to silica gel chromatography. The *N*-oxide was separated by using a 15% ethyl acetate–hexane mixture as the eluent. Evaporation of the solvent under reduced pressure gave 265 mg (80%) of 2-methyl-3-phenyl-4-(phenylsulfonyl)-5-methyleneisoxazolidine *N*-oxide (**55**) as a white solid. Recrystallization from a 10% ethyl acetate–hexane mixture gave colorless crystals: mp 131–132 °C; IR (KBr) 1760, 1450, 1310, 1150, 760, and 690 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.5 (s, 3 H), 4.0 (d, 1 H, J = 6 Hz), 4.4 (d, 2 H), 4.8 (d, 1 H, J = 6 Hz), and 7.2–7.8 (m, 10 H).

A stirred solution containing 331 mg of the above *N*-oxide in 10 mL of methylene chloride was cooled to 0 °C, and to this solution was added 204 mg of acetic anhydride over a 5-min period. The mixture was allowed to warm to room temperature, and after the mixture was stirred for 5 h, 0.2 mL of pyridine was added. The organic layer was washed with water and a dilute hydrochloric acid solution, dried over magnesium sulfate, and concentrated in vacuo to give a white solid (298 mg, 80%). Recrystallization of this material from a 5% ethyl acetate–hexane mixture provided a pure sample of 2-methyl-3-acetoxy-3-phenyl-4-(phenylsulfonyl)-5-methyleneisoxazolidine (**56**): mp 154–155 °C; IR (KBr) 1790, 1660, 1450, 1370, 1310, 1290, 1180, and 1150 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.2 (s, 3 H), 2.3 (s, 3 H), 4.25 (d, 1 H, J = 2.5 Hz), 4.5 (d, 1 H, J = 2.5 Hz), 4.75 (s, 1 H), and 7.1–7.3 (m, 10 H). Anal. Calcd for $C_{19}H_{19}O_5NS$: C, 61.13; H, 5.09; N, 3.75; S, 8.58. Found: C, 61.06; H, 5.17; N, 3.75; S, 8.52.

Acknowledgment. We gratefully acknowledge the National Cancer Institute for generous support of this work. U.C. thanks the NATO Foundation for a travel grant and the MPI for partial financial support.

Registry No. **8**, 19345-08-5; **11**, 113549-18-1; **12**, 106745-24-8; **13**, 113549-19-2; **14**, 113549-20-5; **15**, 113549-21-6; **16**, 17647-39-1; **17** (*E* oxime), 113549-15-8; **17** (*Z* oxime), 113549-22-7; **18**, 113549-23-8; **19**, 113549-24-9; **22**, 113549-25-0; **23**, 107402-99-3; **24**, 113549-26-1; **24** (*o*-trimethylsilylcyanohydrin), 113549-16-9; **25**, 108817-75-0; **26**, 110729-87-8; **27**, 108817-72-7; **28**, 20048-05-9; **29**, 113549-27-2; **30**, 113549-28-3; **31**, 113549-29-4; **32**, 113549-30-7; **33**, 113549-31-8; **33** (mesylate), 113549-17-0; **34**, 113549-32-9; **35**, 113549-33-0; **36**, 113549-34-1; **37**, 113549-35-2; **38**, 109787-18-0; **39**, 113549-36-3; **40**, 87352-10-1; **41**, 107969-78-8; **43**, 87352-09-8; **43** (regioisomer), 87352-06-5; **44**, 109787-19-1; **45**, 113549-37-4; **46**, 113549-38-5; **46** (5-methylene isomer), 113549-42-1; **47**, 113549-39-6; **48**, 113549-40-9; **49**, 113549-41-0; **50**, 107403-02-1; **50** (5-methylene isomer), 107402-98-2; **53**, 113549-43-2; **54**, 108817-77-2; **55**, 113549-44-3; **56**, 113549-45-4; $PhCOCH{=}CHCO_2CH_3$, 14274-07-8; $Ph(CH_2)_2COCH_3$, 2550-26-7; $PhCH{=}CHCOCH_3$, 122-57-6; $PhCH{=}N(O)C_4H_9$-*t*, 3376-24-7; $CH_2{=}C(CH_3)CO_2CH_3$, 80-62-6; $HC{\equiv}CCO_2CH_3$, 922-67-8; $(CH_3)_2C(OC_2H_5)_2$, 77-76-9; $(CH_3)_2C{=}N(O)CH_3$, 72552-73-9; $PhSO_2CH{=}C{=}CH_2$, 2525-42-0; n-$C_3H_7CH{=}N(O)C_4H_9$-*t*, 72552-75-1; $PhSO_2C{\equiv}CCH_3$, 2525-41-9; 1-hydroxypiperidine, 4801-58-5.

Supplementary Material Available: Experimental details for the preparation of compounds **13**, **29**, **31**, **43**, **46**, **48**, and **50**, base-induced alkylations of 2,5-dimethyl-3-phenyl-4-(phenylsulfonyl)isoxazoline (**23**), and crystallographic data for **53** (Tables 1–5) (9 pages). Ordering information is given on any current masthead page.

Acylation of Pyrrole and *N*-Methylpyrrole with 1,3-Benzoxathiolium Tetrafluoroborates. A High-Yield Method for the Synthesis of Diacylpyrroles†

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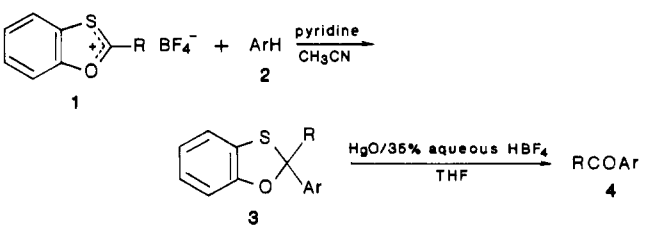
Received July 16, 1987

2-Substituted 1,3-benzoxathiolium tetrafluoroborates (I) were used as masked acylating agents for pyrrole and *N*-methylpyrrole. The reactions on pyrrole (II) were regiospecific, and according to the molar ratio of the reagents (I:II = 1:3 or 2.5–3:1), 2-acylpyrroles were obtained in moderate to good yields (38–82%) and 2,5-diacylpyrroles were obtained in excellent yields (in most cases, quantitative). The reactions on *N*-methylpyrrole (III) were not regioselective, and both α- and β-positions were attacked. So, depending on the molar ratio of the reagents (I:III = 1:3 or 2.5–3:1), 2- and 3-acyl-*N*-methylpyrroles (9–51% and 27–68% yields, respectively) and 2,4- and 2,5-diacyl-*N*-methylpyrroles (60–93% and 17–40%, respectively) were obtained. A very interesting feature of the new method is the possibility of introducing two identical or different acyl groups in the pyrrole ring under mild conditions. ^1H and ^{13}C NMR spectra of all the new compounds and IR spectra, recorded in the gas phase, of 2- and 3-acylpyrroles and of 2,4- and 2,5-diacylpyrroles are reported.

