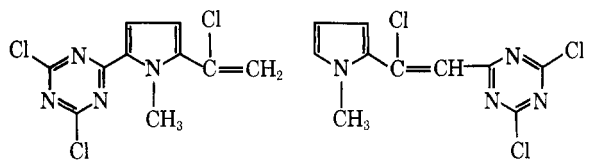
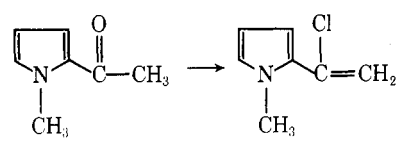
close agreement of the isotopic ratios at *m/e* 253, 255, and 257 with the expected values 9:6:1. In compound **1**, the characteristic feature is shown by the presence of the ion *m/e* 227 due to loss of the chlorovinyl side chain, which is absent in **2**.

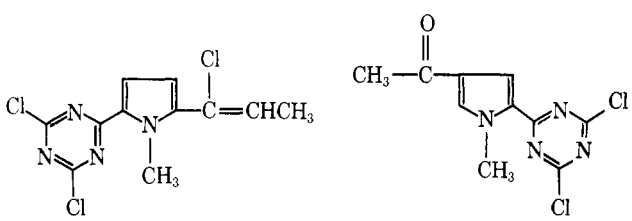
The chlorovinylpyrrole **4**, which is a likely initial product from **3** and cyanuric chloride,[3] is suggested as an intermediate in the formation of **1** and **2**.[4,5] From a similar reaction with 1-methyl-2-propionylpyrrole only the corresponding 5-triazinyl-substituted pyrrole (**5**) was isolated. Attack at the olefinic site may have been hindered by steric factors.



1 **2**



3 **4**



5 **6**

In view of our failure to produce an acylpyrrole substituted with an *s*-triazinyl group by the above reaction, we turned to acylation of pyrroles already having a triazinyl substituent. Thus, Friedel–Crafts acetylation of 2,4-dichloro-6-(1-methylpyrrol-2-yl)-*s*-triazine with acetic anhydride in the presence of $SnCl_4$ produced mainly the 4-acetyl derivative (**6**). This is consistent with our previous observation on electrophilic substitution reactions with pyrroles having a triazinyl group at the 2 position.[6]

Experimental Section

Melting points are not corrected. Spectra were measured with Perkin-Elmer 457, Unicam SP800, Varian A-60A, and LKB-9000S spectrometers.

2,4-Dichloro-6-[5-(α-chlorovinyl)-1-methylpyrrol-2-yl]-*s*-triazine (1) and 2,4-Dichloro-6-[2-chloro-2-(1-methylpyrrol-2-yl)vinyl]-*s*-triazine (2). A mixture of 2-acetyl-1-methylpyrrole (5.0 g, 0.04 mol) and cyanuric chloride (7.4 g, 0.04 mol) in dry bromobenzene (150 ml) was refluxed for 20 hr; the solvent was evaporated under vacuum at 50° and the residue extracted repeatedly with diethyl ether. The extract on chromatography on a silica gel column eluting with CH_2Cl_2 afforded two fractions. Compound **1** was a pale yellow solid: 3.6 g (31%); mp 108–110° (*n*-hexane); ir (KBr) 890, 850 cm^{-1}; NMR (CCl_4) δ 5.62 (d) and 5.77 (d) ($J \simeq 1.5$ Hz, $=CH_2$), 6.35 (d, H_3), 7.42 (d, H_4, $J_{3,4} \simeq 4.2$ Hz), 4.1 (s, NCH_3); MS *m/e* 288 (M^+), 253 ($M^+ - Cl$), 227 ($M^+ - CCl{=}CH_2$), 140 ($M^+ - C_3N_3Cl_2$); λ_{max} (MeOH) 345 nm (log ε 4.5).

Anal. Calcd for $C_{10}H_7Cl_3N_4$: C, 41.47; H, 2.43; N, 19.34; Cl, 36.73. Found: C, 41.24; H, 2.52; N, 19.57; Cl, 36.86.

