la bande est identifiée comme étant une bande $\pi-\pi^*$ d'un état singulet.

En ce qui a trait à la bande de luminescence, on observe par contre un effet hypsochrome par augmentation de la polarité du solvant. D'autre part, l'augmentation du couplage spin-orbite par dissolution de la colchicine dans l'iodure d'éthyle n'apporte aucun changement du spectre. Un tel résultat a été commenté par McGlynn et coll. (5). Enfin des mesures de polarisation aux différentes longueurs d'onde de l'émission, il découle une valeur moyenne $P = +0.2$ (fig. 2).

Chacun de ces résultats présente une preuve directe de la présence d'une bande $n-\pi^*$ (probablement dûe à la délocalisation des électrons du groupement carbonyle de l'anneau tropolone) (6, 7).

Puisque la bande d'absorption à 350 nm possède un caractère $\pi-\pi^*$ et que celle d'émission revêt un caractère $n-\pi^*$, c'est qu'il existe une absorption $n-\pi^*$. Il nous a été cependant impossible de détecter la présence de cette bande, du fait de son faible coefficient d'extinction molaire ($\varepsilon_{n-\pi^*} < 2000$). De plus, la position de la bande 0–0 d'émission se situe à 402 nm, ce qui impliquerait une absorption vers la même longueur d'onde, absorption qui disparaît donc sous la bande $\pi-\pi^*$.

Afin de déterminer la multiplicité de l'état excité de la colchicine, le temps de vie a été mesuré, soit $2 \times 10^{-4}$ s ce résultat permet d'identifier l'émission comme étant de la phosphorescence (8).

L'existence de cette forme de dégradation de l'état excité par émission de phosphorescence laisse entrevoir, pour la molécule de colchicine en particulier, de nombreuses possibilités d'explication de son mode d'action sur l'appareil mitotique cellulaire.

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# Pyrrole Chemistry. XIV. Some Chemical and Physical Properties of 3-Pyrrolecarbaldehyde and 1-Methyl-3-pyrrolecarbaldehyde

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3-Pyrrolecarbaldehyde (1) has been prepared on an increased scale. A general survey of the physical and chemical properties of the 3-aldehyde and 1-methyl-3-pyrrolecarbaldehyde has been carried out. The results indicate similar chemical properties to those of the corresponding 2-aldehydes. The physical properties are generally predictable on the basis of earlier studies.

Le pyrrolecarbaldéhyde-3 (1) a été préparé sur une plus grande échelle. Une revue générale des propriétés physiques et chimiques de l'aldéhyde-3 et du méthyl-1 pyrrolecarbaldéhyde-3 a été menée à bien. Les résultats indiquent des propriétés chimiques semblables à celles des aldéhydes-2 correspondants. Les propriétés physiques sont en général prévisibles en se fondant sur les études précédentes.

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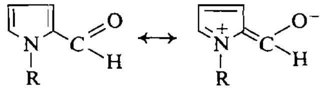
The availability of 3-pyrrolecarbaldehyde (1) has permitted an examination of some of its physical and chemical properties. These properties have been compared with those of 1-methyl-3-pyrrolecarbaldehyde, 2-pyrrolecarbaldehyde, and the 1-methyl-2-aldehyde. The last two compounds have provided considerable discussion over the years (2–4).

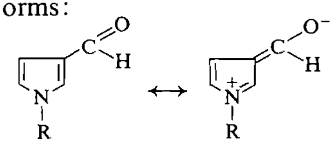
The necessary modifications for optimum yield in larger scale preparation of the 3-aldehyde are described in the Experimental. Standardization trials for the decarbonylation step were tedious and the best means of product analysis was careful filtration of an aliquot, evaporation, and p.m.r. examination of the residue for the various possible products (1). The readily available 1-methyl-2-aldehyde (5) could be formylated by the Friedel–Crafts method to the 1-methyl-2,4-dialdehyde but the yield was only 26%. Thus, although the subsequent decarbonylation step appeared to go satisfactorily, this method was not used to prepare the 1-methyl-3-aldehyde. Instead, this substance was isolated in about 6% yield as a by-product of the Vilsmeier preparation of the 1-methyl-2-aldehyde[1] being used in other work.

