Deacylation of Pyrrole and Other Aromatic Ketones

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Received February 10, 1984

Ethyl 4-acetyl-3,5-dimethyl-1*H*-pyrrole-2-carboxylate (**1a**) reacts rapidly with ethylene glycol in refluxing benzene with *p*-toluenesulfonic acid or perchloric acid as catalyst to give ethyl 3,5-dimethyl-1*H*-pyrrole-2-carboxylate (**3**) in high yield (96%). Various 2- and 3-acylpyrroles can be efficiently deacylated by using this procedure. Other ketones which undergo deacylation include phenyl(2-phenylindol-3-yl)methanone (**19**), 1-(5-methyl-1-phenylpyrazol-4-yl)ethanone (**20**), and 2,4-dimethoxybenzophenone. Certain pyrrole ketones where the acyl group is flanked by two ring methyl groups are also cleaved under acidic conditions by using ethanedithiol.

Discussion

Reaction of formylpyrroles with glycols to give acetal derivatives has been reported by several groups.[2-8] Acetals formed by using ethylene glycol are usually unstable and readily revert to the formylpyrrole on chromatography or crystallization.[3,4] Stability of the acetals is increased when electron-withdrawing substituents are present in the pyrrole ring[3,7] or when ethylene glycol is replaced with a more hindered diol (2-methylpentane-2,4-diol[2,3] or 2,2-dimethylpropane-1,3-diol[5,8]) or ethanedithiol.[3] Some of the more stable acetals have found use in synthesis.[5-7] Although the reaction of formyl pyrroles has been studied in some detail, there have been few reports on the reaction of acetylpyrroles and other pyrrole ketones with glycols.[8-10]

Smith et al.[10] recently reported that certain 3-acetyl- and 3-formylpyrroles can be deacylated by refluxing in benzene with *p*-toluenesulfonic acid (TsOH) and a large excess of ethylene glycol for 24 h. We have obtained similar results and have found that this reaction provides a convenient synthesis for pyrroles such as **3** (Scheme I). We have used this reaction to deacylate not only 3-acylpyrroles but also a variety of 2-acylpyrroles. Many of the reactions are complete in less than 1 h by using only a slight excess of ethylene glycol. In some cases we have found it advantageous to replace TsOH, which is consumed in the reaction, with perchloric acid which functions only as a catalyst. In this paper we describe our results and present some considerations on the scope and limitations of this deacylation reaction.

Most of our reactions were carried out under standardized conditions, which involved addition of TsOH (0.1 equiv) to a refluxing solution of the pyrrole (0.01 mol) and ethylene glycol (2.0 equiv) in benzene (50 mL); water was removed from the reaction using a Dean–Stark trap. The composition of the reaction mixture was determined at various times by gas chromatography and by reverse phase HPLC. HPLC was particularly valuable as it allowed complete analysis of the reaction mixtures, including the products derived from TsOH.

Various pyrrole ketones of structure **1** react with ethylene glycol and TsOH as outlined in Scheme I. Ketone **1a** is completely converted to the deacetylated pyrrole **3** and glycol ester **4a** within minutes under the standardized reaction conditions (Figure 1). If the refluxing is continued for 1 h, the yield of pyrrole **3** is unaffected, but most of the TsOH reacts with **4a** to give a mixture of the sul-

Table I. Products Formed by Refluxing Various Pyrroles with Ethylene Glycol in Benzene[a]

compd	TsOH, equiv	2,[b] %	3,[b] %
1a	0.01	46[c]	30
	0.1	0	100[d]
1b	0.1	0	58
1c	0.1	0	53
1d	0.1	0	18[e]

[a] Reactions were run on 0.01-mol scale with 2.0 equiv of ethylene glycol in 50 mL of benzene; additional information is given in Scheme I and Figure 1. [b] Analysis by GC at 1 h. [c] Identified by GC/MS. The ketal could also be detected by TLC but reverted to the ketone when chromatographed on silica gel. [d] Isolated yield was 96%. Deacetylation did not go to completion when this reaction was carried out in a larger volume of benzene (500 mL). [e] This represents the isolated yield of **3**. Compound **17** (66%) was also isolated from this reaction.

Table II. Deacetylation of 1a Using TsOH and Varying Amounts of Ethylene Glycol[a]

ethylene glycol, equiv	deacetylation, % 1 h	24 h
1.0	30	32
1.5	39	41
2.0	48	52
2.5	59	65
4.0	72	81
5.0	81	94
7.5	87	100

[a] Reactions carried out on 0.01-mol scale by using 0.01 equiv of TsOH in benzene (50 mL); analysis by GC at 1 and 24 h.

Table III. Products Formed by Refluxing 1c with TsOH and Ethylene Glycol in Benzene[a]

TsOH, equiv	time, min	TsOH (% of original)[b]	3c,[c] %
0.1	60	0	53
0.2	60	0	83
0.3	60	0	94
0.4	5	91	59
	15	62	95
	60	0	97
0.5	60	10	100[d]
0[e]	150		72
0[e]	480		100[f]

[a] Reactions carried out on 0.01-mol scale in benzene (50 mL) with 2 equiv of ethylene glycol. [b] Determined by reverse phase HPLC. [c] Percent of pyrrole-related products as determined by GC. [d] Isolated yield after chromatography and crystallization was 92%. [e] 0.01 equiv of perchloric acid used as the catalyst. [f] Isolated yield by crystallization of the crude product from methanol was 73%. Diethylene glycol monobenzoate and triethylene glycol dibenzoate were formed in addition to **4c** in this reaction.

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(2) Chong, R.; Clezy, P. S. *Aust J. Chem.* **1967**, *20*, 935.
(3) Clezy, P. S.; Fookes, C. J. R.; Lau, D. Y. K.; Nichol, A. W.; Smythe, G. A. *Aust. J. Chem.* **1974**, *27*, 357.
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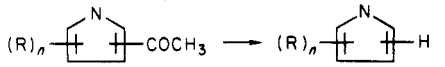
(6) Hudson, M. F.; Smith, K. M. *Synthesis* **1976**, 464.
(7) Loader, C. E.; Anderson, H. J. *Synthesis* **1978**, 295.
(8) Loader, C. E.; Barnet, G. H.; Anderson, H. J. *Can. J. Chem.* **1982**, *60*, 383.
(9) Elguero, J.; Jacquier, R.; Shimizu, B. *Bull. Soc. Chim. Fr.* **1970**, 1585.
(10) Smith, K. M.; Miura, M.; Tabba, H. D. *J. Org. Chem.* **1983**, *48*, 4779.

