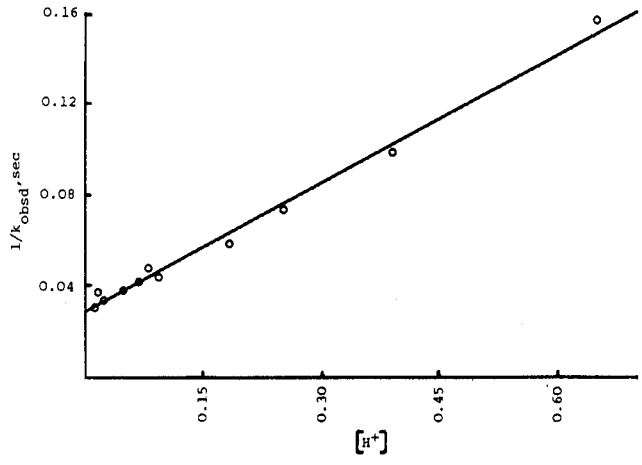

Figure 1. Plot of $1/k_{obsd}$ vs. $[H^+]$ for the proton exchange of the conjugate acid of *N*-methylisoindoline in aqueous HCl at 25°.

$$k_{obsd} = \frac{k_a k_H}{k_H + k_{-a}[H^+]} \quad (1)$$

vs. $[H^+]$ should be linear. This was found to be the case (Figure 1). The slope and intercept of the plot and the pK_a of the amine ($K_a = k_a/k_{-a}$) allowed calculation of all three rate parameters in the mechanism. These are given in Table I along with analogous data for dibenzylmethylamine. The k_a values are seen to differ sevenfold, but this largely reflects the difference in basicity between the two amines. More importantly, the k_H values for *N*-methylisoindoline and dibenzylmethylamine differ by only a small and mechanistically insignificant amount.

Table I
Proton Exchange Data for *N*-Methylisoindoline and Dibenzylmethylamine

Amine	pK_a	k_a, sec^{-1}	k_{-a}, M^{-1} sec^{-1}	k_H, sec^{-1}
N-Methylisoindoline[a]	8.33	35	7.4×10^9	1.1×10^9
Dibenzylmethylamine[b]	7.72	240	1.3×10^{10}	2.7×10^9

[a] 25°, aqueous HCl. [b] 30°, data from ref 3.

Grunwald and Ralph[3] have proposed that *solvent–solute* interactions (rather than *solvent–solvent* interactions) determine the shapes of amine solvation shells. Thus, the solvent molds itself about the contours of the amine; the better the fit, the smaller the rate of desolvation, k_H. If this description is correct, then solvation phenomena can become "extraordinarily specific".[3] Our results show that short-range London dispersion forces between the amine substituents and the water, upon which k_H depends, vary little when the substituents are confined in a ring. In at least one case, therefore, amine solvation is certainly *not* sufficiently form fitting to distinguish a cyclic amine from a conformationally different acyclic analog.[5] This work points out the need to specify the effect of shape on k_H more clearly.

Experimental Section

Materials. *N*-Methylisoindoline was prepared by reducing *N*-methylphthalimide with $LiAlH_4$ in ether in the presence of $MgSO_4$.[6] After the excess $LiAlH_4$ was destroyed with aqueous ethanol, the mixture was filtered and the ether layer was separated and dried over $MgSO_4$. The ether was then removed, leaving a dark residue which was distilled under vacuum, bp 92–93° (25 mm) [lit.[6] bp 81–82° (13 mm)], to give colorless *N*-methylisoindoline in approximately 15% yield. Redistillation gave material of high purity as judged by GLC and an elemental analysis. Although *N*-methylisoindoline was found to be oxygen sensitive to a much greater degree than simple acyclic amines, the compound was quite stable when stored under nitrogen in a freezer. The compound was also found to be stable in >1 *M* aqueous HCl (with a corresponding decrease in stability with increasing pH). All kinetic studies were performed with freshly distilled amine.

