3-Hydroxypyrroles and 1*H*-Pyrrol-3(2*H*)-ones. Part 7.[1,2] Protonation and *O*-Alkylation of Simple 1*H*-Pyrrol-3(2*H*)-ones: Crystal and Molecular Structure of 3-Hydroxy-1-t-butyl-1,2-dihydropyrrolium Picrate

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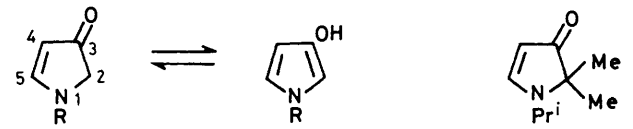
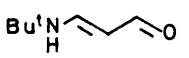
O-Protonation of 1*H*-pyrrol-3(2*H*)-ones gives cations which are stable indefinitely in solution, and can be isolated as picrate salts. An *X*-ray crystal structure of the 1-t-butyl derivative confirms charge delocalisation in these cations, which can be regarded as the Wheland intermediates for protonation of 3-hydroxypyrroles. Deuterium exchange at the 2- and 4-position under acidic conditions takes place *via* the hydroxypyrrole and pyrrolone tautomers, respectively, of the free base. 2,2-Disubstituted 1*H*-pyrrol-3(2*H*)-ones are found to give *O*-alkylated salts on treatment with Meerwein's reagent.

In Part 2 of this series we described a convenient and flexible synthesis of simple 1-substituted, 1,2-disubstituted, and 1,2,2-trisubstituted 1*H*-pyrrol-3(2*H*)-ones (3-hydroxypyrroles), in which the 4- and 5-position of the ring remain unsubstituted.[3] This route complements earlier work[4] leading to 4,5-disubstituted derivatives which are necessarily unsubstituted in the 1- and 2-position. We have therefore embarked upon a study of the chemical properties of typical pyrrolones with these new substitution patterns, and report an n.m.r. and *X*-ray crystallographic study of the protonation and *O*-alkylation of 1-alkyl, 1-aryl, and 1,2,2-trialkyl derivatives [(**1**)—(**3**), respectively.[3]]



(**1**) R = Bu^t
(**2**) R = Ph

(**3**)



(**4**)

(**5**)

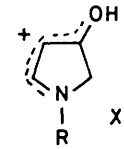
Simple pyrroles show complex behaviour in acid solution.[5–7] Depending on the conditions and the substituents, α- and/or β-protonation leads to dimerisation or polymerisation in the majority of cases, though the formation of monomeric salts is favoured by the presence of electron-withdrawing groups or of multiple alkyl substituents. In addition, t-butyl-substituted pyrroles give stable crystalline tetrafluoroborates on protonation at the 2-position.[8] In earlier studies of the 1*H*-pyrrol-3(2*H*)-one series, spectroscopic evidence was obtained for reversible *O*-protonation, though these examples were generally complicated by the presence of electron-withdrawing[9] or electron-donating[10] groups.[11] This behaviour corresponds to 2-protonation of the hydroxypyrrole tautomer.

The simple pyrrolones (**1**)—(**3**) dissolve in trifluoroacetic acid to give solutions which are stable indefinitely at room temperature. These reactions are accompanied by regular changes in the ^{1}H and ^{13}C n.m.r. spectra compared with the neutral species (Tables 1—3), which are quantitatively similar to those observed for open-chain enaminones[12] [*e.g.* (**4**)] for which there is ample evidence of *O*-protonation.[13] The cations (**6**), (**7**), and (**8**), obtained in the present series, therefore correspond to the Wheland intermediates for electrophilic protonation and alkylation, respectively, of the 3-hydroxypyrrole system.

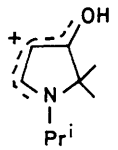
Table 1. Proton chemical shifts and coupling constants of protonated 1*H*-pyrrol-3(2*H*)-ones and enaminones[a]

Substrate	2-H	4-H	5-H	$^3J_{4,5}$	$^4J_{2,5}$
(**6**)	4.81	5.99	8.62	2.2	1.9
	(+0.86)	(+0.9)	(+0.69)	(−1.3)	(+1.1)
(**7**)	5.26	6.26	8.93	2.3	1.7
	(+1.16)	(+1.2)	(+0.53)	(−1.1)	(+1.1)
(**8**)	—	5.98	8.61	2.3	—
		(+0.99)	(+0.75)	(−1.1)	
(**5**)[12]	—	6.12	8.08	11.2	—
		(+1.01)	(+0.71)	(−1.3)	
(**9**)[8]	5.03	6.68	8.84		

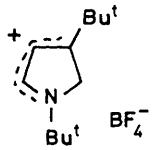
[a] Recorded for solutions in trifluoroacetic acid. Parameters quoted for the protonated species, with difference from neutral species given in brackets.