0022-3263/84/1949-2663$01.50/0

Table IV. Deacylation of Various Pyrroles by Ethylene Glycol (2 equiv) and TsOH

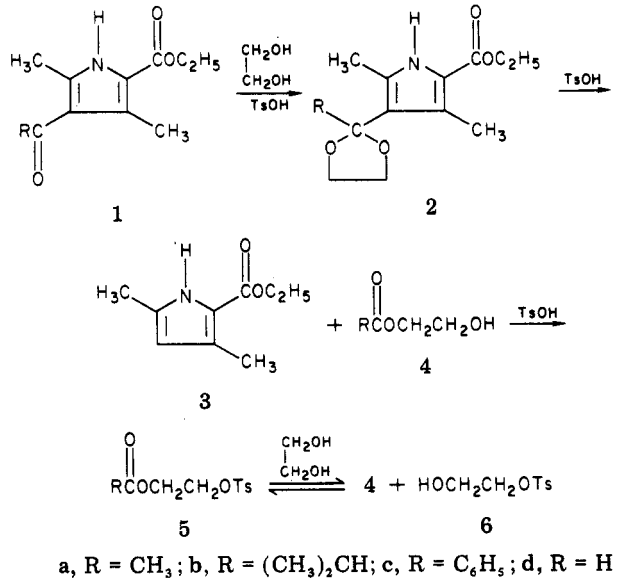


9 10

	substituent groups in 9					TsOH, equiv	time, min	yield of 10,[a] %
	1	2	3	4	5			
a	H	$COCH_3$	CH_3	C_2H_5	CH_3	0.1	15	35[b]
b	H	$COCH_3$	$COOC_2H_5$	H	CH_3	0.1	15	85
c	H	$COOC_2H_5$	CH_3	CH_3	$COCH_3$	0.5	5	88[c]
d	H	CH_3	$COCH_3$	CH_3	H	0.1	15	40[b]
e	CH_3	CH_3	$COCH_3$	H	CH_3	0.1	15	68
f	CH_3	CH_3	$COCH_3$	$COCH_3$	CH_3	0.1	30	72[d]
g	H	H	$COOC_2H_5$	$COCH_3$	CH_3	0.1	15	84
h	H	CH_3	$COCH_3$	CH_3	NO_2	0.4	120	20[e]
						0[f]	45	83

[a] Isolated yield following chromatography or crystallization. [b] Chromatography was required to remove 2-hydroxyethyl acetate from the pyrrole product. [c] Reaction of **9c** with 0.1 equiv of TsOH reached a steady state at 30 min and gave 30% of **10c** and 70% of the ketal derivative of **9c**. This ketal has been reported by Smith et al (ref 10). [d] Four equivalents of ethylene glycol were used; the product of the reaction was 1,2,5-trimethyl-1*H*-pyrrole. [e] Starting material and the ketal of **9h** were also obtained (see Experimental Section). [f] Perchloric acid (0.05 equiv) used as catalyst.

Scheme I. Products Obtained by Reaction of Acylpyrroles with Ethylene Glycol[a]



1 2 3 4 5 6

a, R = CH_3; b, R = $(CH_3)_2CH$; c, R = C_6H_5; d, R = H

[a] Deacetylation of benzyl 4-acetyl-3,5-dimethylpyrrole-2-carboxylate has been described by Smith et al.[10] The fate of the TsOH was not considered by these authors. Reference 26 describes the formation of **5a** from **4a**. For the use of **4a** as a catalyst in the formation of **6** from TsOH and ethylene glycol, see Experimental Section.

fonate esters **5a** and **6**. This participation of TsOH makes it a less than ideal catalyst for deacylation of pyrroles, as an initially rapid reaction may slow and stop before deacylation is complete. For example, reaction of **1a** with a reduced quantity of TsOH (0.01 equiv) was incomplete even after 24 h and gave a mixture of ketone, ketal, and **3** (Figure 1 and Table I). Deacylation can be completed by using 0.01 equiv of TsOH provided larger amounts of ethylene glycol are used and the reaction is refluxed for several hours (Table II).

Deacylation of ketones **1b** and **1c** was also incomplete, using 0.1 equiv of TsOH. These reactions could be completed by using larger amounts of TsOH or by using perchloric acid (0.01 equiv) as catalyst as is illustrated in Table III for **1c**.[11]

(11) The hindered sulfonic acid 2,4,6-trimethylbenzenesulfonic acid also participated in the reaction and offered no advantage over TsOH as a catalyst.

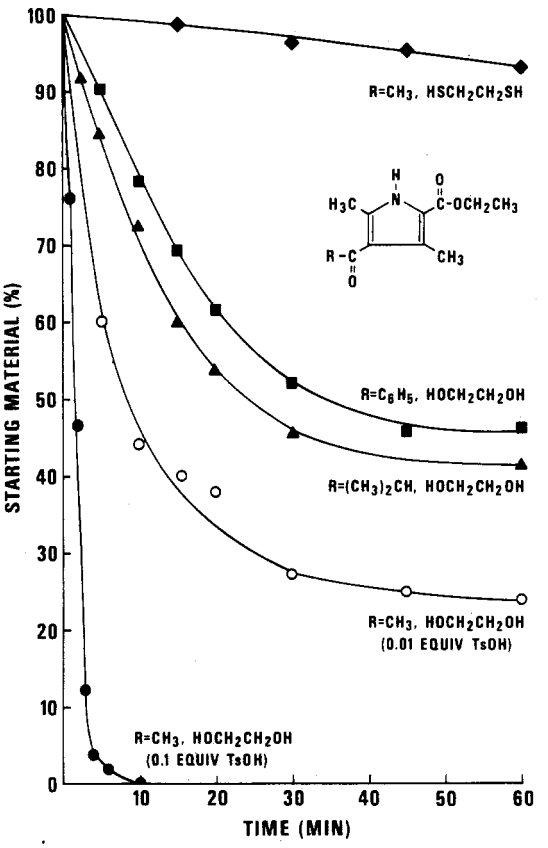
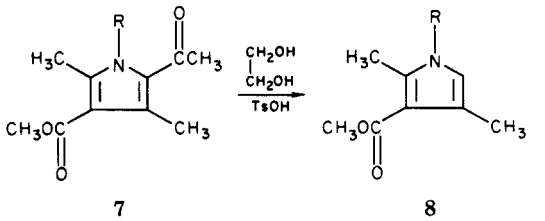


Figure 1. Deacylation of pyrroles of structure 1. The pyrrole (0.01 mol) was refluxed in benzene (50 mL) with ethylene glycol or ethanedithiol (2.0 equiv) and TsOH (0.1 equiv).

Pyrrole deacylations reported by Smith[10] all involve 3-acylpyrroles. We have found that various 2-acetylpyrroles can also be deacetylated. Compound **7a** was



7 8

a, R = H; b, R = CH_3

readily deacetylated by using the standardized conditions

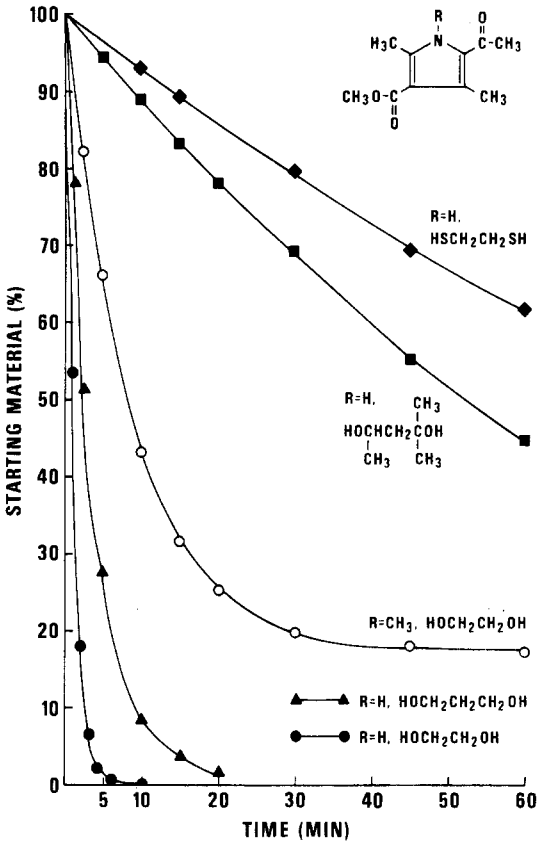


Figure 2. Reaction of methyl 5-acetyl-2,4-dimethyl-1*H*-pyrrole-3-carboxylate with various glycols and ethanedithiol. The pyrrole (0.01 mol) was refluxed in benzene (50 mL) with the glycol (2.0 equiv) and TsOH (0.1 equiv).

