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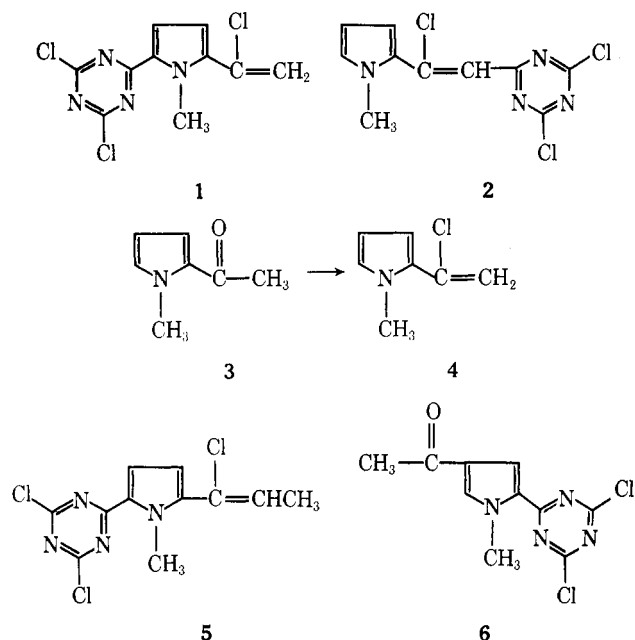
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close agreement of the isotopic ratios at m/e 253, 255, and 257 with the expected values 9:6:1. In compound 1, the characteristic feature is shown by the presence of the ion m/e 227 due to loss of the chlorovinyl side chain, which is absent in 2.

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.



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-(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) ($J \approx 1.5$ Hz, $=\text{CH}_2$), 6.35 (d, H_3), 7.42 (d, H_4 , $J_{3,4} \approx 4.2$ Hz), 4.1 (s, NCH_3); MS m/e 288 (M^+), 253 ($\text{M}^+ - \text{Cl}$), 227 ($\text{M}^+ - \text{CCl}=\text{CH}_2$), 140 ($\text{M}^+ - \text{C}_3\text{N}_3\text{Cl}_2$); λ_{max} (MeOH) 345 nm ($\log \epsilon$ 4.5).

Anal. Calcd for $\text{C}_{10}\text{H}_7\text{Cl}_3\text{N}_4$: 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, $=\text{CH}-$), 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, $=\text{CH}-$), 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 ($\text{M}^+ - \text{Cl}$); λ_{max} (MeOH) 400 nm ($\log \epsilon$ 4.25).

Anal. Calcd for $\text{C}_{10}\text{H}_7\text{Cl}_3\text{N}_4$: 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, $=\text{CH}-$), 6.23 (d, H_3), 7.41 (d, H_4 , $J_{3,4} \approx 4.5$ Hz), two signals at 2.11 (d), 1.98 (d) for $\text{C}-\text{CH}_3$ 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 ($\text{M}^+ - \text{CH}_3$), 267 ($\text{M}^+ - \text{Cl}$), 154 ($\text{M}^+ - \text{C}_3\text{N}_3\text{Cl}_2$); λ_{max} (MeOH) 348 nm ($\log \epsilon$ 4.56).

Anal. Calcd for $\text{C}_{11}\text{H}_9\text{Cl}_3\text{N}_4$: 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 , $J_{3,5} \approx 2.0$ Hz), 2.43 (s, $\text{C}-\text{CH}_3$), 4.12 (s, NCH_3); λ_{max} (MeOH) 232 nm ($\log \epsilon$ 4.24), 328 (4.43).

Anal. Calcd for $\text{C}_{10}\text{H}_8\text{Cl}_2\text{N}_4\text{O}$: 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.

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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 (P-AlCl_3) to be an effective catalyst for the formation of ethers³ and esters.⁴

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

The scope of the reaction of various aldehydes and alcohols with P-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 | P-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 | <i>o</i> -Nitrobenzaldehyde | 1-Butanol | 0.21 | 45 | 3 | 1 | 40 |
| | <i>o</i> -Nitrobenzaldehyde | 1-Butanol | 0.21 | 95 | 18 | 0 | 62 |
| 104-88-1 | <i>p</i> -Chlorobenzaldehyde | 1-Butanol | 0.21 | 95 | 18 | 1 | 32 |
| 123-11-5 | <i>p</i> -Anisaldehyde | 1-Butanol | 0.21 | 95 | 93 | 0 | 0 |
| 90-02-8 | <i>o</i> -Salicylaldehyde | 1-Butanol | 0.21 | 95 | 47 | 0 | 0 |
| 535-16-8 | <i>p</i> -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 P-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 |
| $\text{N}(\text{CH}_3)_2^b$ | 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 P-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 P-AlCl_3 .

Consistency of P-AlCl_3 preparation was demonstrated by two different batches which gave yields of the acetal from *o*-nitrobenzaldehyde 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 P-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 P-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 P-AlCl_3 was also an effective catalyst for the hydrolysis of acetals. For example, heating the diethyl acetal of *o*-chlorobenzaldehyde with P-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 P-AlCl_3 produced only 4% of the aldehyde and 2% of the mixed methyl ethyl acetal.

P-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, P-AlCl_3 may well be the reagent of choice. Extensive electron microscopic studies detailing the exact structure of P-AlCl_3 will be published shortly.

Experimental Section

All alcohols and aldehydes were reagent grade and the latter were redistilled prior to use. P-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 P-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 \times 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 P-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.

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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 $\text{Eu}(\text{hfac})_3$, 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 $\text{Eu}(\text{hfac})_3$ (europium 3-trifluoroacetyl-*d*-camphorate) to the determination of the configuration at C-2 of a series of derivatives of 2-methyl-