In previous work we have shown the synthetic effectiveness of 1,3-benzoxathiolium tetrafluoroborates **1** as masked acylating agents.[2] In particular, we have recently found that in certain cases the salts **1** can be advantageously utilized for a two-step acylation of electron-rich aromatic and heteroaromatic compounds.[3] Indeed, according to Scheme I, various 2,2-disubstituted 1,3-benzoxathioles **3** were first obtained by electrophilic aromatic substitution from reaction of **1** with **2**, under mild conditions; subsequently, hydrolysis of **3** easily yielded the acyl derivatives **4**.

Scheme I



In connection with these last investigations, we have undertaken a specific study on the acylation of pyrrole and

† Part 18 in Pentaatomic Heteroaromatic Cations series. Part 17 is ref. 1. Presented in part at XVI Convegno Nazionale della Divisione di Chimica Organica della Società Chimica Italiana, Urbino, Italy, September 7–14, 1986 (Atti, p 42).

(1) Barbero, M.; Cadamuro, S.; Ceruti, M.; Degani, I.; Fochi, R.; Regondi, V. *Gazz. Chim. Ital.* **1987**, *117*, 227.

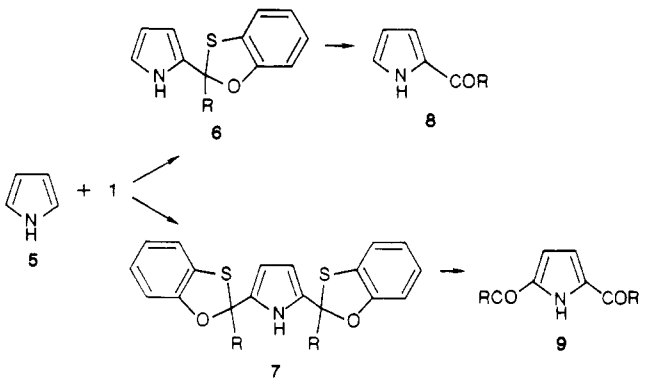
0022-3263/88/1953-2245$01.50/0

Table I. Acylation of Pyrrole (5) and *N*-Methylpyrrole (12): Reaction Conditions and Yields

entry	R	reagent ratio 5:1	reagent ratio 12:1	time, h	chromatographic solvent[a]	products,[b] % yields[c] 6	7	13	14	15	16
1	C_6H_5	3:1[d]		0.5	A/B (9.5:0.5)	70	tr[e]				
2	C_6H_5	1:2.5[d]		0.5	*f*	–	100				
3	4-$CH_3OC_6H_4$	3:1		0.5	A/B (1:1)	84	tr[e]				
4	4-$CH_3OC_6H_4$	1:2.5		0.5	*g*	–	100				
5	4-ClC_6H_4	3:1		0.5	A/C (9.8:0.2)	66	tr[e]				
6	4-ClC_6H_4	1:2.5		0.5	*g*	–	100				
7	CH_3	3:1		1	A/C (9.8:0.2)	45	2				
8	CH_3	1:3[h]		1	A/C (9.8:0.2)	tr[e]	45				
9	*t*-C_4H_9	3:1		1	A/C (9.8:0.2)	70	6				
10	*t*-C_4H_9	1:3		1	*g*	–	100				
11	*n*-C_5H_{11}	3:1		3	A/C (9.8:0.2)	40	6				
12	*n*-C_5H_{11}	1:3		3	A/C (9.8:0.2)		45				
13	c-C_6H_{11}	3:1		1	A/C (9.8:0.2)	42	5				
14	c-C_6H_{11}	1:3		1	A/C (9.8:0.2)	19	81				
15	C_6H_5		3:1	1	A/C (9.8:0.2)			40	44	–	–
16	C_6H_5		1:2.5	1	A/C (9.8:0.2)			–	–	62	30
17	4-$CH_3OC_6H_4$		3:1	1	A/B (4:1)			47	28	–	–
18	4-$CH_3OC_6H_4$		1:2.5	3	A/C (9:1)			–	–	60	40
19	4-ClC_6H_4		3:1	1	A/C (9.8:0.2)			53	34	–	–
20	4-ClC_6H_4		1:2.5	0.17	A/B (9:1)			–	–	70	26
21	*t*-C_4H_9		3:1	1	A/B (9.5:0.5)			10	70	2	–
22	*t*-C_4H_9		1:3	1	A/D (4:1)			–	–	63[i]	17[i]
23	*n*-C_5H_{11}		3:1	3	A/B (9.5:0.5)			12	44	3	–
24	*n*-C_5H_{11}		1:3	3	A/B (9.5:0.5)			17	26	47	–
25	c-C_6H_{11}		3:1	3	A/B (9.5:0.5)			14	72	4	–
26	c-C_6H_{11}		1:3	3	A/B (9.5:0.5)			2	4	93	–

[a] A = petroleum ether; B = ethyl ether; C = acetone; D = benzene. [b] Physical data and MS data are reported in Table II. [c] Yields of pure isolated products. In entries 1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, and 25, the yields were calculated with regard to 2-substituted 1,3-benzoxathiolium tetrafluoroborates. [d] Reported in ref 3b. [e] Traces. Determined by TLC and MS analyses. [f] Crude residue from the reaction was purified simply by two washings with hot methanol (2 × 5 mL).[3b] [g] Crude residue from the reaction was purified simply by two washings with acetonitrile (2 × 5 mL). [h] For 10 mmol of pyrrole, 15 mL of acetonitrile was used. [i] Two fractions were isolated by chromatography with petroleum ether/benzene (4:1): the first was 2,5-bis[2-(2-*tert*-butyl-1,3-benzoxathiolyl)]-*N*-methylpyrrole (**16d**) as a mixture of diastereoisomers (meso and racemic forms); the second was a mixture of 2,4-bis[2-(2-*tert*-butyl-1,3-benzoxathiolyl)]-*N*-methylpyrrole (**15d**) and an unidentified byproduct. The presence of two products in the second fraction was put in evidence by TLC (petroleum ether/acetone, 9.8:0.2, as eluent showed two almost-overlapping spots). These could not be separated by further chromatographies. The separation of **15d** was however achieved by several fractional crystallizations of the mixture with chloroform/methanol. The yield reported is of the pure product.