Herz and Brasch (3) compared the physical and chemical properties of the 2-aldehyde and its 1-methyl derivative and concluded that a resonance hybrid:



$R = H$ or $CH_3$

best accounted for the observations made. Similar forms:



$R = H$ or $CH_3$

may be drawn for the 3-aldehydes.

The 3-aldehyde carbonyl stretching frequency in carbon tetrachloride was found to be at 1683 $cm^{-1}$ (6) while we find that of the 1-methyl derivative to be at 1685 $cm^{-1}$. The most recent values for the carbonyl bands of the 2-aldehyde and its 1-methyl derivative are 1667 and 1671.5 $cm^{-1}$, respectively, in the same solvent (7). These values support the usual statement that electron release is easier through the 2- than through the 3-position. However, the small, and similar, effect of the 1-methyl group on the carbonyl band positions makes it difficult to see that intramolecular hydrogen bonding is important to the low frequency of the 2-aldehyde carbonyl absorption (8).

In a footnote, Herz and Brasch (3) reported that the u.v. spectrum of the 2-aldehyde did not obey Beer's Law. However, we found no deviation greater than experimental error:[2] $\lambda_{max}$ 290 nm ($\varepsilon$ 16 500 $\pm$ 2.5%) in the range from $3.3 \times 10^{-2}$ to $1.1 \times 10^{-5}$ $M$ in 95% ethanol, and $\lambda_{max}$ 281 nm ($\varepsilon$ 16 000 $\pm$ 6%) from $5.8 \times 10^{-2}$ to $1.1 \times 10^{-4}$ $M$ in methylcyclohexane. Our spectra of the 2-aldehyde and its 1-methyl derivative in alcohol agree well with those reported by Andrisano *et al.* (9). The 3-aldehyde also obeys Beer's Law over a wide range of concentration in ethanol. Insolubility of the 3-aldehydes prevents u.v. measurement in hydrocarbon solvent. In ethanol there does not seem to be any consistent spectral change arising from the introduction of the 1-methyl group in these two aldehydes. Eisner and Gore (10) observed that the longer wavelength absorption band of 3-substituted compounds is much less intense than that of the 2-substituted ones. This is true here, although that band is a shoulder in the 3-aldehyde spectra and measurement is not precise. Also this band is 15–18 nm lower for the 3- than for the corresponding 2-derivative as noted before (10) in more highly substituted examples.

The p.m.r. spectra of the 3-aldehyde and 1-methyl-3-aldehyde of pyrrole showed no observable coupling of the aldehyde and ring protons at probe temperature. This contrasts with the spectra of the 3-aldehyde of furan (11) and of thiophene (12) where —C*H*O to H-5 and to H-4 coupling was observed. In both 2,4-pyrroledicarbaldehyde and its 1-methyl derivative the 2-C*H*O is coupled to H-5, but the 4-C*H*O signal is again a singlet.

The mass spectra of the four aldehydes were found to be entirely as expected on the basis of earlier work (13)[3]. In each, the important peaks are $M^{+\cdot}$, $M - 1$, $M - CHO$, as well as the peak at *m*/*e* 39 and, for the 1-methyl derivatives, the peak at *m*/*e* 53.

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[1] Observed by Dr. C. E. Loader of this Department. In large scale preparations of 2-pyrrolecarbaldehyde, he also obtained about 1/2% of the 3-aldehyde from the residue.

[2] In a personal communication Professor Herz agrees that their observation may have been an effect of stray light at high absorbance.

[3] Under the instrument conditions we used, the spectrum of the 2-aldehyde showed good agreement with ref. 13 for higher masses but was less satisfactory for lower masses.