(**6**) R = Bu^t
(**7**) R = Ph



(**8**)



(**9**)

In the ^{1}H n.m.r. spectra (Table 1) all the peaks are shifted to high frequency reflecting the overall positive charge, and, significantly, the vicinal coupling constant ($^3J_{4,5}$) is markedly decreased, consistent with the reduction in bond order caused by delocalisation.

Protonation leads to large changes in the ^{13}C n.m.r. chemical shifts of the 3- and 5-position as found for the open-chain model compound (**4**)[12] (Table 2). Despite the effect of the charge, the signal due to the 3-position is *shielded* by *ca.* 10 p.p.m. because of a reduction in the anisotropic effect of the carbonyl group on *O*-protonation. The marked deshielding of the C-5 signal is

Table 2. ^{13}C Chemical shifts for protonated 1*H*-pyrrol-3(2*H*)-ones and enaminones[a]

Substrate	C-2	C-3	C-4	C-5
(**6**)	56.51	186.84	100.86	170.04
	(+3.32)	(−11.87)	(+1.73)	(+7.46)
(**7**)	59.06	189.52	102.35	168.89
	(+3.41)	(−10.24)	(−1.46)	(+10.58)
(**8**)	74.13	192.65	96.32	166.71
	(+6.57)	(−12.03)	(+2.04)	(+7.93)
(**5**)[12]	—	176.93	104.68	167.53
		(−10.79)	(+2.63)	(+10.68)
(**9**)[8]	63.34		121.76	169.79

[a] Recorded for solutions in trifluoroacetic acid. Parameters quoted for the protonated species with difference from neutral species given in brackets.

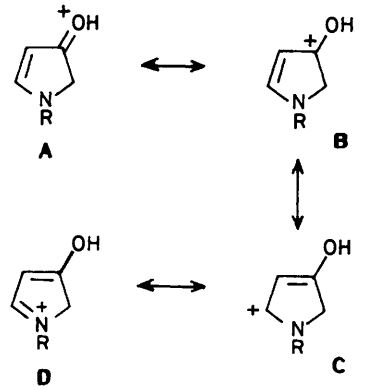


Figure 1.

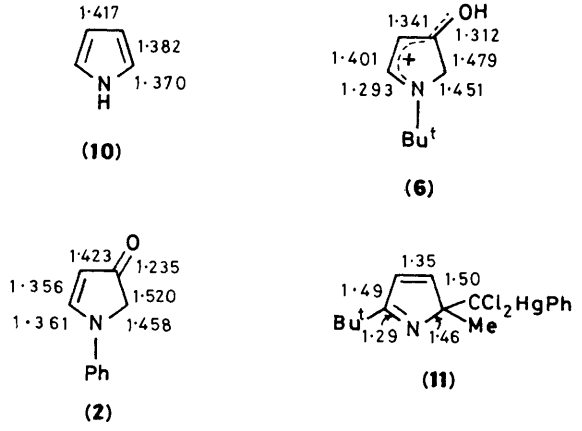


Figure 2. Bond lengths (Å) of pyrrole (**10**) and its derivatives (**6**), (**2**), and (**11**)

expected, since this site is one of low electron density (Figure 1), and is in contrast with the C-4 signal, whose chemical shift is little affected by protonation. In the conjugated system, the one-bond coupling constants $^1J_{CH}$ are uniformly increased (Table 3), which has been ascribed to the effect of the overall charge.[12] Minor couplings present in the non-protonated species[1] are affected by small but uniform amounts (Table 3).

* *Supplementary data* (see section 5.6.3 Instructions for Authors in the January issue). Calculated hydrogen-atom co-ordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

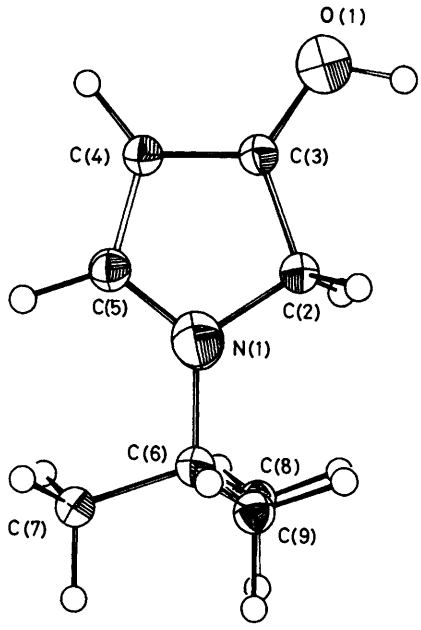


Figure 3. View of the cation (**6**) showing the crystallographic numbering scheme

A comparison of the spectra of the t-butylpyrrolium salts (**6**) and (**9**)[8] is also illuminating (Tables 1—3). The electron-donating effect of the hydroxy substituent in (**6**) is particularly marked at the 4-position, which is shielded by 0.68 and 20.90 p.p.m. in the ^1H and ^{13}C n.m.r. spectra, respectively, relative to the corresponding spectra of the 3-t-butyl analogue. Otherwise, the trends in chemical shifts and coupling constants are remarkably similar, especially since it should be noted that in other examples[8] a more typical $^1J_{CH}$ for the β-position of t-butylpyrrolium species (Table 3) is *ca.* 180 Hz, which is clearly in line with the values in the 3-hydroxy series.