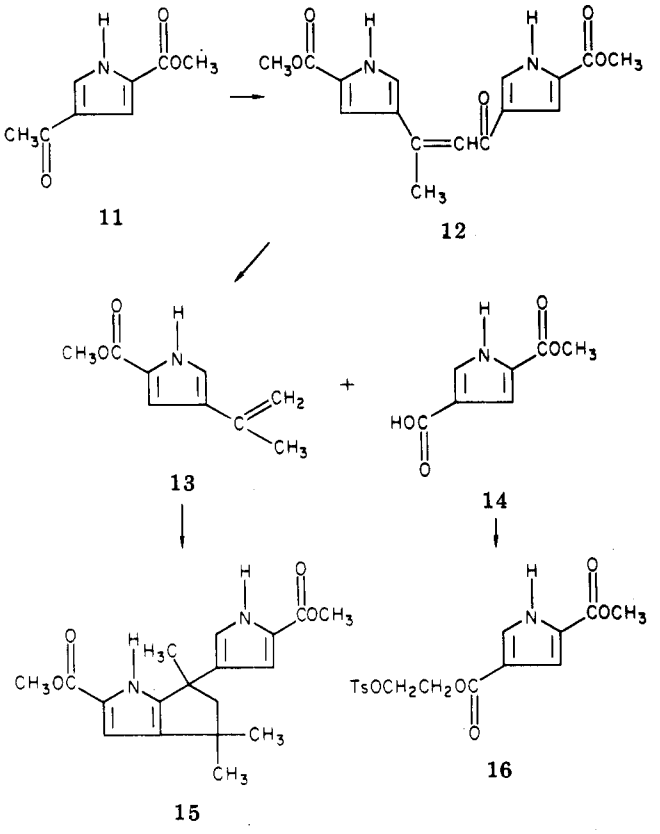
(Figure 2). While no deacetylation occurred with alcohols (e.g., butanol), other diols could be used, but the reaction rate was slower (Figure 2). The N-methylated pyrrole **7b** was also deacetylated but more slowly than **7a** (Figure 2).

Many pyrrole ketones can be rapidly deacylated in high yield with ethylene glycol and TsOH. Table IV shows additional examples. Although the reaction is quite general, certain ketones are not deacylated, or the deacylated pyrrole initially obtained is transformed to other products under the acidic reaction conditions.

We have found that a ketal derivative is formed from diethyl 5-formyl-3-methyl-1*H*-pyrrole-2,4-dicarboxylate and ethylene glycol even under forcing conditions with perchloric acid or large amounts of TsOH as catalyst; similar results for this pyrrole have been reported by Clezy et al.[3] It is probable that pyrrole ketones which are deactivated by two electron-withdrawing substituents in addition to the acyl group form ketal derivatives which resist protonation of the pyrrole ring and therefore are not readily deacylated.

An unstable ketal can be formed from compound **11** (Scheme II) under the conditions described by Elguero et al.[9] We have found that attempted ketalization of **11** under the standardized conditions gave a complex mixture from which **15** and **16** were isolated as the major products. Acid-catalyzed dimerization of the ketone as shown in Scheme II, a reaction reported for acetophenone,[12] may account for formation of these products. Methyl 1*H*-pyrrole-2-carboxylate and esters **5a** and **6** are also formed

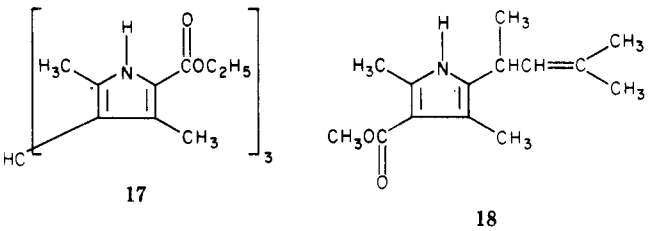
Scheme II. Products Formed on Attempted Ketalization of Pyrrole **11**[a]



[a] Reaction of **11** with ethanedithiol (2 equiv) and TsOH (0.1 equiv) in refluxing benzene for 15 min gives methyl 4-(2-methyl-1,3-dithiolan-2-yl)-1*H*-pyrrole-2-carboxylate (62%), mp 74–76 °C.

in low yield in the reaction, indicating that deacylation of **11** is also taking place.[13]

A further limitation to the scope of the deacylation reaction is encountered when the pyrrole initially produced undergoes further transformation under the reaction conditions. Deacetylation of 3-acetyl-2,4-dimethylpyrrole (**9d**) gives a low yield of 2,4-dimethylpyrrole (Table IV). A major reason for the low yield is the instability of the product under the acidic reaction conditions. Similar results may be expected in other reactions where the pyrrole product is sensitive to acid. Another problem was encountered in the deformylation of **1d**. Compound **17**,



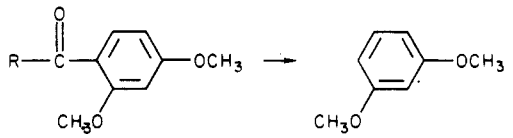
formed by reaction of **3** with **1d** under the reaction conditions, was the major product.[14] Reaction of **7a** with 2-methyl-2,4-pentanediol afforded **18** as the major product. This is formed by further reaction of **8a** with the allylcarbonium ion generated from the diol under the reaction conditions.

(12) Juge, F. E.; Fry, A. *J. Org. Chem.* **1970**, *35*, 1876. The reaction reported by Juge and Fry occurs at high temperature over a phosphoric acid catalyst. We have found that (1,1,3-trimethyl-3-phenyl)indan (42%) is formed when 0.01 mol of acetophenone is refluxed with ethylene glycol (1.0 equiv) and TsOH (1.0 equiv) in benzene for 18 h.

(13) A higher yield of methyl pyrrole-2-carboxylate (45%) is obtained if 1 equiv of TsOH is used in the reaction; we have not studied this reaction in detail to further optimize the reaction conditions.

(14) A related tripyrrylmethane was obtained by Clezy on attempted ketalization of ethyl 5-formyl-4-methylpyrrole-2-carboxylate (see ref. 3).

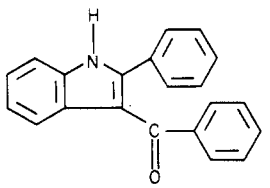
Table V. Deacylation of 2,4-Dimethoxyacetophenone and 2,4-Dimethoxybenzophenone[a]



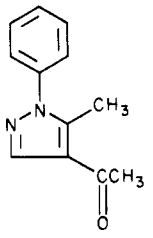
R	acid	equiv	deacylation,[b] % 2h	24h
CH_3	TsOH	0.1	14	15
		0.5	76	75
		1.0	100	
	$HClO_4$	0.01	35	72
		0.05	80	100
C_6H_5	TsOH	0.1	9	11
		0.5	60	65
		1.0	100	
	$HClO_4$	0.01	3	34
		0.05	18	97[c]

[a] All reactions run on 0.01-mol scale with 2.0 equiv of ethylene glycol in benzene (50 mL). Grözinger and Hess (ref 16) report 87% deacetylation of 2,4-dimethoxyacetophenone in 100 h using 5 equiv of ethylene glycol and 0.1 equiv of TsOH. [b] Determined by GC. [c] Products isolated from this reaction were 2,4-dimethoxybenzene (1.05 g), diethylene glycol dibenzoate (0.12 g), and triethylene glycol dibenzoate (0.96 g).