It has been reported (2, 3) that 2-pyrrolecarbaldehyde does not show positive Schiff's, Fehling's, or Tollen's tests. Herz and Brasch (3) stated that the 1-methyl-2-aldehyde also failed these tests. As the usual Fehling's test generally fails for aromatic aldehydes (14) that result is not surprising. We confirmed that the Schiff test fails for both the 2- and 3-aldehydes as well as their 1-methyl derivatives. However, Tollen's reagent with either the 2- or the 3-aldehyde gave a silver mirror rapidly on warming or within 5 min in the dark at room temperature. Surprisingly, neither 1-methyl derivative reacted within several hours, nor on warming. All four aldehydes may be converted to their acids using fresh silver oxide in the method of Hodge and Rickards (15).

Attempts to convert the 2- or the 3-aldehyde to its acetal failed. However, the ethylene acetal of the 3-aldehyde, 3-(1,3-dioxolan-2-yl)-pyrrole, could be made by conversion of ethyl 4-formyl-2-pyrrolethiolcarboxylate to its ethylene acetal followed by removal of the ethyl thiolcarboxylate group by Raney nickel. Both acetals were highly unstable toward light and to the most weakly acidic conditions. Similar instability of the ethylene ketal of methyl 4-acetyl-2-pyrrolecarboxylate has been observed (16). Attempts to convert the 3-acetal to a pyrrole Grignard reagent were unsuccessful.

It has been reported (17) that in Wittig reactions with the 2-aldehyde and with its 1-methyl derivative the yields are very sensitive to relative basicities and reaction conditions. We found that the yield of 1-methyl-3-styrylpyrrole from the 1-methyl-3-aldehyde was low under a variety of conditions and that the only apparently successful reaction of 3-pyrrolecarbaldehyde with triphenylbenzylphosphonium chloride could not be repeated.

Although the Knoevenagel reaction with ethyl malonate succeeded with the 3-aldehyde, the benzoin and Perkin condensations failed. The lithium aluminum hydride reduction was also unsuccessful, but Wolff–Kischner reduction to 3-methylpyrrole worked well. We have already reported the direct Wolff–Kischner conversion of ethyl 4-formyl-2-thiolcarboxylate to 3-methylpyrrole (18).

In general, the chemical reactivities of the 3-aldehyde of pyrrole and its 1-methyl derivative are not greatly different from those of the corresponding 2-aldehydes. In both simple aldehydes the N—H is decidedly acidic and this complicates some base-catalyzed reactions.

## Experimental

Melting points (uncorrected) were determined on a Fisher–Johns apparatus. Elemental analyses were by Alfred Bernhardt, West Germany. The i.r. spectra were recorded on a Perkin–Elmer 237B grating spectrophotometer using potassium chloride discs, while u.v. spectra were recorded on a Perkin–Elmer 202 spectrophotometer. The p.m.r. spectra were determined using a Varian A-60 or HA100 instrument. Values are given using the $\tau$ scale with tetramethylsilane as internal reference. Mass spectra were recorded on a Hitachi–Perkin–Elmer RMU-6E spectrometer using the direct inlet system. Spectra were normalized when the variation of total ion current was less than 6% peak. Peak intensities are given as a percentage of the base peak.

### *3-Pyrrolecarbaldehyde*[4]

*(a) Ethyl 4-Formyl-2-thiolcarboxylate*

The dichloromethyl methyl ether was fractionated through a 50 cm Widmer column prior to use. The crude reaction product was extracted 48 h in a Soxhlet using petroleum (80–100°); yield about 88% starting from 10–25 g thiol ester.

*(b) Raney Nickel W-5*

The literature method (19) could be increased fourfold in scale by increasing the diameter of the washing chamber to 10 cm while other dimensions remained the same. A Teflon paddle gave good agitation of the nickel. Deionized water (40 l) was used for washing the catalyst.