The pyrrolones (**1**)—(**3**) are sufficiently basic to give monomeric crystalline salts with picric acid [(**6**)—(**8**), X = picrate; 65—95%], which can be stored in the solid state at room temperature, though the *N*-phenyl example (**7**) decomposed in solution on attempted recrystallisation. The *N*-t-butyl derivative (**6**; X = picrate) gave crystals suitable for *X*-ray analysis. The bond lengths, bond angles, and torsion angles are given in Tables 4—6: refined positional parameters are given in Table 7.* Two molecules, unrelated by symmetry, were observed, and the parameters for both are listed with A and B classifications. Average bond lengths are quoted in Figure 2, together with data for pyrrole itself (**10**),[14] for a representative pyrrolone (**2**),[15] and for a 2*H*-pyrrole (**11**).[16,17] The results confirm that *O*-protonation of the pyrrolone takes place (Figure 3), stabilised by intermolecular hydrogen-bonding to the phenolate group of the picrate counterion (Figure 4). The hydroxy group, the five-membered ring, and one methyl group [C(7)] are approximately coplanar, but a curious feature of the structure is the eclipsing which is present between the t-butyl methyl groups and the hydrogen atoms at C(2) and C(5). This may be responsible for a deformation of the t-butyl group, reflected in an expansion to 112° of one of the angles at its central carbon atom [C(7)–C(6)–C(9)].

The bond length changes which are found on protonation are clearly in accord with the delocalisation represented by Figure 1. Thus the C(3)–C(4), C(4)–C(5), and C(5)–N bond lengths in (**6**) are respectively shorter, longer, and shorter than in the parent pyrrolone system (**3**), or in pyrrole itself (**10**). In view of the similarity of the C(3)–C(4) and C(5)–N bond lengths in (**6**)

Table 3. Carbon-proton coupling constants of protonated 1*H*-pyrrol-3(2*H*)-ones and enaminones[a]

	C-2		C-3[b]	C-4		C-5		
Substrate	^1J	$^3J_{4\text{-H}} = {}^3J_{5\text{-H}}$		^1J	$^2J_{5\text{-H}}$	^1J	$^2J_{4\text{-H}}$	$^3J_{\text{H}}$
(6)	144.6	5.6		185.0	7.8	184.6	6.8	5.0[c]
	(+3.4)	(+0.4)		(+8.5)	(+1.0)	(+11.6)	(−1.7)	(+1.0)
(7)	146.3	5.6		186.2	7.8	186.9	7.9	5.0[c]
	(+3.1)	(+1.2)		(+7.0)	(+1.6)	(+10.2)	(−1.5)	(+1.4)
(8)	—	—		185.6	7.6	183.2	6.5	6.5[d]
				(+9.5)	(+1.6)	(+13.2)	(−2.1)	(+0.6)
(5)[12]	—	—		164.9	—	168.4	—	—
				(+9.6)		(+7.5)		
(9)[8]	143.7			170.0		185.0		

[a] Protonated species quoted with difference from neutral species in brackets. [b] Couplings of ~4.5 Hz observed to at least two protons but not assigned. [c] Coupling to 2-H. [d] Coupling to α-CH on nitrogen atom substituent.

Table 4. Bond lengths (Å) with standard deviations

O(1A)–H(1A)	0.96(3)	O(1B)–H(1B)	0.94(4)
O(1A)–C(3A)	1.311(4)	O(1B)–C(3B)	1.313(5)
C(3A)–C(4A)	1.352(5)	C(3B)–C(4B)	1.330(6)
C(3A)–C(2A)	1.478(5)	C(3B)–C(2B)	1.479(5)
C(4A)–C(5A)	1.406(5)	C(4B)–C(5B)	1.396(6)
C(5A)–N(1A)	1.295(5)	C(5B)–N(1B)	1.290(5)
C(2A)–N(1A)	1.450(5)	C(2B)–N(1B)	1.451(5)
N(1A)–C(6A)	1.491(5)	N(1B)–C(6B)	1.494(5)
C(6A)–C(7A)	1.489(7)	C(6B)–C(7B)	1.506(6)
C(6A)–C(8A)	1.517(7)	C(6B)–C(8B)	1.517(6)
C(6A)–C(9A)	1.481(8)	C(6B)–C(9B)	1.494(6)