The reaction can also be used to deacylate other heterocyclic and aromatic ketones. Kametani et al.[15] have reported the deformylation of an indole, and we have found that other indoles, e.g., **19**, can be efficiently deacylated.



19

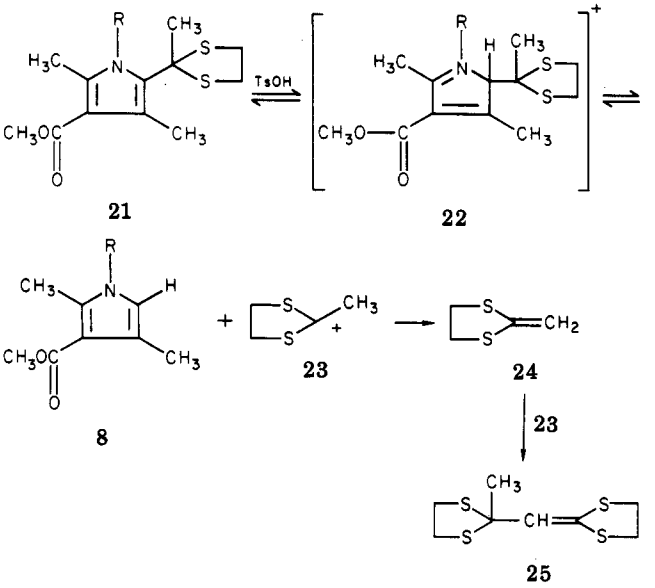


20

Pyrazole **20** can also be deacetylated, although the reaction is extremely slow and 3 equiv of TsOH and a 48-h reaction period are required to complete the deacylation. While these reaction conditions are forcing, ketone **20** is recovered unchanged when refluxed with TsOH in absence of ethylene glycol.

Grözinger and Hess have reported the slow deacetylation of various methoxy-substituted acetophenones including 2,4-dimethoxyacetophenone.[16] We have found that these reactions follow the course outlined in Scheme I. An unstable ketal can be identified as a reaction intermediate by GC/MS. Following an initially rapid reaction, the rate of the deacylation reaction slows as the TsOH is converted to **5a** and **6**. By modifying the reaction conditions we have been able to deacylate 2,4-dimethoxyacetophenone in 2 h using 1.0 equiv of TsOH (Table V). If perchloric acid (0.05 equiv) is substituted for TsOH in this reaction, deacetylation is complete in 24 h (Table V). We have also found that 2,4-dimethoxybenzophenone undergoes the same cleavage reaction (Table V). With perchloric acid as catalyst the reaction products at 18 h are 2,4-dimethoxybenzene, diethylene glycol dibenzoate, and triethylene glycol dibenzoate. As reported by Grözinger and Hess the

Scheme III. Products Obtained by Reaction of Thioketals of Structure 21 with TsOH



a, R = H; b, R = CH_3

scope of this deacylation reaction is fairly limited; *o*-methoxyacetophenone and acetophenone are not deacylated by ethylene glycol even when large amounts of TsOH are used.[12]

Ethanedithiol can also be used to deacylate certain pyrrole ketones.[10] We have not studied this reaction in detail, as it offers no advantage over the ethylene glycol procedure for deacylating pyrrole ketones. The reaction is much slower (see Figures 1 and 2) and is also more limited in scope, as many pyrrole ketones afford stable thioketal derivatives when refluxed with ethanedithiol (2 equiv) and TsOH (0.1 equiv) in benzene.[3] Ketones which are deacylated under these reaction conditions can be regarded as sterically hindered. Compound **1a** (Scheme I), where the acetyl group is flanked by two ring methyl groups, is completely deacylated in 24 h, while the *N*-methylpyrrole **7b** is deacylated more slowly (25% in 24 h; 40% in 48 h); thioketal intermediates could not be detected in the reactions of **1a** and **7b** with ethanedithiol. Compound **11** (Scheme II), where the ketone group lacks adjacent alkyl substituents, reacts rapidly (15 min) with ethanedithiol to give a stable thioketal in high yield, while **7a** gives thioketal **21a** (Scheme III) as the major product together with some deacylated pyrrole **8a** (10%).

While thioketal **21a** appears to be stable, we have shown that it exists in equilibrium with **8a** and **23** under acidic conditions (Scheme III), with equilibrium favoring **21a**. Ion **23** appears to be a relatively stable intermediate under the reaction conditions.[17] Under similar reaction conditions thioketal **21b**, prepared by methylation of **21a**, is rapidly converted to **8b** and **25** (Scheme III). Dimerization of **23** as shown in Scheme III accounts for the formation of **25**.[18]

Evidence to support the existence of **23** as a relatively stable reaction intermediate and the equilibrium proposed for **21a** in Scheme III comes from the following experiments. When thioketal **21b** and pyrrole **8a** are heated in benzene in the presence of TsOH the 2-methyl-1,3-di-

(15) Kametani, T.; Kigawa, Y.; Takahashi, K., Nemoto, H.; Fukumoto, K. *Chem. Pharm. Bull.* **1978**, 26, 1918.
(16) Grözinger, K.; Hess, F. *Synthesis* **1977**, 411.

(17) TsOH functions only as a catalyst in the reactions of pyrrole ketones with ethanedithiol; 2-[[(4-methylphenyl)sulfonyl]thio]ethyl thiolacetate, the sulfur analogue of **5a** (Scheme I), is not formed in these reactions.

thiolan-2-yl group is transferred to the less hindered pyrrole, giving **8b** and thioketal **21a** in good yield. Also, if pyrrole **8a** is treated with 2-methyl-1,3-dithiolan-2-yl perchlorate[18] at room temperature in acetonitrile a 3:1 mixture of the thioketal **21a** and unreacted **8a** is obtained. This reaction provides an alternate synthesis for **21a**; the perchlorate salt of **23** should be a useful reagent for the synthesis of thioketal derivatives of other pyrroles.

In summary, pyrrole deacylation is a more general reaction than has previously been reported. Where deacylation is incomplete or slow with use of TsOH, perchloric acid may be preferred as the acid catalyst. This reaction provides an extremely convenient synthesis for selected pyrroles (e.g., **3** from **1a** and **8a** from **7a**). The ketone group may also find use as a removable protecting group in pyrrole synthesis.