Kinetics. Observed rate constants at 25.0 ± 0.8° for NH-proton exchange of *N*-methylisoindoline in aqueous HCl were determined from the singlet-to-doublet transition of the NCH_3 NMR signal. The instrumental settings and treatment of the NMR data were similar to those described in a previous publication.[7] Rate constants in Table I determined at Emory with a Jeol JNM-MH-100 spectrometer were within 10% of those determined at Georgia with a Hitachi Perkin-Elmer R-20 spectrometer. Solutions were used immediately after their preparation, and pH values were measured both before and after each kinetic run. The pK_a of *N*-methylisoindoline (Table I) was obtained by differential potentiometric titration.

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Registry No.—*N*-Methylisoindoline, 3474-87-1.

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s-Triazines. VI.[1] Novel Reaction Products from *s*-Triazinylation of 2-Acyl-1-methylpyrroles Using 2,4,6-Trichloro-*s*-triazine

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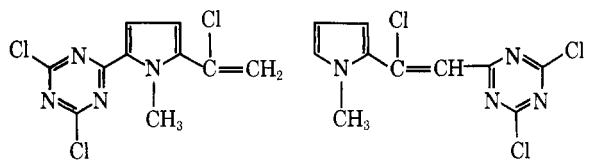
The direct *s*-triazinylation reactions using 2,4,6-trichloro-*s*-triazine (cyanuric chloride) on pyrrole and various substituted pyrroles to give 2,4-dichloro-6-(pyrrolyl)-*s*-triazines have been described in our earlier paper.[2] Here we report on the novel reaction products obtained by treating cyanuric chloride with 2-acyl-1-methylpyrroles.

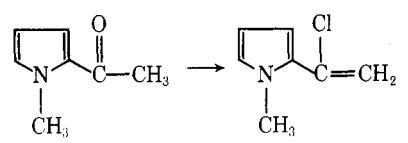
2-Acetyl-1-methylpyrrole (**3**), when treated with 1 equiv of cyanuric chloride in refluxing bromobenzene, led to an equimolar mixture of two isomeric products, **1** and **2**. The ir spectrum in either case did not show any carbonyl or hydroxyl absorptions. The NMR spectrum in CCl_4 for **1** exhibited two vinyl protons at δ 5.62 (d) and 5.77 (d) ($J \simeq 1.5$ Hz) besides the expected pyrrole ring protons. The single olefinic proton in **2** appeared as a singlet at δ 6.72 amidst a multiplet at δ 6.65–6.86 due to two other pyrrole protons. However, in C_6D_6 the olefinic proton appeared as a sharp singlet at δ 6.42 and the three pyrrole ring protons in a normal ABX pattern. Mass spectra (20 eV) for both compounds show the same parent ion, M^+ 288. The relative abundance ratios of the four peaks corresponding to the molecular ion group at 288, 290, 292, and 294 are consistent with the expected ratios 27:27:9:1 for three chlorine atoms. The loss of a chlorine atom in each case is shown by the

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**.

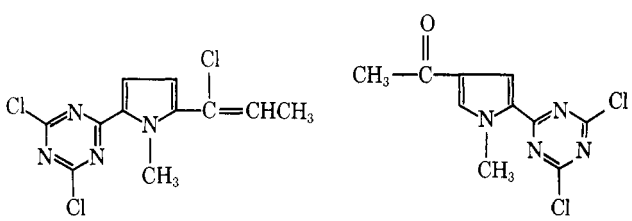
The chlorovinylpyrrole **4**, which is a likely initial product from **3** and cyanuric chloride,[3] is suggested as an intermediate in the formation of **1** and **2**.[4,5] From a similar reaction with 1-methyl-2-propionylpyrrole only the corresponding 5-triazinyl-substituted pyrrole (**5**) was isolated.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

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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 (Ⓟ-$AlCl_3$) 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-