuum distillation.

Reaction of (1) and (2) with thiophene

A) (2) was added slowly to thiophene at $-20 - 0^{\circ}C$ while stirring after which the temperature was allowed to rise to $20^{\circ}C$. The product was purified by vacuum distillation.

B) A rapid, exothermic reaction occured as CF_3COOH was slowly added to a mixture of (3) and thiophene. After 2 h, distillation afforded the 2-substituted thiophene.

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