Experimental Section

Melting points were taken in open capillary tubes on a Thomas Hoover melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on a Varian CFT 20 spectrometer, chemical shifts are reported in δ units with $CDCl_3$ as solvent and tetramethylsilane as the internal standard (in NMR description s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet). GC data were obtained on a Hewlett-Packard Model 5840A gas chromatograph, a column (45 cm × 3 mm i.d.) of 3% SE-30 on 100–120 mesh Gas Chrom Q, a nitrogen carrier gas (flow rate 20 mL/min), and a hydrogen flame ionization detector. Samples were injected at 100 °C and after 1 min the column temperature was raised 20 °C/min to a final temperature of 250 °C. Mass spectra were recorded on a Hewlett Packard Model 5990A gas chromatograph/mass spectrometer. HPLC data were obtained on two Waters Associates 6000A pumps, a Waters Associates Model 660 solvent programmer, a Valco 60-N injector with 20-μL sample loop, a Tracor 970A detector set at 215 nM, a Hewlett-Packard 3390A integrator, and a reverse phase μ-Bondapak-C_{18} column (30 cm × 3.9 mm i.d.). Solvents were prepared by mixing acetonitrile (Burdick and Jackson UV grade) with aqueous 0.01 M sodium dihydrogen phosphate (adjusted to pH 2.9 by addition of 1.0 mL/L of 17% phosphoric acid). Samples were evaporated under reduced pressure and reconstituted in methanol, and 20 μL was injected and analyzed by using a linear gradient of acetonitrile (10–75%) over a period of 15 min (flow rate 2.0 mL/min); elution of the column was continued for an additional 6 min with 75% acetonitrile.

Preparation of Pyrroles and Glycol Derivatives. Many of the compounds prepared in this study have been reported in the literature. These compounds were identical by GC, HPLC, TLC, and NMR analysis to samples of the same product prepared by literature methods. Satisfactory elemental analyses (±0.3%) were obtained for all new solids. Information on the compounds is provided below (compound number, melting point or boiling point/mm (ref), GC retention time, HPLC retention time). Compound **1a**, 143–144 °C (lit.[45] 143–144 °C), 4.8 min, 9.8 min; **1b**, 109–111 °C (lit.[19] 108 °C), 5.3 min, 12.4 min; **1c**, 112–114 °C (lit.[20] 112–114 °C), 6.9 min, 13.3 min; **1d**, 144 °C (lit.[21] 145 °C), 4.6 min, 9.5 min; **2a**,[22] 5.1 min;[23] **3**, 122–124 °C (lit.[21] 125 °C), 2.4 min, 11.6 min; **4a**, 93 °C (25 mm), 2.9 min,[24] 4.8 min; **4c**, 133 °C (0.1 mm) (lit.[25] 154–157 °C (10 mm)), 3.1 min, 7.6 min; **5a**,[22] (ref 26),[27] 11.7 min; **5c**, 75–77 °C (lit.[28] 74–75 °C),[27] 14.8 min; ethylene glycol dibenzoate, 71–73 °C (lit.[29] 73–74 °C), 6.2 min, 15.4 min; diethylene glycol monobenzoate,[30] (lit.[31] 153–155 °C (2 mm)), 4.3 min, 8.4 min; diethylene glycol dibenzoate,[30] (lit.[31] 235–237 °C (7 mm)), 7.4 min, 14.9 min; triethylene glycol monobenzoate,[30] 5.5 min, 8.7 min; triethylene glycol dibenzoate,[30] (ref 32), 8.5 min, 14.9 min; **6**,[22] ref 28,[27] 8.7 min; **7a**, 161–163 °C,[33] 4.5 min, 9.0 min; **7b**, 66–68 °C, 4.5 min, 10.7 min; **8a**, 101–104 °C (lit.[34] 101–103 °C), 2.7 min, 9.1 min; **8b**, 84–86 °C (lit.[35] 85–86 °C), 2.6 min, 11.1 min; **9a**, 112–114 °C (lit.[36] 112 °C), 3.3 min, 11.2 min; **9b**, 120–122 °C (lit.[37] 124 °C), 3.9 min, 9.9 min; **9c**, 106–108 °C (lit.[38] 106 °C), 4.4 min, 11.9 min; **9d**, 139–141 °C (lit.[39] 137 °C), 3.0 min, 6.9 min; **9e**, 51–54 °C, 2.7 min, 8.7 min; **9f**, 140–142 °C (lit.[40] 143–144 °C), 4.9 min, 7.4 min; **9g**, 59–62 °C, 5.1 min, 7.8 min; **9h**, 214–215 °C, 5.8 min, 8.2 min; **10a**, 105 °C (25 mm) (lit.[41] 84 °C (10 mm)), 3.1 min,[24] 11.5 min; **10b**, 69–71 °C (lit.[42] 70–71 °C), 3.2 min, 8.8 min; **10c**, 94–96 °C (lit.[43] 95–96 °C), 2.3 min, 12.1 min; **10d**, 80 °C (30 mm) (lit.[44] 165 °C (743 mm)), 1.7 min,[24] 8.20 min; **10e**, 85 °C (30 mm) (lit.[44] 165 °C (740 mm)), 2.1 min,[24] 10.8 min; **10h**, 108–110 °C, 2.8 min, 8.7 min; **11**, 111–113 °C (ref 9), 4.1 min, 6.2 min; **15**, 192–195 °C,[27] 14.5 min; **16**,[27] 2.6 min; methyl pyrrole-2-carboxylate, 74–76 °C, 0.90 min, 6.9 min; **17**, 193–195 °C,[27] 16.1 min; **18**, 92–94 °C, 4.8 min, 15.1 min; **19**, 225–226 °C (lit.[46] 222 °C), 9.3 min, 14.8 min; 2-phenylindole, 188–189 °C (lit.[47] 187 °C), 6.0 min, 15.1 min; **20**, 103–104 °C, (lit.[48] 107–108 °C), 4.5 min, 10.0 min; 5-methyl-1-phenylpyrazole, 178 °C (25 mm) (lit.[49] 263 °C (762 mm)), 2.4 min, 10.5 min; 2,4-dimethoxyacetophenone, 39–41 °C, 6.4 min,[24] 10.5 min; 2,4-dimethoxybenzophenone, 82–84 °C, 8.5 min,[24] 13.8 min; 2,4-dimethoxybenzene, 85–87 °C (7 mm), 3.5 min,[24] 11.3 min; **21a**, 98–101 °C, 6.6 min, 13.7 min; **21b**, 88–89 °C, 7.4 min, 15.2 min; **25**, 170 °C (0.2 mm), 5.8 min, 14.5 min.

Standardized Conditions for Deacylation of Pyrroles. A solution of the pyrrole (0.01 mol) and *p*-toluenesulfonic acid monohydrate (190 mg, 0.001 mol) in benzene (50 mL) was stirred and refluxed under a Dean–Stark trap for 5 min. Ethylene glycol (1.22 g, 0.02 mol) was added to give a two-phase system which became homogeneous within a few minutes. Samples were removed at various times for GC and HPLC analysis. When reaction was complete the solution was cooled, diluted with benzene, and washed successively with sodium carbonate solution and water. The benzene was removed under reduced pressure and the deacylated pyrrole was purified by crystallization or by chromatography on silica gel (ethyl acetate/Skellysolve B as eluant) followed by crystallization or distillation.

Deacetylation of Ethyl 4-Acetyl-3,5-dimethyl-1*H*-pyrrole-2-carboxylate (1a) Using TsOH. A mixture of compound **1a** (20.9 g, 0.10 mol), ethylene glycol (6.2 g, 0.10 mol), and $TsOH·H_2O$ (1.90 g, 0.01 mol) in benzene (200 mL) was stirred and refluxed for 1 h under a Dean–Stark trap. The benzene was removed by evaporation at 50 °C (25 mm), and 2-hydroxyethyl

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acetate (**5a**) was then removed at 120 °C (0.2 mm); redistillation of this fraction afforded 5.2 g of **5a**, bp 95 °C (25 mm).

The solid remaining after removal of solvents was crystallized from methanol to give 15.1 g (90%) of ethyl 3,5-dimethyl-1*H*-pyrrole-2-carboxylate (**3**), mp 122–124 °C. Chromatography of the mother liquors on silica gel followed by crystallization from methanol gave an additional 1.0 g (6%) of **3**, mp 122–124 °C.