Table 5. Angles (°) with standard deviations

H(1A)–O(1A)–C(3A)	113.4(19)	H(1B)–O(1B)–C(3B)	108.2(22)
O(1A)–C(3A)–C(4A)	126.2(3)	O(1B)–C(3B)–C(4B)	126.9(4)
O(1A)–C(3A)–C(2A)	124.2(3)	O(1B)–C(3B)–C(2B)	124.0(3)
C(4A)–C(3A)–C(2A)	109.6(3)	C(4B)–C(3B)–C(2B)	109.2(4)
C(3A)–C(4A)–C(5A)	105.8(3)	C(3B)–C(4B)–C(5B)	107.0(4)
C(4A)–C(5A)–N(1A)	113.3(3)	C(4B)–C(5B)–N(1B)	112.8(4)
C(3A)–C(2A)–N(1A)	102.7(3)	C(3B)–C(2B)–N(1B)	102.6(3)
C(5A)–N(1A)–C(2A)	108.6(3)	C(5B)–N(1B)–C(2B)	108.4(3)
C(5A)–N(1A)–C(6A)	128.4(3)	C(5B)–N(1B)–C(6B)	128.2(3)
C(2A)–N(1A)–C(6A)	123.0(3)	C(2B)–N(1B)–C(6B)	123.3(3)
N(1A)–C(6A)–C(7A)	109.5(4)	N(1B)–C(6B)–C(7B)	109.0(3)
N(1A)–C(6A)–C(8A)	107.5(4)	N(1B)–C(6B)–C(8B)	107.5(3)
N(1A)–C(6A)–C(9A)	108.8(4)	N(1B)–C(6B)–C(9B)	108.3(3)
C(7A)–C(6A)–C(8A)	109.2(4)	C(7B)–C(6B)–C(8B)	109.1(4)
C(7A)–C(6A)–C(9A)	112.0(4)	C(7B)–C(6B)–C(9B)	112.5(4)
C(8A)–C(6A)–C(9A)	109.7(4)	C(8B)–C(6B)–C(9B)	110.4(4)

Table 6. Torsion angles (°) with standard deviations

H(1A)–O(1A)–C(3A)–C(4A)	167.7(21)
H(1A)–O(1A)–C(3A)–C(2A)	−13.8(21)
O(1A)–C(3A)–C(4A)–C(5A)	−178.8(3)
C(2A)–C(3A)–C(4A)–C(5A)	2.5(4)
O(1A)–C(3A)–C(2A)–N(1A)	178.6(3)
C(4A)–C(3A)–C(2A)–N(1A)	−2.6(4)
C(3A)–C(4A)–C(5A)–N(1A)	−1.4(4)
C(4A)–C(5A)–N(1A)–C(2A)	−0.3(4)
C(4A)–C(5A)–N(1A)–C(6A)	−178.4(3)
C(3A)–C(2A)–N(1A)–C(5A)	1.7(4)
C(3A)–C(2A)–N(1A)–C(6A)	180.0(3)
C(5A)–N(1A)–C(6A)–C(7A)	4.3(5)
C(5A)–N(1A)–C(6A)–C(8A)	122.8(4)
C(5A)–N(1A)–C(6A)–C(9A)	−118.4(4)
C(2A)–N(1A)–C(6A)–C(7A)	−173.6(4)
C(2A)–N(1A)–C(6A)–C(8A)	−55.0(5)
C(2A)–N(1A)–C(6A)–C(9A)	63.7(5)
H(1B)–O(1B)–C(3B)–C(4B)	171.1(23)
H(1B)–O(1B)–C(3B)–C(2B)	−9.6(23)
O(1B)–C(3B)–C(4B)–C(5B)	179.8(4)
C(2B)–C(3B)–C(4B)–C(5B)	0.3(5)
O(1B)–C(3B)–C(2B)–N(1B)	179.9(3)
C(4B)–C(3B)–C(2B)–N(1B)	−0.7(4)
C(3B)–C(4B)–C(5B)–N(1B)	0.2(5)
C(4B)–O(5B)–N(1B)–C(2B)	−0.7(5)
C(4B)–C(5B)–N(1B)–C(6B)	174.2(4)
C(3B)–C(2B)–N(1B)–C(5B)	0.8(4)
C(3B)–C(2B)–N(1B)–C(6B)	−174.3(3)
C(5B)–N(1B)–C(6B)–C(7B)	18.9(5)
C(5B)–N(1B)–C(6B)–C(8B)	136.9(4)
C(5B)–N(1B)–C(6B)–C(9B)	−103.8(5)
C(2B)–N(1B)–C(6B)–C(7B)	−167.0(3)
C(2B)–N(1B)–C(6B)–C(8B)	−49.0(4)
C(2B)–N(1B)–C(6B)–C(9B)	70.3(4)