Scheme II



1, 6-9a: R = C_6H_5
b: R = 4-$CH_3OC_6H_4$
c: R = 4-ClC_6H_4
d: R = CH_3
e: R = *t*-C_4H_9
f: R = *n*-C_5H_{11}
g: R = c-C_6H_{11}

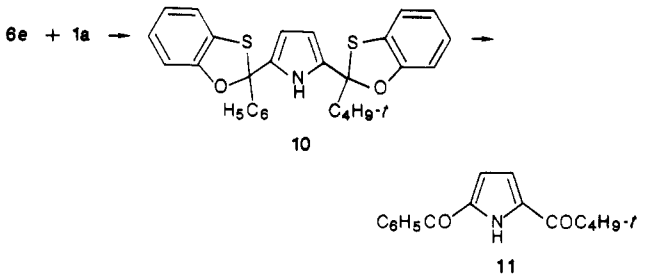
N-methylpyrrole with reagents 1 and we now report these findings.

Results

According to the conditions of the general procedure previously reported,[3] the reactions of pyrrole and *N*-methylpyrrole with some representative 2-substituted 1,3-benzoxathiolium tetrafluoroborates were carried out in the presence of pyridine in dry acetonitrile at room temperature.

In the case of pyrrole (**5**), the reactions produced mixtures of 2-monosubstituted pyrroles **6** (racemic forms) and 2,5-disubstituted pyrroles **7** (meso and racemic forms) (Scheme II) in varying amounts, depending on the molar ratio of the reagents. Thus pyrrole, salts **1**, and pyridine in a 3:1:1 molar ratio gave **6** in good yields as major products, accompanied by low amounts of 2,5-disubstituted pyrroles **7**; with excess of salts **1**, **7** were formed as the only products (with the exception of entry 14) in good to excellent yields (Tables I and II). The reaction of 2-[2-(2-*tert*-butyl-1,3-benzoxathiolyl)]pyrrole (**6e**) with 2-phenyl-1,3-benzoxathiolium tetrafluoroborate (**1a**) in a 1:1.25 molar ratio produced unsymmetrical 2,5-disubstituted pyrrole **10** (Scheme III) in 93% yield.

Scheme III



In the case of the reactions between *N*-methylpyrrole (**12**) and the salts **1**, more complex reaction mixtures were

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Table II. 2-Substituted and 2,5-Disubstituted Pyrroles 6, 7, and 10 and 2- and 3-Substituted and 2,4- and 2,5-Disubstituted *N*-Methylpyrroles 13–16

compd	mp,[a] °C (solv)[b] or bp, °C/Torr	formula[c]	MS,[d] *m/e* (M^+)	compd	mp,[a] °C (solv)[b] or bp, °C/Torr	formula[c]	MS,[d] *m/e* (M^+)
6a	81–82[e] (E/A)		*e*	**13e**	152–154/0.3	$C_{17}H_{21}NOS$	287
6b	129 (F/G)	$C_{18}H_{15}NO_2S$	309	**13f**	157–159/0.3	$C_{18}H_{21}NOS$	299
6c	121 (H)	$C_{17}H_{12}ClNOS$	313	**14a**	84–85 (E/I)	$C_{18}H_{15}NOS$	293
6d	131–133/0.4	$C_{12}H_{11}NOS$	217	**14b**	thick oil	$C_{19}H_{17}NO_2S$	323
6e	75 (A)	$C_{15}H_{17}NOS$	259	**14c**	103–105 (F/H)	$C_{18}H_{14}ClNOS$	327
6f	161–163/0.02	$C_{16}H_{19}NOS$	273	**14d**	96–97 (G)	$C_{16}H_{19}NOS$	273
6g	87–89 (H)	$C_{17}H_{19}NOS$	285	**14e**	179–180/0.3	$C_{17}H_{21}NOS$	287
7a	173–174[e] (F/A)		*e*	**14f**	74–75 (H)	$C_{18}H_{21}NOS$	299
7b	184–185 (F/G)	$C_{32}H_{25}NO_4S_2$	551[f]	**15a**	132–134 (E/H)	$C_{31}H_{23}NO_2S_2$	505[f]
7c	154–155 (F/G)	$C_{30}H_{19}Cl_2NO_2S_2$	559[f]	**15b**	86–88 (J)	$C_{33}H_{27}NO_4S_2$	565[f]
7d	100–101 (H)	$C_{20}H_{17}NO_2S_2$	367	**15c**	168–170 (C/A)	$C_{31}H_{21}Cl_2NO_2S_2$	573[f]
7e	226–227 (D)	$C_{26}H_{29}NO_2S_2$	451	**15d**	152–153 (F/G)	$C_{27}H_{31}NO_2S_2$	465[f]
7f	64–65 (I)	$C_{28}H_{33}NO_2S_2$	479	**15e**	thick oil	$C_{29}H_{35}NO_2S_2$	493[f]
7g	131–132 (E/G)	$C_{30}H_{33}NO_2S_2$	503	**15f**	83–87 (G)	$C_{31}H_{35}NO_2S_2$	517[f]
10	145–146 (D)	$C_{28}H_{25}NO_2S_2$	471[f]	**16a**	154–155 (E/H)	$C_{31}H_{23}NO_2S_2$	505[f]
13a	88–89 (E/H)	$C_{18}H_{15}NOS$	293	**16b**	153–154 (E/G)	$C_{33}H_{27}NO_4S_2$	565[f]
13b	108–109 (E/H)	$C_{19}H_{17}NO_2S$	323	**16c**	98–101 (C/A)	$C_{31}H_{21}Cl_2NO_2S_2$	573[f]
13c	84–85 (H)	$C_{18}H_{14}ClNOS$	327	**16d**-I (meso or dl)[g]	213–214 (F/A)	$C_{27}H_{31}NO_2S_2$	465[f]
13d	99 (G)	$C_{16}H_{19}NOS$	273	**16d**-II (meso or dl)[d]	171 (F/A)	$C_{27}H_{31}NO_2S_2$	465[f]