*(c) 3-Pyrrolecarbaldehyde*

On the larger scale a short-path distillation of the product (132–142° at 1 mm) was more convenient than column chromatography for initial product isolation. Storage of the purified material in the dark over sodium hydroxide pellets was found most satisfactory; $\lambda_{max}$ (ethanol) 246 ($\varepsilon$ 10 800), 272 nm (sh $\varepsilon$ 6500).

### *3-Pyrrolecarboxylic Acid*

The 3-aldehyde was oxidized by the method of Hodge and Rickards (15) to the 3-acid (75%), m.p. 144–144.5°, lit. (20) m.p. 144.5–145.5°.

### *1-Methyl-3-pyrrolecarboxylic Acid (by N. C. Wang)*

The 1-methyl-3-aldehyde was oxidized in the same manner to give 1-methyl-3-pyrrolecarboxylic acid (72%), m.p. 145–145.5° (benzene–hexane); $\lambda_{max}$ (ethanol) 233 ($\varepsilon$ 9160), 246 nm (sh $\varepsilon$ 7250); p.m.r. ($CDCl_3$) $\tau$ 1.02 (s, 1H), 2.66 (m, 1H), 3.40 (m, 2H), 6.30 (s, 3H).

Anal. Calcd. for $C_6H_7NO_2$: C, 57.60; H, 5.60; N, 11.20. Found: C, 57.74; H, 5.69; N, 11.36.

### *1-Methyl-2,4-pyrroledicarbaldehyde*

1-Methyl-2-pyrrolecarbaldehyde (2.75 g, 25 mmol) was dissolved in methylene chloride (25 ml). Nitromethane (3 ml) in methylene chloride (75 ml) was added, with stirring, followed by aluminum chloride (15.6 g, 117 mmol) and dichloromethyl methyl ether (7.6 g, 66 mmol) in methylene

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[4] Modifications to method of ref. 1 for larger scale synthesis.

chloride (25 ml). The mixture was stirred at room temperature 1 h, then refluxed 10 min, cooled, and poured onto ice. The organic phase was separated and the aqueous phase extracted with chloroform. The combined organic phase was washed with water and dried ($MgSO_4$). Vacuum evaporation of the solvent was followed by distillation of unreacted starting material (680 mg). The black residue was chromatographed on neutral alumina using chloroform as eluant. The solid product was recrystallized from petroleum (80–100°) to give light yellow crystals (980 mg, 26%), m.p. 95°; $\lambda_{max}$ (ethanol) 237 ($\varepsilon$ 24 700), 260 (sh $\varepsilon$ 9600), 290 nm ($\varepsilon$ 15 400); p.m.r. ($CDCl_3$) $\tau$ 0.18 (s, 1H), 0.33 (d, 1H); 2.5 (m, 1H), 2.7 (m, 1H), 5.99 (s, 3H).

Anal. Calcd. for $C_7H_7NO_2$: C, 61.31; H, 5.15. Found: C, 61.30; H, 5.20.

### *1-Methyl-3-pyrrolecarbaldehyde*

Following the Vilsmeier synthesis of 1-methyl-2-pyrrolecarbaldehyde on a 2-mol scale (4), the principal product was distilled at 45°/1 mm. The residue was then distilled at 75°/1 mm and was found to consist mainly of the 1-methyl-3-aldehyde. After redistillation the yield was 10.4 g (~6%). The material was dissolved in ether and chilled to −70° producing crystals from which the ether was decanted. The crystals melted well below 0° to a colorless oil that gave a single peak on the gas chromatograph; $\lambda_{max}$ (ethanol) 254 ($\varepsilon$ 12 000), 274 nm (sh, $\varepsilon$ 8600); p.m.r. ($CDCl_3$) $\tau$ 0.25 (s, 1H), 2.72 (m, 1H), 3.37 (m, 2H), 6.32 (s, 3H).

Anal. Calcd. for $C_6H_7NO$: C, 66.03; H, 6.47. Found: C, 65.72; H, 6.42.