and in the 2*H*-pyrrole (**11**),[16] the resonance structure **D** (Figure 1) apparently gives the best approximation to the structure of the cation, and in agreement with this the C–O bond length (1.312 Å) shows evidence of considerable single-bond character. The C(2)–C(3) bond is shortened, relative to that of the neutral species (**2**) but there is little change in the N–C(2) bond length, while the geometrical constraints of the ring ensure that the bond angles (Table 5 and ref. 1) remain relatively constant on protonation, except for a slight change at C(3).

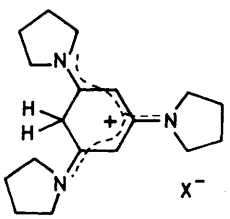
These data represent the first structural information for a Wheland-like intermediate in the pyrrole series. Recent crystallographic studies of benzenoid σ-complexes [*e.g.* (**12**)] have also employed electron-donating substituents to stabilise the positive charge.[18]

The enaminone-like behaviour of the pyrrolone (**3**) on protonation[13] is also reflected in its reactions with hard alkylating agents.[19] Thus, the salt (**13**) was obtained as a crystalline solid in 70% yield, on treatment of (**3**) with triethyloxonium tetrafluoroborate. The ^{1}H and ^{13}C n.m.r. spectra of this material (see Experimental section) are similar to those of the protonated species, which is therefore consistent with *O*-alkylation. Reaction of the 2-unsubstituted derivatives (**1**) and (**2**) with Meerwein's reagent was more complex, and will be considered in a later paper in this series, in the context of *O-versus-C* alkylation.[20]

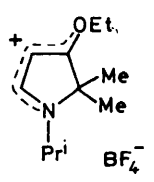
Further information on the exchange processes involved in the protonation of the pyrrolones is obtained by using [^{2}H]-trifluoroacetic acid; deuterium incorporation in the substrate also reveals the potential of the system to undergo electrophilic substitution reactions. Under these conditions, the half-life for deuterium exchange at the 4-position of the 1-t-butyl compound (**1**) is <1 min, while that at the 2-position is *ca.* 6 min. No

Table 7. Fractional co-ordinates of atoms with standard deviations

	x	*y*	*z*
O(1A)	0.344 40(21)	0.813 50(14)	0.415 1(3)
H(1A)	0.385 4(27)	0.859 1(16)	0.495(4)
C(3A)	0.238 4(3)	0.809 12(18)	0.332 1(4)
C(4A)	0.168 9(3)	0.757 76(19)	0.189 9(5)
C(5A)	0.065 6(3)	0.776 15(19)	0.145 4(5)
C(2A)	0.175 9(3)	0.859 91(18)	0.384 8(4)
N(1A)	0.065 95(23)	0.833 26(15)	0.250 9(4)
C(6A)	−0.028 5(3)	0.867 52(20)	0.247 8(5)
C(7A)	−0.134 1(4)	0.822 4(3)	0.107 9(8)
C(8A)	−0.057 8(5)	0.869 2(4)	0.433 2(8)
C(9A)	0.015 6(5)	0.943 1(3)	0.212 3(10)
O(1B)	0.209 95(25)	0.334 34(16)	0.219 9(4)
H(1B)	0.190(3)	0.374 7(18)	0.267(5)
C(3B)	0.289 0(3)	0.323 54(21)	0.345 8(5)
C(4B)	0.329 6(4)	0.266 96(23)	0.341 0(6)
C(5B)	0.412 2(4)	0.278 59(22)	0.502 9(6)
C(2B)	0.348 2(3)	0.374 80(20)	0.518 1(5)
N(1B)	0.425 26(24)	0.338 61(16)	0.607 9(4)
C(6B)	0.497 2(3)	0.366 06(20)	0.796 9(5)
C(7B)	0.586 1(4)	0.326 5(3)	0.831 0(7)
C(8B)	0.560 5(4)	0.446 86(24)	0.810 8(6)
C(9B)	0.417 0(4)	0.354 8(3)	0.924 9(6)
O(1)	0.409 64(21)	0.942 48(13)	0.603 3(3)
C(1)	0.485 6(3)	0.989 83(18)	0.721 6(4)
C(2)	0.597 3(3)	0.984 78(19)	0.804 2(5)
C(3)	0.680 4(3)	1.038 29(21)	0.934 7(5)
C(4)	0.657 9(3)	1.100 99(20)	0.988 3(4)
C(5)	0.554 3(3)	1.111 96(19)	0.916 9(5)
C(6)	0.471 3(3)	1.058 28(19)	0.788 1(5)
N(1)	0.624 6(3)	0.919 11(20)	0.760 0(5)
O(11)	0.555 6(3)	0.867 01(21)	0.673 3(7)
O(12)	0.720 1(4)	0.916 61(24)	0.815 7(9)
N(2)	0.744 1(4)	1.156 85(22)	1.128 6(4)
O(21)	0.839 0(3)	1.147 23(19)	1.180 8(4)
O(22)	0.719 6(3)	1.210 04(20)	1.184 6(5)
N(3)	0.363 1(3)	1.071 79(20)	0.720 7(5)
O(31)	0.364 8(3)	1.135 23(23)	0.729 4(8)
O(32)	0.275 5(3)	1.024 33(21)	0.660 1(6)
O(1′)	0.201 48(22)	0.456 77(14)	0.367 8(4)
C(1′)	0.146 0(3)	0.500 97(18)	0.372 7(4)
C(2′)	0.191 9(3)	0.570 45(18)	0.493 9(4)
C(3′)	0.138 4(3)	0.622 16(18)	0.502 7(4)
C(4′)	0.029 3(3)	0.607 47(18)	0.392 6(5)
C(5′)	−0.024 2(3)	0.542 58(19)	0.273 0(4)
C(6′)	0.032 2(3)	0.491 53(17)	0.262 0(4)
N(1′)	0.304 7(3)	0.585 80(20)	0.618 1(4)
O(11′)	0.324 8(3)	0.537 16(19)	0.693 6(5)
O(12′)	0.371 0(3)	0.647 38(20)	0.648 2(5)
N(2′)	−0.032 3(3)	0.660 42(18)	0.403 2(5)
O(21′)	0.009 7(3)	0.713 75(17)	0.522 8(5)
O(22′)	−0.122 70(25)	0.649 82(16)	0.290 9(4)
N(3′)	−0.029 7(3)	0.424 74(17)	0.136 3(4)
O(31′)	−0.131 12(25)	0.413 31(17)	0.065 9(4)
O(32′)	0.021 7(3)	0.382 90(18)	0.098 9(5)