2-Hydroxyethyl *p*-Toluenesulfonate (6). A mixture of ethylene glycol (12.4 g, 0.2 mol), $TsOH·H_2O$ (19.0 g, 0.10 mol), and 2-hydroxyethyl acetate (1.0 g, 0.01 mol) was stirred and refluxed in benzene (400 mL) under a Dean–Stark trap for 18 h. The benzene was removed under reduced pressure and the product was chromatographed on silica gel. Elution of the column with ethyl acetate/Skellysolve B gave 1.4 g of 2-[[(4-methylphenyl)-sulfonyl]oxy]ethyl acetate (**5a**): NMR δ 1.99 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3), 4.22 (s, 4 H, CH_2CH_2), 7.35 (d, 2 H, Ar H), 7.80 (d, 2 H, Ar H).

Continued elution of the column gave 16.4 g (81%) of compound **6**: NMR δ 1.89 (s, 1 H, OH), 2.45 (s, 3 H, CH_3), 3.70 (m, 2 H, CH_2), 4.15 (m, 2 H, CH_2), 7.35 (d, J = 8 Hz, 2 H, Ar H), 7.81 (d, J = 8 Hz, 2 H, Ar H). Anal. Calcd for $C_9H_{12}O_4S$: C, 50.00; H, 5.60; S, 14.82. Found: C, 50.09; H, 5.78; S, 14.62.

Debenzoylation of Ethyl 4-Benzoyl-3,5-dimethyl-1*H*-pyrrole-2-carboxylate (1c) Using TsOH. A mixture of compound **1c** (2.71 g, 0.01 mol), ethylene glycol (1.22 g, 0.02 mol), and $TsOH·H_2O$ (0.95 g, 0.005 mol) was refluxed in benzene (50 mL) under a Dean–Stark trap for 1 h. After removal of the benzene, the product was chromatographed on silica gel by using ethyl acetate/Skellysolve B (1:1) as eluant. The first product eluted from the column was crystallized from methanol (15 mL) to give 1.54 g (92%) of ethyl 3,5-dimethyl-1*H*-pyrrole-2-carboxylate (**3**), mp 123–124 °C.

Continued elution of the column gave 1.21 g of 2-[[(4-methylphenyl)sulfonyl]oxy]ethyl benzoate (**5c**) followed by 0.86 g of 2-hydroxyethyl benzoate (**4c**).

Deacetylation of Methyl 5-Acetyl-2,4-dimethyl-1*H*-pyrrole-3-carboxylate (7a) Using $HClO_4$. A mixture of compound **7a** (1.95 g, 0.01 mol), ethylene glycol (1.24 g, 0.02 mol), and 70% $HClO_4$ (28 mg, 0.02 equiv) was refluxed in benzene (50 mL) under a Dean–Stark trap for 30 min. After evaporation of the benzene under reduced pressure the product was purified by chromatography on silica gel and crystallized from ethyl acetate/Skellysolve B to give 1.19 g (77%) of methyl 2,4-dimethyl-1*H*-pyrrole 3-carboxylate, mp 139–140 °C.

1-(2,4-Dimethyl-5-nitro-1*H*-pyrrol-3-yl)ethanone (9h). Fuming nitric acid (24 mL) in acetic anhydride (250 mL) was added at 0 °C to a stirred solution of 2,4-diacetyl-3,5-dimethyl-1*H*-pyrrole (40 g) in acetic anhydride (480 mL). The mixture was stirred 30 min and was diluted with water (500 mL), and the product was extracted into chloroform. Evaporation of the chloroform gave a solid which was crystallized twice from methanol to give 8.0 g of **9h**: mp 214–216 °C; NMR δ 2.36 (s, 3 H, CH_3), 2.46 (s, 3 H, CH_3), 2.55 (s, 3 H, CH_3), 13.05 (s, 1 H, NH). Anal. Calcd for $C_8H_{10}N_2O_3$: C, 52.74; H, 5.53; N, 15.38. Found: C, 52.44; H, 5.78; N, 15.03.

3-(2-Methyl-1,3-dioxolan-2-yl)-2,4-dimethyl-5-nitro-1*H*-pyrrole. A mixture of **9h** (8.0 g, 0.049 mol), TsOH (400 mg, 0.043 equiv), and ethylene glycol (6.0 g, 0.097 mol) was refluxed in benzene (400 mL) for 2 h. The benzene was evaporated under reduced pressure, and the residual oil was crystallized from ethyl acetate/Skellysolve B. The solid obtained was recrystallized twice from ethyl acetate/Skellysolve B to give 2.3 g of 3-(2-methyl-1,3-dioxolanyl-2-yl)-2,4-dimethyl-5-nitro-1*H*-pyrrole: mp 121–123 °C; NMR δ 1.62 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3), 2.53 (s, 3 H, CH_3), 3.82 (m, 4 H, CH_2CH_2). Anal. Calcd for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.25; N, 12.38. Found: C, 52.91; H, 6.33; N, 12.01.

The mother liquors were combined and chromatographed on silica gel (chloroform as eluant) to give 1.4 g of 2-nitro-3,5-dimethyl-1*H*-pyrrole which was crystallized from ethyl acetate/Skellysolve B; mp 108–110 °C; NMR δ 2.29 (s, 3 H, CH_3), 2.39 (s, 3 H, CH_3), 5.88 (s, 1 H, Ar H). Anal. Calcd for $C_6H_8N_2O_2$: C, 51.42; H, 5.75; N, 19.99. Found: C, 51.48; H, 5.86; N, 20.19.

Methyl 1,4,5,6-Tetrahydro-6-[5-(methoxycarbonyl)-1*H*-pyrrol-3-yl]-4,4,6-trimethylcyclopenta[*b*]pyrrole-2-carboxylate (15). A mixture of methyl 4-acetyl-1*H*-pyrrole-2-carboxylate (1.67 g, 0.01 mol), $TsOH·H_2O$ (0.19 g, 0.1 equiv), and ethylene glycol (1.24 g, 0.02 mol) was refluxed for 6 h in benzene (50 mL) under a Dean–Stark trap. The benzene was removed under reduced pressure to give an oil which was chromatographed on silica gel by using ethyl acetate/Skellysolve B (1:1) as eluant. Methyl 1*H*-pyrrole-2-carboxylate (71 mg, 6%) was the first product eluted from the column, followed by compound **15** (420 mg, 25%). Two crystallizations from ethyl acetate/Skellysolve B gave the analytical sample; mp 192–195 °C; NMR δ 1.19 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3), 1.60 (s, 3 H, CH_3), 2.32 (d, J = 12 Hz, 1 H, CH), 2.55 (d, J = 12 Hz, 1 H, CH), 3.80 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 6.75 (m, 3 H, Ar H); mass spectrum, m/e (relative intensity) 330 (25), 315 (100), 283 (72), 251 (25). Anal. Calcd for $C_{18}H_{22}N_2O_4$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.21; H, 6.66; N, 8.36.

The next fraction eluted from the column was 275 mg (7%) of compound **16**: NMR δ 2.41 (s, 3 H, CH_3), 3.88 (s, 3 H, OCH_3), 4.33 (m, 4 H, CH_2CH_2), 7.20 (m, 1 H, Ar H), 7.30 (d, 2 H, Ar H), 7.53 (m, 1 H, Ar H), 7.79 (d, 2 H, Ar H).