[a] 2,5-Disubstituted pyrroles and *N*-methylpyrroles **7a–g** and **16a–c**, 2,5-disubstituted pyrrole **10**, and 2,4-disubstituted *N*-methylpyrroles **15a–f** are mixtures of diastereoisomers (meso and racemic and two racemic forms, respectively). Reported melting points refer to the mixture crystallized once; they are only indicative because, in general, they vary with the crystallization solvents and with the crystallization times; in some cases, moreover, the melted mass remains cloudy. [b] E = carbon tetrachloride; F = chloroform; G = methanol; H = ethanol; I = pentane; J = cyclohexane. For A, B, C, and D, see footnote *a* of Table I. [c] Satisfactory microanalyses were obtained: C ± 0.14; H ± 0.10; N ± 0.11; S ± 0.11. [d] Unless otherwise noted, MS were recorded at 70 eV with a HP 5970 B mass selective detector connected to a HP 5890 GC; cross-linked methyl silicone capillary column. [e] Reported in ref 3b. [f] Recorded on a double-focusing Kratos MS 80 instrument (operating with direct inlet system at 70 eV). [g] The mixture obtained from the reaction, crystallized once from chloroform/petroleum ether, had mp 157–159 °C. Separation of diastereoisomers (meso and racemic forms) was extremely laborious. It was achieved by several sequential chromatographies of the mixture on a silica gel long column, with petroleum ether/acetone (9.8:0.2) as eluent.

obtained. Indeed, in addition to the products arising from attack at α-positions, i.e., **13** (racemic forms) and **16** (meso and racemic forms), the products arising from attack at β-positions, i.e., **14** (racemic forms) and **15** (two racemic forms), were also isolated (Scheme IV).

The amounts of the various products varied, depending on the molar ratio of the reagents: thus, *N*-methylpyrrole, salts **1**, and pyridine in a 3:1:1 molar ratio gave almost exclusively monosubstituted pyrroles **13** and **14**; with excess of the salts **1**, exclusively disubstituted pyrroles **15** and **16** were, in most cases, formed. Among these, 2,4-disubstituted derivatives **15** were isolated as the major products in good to excellent yields (Tables I and II).

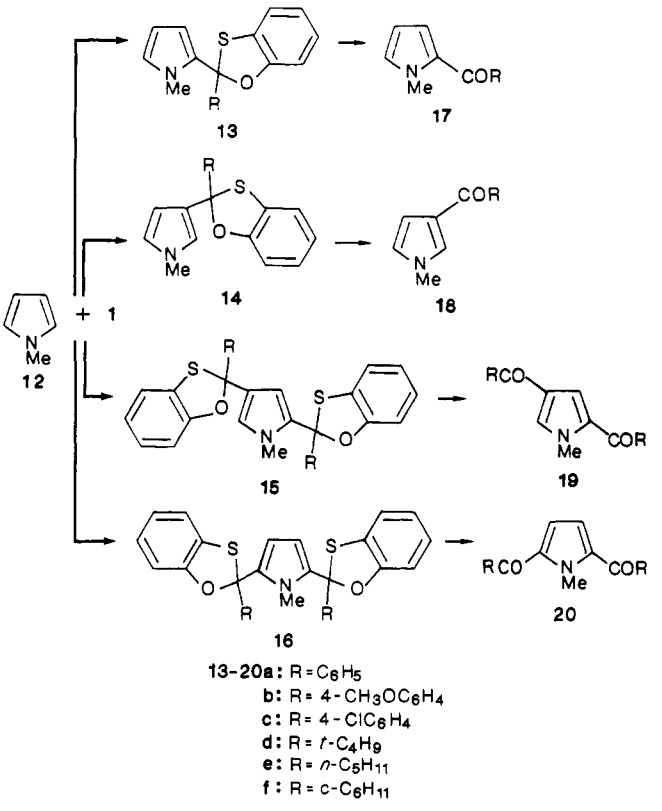
Subsequent hydrolysis of the substituted pyrroles **6**, **7**, **10**, **13**, **14**, **15**, and **16**, carried out by utilizing a very efficient procedure previously reported,[4] gave acyl derivatives **8**, **9**, **11**, **17**, **18**, **19**, and **20**, respectively, in essentially quantitative yield (Table III).

In some cases, the hydrolyses were also directly accomplished on the crude reaction mixtures, without isolation of the intermediate benzoxathiole derivatives, in comparable yields.

Discussion

The acylation of pyrroles is a much-studied reaction.[5-9] The principal emphasis has been in monoacylation and, most recently, in setting up the conditions and in understanding the factors that control the orientation of the substitution in this reaction. By contrast, relatively few examples of diacylated pyrroles have been reported[10-13] and

Scheme IV



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(12) Anderson, A. G.; Exner, M. M. *J. Org. Chem.* **1977**, *42*, 3952.