Compound **2** was an intense yellow solid: 3.3 g (29%); mp 124–126° (*n*-hexane); ir (KBr) 860, 840 cm^{-1}; NMR (CCl_4) δ 6.72 (s, =CH–), 6.65–6.85 (m, H_5, H_3), 6.12 (dd, H_4), 3.87 (s, NCH_3); NMR (C_6D_6) δ 6.42 (s, =CH–), 6.68 (dd, H_3), 5.99 (dd, H_4), 6.15 (dd, H_5), 2.87 (s, NCH_3); MS *m/e* 288 (M^+), 253 ($M^+ - Cl$); λ_{max} (MeOH) 400 nm (log ε 4.25).

Anal. Calcd for $C_{10}H_7Cl_3N_4$: C, 41.47; H, 2.43; N, 19.34; Cl, 36.73. Found: C, 41.30; H, 2.39; N, 19.49; Cl, 36.66.

2,4-Dichloro-6-[5-(1-chloro-1-propenyl)-1-methylpyrrol-2-yl]-*s*-triazine (5) was similarly prepared from 1-methyl-2-propionylpyrrole in ca. 31% yield: mp 108–110° (*n*-hexane); ir (KBr) 850 cm^{-1}; NMR (CCl_4) δ 6.09 (q, =CH–), 6.23 (d, H_3), 7.41 (d, H_4, $J_{3,4} \simeq 4.5$ Hz), two signals at 2.11 (d), 1.98 (d) for C–CH_3 and 4.07 (s), 4.03 (s) for NCH_3 in each case indicated a mixture of cis/trans isomers in the ratio of ca. 1:9; MS *m/e* 302 (M^+), 287 ($M^+ - CH_3$), 267 ($M^+ - Cl$), 154 ($M^+ - C_3N_3Cl_2$); λ_{max} (MeOH) 348 nm (log ε 4.56).

Anal. Calcd for $C_{11}H_9Cl_3N_4$: C, 43.51; H, 2.98; N, 18.45; Cl, 35.03. Found: C, 43.83; H, 2.84; N, 18.25; Cl, 34.78.

2,4-Dichloro-6-(4-acetyl-1-methylpyrrol-2-yl)-*s*-triazine (6). To 2,4-dichloro-6-(1-methylpyrrol-2-yl)-*s*-triazine[2,6] (2.3 g, 0.01 mol) and Ac_2O (1.02 g) in dry benzene (25 ml) was added dropwise $SnCl_4$ (2.6 g, 0.01 mol) with stirring at room temperature; stirring was continued for 2 hr. The reaction mixture was evaporated to dryness and partitioned between $CHCl_3$ and water. The chloroform layer was separated, dried ($MgSO_4$), treated with charcoal, and evaporated to give a solid residue (2.2 g, 81%). This on sublimation at 130° (0.02 mm) produced analytically pure compound: mp 172–174°; ir (KBr) 1675, 1665 cm^{-1}; NMR ($CDCl_3$) δ 7.85 (d, H_3), 7.53 (d, H_5, $J_{3,5} \simeq 2.0$ Hz), 2.43 (s, C–CH_3), 4.12 (s, NCH_3); λ_{max} (MeOH) 232 nm (log ε 4.24), 328 (4.43).

Anal. Calcd for $C_{10}H_8Cl_2N_4O$: C, 44.30; H, 2.97; N, 20.66; Cl, 26.15. Found: C, 44.51; H, 2.97; N, 20.38; Cl, 26.33.

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Registry No.—**1**, 53993-20-7; **2**, 53993-21-8; **3**, 932-16-1; **5**, 53993-22-9; **6**, 53993-23-0; cyanuric chloride, 108-77-0; 1-methyl-2-propionylpyrrole, 17180-59-5; 2,4-dichloro-6-(1-methylpyrrol-2-yl)-*s*-triazine, 35252-42-7.