### *Ethyl 4-(1,3-Dioxolan-2-yl)-2-pyrrolethiolcarboxylate*

Ethyl 4-formyl-2-pyrrolethiolcarboxylate (11.7 g, 0.075 mol) and ethylene glycol (192 ml) were added to benzene (940 ml) containing *p*-toluenesulfonic acid (768 mg). "Molecular Sieves" (10 g) were added and the mixture was refluxed, using a Dean and Stark separator, for 72 h. The benzene solution was washed with sodium bicarbonate solution and dried ($MgSO_4$). Evaporation gave a yellow solid which was recrystallized from petroleum (40–60°) to give pale yellow needles (12 g, 83%), m.p. 61–61.5°, $\lambda_{max}$ (ethanol) 227 ($\varepsilon$ 25 000), 260 (sh, $\varepsilon$ 9900), 270 ($\varepsilon$ 10 800), 298 nm ($\varepsilon$ 20 600); p.m.r. ($CDCl_3$) $\tau$ 2.76 (m, 1H), 2.81 (m, 1H), 4.04 (s, 1H), 5.88 (m, 4H), 6.91 (q, 2H), 8.68 (t, 3H).

Anal. Calcd. for $C_{10}H_{13}NO_3S$: C, 52.86; H, 5.77. Found: C, 52.68; H, 5.77.

### *3-(1,3-Dioxolan-2-yl)pyrrole*

W-5 Raney nickel (32 g) was washed with acetone (3 × 100 ml). Ethyl 4-(1,3-dioxolan-2-yl)-2-pyrrolethiolcarboxylate (2.0 g, 8.8 mmol) in acetone (125 ml) was added and the mixture stirred 70 min. After the Raney nickel was filtered off and washed well with acetone the filtrate was evaporated to give 950 mg oil. Solution in ether and cooling to −70° induced crystallization. The ethylene acetal of 3-pyrrolecarbaldehyde (650 mg, 53%), m.p. 63–63.5° (ether), p.m.r. ($CDCl_3$) $\tau$ 3.28 (m, 1H), 3.44 (m, 1H), 3.71 (m, 1H), 4.18 (s, 1H), 6.03 (m, 4H).

Anal. Calcd. for $C_7H_9NO_2$: C, 60.42; H, 6.52. Found: C, 60.41; H, 6.64.

### *1-Methyl-3-styrylpyrrole*

Potassium (234 mg, 6 mmol) was dissolved in *t*-butyl alcohol (7 ml) under nitrogen. Ether (5 ml) was added, with stirring, followed by benzyltriphenylphosphonium chloride (1.94 g, 5 mmol). The mixture was cooled and 1-methyl-3-pyrrolecarbaldehyde (444 mg, 4 mmol) in ether (5 ml) was added dropwise to the mixture. The stirring was continued at room temperature for 3 h. The mixture was poured into water (30 ml), the phases separated and the aqueous layer extracted with ether. The combined organic phase was then washed with water and dried ($MgSO_4$). After evaporation, the crude product was chromatographed on silica gel (BDH) with benzene. The early fractions gave an oil which was crystallized from petroleum (80–100°) and then sublimed. Colorless crystals (130 mg, 13%), m.p. 95°, $\lambda_{max}$ (ethanol) 314 ($\varepsilon$ 28 300), 303 (sh, $\varepsilon$ 26 600), 236 (sh, $\varepsilon$ 12 700), 230 nm ($\varepsilon$ 13 300); p.m.r. ($CDCl_3$) $\tau$ 2.5–2.8 (m, 5H), 3.09 (d, 2H), 3.27 (m, 1H), 3.41 (m, 1H), 3.51 (m, 1H), 6.39 (s, 3H).

Anal. Calcd. for $C_{13}H_{13}N$: C, 85.20; H, 7.15. Found: C, 85.01; H, 7.12.

### *Attempted Preparation of 3-Styrylpyrrole*

The procedure used to prepare the 1-methyl derivative was applied to 3-pyrrolecarbaldehyde. Although a small amount of crystalline material with the expected p.m.r. and mass spectrum was obtained on one occasion the preparation could not be repeated. Several variations of the method were equally unsuccessful.