(12)



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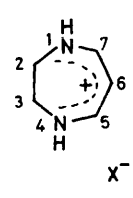


(14)

exchange was observed at the 5-position after several days, even though non-hydroxylated pyrroles give the most thermo-

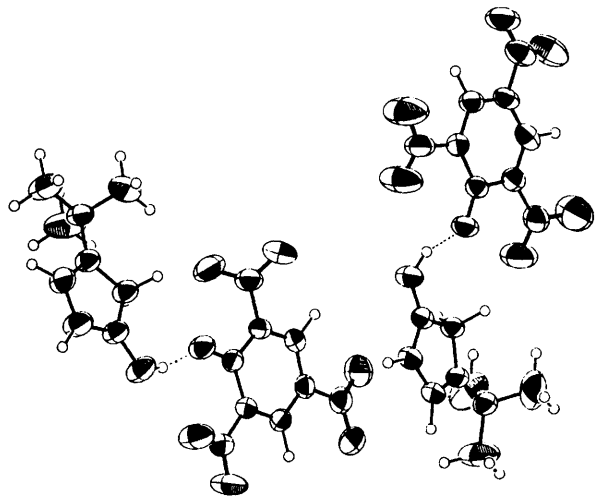


Figure 4. Contents of one asymmetric unit of the picrate salt of (**6**) showing hydrogen-bonded contacts

dynamically stable cation by reaction at the α-position.[5] When the 2-position is blocked, as in the 2,2-dimethyl derivative (**3**), exchange occurs exclusively at the 4-position, though the related salt (**13**) is completely unreactive despite extended reaction times. Hence the observed exchange in (**1**) and (**3**) at the 4-position must take place *via* *C*-protonation of the free base [Scheme 1, route (*a*)], which is not available to the salt (**13**). This behaviour is in complete contrast to that of the isoelectronic dihydrodiazepinium system (**14**), for which there is kinetic evidence that exchange at the corresponding (6)-position takes place through the *N*-protonated form *via* a dication intermediate.[21] Clearly the difference is controlled by the relative electronegativities of the nitrogen and oxygen atoms in the conjugated systems.