References and Notes

(1) Part V: J. K. Chakrabarti, A. F. Cockerill, G. L. O. Davies, T. M. Hotten, D. M. Rackham, and D. E. Tupper, *J. Chem. Soc., Perkin Trans. 2*, 861 (1974).
(2) J. K. Chakrabarti and D. E. Tupper, *J. Heterocycl. Chem.*, **11**, 417 (1974).
(3) J. R. Sandler, *J. Org. Chem.*, **35**, 3967 (1970).
(4) Similar nucleophilic substitutions of cyanuric chloride by the ethylenic double bond of ketene diethyl acetal (a) and by diazomethane (b) are known: (a) E. Kober, *J. Org. Chem.*, **26**, 4705 (1961). (b) C. Grundmann and E. Kober, *J. Am. Chem. Soc.*, **79**, 944 (1957).
(5) We are grateful to one of the reviewers for this suggestion.
(6) J. K. Chakrabarti, R. W. Goulding, and A. Todd, *J. Chem. Soc., Perkin Trans. 1*, 2499 (1973).

Polymer-Protected Reagents. III. Acetal Formation with Polymer-Protected Aluminum Chloride

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Previous communications from this laboratory demonstrated polymer-protected aluminum chloride (Ⓟ-$AlCl_3$) to be an effective catalyst for the formation of ethers[3] and esters.[4]

As an adjunct to these studies we wish to report the use of Ⓟ-$AlCl_3$ as a catalyst for acetal formation. Our results indicate that Ⓟ-$AlCl_3$ is useful for most acid-catalyzed dehydration reactions.

The scope of the reaction of various aldehydes and alcohols with Ⓟ-$AlCl_3$ and noncatalyzed conditions is shown in Table I. These results indicate that the more sterically hindered alcohols react more slowly and that electron-withdrawing groups attached to the benzaldehyde enhance acetal formation. The latter point is demonstrated by compet-

Table I
Acetal Formation

Registry no.	Aldehyde	Alcohol	Mole ratio aldehyde/alcohol	Temp, °C	Time, hr	% yield[a] No catalyst	% yield[a] Ⓟ-$AlCl_3$[b]
100-52-7	Benzaldehyde	1-Butanol[c]	0.21	95	2.5	8	21
	Benzaldehyde	2-Butanol[d]	0.21	95	92	0	0
552-89-6	*o*-Nitrobenzaldehyde	1-Butanol	0.21	45	3	1	40
	o-Nitrobenzaldehyde	1-Butanol	0.21	95	18	0	62
104-88-1	*p*-Chlorobenzaldehyde	1-Butanol	0.21	95	18	1	32
123-11-5	*p*-Anisaldehyde	1-Butanol	0.21	95	93	0	0
90-02-8	*o*-Salicylaldehyde	1-Butanol	0.21	95	47	0	0
535-16-8	*p*-Nitrobenzaldehyde	1-Butanol	0.21	95	24	0	48

[a] Yields determined by VPC with added internal standard of *m*-chlorotoluene. [b] One-half gram of Ⓟ-$AlCl_3$ used per 20 mmol of aldehyde [c] Registry no., 71-36-3. [d] Registry no., 78-92-2.

Table II
Competitive Rate Factors for Dibutyl Acetal Formation from Para-Substituted Benzaldehydes[a]

Substituent	R_x/k_H
NO_2	1.36
$N(CH_3)_2$[b]	0.00
H	1.00
Cl	1.06

[a] 20 mmol of substituted benzaldehyde, 20 mmol of benzaldehyde, excess 1-butanol, and 0.55 g of Ⓟ-$AlCl_3$ stirred at 55°. [b] Registry no., 100-10-7.

itive rate data (see Table II) for various para-substituted benzaldehyde reactions with 1-butanol and Ⓟ-$AlCl_3$.

Consistency of Ⓟ-$AlCl_3$ preparation was demonstrated by two different batches which gave yields of the acetal from *o*-nitrobenzylaldehyde and 1-butanol within 0.1%. Some catalysis by polymer (styrene–1.8% divinylbenzene copolymer) alone was also shown in the case of the *o*-nitrobenzaldehyde–1-butanol reaction. Yields of 67% acetal compared to the Ⓟ-$AlCl_3$ catalysts were observed. The cross-linked polystyrene alone probably works as an entrapment agent for the water formed in the reaction. The total catalytic activity of Ⓟ-$AlCl_3$ is no doubt derived from both its Lewis acid nature of the bound aluminum chloride plus the ability of the cross-linked polystyrene to entrap water.