Continued elution of the column gave 130 mg (8%) of methyl 4-acetyl-1*H*-pyrrole-2-carboxylate followed by 167 mg of 1*H*-pyrrole-2,4-dicarboxylic acid, 4-hydroxyethyl 2-methyl diester: NMR δ 3.84 (s, 3 H, OCH_3), 3.85 (m, 2 H, OCH_2), 4.35 (m, 2 H, OCH_2), 7.20 (m, 1 H, Ar H) 7.50 (m, 1 H, Ar H); mass spectrum, m/e (relative intensity) 213 (22), 170 (42), 152 (73), 120 (100).

Triethyl 4,4′,4″-Methylidynetris(3,5-dimethyl-1*H*-pyrrole-2-carboxylate) (17). A mixture of ethyl 4-formyl-3,5-dimethyl-1*H*-pyrrole-2-carboxylate (1.95 g, 0.01 mol), ethylene glycol (1.24 g, 0.02 mol), and $TsOH·H_2O$ (0.16 g) was stirred and refluxed in benzene (50 mL) for 1 h. After removing the solvent, the residue was chromatographed on silica gel by using chloroform as eluant to give 0.32 g of ethyl 3,5-dimethyl-1*H*-pyrrole-2-carboxylate. Elution of the column with chloroform/methanol (9:1) gave compound **17** which was crystallized from methanol (1.1 g, mp 188 °C). The analytical sample was recrystallized from methanol: mp 193–195 °C; NMR δ 1.34 (t, 9 H, CH_3), 1.69 (s, 9 H, CH_3), 2.05 (s, 9 H, CH_3), 4.29 (q, 6 H, OCH_2), 5.14 (s, 1 H, CH), 8.72 (s, 1 H, NH); mass spectrum, m/e (relative intensity), 511 (100), 496 (56), 450 (30), 438 (69) and 329 (69). Anal. Calcd for $C_{28}H_{37}N_3O_6$: C, 65.73; H, 7.29; N, 8.21. Found: C, 65.54; H, 7.18; N, 8.20.

Methyl 5-(1,3-Dimethyl-2-butenyl)-2,4-dimethyl-1*H*-pyrrole-3-carboxylate (18). A mixture of methyl 2-acetyl-3,5-dimethyl-1*H*-pyrrole-3-carboxylate (19.5 g, 0.10 mol), 2-methyl-2,4-pentanediol (24.0 g, 0.20 mol), and $TsOH·H_2O$ (1.90 g, 0.01 mol) was stirred and refluxed in benzene (200 mL) for 18 h under a Dean–Stark trap. The benzene was evaporated and the residual oil was chromatographed on silica gel by using ethyl acetate/Skellysolve B as eluant. The first product eluted from the column was recrystallized from Skellysolve B to give 9.2 g (39%) of **18**, mp 90–95 °C. The analytical sample was recrystallized from methanol: mp 94–96 °C; NMR δ 1.22 (d, 3 H, CH_3), 1.60 (s, 3 H, CH_3), 1.69 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3), 3.65 (q, 1 H, CH), 3.77 (s, 3 H, OCH_3), 5.20 (m, 1 H, =CH), 7.70 (s, 1 H, NH). Anal. Calcd for $C_{14}H_{21}NO_2$: C, 71.45; H, 9.00; N, 5.95. Found: C, 71.48; H, 9.15; N, 6.32.

Continued elution of the column gave 4.2 g of methyl 3,5-dimethyl-1*H*-pyrrole-3-carboxylate.

2-Phenylindole. A mixture of phenyl (2-phenylindol-3-yl)-methanone (744 mg, 2.5 mmol), ethylene glycol (300 mg, 5.0 mmol), and $TsOH·H_2O$ (238 mg, 1.25 mmol) was stirred and refluxed in benzene (50 mL) under a Dean–Stark trap for 1 h. The benzene was evaporated under reduced pressure and the residual oil was applied to a silica gel column which was eluted with chloroform. The first fraction obtained from the column was crystallized from cyclohexane (50 mL) to give 407 mg (84%) of 2-phenylindole, mp 188–189 °C.

The second fraction eluted from the column was crystallized from ethyl acetate/Skellysolve B to give 242 mg of 2-[[(4-methylphenyl)sulfonyl]oxy]ethyl benzoate (**5c**), mp 75–77 °C.

5-Methyl-1-phenylpyrazole. A mixture of 1-(5-methyl-1-phenylpyrazol-4-yl)ethanone (**20**, 500 mg, 2.5 mmol), $TsOH·H_2O$ (1.45 g, 7.6 mmol), and ethylene glycol (310 mg, 5.04 mmol) was refluxed in benzene (50 mL) under a Dean–Stark trap. After 24 h ethylene glycol (125 mg, 2.0 mmol) was added and the refluxing was continued for an additional 24 h. The reaction solution was cooled and diluted with ether (100 mL) and was extracted with

4 N sodium hydroxide solution (20 mL). The organic phase was washed with water (2 × 5 mL), the solvents were removed, and the residual oil was chromatographed on silica gel. Elution of the column with ethyl acetate/Skellysolve B (1:9) gave 255 mg (64%) of 5-methyl-1-phenylpyrazole. Continued elution of the column gave, in order, 2-[[(4-methylphenyl)sulfonyl]oxy]ethyl acetate (**5a**, 228 mg), compound **25** (28 mg), and 2-hydroxyethyl *p*-toluenesulfonate (**6**, 452 mg).

Methyl 2,4-Dimethyl-5-(2-methyl-1,3-dithiolan-2-yl)-1*H*-pyrrole-3-carboxylate (21a). A mixture of methyl 5-acetyl-2,4-dimethyl-1*H*-pyrrole-3-carboxylate (19.5 g, 0.10 mol), ethanedithiol (14.4 g, 0.15 mol), and $TsOH·H_2O$ (1.90 g, 0.01 mol) was refluxed in benzene (200 mL) for 18 h under a Dean–Stark trap. The benzene was evaporated and the product was dissolved in chloroform and chromatographed on silica gel. Elution of the column with chloroform gave 15.2 g of **21a** which was crystallized from ethyl acetate/Skellysolve B to give 13.8 g (51%) of product, mp 98–100 °C. The analytical sample was recrystallized from ethyl acetate/Skellysolve B: mp 98–100 °C; NMR δ 2.12 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3), 3.35 (m, 4 H, CH_2CH_2), 3.77 (s, 3 H, OCH_3), 8.73 (s, 1 H, NH). Anal. Calcd for $C_{12}H_{17}NO_2S_2$: C, 53.11; H, 6.32; N, 5.16; S, 23.63. Found: C, 53.30; H, 6.32; N, 5.08; S, 23.44.

Continued elution of the column gave 1.62 g of methyl 2,4-dimethyl-1*H*-pyrrole-3-carboxylate.

Alternate Synthesis of 21a. 2-Methyl-1,3-dithiolan-2-yl perchlorate[18] (211 mg, 1.0 mmol) was added to a stirred solution of methyl 2,4-dimethyl-1*H*-pyrrole-3-carboxylate (306 mg, 2.0 mmol) in acetonitrile (25 mL). After 5 min a solution of triethylamine (100 mg, 1.0 mmol) in acetonitrile (8 mL) was added dropwise. Three further additions of the perchlorate salt (0.5 mmol) followed by triethylamine (0.5 mmol) were made over a 30-min period. The reaction solution was evaporated and partitioned between ethyl acetate (200 mL) and water (20 mL). The ethyl acetate was evaporated and the residual oil was chromatographed on silica gel to give, in order of elution from the column, 357 mg (66%) of methyl 2,4-dimethyl-5-(2-methyl-1,3-dithiolan-2-yl)-1*H*-pyrrole-3-carboxylate and 32 mg of compound **8a**.