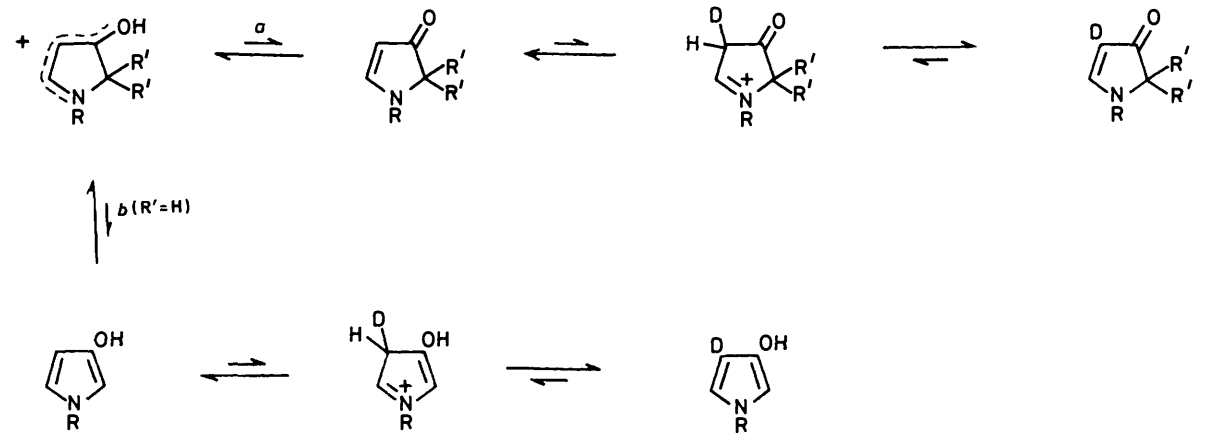
In the 2,2-unsubstituted series, exchange at the 4-position may take place by the above mechanism, or by *C*-deprotonation to the hydroxypyrrole tautomer [Scheme 1, route (*b*)] which can undergo typical pyrrolic substitution. However, preliminary experiments with 3-alkoxypyrroles,[20] for which route (*b*) is the only viable mechanism, reveal that complete deuterium incorporation at position 4 requires many days rather than a few minutes. Hence route (*a*) is the dominant mechanism for the pyrrolones whether or not position 2 is substituted. Nevertheless, the hydroxypyrrole tautomer remains the most likely intermediate for exchange at the 2-position (Scheme 2), which appears to be equally facile in the alkoxypyrrole, and pyrrolone series.[20]

It should be noted that although these results indicate that the 2- and 4-position of the 1*H*-pyrrol-3(2*H*)-one system are open to attack by electrophiles, the rates of deuterium incorporation do not necessarily give the relative reactivity of each site, since these rates are additionally dependent on the rates—and equilibrium constants—for *O*- and *C*-deprotonation.

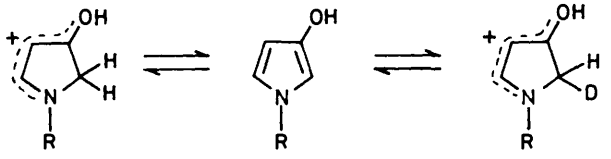
Experimental

^1H and ^{13}C N.m.r. spectra were recorded at 80 MHz and 20 MHz respectively, unless otherwise stated.

Preparation of Samples for N.m.r. Spectroscopy.—The appropriate 1*H*-pyrrol-3(2*H*)-one[3] was dissolved in trifluoroacetic acid and spectra were recorded using an external [$^2H_2$]water lock. The deuterium exchange of the protonated form was observed using neat [^2H]trifluoroacetic acid. Data are given in Tables 1—3.



Scheme 1.



Scheme 2.

Preparation of Picrates.—The 1*H*-pyrrol-3(2*H*)-one[3] (0.5 mmol) was dissolved in ethanol (4 ml) and an excess of a saturated solution of picric acid in ethanol was added. The salts precipitated when the side of the flask was scratched with a glass rod. In neutral solutions a rapid equilibrium between the free base and protonated forms exists which gives rise to unresolved peaks in the ^{1}H n.m.r. spectra. Proton spectra of the salts were therefore obtained in acid solution. The following *pyrrolium picrates* were prepared: 3-*hydroxy*-1-*t*-*butyl*-1,2-*dihydro* (175 mg, 95%), m.p. 80—82 °C (from ethanol) (Found: C, 45.55; H, 4.1; N, 15.2. $C_{14}H_{16}N_4O_8$ requires C, 45.65; H, 4.35; N, 15.2%), $\delta_H(CF_3CO_2H)$ 9.24 (2 H, s), 8.56 (1 H, apparent q, ^3J and ^4J 2.0 Hz), 5.94 (1 H, d, ^3J 2.1 Hz), 4.75 (2 H, d, ^4J 2.0 Hz), and 1.59 (9 H, s); 3-hydroxy-1-phenyl-1,2-dihydro (145 mg, 75%), m.p. 102—104 °C (decomposed on attempted recrystallisation) (Found: C, 48.6; H, 3.05; N, 13.4. $C_{16}H_{12}N_4O_8 \cdot 0.5H_2O$ requires C, 48.35; H, 3.25; N, 14.1%); $\delta_H(CF_3CO_2H)$ 9.32 (2 H, s), 8.94 (1 H, dd, ^3J 2.6 and ^4J 1.8 Hz), 7.4—7.7 (5 H, m), 6.30 (1 H, d, ^3J 2.6 Hz), and 5.29 (2 H, d, ^4J 1.8 Hz); 3-*hydroxy*-1-*isopropyl*-2,2-*dimethyl*-1,2-*dihydro* (120 mg, 63%), m.p. 135—136 °C (from methanol) (Found: C, 47.5; H, 4.75; N, 14.6. $C_{15}H_{18}N_4O_8$ requires C, 47.1; H, 4.7; N, 14.65%); $\delta_H(CF_3CO_2H)$ 9.32 (2 H, s), 8.64 (1 H, d, ^3J 2.0 Hz), 6.00 (1 H, d, ^3J 2.0 Hz), 4.23 (1 H, m), 1.69 (6 H, s), and 1.60 (6 H, d, ^3J 6.7 Hz).