Table III. Acylpyrroles 8, 9, 11, and 17-20

compd	reag ratio[a]	time, h/temp, °C	extractn solv[b]	yield,[c] %	mp, °C (solv)[b] or bp, °C/Torr	lit. data or formula[d]	MS,[e] m/e (M^+)
8a	A	0.5/rt[n]	D	95[f]	77–78 (E/A)	77–78[f]	*f*
8b	A	0.5/rt	F	98	111–112 (D)	110–111[19]	
8c	A	1/rt	F	100	116–117 (F)	114–115[19]	
8d	*g*	0.17/45	F	92	86–88 (A)	89.5–90.5[12]	
8e	A	1/50	D	100	51–53 (I)	46–48[20]	
8f	A	0.5/rt	D	96	37–39 (I)	35–37[21]	
8g	A	0.5/rt	D	100	87 (K)	85–86[22]	
9a	B	0.5/rt	F	95[f]	149–150 (E)	149–150[f]	*f*
9b	B	1/rt	F[h]	90	189–190 (F/G)	$C_{20}H_{17}NO_4$	335
9c	B	1/rt	F[h]	94	260–261 (F)	$C_{18}H_{11}Cl_2NO_2$	343
9d	*g*	0.5/45	F	90	158–159 (L)	159.5–160[12]	
9e	B	3/50	D	100	169–170 (D/A)	$C_{14}H_{21}NO_2$	235
9f	B	0.5/50	D	95	98–99 (D/A)	$C_{16}H_{25}NO_2$	263
9g	B	0.5/rt	D	100	137–138 (I)	$C_{18}H_{25}NO_2$	287
11	B	0.5/50	F	100	105–106 (E/A)	$C_{16}H_{17}NO_2$	255
17a	A	0.5/rt	D	92	114–115/0.5	115–120/0.5[23]	
17b	A	0.17/rt	D	93	69–71 (H)	$C_{13}H_{13}NO_2$	215
17c	A	0.17/rt	D	97	69–71 (H)	70–71[15]	
17d	A	0.5/50	D	94	106–107/15	225–226[g]	
17e	A	0.5/rt	D	100	91–93/0.3	$C_{11}H_{17}NO$	179
17f	A	0.5/rt	D	100	102–103/0.3	$C_{12}H_{17}NO$	191
18a	A	0.5/rt	F	96	90–91 (E/A)	90–93[23]	
18b	A	0.17/rt	F	95	166/0.4	$C_{13}H_{13}NO_2$	215
18c	A	0.5/rt	F	90	51–52 (K)	48–49[15]	
18d	A	0.5/rt	D	100	157–158/19	150/17[9]	
18e	A	0.5/rt	D	100	124–126/0.3	$C_{11}H_{17}NO$	179
18f	A	0.5/rt	D	95	47–48 (A)	$C_{12}H_{17}NO$	191
19a	B	0.5/rt	D	97	126–127 (D)	$C_{19}H_{15}NO_2$	289
19b	B	0.5/rt	F	100	96 (A)	$C_{21}H_{19}NO_4$	349
19c	B	0.5/rt	F	97	148–149[i] (F/G)	$C_{19}H_{13}Cl_2NO_2$	357
19d	B	0.5/rt	D	100[l]	72–73 (G)	72–72.5[9]	
19e	B	0.5/rt	D	100	176–178/0.5	$C_{17}H_{27}NO_2$	277
19f	B	1/rt	D	100	84–85 (G)	$C_{19}H_{27}NO_2$	301
20a	B	0.5/rt	D	95	135–136 (H)	135.5–137.5[14]	
20b	B	1/rt	F	100	218–219 (F)	$C_{21}H_{19}NO_4$	349
20c	B	0.5/rt	F[h]	93	270–272 (M/H)	$C_{19}H_{13}Cl_2NO_2$	357
20d	B	0.5/rt[m]	D	100	65–66 (G)	$C_{15}H_{23}NO_2$	249

[a] A: HgO (1.09 g, 5 mmol), 35% aqueous HBF_4 (2.5 mL), and THF (12.5 mL) for 5 mmol of monosubstituted pyrroles and *N*-methylpyrroles **6**, **13**, and **14**. B: HgO (2.17 g, 10 mmol), 35% aqueous HBF_4 (5 mL), and THF (25 mL) for 5 mmol of disubstituted pyrroles and *N*-methylpyrroles **7**, **10**, **15**, and **16**. [b] For extraction solvent, see footnotes *a* of Table I and *b* of Table II; K = hexane; L = nitromethane; M = DMSO. [c] Yields of pure isolated products. [d] Satisfactory microanalyses were obtained: C ± 0.14; H ± 0.11; N ± 0.11. [e] See footnote *d* of Table II. [f] Reported in ref 3b. [g] The general method reported in the experimental part for the hydrolysis did not give good results. In fact, the extraction of 2-acetylpyrrole (**8d**) and 2,5-diacetylpyrrole (**9d**) was not possible owing to their low solubility in all the solvents tested (e.g., benzene, chloroform, etc.). However, it was possible to hydrolyze **6d** and **7d** with H_2O_2/CH_3COOH according to the method previously reported by us for the hydrolysis of 2,2-disubstituted 1,3-benzoxathioles.[24] In particular, the hydrolyses of **6d** and **7d** (2 mmol) were run in CH_3COOH (6 and 12 mL) with 4 and 8 mmol respectively of H_2O_2. The reactions were complete after 10 and 30 min at 40–45 °C. After the usual workup of the reaction mixtures, 2-acetylpyrrole (**8d**) and 2,5-diacetylpyrrole (**9d**) were continuously extracted with chloroform. Ketones so obtained are pure. [h] The reaction mixture is treated with chloroform (about 100 mL). The solution so obtained is then filtered through a silica gel column (20 cm in height and 4–5 cm in diameter), with the same solvent as eluent. The first portion of chloroform (about 500 mL) is rejected, while the following portion (about 1000 mL) is collected and evaporated under vacuum to afford pure ketone. [i] In ref 15, 2,4-bis(4-chlorobenzoyl)-*N*-methylpyrrole was reported in 12% yield; however, the melting point was not reported. [l] Hydrolysis could be carried out by starting from pure **15d** and also by starting from the mixture of **15d** and the byproduct (see footnote *h* of Table II). The overall yield of ketone **19d** was the same. [m] Hydrolysis was carried out by starting from the separated diastereoisomers **16d**-I and **16d**-II and also from the mixture of the diastereoisomers. Yields were always quantitative. [n] Room temperature.

the methods for their preparation are of limited value.

Although our new method can be employed for the monoacylation of pyrrole itself, the introduction of an acyl group at the 2-position can be more easily achieved by other well-known routes.[5-8] However, our method for synthesizing diacylpyrroles bearing identical or different acyl groups at the 2- and 5-positions represents the first general route to these derivatives. Indeed, the introduction of a second acyl group by electrophilic acylation of 2-acylpyrroles takes place with prevalent or exclusive attack at the 4-position, in accordance with the usual behavior of pyrroles bearing an electron-withdrawing substituent at the 2-position. Thus, the acetylation of 2-acetylpyrrole with acetic acid, catalyzed by trifluoroacetic anhydride, affords 2,4-diacetylpyrrole as the major product (47%), accompanied by 2,5-diacetylpyrrole (19%).[12] Furthermore, the $AlCl_3$-catalyzed Friedel–Crafts acetylation of 2-(trichloroacetyl)pyrrole with acetyl chloride gives 4-acetyl-2-(trichloroacetyl)pyrrole in 93% yield.[11] The formation of 2,5-diacetylpyrrole by reaction of acetic anhydride with pyrrole at high temperature in 33% yield[10] appears anomalous, but this reaction probably proceeds by the thermal rearrangement of 1,2-diacetylpyrrole.[5a,b] When salts **1** are used, both the mono- and disubstitution obviously proceed by electrophilic attack. The first substitution takes place at the 2-position; the second proceeds by regiospecific attack at the 5-position. This is due to the presence at the 2-position of the pyrrole ring of a substituent, the masked acyl group, which not only does not exert –M effect but also probably activates the 5-position.