The Ⓟ-$AlCl_3$ was also an effective catalyst for the hydrolysis of acetals. For example, heating the diethyl acetal of *o*-chlorobenzaldehyde with Ⓟ-$AlCl_3$ in benzene–methanol–water (2:6:1) for 17.5 hr gave a 61% yield of *o*-chlorobenzaldehyde together with 34% of *o*-chlorobenzaldehyde dimethyl acetal and 5% of a product tentatively identified as the methyl ethyl acetal. Under similar conditions a blank containing all reagents but Ⓟ-$AlCl_3$ produced only 4% of the aldehyde and 2% of the mixed methyl ethyl acetal.

Ⓟ-$AlCl_3$ is a useful catalyst for synthetic reactions which require both a dehydrating agent and a Lewis acid. Though its versatility is rather limited, on a larger scale, it may be quite useful because the reagents can be recycled and because the catalyst's reactivity is somewhat attenuated because of the presence of the polymer. For reactions requiring an acid catalyst in compounds with a sensitive secondary functional group, Ⓟ-$AlCl_3$ may well be the reagent of choice. Extensive electron microscopic studies detailing the exact structure of Ⓟ-$AlCl_3$ will be published shortly.

Experimental Section

All alcohols and aldehydes were reagent grade and the latter were redistilled prior to use. Ⓟ-$AlCl_3$ was prepared as before.[3]

General Procedure. Reactant concentrations, temperatures, times, product, and yield data are given in Table I. The aldehyde, alcohol, anhydrous benzene (5 ml/20 mmol of aldehyde), and 0.5 g of Ⓟ-$AlCl_3$ per 20 mmol of aldehyde were stirred in a closed reaction tube for the appropriate temperature. After the desired reaction time, aliquots were removed and analyzed by gas–liquid chromatography on a Hewlett-Packard Model 5750 flame ionization gas chromatograph. The columns used were 6 ft × 0.125 in. 3% silicon gum rubber on Chromosorb W and 10% Carbowax 20M on Chromosorb P. Yields were determined by the addition of the internal standard of *m*-chlorotoluene. Preparative reactions were performed as above. Isolation of products was accomplished by filtration of Ⓟ-$AlCl_3$ and distillation of the filtrate. Products were identified by VPC, NMR, ir, and comparison with authentic samples.

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Registry No.—*p*-Nitrobenzaldehyde dibutyl acetal, 19706-87-7; *p*-(dimethylamino)benzaldehyde dibutyl acetal, 53951-32-9; benzaldehyde dibutyl acetal, 5395-08-4; *p*-chlorobenzaldehyde dibutyl acetal, 53951-33-0; *o*-nitrobenzaldehyde dibutyl acetal, 53951-34-1; $AlCl_3$, 7446-70-0.

References and Notes

(1) On leave from Rollins College, 1972–1973.
(2) Fellow of the Alfred P. Sloan Foundation, 1971–1973.
(3) D. C. Neckers, D. A. Kooistra, and G. W. Green, *J. Am. Chem. Soc.*, **94**, 9284 (1972).
(4) E. C. Blossey, L. M. Turner, and D. C. Neckers, *Tetrahedron Lett.*, 1823 (1973).

Application of an Optically Active Nuclear Magnetic Resonance Shift Reagent to Configurational Problems

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The use of an optically active NMR shift reagent, such as $Eu(hfac)_3$, offered an interesting approach to the problem of the determination and correlation of configuration, or the evaluation of the optical yield of reactions. The principal effect of such optically active shift reagents is the separation of NMR signals for the corresponding enantiomers by the selective complexation of one enantiomer. In this study we report the application of $Eu(hfac)_3$ (europium 3-trifluoroacetyl-*d*-camphorate) to the determination of the configuration at C-2 of a series of derivatives of 2-methyl-