3-*Ethoxy*-1-*isopropyl*-2,2-*dimethyl*-1,2-*dihydropyrrolium Tetrafluoroborate.*—1-Isopropyl-2,2-dimethyl-1*H*-pyrrol-3(2*H*)-one[3] (0.6 g, 4 mmol) was dissolved in methylene dichloride (15 ml) and a solution of triethyloxonium tetrafluoroborate in methylene dichloride (0.83M; 5.5 ml) was added dropwise while the mixture was stirred, and cooled, in an ice-bath. The reaction mixture was allowed to warm to room temperature and left to stand for 30 min. The methylene dichloride was then removed *in vacuo* and ether was added to the oily residue. It was stored at −20 °C overnight and this yielded the salt as a solid which was purified by reprecipitation from acetone by addition of ether, to give the pure *tetrafluoroborate* (0.75 g, 70%), m.p. 70—72 °C (Found: C, 48.85; H, 7.25; N, 5.05. $C_{11}H_{20}BF_4NO$ requires C, 49.05; H, 7.45; N, 5.2%); δ_H(200 MHz, C[^{2}H]Cl$_3$) 8.93 (1 H, d, ^3J 2.4 Hz), 6.03 (1 H, d, ^3J 2.4 Hz), 4.34 (2 H, q, ^3J 7.1 Hz), 4.14 (1 H, m, ^3J 6.7 Hz), 1.53 (6 H, s) 1.50 (6 H, d, ^3J 6.7 Hz), and 1.46 (3 H, t, ^3J 7.1 Hz); δ_C([$^2H_6$]DMSO) 190.25(q), 168.28, 95.14, 73.78(q), 70.61, 49.50, 23.24, 20.69, and 13.59; no reasonable mass spectrum could be obtained.

Crystal Data for 3-*Hydroxy*-1-*t*-*butyl*-1,2-*dihydropyrrolium Picrate.*—$C_8H_{14}NO \cdot C_6H_2N_3O_7$, M = 368.3. Triclinic, a = 12.261(7), b = 19.403(11), c = 7.607 1(27) Å, α = 96.21(4), β = 100.49(5), γ = 106.83(6)°, V = 1 678.2 Å^3 (by least-squares refinement on diffractometer angles for 12 centred reflections. 7.8 < θ < 10.2°, $\bar{\lambda}$ = 0.710 69 Å), space group $P\bar{1}$, Z = 4, D_x = 1.458 g cm^{-3}. Pale yellow-green, equant crystal, 0.7 × 0.7 × 0.6 mm, μ (Mo-K_α) = 0.04 mm^{-1}.

Data Collection and Processing.—CAD4 diffractometer, ω/2θ mode with ω scan width 0.80° + 0.347 tanθ°, graphite-monochromated Mo-K_α radiation; 4 371 reflections measured (2.0 < θ < 22.5°, h −13 ⟶ 13, k −20 ⟶ 20, l 0 ⟶ 6), 4 357 unique, giving 3 663 with $F \geqslant 2\sigma(F)$. Decay correction (min. 0.977, max. 1.019) applied, no absorption correction.

Structure Analysis and Refinement.—Direct methods[22] yielded the positions of all non-H atoms; H-atoms were located from subsequent difference Fourier syntheses. Full-matrix least-squares refinement[23] with the O–H distance fixed at 1.00(5) Å, the remaining H atoms in calculated positions, and all non-H atoms anisotropic. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,179\,F^2$ gave satisfactory agreement analyses and at final convergence R, wR = 0.0615, 0.0872, S = 1.55 for 475 refined parameters. The final ΔF synthesis had no feature above 0.57 e Å^{-3}. Molecular geometry calculations utilised CALC[24] and illustrations were produced using ORTEP.[25]

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