The reactions of the salts **1** with *N*-methylpyrrole have been chiefly examined in order to explore the synthetic

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potential of the new procedure toward the simplest N-substituted pyrrole, in view of the more extensive research on this subject. It is known that substituents at the 1-position can exert significant steric and electronic influence on electrophilic substitution. Therefore, in comparison with the reactions carried out on unsubstituted pyrrole, a different orientation of the substitutions was to be expected by attack of bulky electrophiles, such as 2-substituted 1,3-benzoxathiolyl cations, even in the presence of a group as simple as a methyl at the 1-position. Actually, the first substitution is not regioselective: both 2- and 3-substituted *N*-methylpyrroles were isolated. However, the second substitution in any case gives 2,4-disubstituted *N*-methylpyrroles as the major products, whatever the nature of the R group present in **1**. These results in general, but the second substitution in particular, appear to prove the importance of the steric effect of the methyl group, and of the 1,3-benzoxathiolyl group, once present. From a synthetic point of view, it is important that, even in the case of *N*-methylpyrrole, the new procedure allows the introduction of two acyl groups in the pyrrole ring, under mild reaction conditions, thus filling a void in the preparation of diacyl derivatives of N-substituted pyrroles, of which very few examples have been reported.[9,14,15]

Experimental Section

^1H and ^{13}C NMR spectra were recorded on a Bruker WP 80 SY spectrometer in deuteriochloroform or in deuterioacetone, and the chemical shifts are expressed in parts per million (δ) relative to internal tetramethylsilane. Unless otherwise noted, MS were recorded with a HP 5970 B mass selective detector connected to a HP 5890 GC; cross-linked methyl silicone capillary column. IR spectra were recorded in the gas phase on a Bruker IFS 85 infrared Fourier spectrophotometer equipped with a GC–IR coupling system; cross-linked methyl silicone capillary column; data are given in cm^{-1} by using the following convention: vw, very weak; w, weak; m, medium; s, strong; vs, very strong.

2-Substituted 1,3-Benzoxathiolium Tetrafluoroborates (1a–g). 2-Phenyl-, 2-(4-methoxyphenyl)-, 2-(4-chlorophenyl)-, 2-*tert*-butyl-, 2-pentyl-, and 2-cyclohexyl-1,3-benzoxathiolium tetrafluoroborates (**1a–c,e–g**) were prepared as previously reported by starting from *o*-mercaptophenol[16] (1.26 g, 10 mmol) and the appropriate acyl chloride[2,16b] or carboxylic acid[17] (10 mmol) plus 5 mL of 54% tetrafluoroboric acid–ether complex. 2-Methyl-1,3-benzoxathiolium tetrafluoroborate (**1d**) was prepared in the same way by starting from acetic acid, with 70–75% yield; mp 87–88 °C dec. Salt **1d** is very sensitive to moisture, and its immediate use is advisable. However, it can be stored in well-closed bottles at a low temperature: ^1H NMR (CF_3COOD) δ 7.61–8.47 (m, 4 H benzo), 3.54 (s, 3 H, CH_3); ^{13}C NMR (CF_3COOD) δ 211.66 (s, C^+), 159.95 (s, OC benzo), 134.71, 132.14, 126.19, 117.26 (d, C benzo), 125.99 (s, SC benzo), 21.82 (q, CH_3). Anal. Calcd for $C_8H_7BF_4OS$: C, 40.37; H, 2.96; S, 13.47. Found: C, 40.26; H, 3.02; S, 13.54.

Reaction of Pyrrole (5) with 2-*tert*-Butyl-1,3-benzoxathiolium Tetrafluoroborate (1e). Typical Procedure. In entry 9, 2-*tert*-butyl-1,3-benzoxathiolium tetrafluoroborate (**1e**; 2.80 g, 10 mmol) was added, in one portion and with stirring, to a mixture of pyrrole (**5**; 2.01 g, 30 mmol) and dry pyridine (0.79 g, 10 mmol) in dry acetonitrile (5 mL). The reaction was exothermic, salt **1e** dissolved at once, and a white precipitate was formed. The reaction mixture was stirred at room temperature for 60 min, then treated with water (100 mL), and extracted with chloroform (3 × 150 mL). The collected extracts were washed with sodium hydroxide solution (5%; 100 mL) and then with water (100 mL), dried, and evaporated. The crude residue was chromatographed on a silica gel column, with petroleum ether/acetone (9.8:0.2) as eluent, to afford 2,5-bis[2-(2-*tert*-butyl-1,3-benzoxathiolyl)]pyrrole (**7e**) as a minor product, 6% yield (calculated on 2-*tert*-butyl-1,3-benzoxathiolium tetrafluoroborate; 0.26 g), and 2-[2-(2-*tert*-butyl-1,3-benzoxathiolyl)]pyrrole (**6e**) as the major product, 70% yield (calculated on 2-*tert*-butyl-1,3-benzoxathiolium tetrafluoroborate; 1.81 g). **7e**: mp 226–227 °C, from benzene; MS, *m/e* 451 (M^+); ^1H NMR ($CDCl_3$) δ 8.57 (br m, 1 H, NH), 6.73–7.10 (m, 8 H benzo), 6.12 (d, 2 H, H-3 and H-4; J = 2.78 Hz), 1.06 (s, 18 H, 2 t-C_4H_9); ^{13}C NMR (owing to low solubility in $CDCl_3$ and in CD_3COCD_3, the spectra were recorded in C_6D_6 and in hexamethylphosphoramide where the signals marked with one or two asterisks could be respectively observed) δ 156.55* (s, OC benzo), 107.84* (s, OCS), 132.31* (s, C-2 and C-5 pyrrole), 125.96, 122.70, 122.17, 110.81, 109.20** (d, C pyrrole and C benzo), 40.81* [s, $C(CH_3)_3$], 26.75 [q, $C(CH_3)_3$]. Anal. Calcd for $C_{26}H_{29}NO_2S_2$: C, 69.15; H, 6.47; N, 3.10; S, 14.20. Found: C, 69.21; H, 6.52; N, 3.18; S, 14.31. **6e**: mp 75 °C, from petroleum ether; MS, *m/e* 259 (M^+); ^1H NMR ($CDCl_3$) δ 8.47 (br m, 1 H, NH), 6.73–7.16 (m, 4 H benzo), 6.61–6.73 (m, 1 H, H-5), 6.24 (7 lines, 1 H, H-3, $J_{1,3}$ = 2.44, $J_{3,4}$ = 3.50, $J_{3,5}$ = 1.40), 6.09–6.20 (m, 1 H, H-4), 1.13 (s, 9 H, t-C_4H_9); ^{13}C NMR ($CDCl_3$) δ 155.93 (s, OC benzo), 125.90 (s, SC benzo), 107.35 (s, OCS), 132.47 (s, C-2 pyrrole), 125.52, 122.19, 122.05, 116.40, 110.31, 108.32 (two overlapping signals) [d, C pyrrole and C benzo], 40.72 [s, $C(CH_3)_3$], 26.28 [q, $C(CH_3)_3$]. Anal. Calcd for $C_{15}H_{17}NOS$: C, 69.46; H, 6.61; N, 5.40; S, 12.36. Found: C, 69.39; H, 6.67; N, 5.50; S, 12.42.