### *Ethyl 1-Carbethoxy-3-(3-pyrrolyl)acrylate*

3-Pyrrolecarbaldehyde (200 mg, 2.1 mmol) was dissolved in a few drops of ethanol. Ethyl malonate (600 mg, 3.7 mmol), methylammonium chloride (100 mg, 1.3 mmol), and anhydrous potassium carbonate (200 mg, 1.5 mmol) were added. After 4 days at room temperature the mixture was poured into water and extracted with ether. The ether layer was washed with water and dried ($MgSO_4$). It was then evaporated giving 190 mg of yellow oil. Chromatography on neutral alumina (benzene) gave several fractions, one of which crystallized 3 months later. The product (89 mg, 18%) was pale yellow m.p. 62–63° (ether–petroleum (60–80°)), $\lambda_{max}$ 314 nm ($\varepsilon$ 15 100); p.m.r. ($CDCl_3$) $\tau$ 2.22 (s, 1H), 2.85 (m, 1H), 3.18 (m, 1H), 3.58 (m, 1H), 5.70 (m, 4H), 8.68 (m, 6H).

Anal. Calcd. for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37. Found: C, 60.56; H, 6.29.

### *Mass Spectra*

*2-Pyrrolecarbaldehyde*: $M^+$ 95(100%), 94(63), 66(43), 39(16). *3-Pyrrolecarbaldehyde*: $M^+$ 95(100%), 94(72), 66(43), 39(24). *1-Methyl-2-pyrrolecarbaldehyde*: $M^+$ 109(100), 108(76), 80(23), 53(28), 39(16). *1-Methyl-3-pyrrolecarbaldehyde*: $M^+$ 109(100), 108(99), 80(16), 53(22), 39(18).

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# The Conformational Enthalpy, Entropy, and Free Energy of The Formyl Group Determined by Low Temperature Proton Magnetic Resonance

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The low temperature proton n.m.r. peak area method has been applied to the formyl proton of cyclohexanecarboxaldehyde. The conformational enthalpy and entropy of the CHO group have been measured for the first time. The results indicate that the axial conformation has the higher entropy and $-\Delta G^0$ for the CHO function is about 0.8 kcal/mol.

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La méthode de la surface des pics par r.m.n. à basse température a été appliquée au proton formyle du cyclohexanecarboxaldéhyde. L'enthalpie et l'entropie conformationnelle du groupe CHO ont été mesurées pour la première fois. Les résultats indiquent que la conformation axiale possède l'entropie la plus élevée et que $-\Delta G^0$ pour la fonction CHO est environ de 0.8 kcal/mol.

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## Introduction

Considerable discrepancy exists between the published results for the conformational energy $(-\Delta G^0)$ of the formyl group. Based on room temperature $^1$H n.m.r. chemical shifts and couplings for the aldehyde proton of cyclohexanecarboxaldehyde and its *cis*- and *trans*-4-*t*-butyl derivatives, a value of 1.35 kcal/mol has been obtained (1, 2). A subsequent report by Eliel *et al.* gives a range of 0.56 to 0.78 kcal/mol as determined from equilibration experiments (3).

The n.m.r. procedure employing model compounds contains the inherent assumption that the 4-*t*-butyl group does not affect appreciably the properties of the axial and equatorial formyl groups respectively. In other substituted cyclohexanes, this method has been shown to be sometimes inaccurate for C-1 methine ring protons (4). No doubt similar perturbations exist for exocyclic protons although they are spatially further from the *t*-butyl group. This factor may be particularly important in these aldehydes, where the chemical shift difference between formyl protons in the *cis*- and *trans*-4-*t*-butylcyclohexyl compounds is only *ca.* 0.1 p.p.m.

The formyl group is not ideally suited for equilibration studies. Under some of the conditions employed in the previous work, condensation reactions occur and some doubt is cast on the assumption that true equilibrium was attained (3).

In view of the above data and assumptions in