Methyl 5-(2-Methyl-1,3-dithiolan-2-yl)-1,2,4-trimethyl-1*H*-pyrrole-3-carboxylate (21b). Sodium hydride (50% in oil, 0.96 g, 0.02 mol) was added to a stirred solution of **21a** (5.4 g, 0.02 mol) in THF (150 mL). After 30 min methyl iodide (5.6 g, 0.04 mol) was added and the solution was stirred for an additional 60 min. The THF was evaporated under reduced pressure and the residue was partitioned between ethyl acetate and water. The ethyl acetate phase was separated, washed with water, and dried over sodium sulfate, and the ethyl acetate was evaporated. The crude product was chromatographed on silica gel by using ethyl acetate/Skellysolve B as eluant and the purified product was crystallized from Skellysolve B to give 2.8 g of **21b**: mp 83–85 °C; NMR δ 2.31 (s, 3 H, CH_3), 2.42 (s, 3 H, CH_3), 2.49 (s, 3 H, CH_3), 3.48 (s, 4 H, CH_2CH_2), 3.77 (s, 6 H, OCH_3 and NCH_3). Anal. Calcd for $C_{13}H_{19}NO_2S_2$: C, 54.70; H, 6.71; N, 4.91; S, 22.47. Found: C, 54.80; H, 6.72; N, 5.05; S, 22.56.

Action of TsOH on Compound 21b. Methyl 5-(2-methyl-1,3-dithiolan-2-yl)-1,2,4-trimethyl-1*H*-pyrrole-3-carboxylate (2.85 g, 0.01 mol) was refluxed in benzene (100 mL) with TsOH (10 mg) for 30 min and the benzene was evaporated under reduced pressure. The product was chromatographed on silica gel by using ethyl acetate/Skellysolve B (1:9) as eluant to give, as the first product eluted from the column, 1.1 g (93%) 2-(1,3-dithiolan-2-ylidenemethyl)-2-methyl-1,3-dithiolane (**25**). A sample was distilled for analysis: bp 150 °C (0.2 mm); NMR δ 1.97 (s, 3 H, CH_3), 3.30 (m, 8 H), 5.88 (s, 1 H, =CH); mass spectrum, *m/e* (relative intensity) 236 (80), 221 (23), 208 (48), 180 (84), 148 (100) 83, (66), 59 (78). Anal. Calcd for $C_8H_{12}S_4$: C, 40.64; H, 5.12; S, 54.25. Found: C, 40.68; H, 5.37; S, 54.44.

Continued elution of the column gave 1.52 g (93%) of methyl 1,2,4-trimethyl-1*H*-pyrrole-3-carboxylate which was crystallized from ethyl acetate/Skellysolve B; mp 84–85 °C.

Alternate Synthesis of 2-(1,3-Dithiolan-2-ylidenemethyl)-2-methyl-1,3-dithiolane (25). Triethylamine (3.0 g, 0.03 mol) was added to a stirred solution of 2-methyl-1,3-dithiolan-2-yl perchlorate[18] (3.3 g, 0.014 mol) in acetonitrile (50 mL). After 15 min the solution was evaporated and partitioned between ethyl acetate and 1 N sodium hydroxide solution. The ethyl acetate phase was washed with water and evaporated. The residual oil was chromatographed on silica gel to give 0.85 g of compound **25**, identical with the previously prepared sample by NMR, GC, and mass spectral analysis.

Transfer of 2-Methyl-1,3-dithiolan-2-yl Residue from 21b to 8a. A mixture of methyl 5-(2-methyl-1,3-dithiolan-2-yl)-1,2,4-trimethyl-1*H*-pyrrole-3-carboxylate (285 mg, 1.0 mmol), methyl 2,4-dimethyl-1*H*-pyrrole-3-carboxylate (200 mg, 1.3 mmole), and $TsOH·H_2O$ (10 mg) was stirred and refluxed in benzene for 5 min. The benzene was removed under reduced pressure and the residual oil was chromatographed on silica gel by using chloroform as the eluant. The first product eluted from the column was 162 mg of methyl 1,2,4-trimethyl-1*H*-pyrrole-3-carboxylate followed by 221 mg (82%) of methyl 5-(2-methyl-1,3-dithiolan-2-yl)-2,4-dimethyl-1*H*-pyrrole-3-carboxylate. Continued elution of the column gave 24 mg of methyl 2,4-dimethyl-1*H*-pyrrole-3-carboxylate.

Registry No. **1a**, 2386-26-7; **1b**, 90433-73-1; **1c**, 90433-74-2; **1d**, 2199-64-6; **2a**, 90433-75-3; **2b**, 90433-76-4; **2c**, 90433-77-5; **2d**, 90433-78-6; **3**, 2199-44-2; **4a**, 542-59-6; **4b**, 6942-58-1; **4c**, 94-33-7; **4d**, 628-35-3; **5a**, 19859-09-7; **5b**, 90433-79-7; **5c**, 90433-80-0; **5d**, 90433-81-1; **6**, 42772-85-0; **7a**, 62264-99-7; **7b**, 90433-82-2; **8a**, 52459-90-2; **8b**, 14186-59-5; **9a**, 1500-91-0; **9b**, 90433-83-3; **9c**, 90433-84-4; **9d**, 2386-25-6; **9e**, 90433-85-5; **9f**, 55341-97-4; **9g**, 90433-86-6; **9h**, 90433-87-7; **10a**, 517-22-6; **10b**, 2199-50-0; **10c**, 938-75-0; **10d**, 625-82-1; **10e**, 930-87-0; **10h**, 90433-88-8; **11**, 40611-82-3; **12**, 90433-89-9; **13**, 90433-90-2; **14**, 67858-48-4; **15**, 90433-91-3; **16**, 90433-92-4; **17**, 37059-21-5; **18**, 90433-93-5; **19**, 26862-65-7; **20**, 6123-63-3; **21a**, 90433-94-6; **21b**, 90433-95-7; **23**, 90433-96-8; **24**, 26728-22-3; **25**, 90433-97-9; ethylene glycol dibenzoate, 94-49-5; diethylene glycol monobenzoate, 20587-61-5; diethylene glycol dibenzoate, 120-55-8; triethylene glycol monobenzoate, 23022-51-7; triethylene glycol dibenzoate, 120-56-9; methyl pyrrole-2-carboxylate, 1193-62-0; 2-phenylindole, 948-65-2; 5-methyl-1-phenylpyrazole, 6831-91-0; 2,4-dimethoxyacetophenone, 22924-18-1; 2,4-dimethoxybenzophenone, 3555-84-8; 1,3-dimethoxybenzene, 151-10-0; 3-(2-methyl-1,3-dioxolan-2-yl)-2,4-dimethyl-5-nitro-1*H*-pyrrole, 90433-98-0; 2-methyl-1,3-dithiolan-2-yl perchlorate, 90433-99-1; (1,1,3-trimethyl-3-phenyl)indan, 3910-35-8; acetophenone, 98-86-2; *o*-methoxyacetophenone, 579-74-8.