In entry 10, the reaction mixture consisted of 2-*tert*-butyl-1,3-benzoxathiolium tetrafluoroborate (**1e**; 8.40 g, 30 mmol), pyrrole (**5**; 0.67 g, 10 mmol), and dry pyridine (2.37 g, 30 mmol) in dry acetonitrile (8 mL). After the mixture was stirred for 30 min at room temperature, the precipitate consisting of 2,5-bis-[2-(2-*tert*-butyl-1,3-benzoxathiolyl)]pyrrole (**7e**) and pyridinium tetrafluoroborate was filtered, washed with 2–3 mL of acetonitrile, and then dissolved in chloroform/water (500:100 mL). The chloroform solution was separated and washed with sodium hydroxide solution (5%; 100 mL) and water (100 mL), as described above. After evaporation of the solvent, the crude residue was washed with hot methanol (2 × 5 mL) to afford pure product **7e** in quantitative yield [4.41 g; purity monitored by TLC (petroleum ether/acetone, 9.8:0.2) and ^1H NMR; mp 226–227 °C, from benzene]. This was identical with that isolated in entry 9.

2-[2-(2-Phenyl-1,3-benzoxathiolyl)]-5-[2-(2-*tert*-butyl-1,3-benzoxathiolyl)]pyrrole (10) was prepared according to the above procedure by starting from 2-phenyl-1,3-benzoxathiolium tetrafluoroborate (**1a**; 3.75 g, 12.5 mmol), 2-[2-(2-*tert*-butyl-1,3-benzoxathiolyl)]pyrrole (**6e**; 2.58 g, 10 mmol), dry pyridine (0.99 g, 12.5 mmol), and dry acetonitrile (5 mL). The reaction time was 30 min at room temperature. The crude residue obtained after the usual workup was chromatographed on silica gel with petroleum ether/ethyl ether (9.5:0.5) as eluent. Compound **10** was obtained in 93% yield (4.38 g): mp 145–146 °C, from benzene; MS, *m/e* 471 (M^+); ^1H NMR ($CDCl_3$) δ 8.70 (br m, 1 H, NH), 7.31–7.61 and 7.01–7.31 (2 m, 2:3, 5 H phenyl), 6.52–7.01 (m, 8 H benzo), 6.01 and 5.73 (2 dd, 1:1, 2 H, H-3 and H-4, $J_{3,4}$ = 3.94, $J_{1,3}$ = $J_{1,4}$ = 2.25 Hz), 1.00 (s, 9 H, t-C_4H_9); ^{13}C NMR ($CDCl_3$) δ 154.80, 154.21 (s, OC benzo), 141.99, 134.82, 126.04 (s, C arom), 128.56, 128.31, 127.77, 126.55, 126.22, 125.63, 122.72, 122.27, 121.99, 121.80, 121.42, 111.60, 111.48, 110.93, 110.43, 108.52, 108.39 (d, C arom), 106.73, 98.37 (s, OCS), 40.52 [s, $C(CH_3)_3$], 26.18 [q, $C(CH_3)_3$]. Anal. Calcd for $C_{28}H_{25}NO_2S_2$: C, 71.31; H, 5.34; N, 2.97; S, 13.60. Found: C, 71.25; H, 5.40; N, 3.04; S, 13.67.

2,5-Dipivaloylpyrrole (9e). Typical Procedure. According to the procedure previously reported, 2,5-bis[2-(2-*tert*-butyl-

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1,3-benzoxathiolyl)]pyrrole (**7e**; 2.20 g, 5 mmol) was added to the hydrolysis reagent constituted of mercury (II) oxide (2.17 g, 10 mmol) in THF (25 mL) and 35% aqueous tetrafluoroboric acid (5 mL). The reaction was exothermic, and mercury(II) oxide dissolved at once. The mixture was heated at 50 °C with stirring for 3 h until the disappearance of the starting material (TLC test: petroleum ether/ethyl ether, 9.5:0.5). The reaction mixture was then extracted several times with hot benzene until a test by TLC of the last extract showed that the ketone **9e** was no longer present. The combined extracts were washed successively with 10% potassium iodide solution (2 × 80 mL), 5% sodium hydroxide solution (80 mL), and water (80 mL). After evaporation of the solvent, pure 2,5-dipivaloylpyrrole (**9e**) was obtained in quantitative yield (1.11 g; purity monitored by TLC with petroleum ether/ethyl ether, 9.5:0.5, GC–MS, ^{1}H NMR): mp 169–170 °C, from benzene/petroleum ether; MS, m/e 235 (M^+); ^{1}H NMR ($CDCl_3$) δ 9.99 (br m, 1 H, NH), 6.88 (d, 2 H, H-3 and H-4, $J_{1,3} = J_{1,4} = 2.56$ Hz), 1.36 (s, 18 H, 2 t-C_4H_9); ^{13}C NMR ($CDCl_3$) δ 196.78 (s, CO), 130.67 (s, C-2 and C-5), 115.21 (d, C-3 and C-4, $J_{C,H} = 173$ Hz), 43.21 [s, $C(CH_3)_3$], 27.87 [q, $C(CH_3)_3$]; IR (gas phase) 3444 (w), 2981 (w), 2943 (w), 2921 (w), 2884 (vw), 1672 (m), 1529 (vw), 1481 (w), 1398 (w), 1372 (vw), 1279 (w), 1161 (vs), 1063 (vw), 1016 (vw), 899 (w), 798 (vw), 763 cm^{-1} (vw). Anal. Calcd for $C_{14}H_{21}NO_2$: C, 71.46; H, 9.00; N, 5.95. Found: C, 71.53; H, 9.09; N, 6.01.

2-(Cyclohexylcarbonyl)-*N*-methylpyrrole (17f), 3-(Cyclohexylcarbonyl)-*N*-methylpyrrole (18f), and 2,4-Bis(cyclohexylcarbonyl)-*N*-methylpyrrole (19f). Direct Hydrolysis. The crude reaction mixture (3.10 g) obtained in entry 25 by reaction of 2-cyclohexyl-1,3-benzoxathiolium tetrafluoroborate (**1g**; 3.06 g, 10 mmol), *N*-methylpyrrole (**12**; 2.43 g, 30 mmol), and dry pyridine (0.79 g, 10 mmol) in dry acetonitrile (5 mL) was directly hydrolyzed by treatment with mercury(II) oxide (2.24 g) and 35% aqueous tetrafluoroboric acid (5 mL) in THF (50 mL). The reaction was complete after 60 min at room temperature. The usual workup afforded a mixture of **17f**, **18f**, and **19f**. By chromatography on silica gel with petroleum ether/ethyl ether, 1:1, as eluent, pure ketones were isolated with the following yields: **17f** (14%), **18f** (68%), and **19f** (4%).

Acknowledgment. This work was supported by the National Research Council of Italy (CNR), Progetto Finalizzato "Chimica Fine e Secondaria", and by Ministero della Pubblica Istruzione (MPI).

Registry No. **1a**, 58948-35-9; **1b**, 58948-36-0; **1c**, 58948-38-2; **1d**, 112816-51-0; **1e**, 59045-53-3; **1f**, 70737-93-8; **1g**, 58948-47-3; **5**, 109-97-7; (±)-**6a**, 112816-52-1; (±)-**6b**, 112816-53-2; (±)-**6c**, 112816-54-3; (±)-**6d**, 112816-55-4; (±)-**6e**, 112816-56-5; (±)-**6f**, 112816-57-6; (±)-**6g**, 112816-58-7; *meso*-**7a**, 112816-59-8; (±)-**7a**, 112816-60-1; *meso*-**7b**, 112816-60-1; (±)-**7b**, 112816-62-3; *meso*-**7c**, 112816-63-4; (±)-**7c**, 112839-64-2; *meso*-**7d**, 112816-64-5; (±)-**7d**, 112816-65-6; *meso*-**7e**, 112816-66-7; (±)-**7e**, 112816-67-8; *meso*-**7f**, 112816-68-9; (±)-**7f**, 112816-69-0; *meso*-**7g**, 112816-92-9; (±)-**7g**, 112816-93-0; **8a**, 7697-46-3; **8b**, 1963-43-5; **8c**, 13169-71-6; **8d**, 1072-83-9; **8e**, 91539-34-3; **8f**, 89789-54-8; **8g**, 75211-59-5; **9a**, 111122-84-0; **9b**, 112816-70-3; **9c**, 112816-71-4; **9d**, 31685-34-4; **9e**, 112816-72-5; **9f**, 112816-73-6; **9g**, 112816-74-7; (±)-(*R**,*R**)-**10**, 112816-95-2; (±)-(*R**,*S**)-**10**, 112816-94-1; **11**, 112816-75-8; **12**, 96-54-8; (±)-**13a**, 112925-40-3; (±)-**13b**, 112925-41-4; (±)-**13c**, 112925-42-5; (±)-**13d**, 112816-96-3; (±)-**13e**, 112816-87-2; (±)-**13f**, 112816-88-3; (±)-**14a**, 112816-89-4; (±)-**14b**, 112816-90-7; (±)-**14c**, 112816-91-8; (±)-**14d**, 112895-66-6; (±)-**14e**, 112895-67-7; (±)-**14f**, 112895-68-8; (±)-(*R**,*S**)-**15a**, 112816-97-4; (±)-(*R**,*R**)-**15a**, 112816-98-5; (±)-(*R**,*S**)-**15b**, 112816-99-6; (±)-(*R**,*R**)-**15b**, 112817-00-2; (±)-(*R**,*S**)-**15c**, 112817-01-3; (±)-(*R**,*R**)-**15c**, 112817-02-4; (±)-(*R**,*S**)-**15d**, 112817-03-5; (±)-(*R**,*R**)-**15d**, 112817-04-6; (±)-(*R**,*S**)-**15e**, 112817-05-7; (±)-(*R**,*R**)-**15e**, 112817-06-8; (±)-(*R**,*S**)-**15f**, 112817-07-9; (±)-(*R**,*R**)-**15f**, 112817-08-0; *meso*-**16a**, 112817-09-1; (±)-**16a**, 112817-10-4; *meso*-**16b**, 112817-11-5; (±)-**16b**, 112817-12-6; *meso*-**16c**, 112817-13-7; (±)-**16c**, 112817-14-8; *meso*-**16d**, 112817-15-9; (±)-**16d**, 112817-16-0; **17a**, 37496-06-3; **17b**, 35421-09-1; **17c**, 62128-32-9; **17d**, 108213-03-2; **17e**, 112816-76-9; **17f**, 112816-77-0; **18a**, 62128-30-7; **18b**, 111223-35-9; **18c**, 62128-44-3; **18d**, 108213-04-3; **18e**, 112816-78-1; **18f**, 112816-79-2; **19a**, 112816-80-5; **19b**, 112816-81-6; **19c**, 76024-67-4; **19d**, 108213-05-4; **19e**, 112816-82-7; **19f**, 112816-83-8; **20a**, 37496-10-9; **20b**, 112816-84-9; **20c**, 112816-85-0; **20d**, 112816-86-1; *o*-mercaptophenol, 1121-24-0.

Supplementary Material Available: ^{1}H and ^{13}C NMR data of substituted pyrroles and *N*-methylpyrroles **6**, **7**, and **13–16**, ^{1}H and ^{13}C NMR and IR (gas phase) data of acylpyrroles and acyl-*N*-methylpyrroles **8**, **9**, **11**, and **17–20** (9 pages). Ordering information is given on any current masthead page.