3-Hydroxypyrroles and 1*H*-Pyrrol-3(2*H*)-ones. Part 10.[1] Alkylation of Pyrrolones under Basic Conditions: Regiospecific Formation of 3-Alkoxypyrroles

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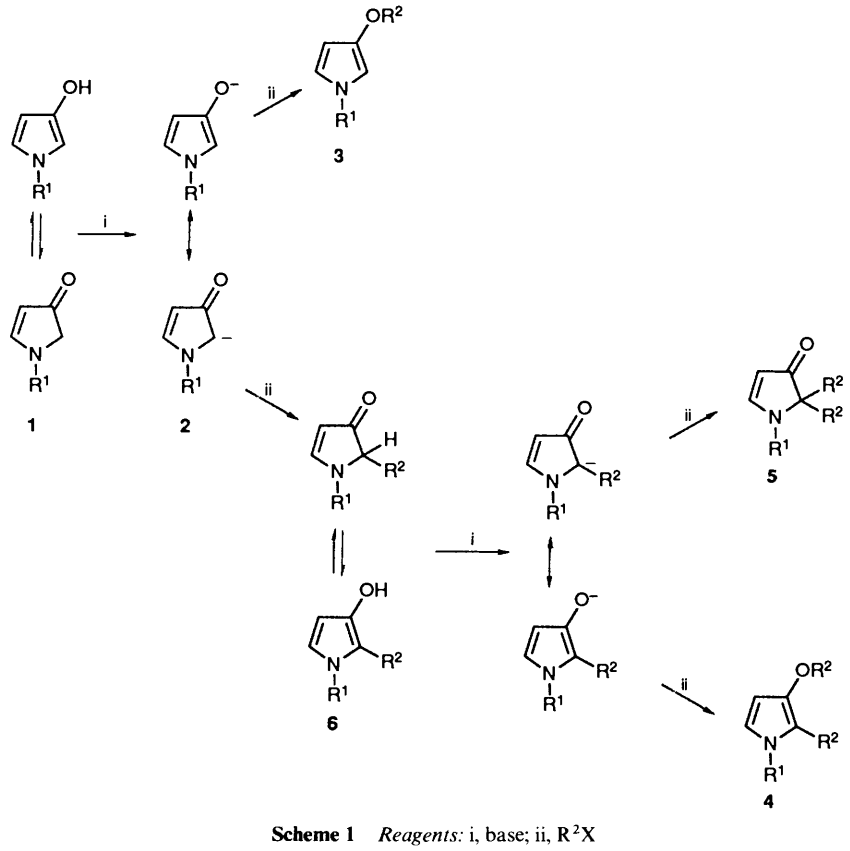
Alkylation of 1-substituted 1*H*-pyrrol-3(2*H*)-ones **1** in the presence of base generally gives a mixture of *O*-alkylated **3**, *C,O*-dialkylated **4** and *C,C*-dialkylated **5** products. The proportion of *C*-alkylation is increased by the use of a soft alkylating agent (*e.g.* iodomethane) and a solvent of low polarity (*e.g.* THF), whereas *O*-alkylation is favoured by hard alkylating agents (*e.g.* methyl toluene-*p*-sulphonate), and dipolar aprotic solvents (*e.g.* dimethylimidazolidinone). These latter conditions give a good preparative route to a wide range of 1-substituted and 1,2-disubstituted 3-alkoxypyrroles **3** (65–90% yield). The X-ray crystal structure of 1-*tert*-butyl-3-methoxy-2-phenylpyrrole **22** is reported.

In this paper, we describe the results of a systematic study of the alkylation of the 3-hydroxypyrrole-1*H*-pyrrol-3(2*H*)-one system **1** under basic conditions (Scheme 1). Depending on the substitution pattern of the pyrrole, and on the reaction conditions, such reactions are known to give either *O*-alkylated products **3**,[2] *C*-alkylated products **5**,[3] or a mixture of both.[4] In view of the ready availability of simple 3-hydroxypyrroles **1** (and **6**) by the Meldrum's acid pyrolysis route,[5] we hoped to develop *regiospecific* methods which could lead to either 3-alkoxypyrroles **3** or 2,2-dialkyl-1*H*-pyrrol-3(2*H*)-ones **5**. This route to the latter compounds would complement the direct pyrolysis method,[5] while the alkoxypyrroles were required as tautomerically locked model compounds in a general study of 3-hydroxypyrrole reactivity.[6] The disadvantages of earlier routes to 3-alkoxypyrroles have been reviewed by Pinnick,[7,8] who discovered an alternative (reductive) method which does not involve alkylation.[7]

At an early stage of our work, we discovered that standard methods of alkylating phenols (*e.g.* alkyl halide plus anhydrous potassium carbonate in dimethylformamide) were ineffective in the 3-hydroxypyrrole series, presumably due to their lower acidity. However, treatment of either 1-*tert*-butyl-3-hydroxypyrrole **7** or its 1-phenyl analogue **8** with sodium hydride in [$^2H_6$]DMSO gave a deep-red solution though only broad peaks were present in the ^1H NMR spectrum; the colour was discharged, and a characteristic hydroxypyrrole spectrum[9] was regenerated when the sample was quenched with [$^2H_4$]acetic acid. Although attempts to analyse the spectrum of the red



Scheme 1 *Reagents:* i, base; ii, R^2X

Table 1 Effect of solvent on the alkylation of **8** and **9**

Substrate	Solvent	Alkylating agent	Yield (%) 5	4	3
8	THF	MeI	100	0	0
8	DMSO	MeI	75	12	13
8	DMI[a]	MeI	25	31	44
9	THF	MeI	77	23	
9	DMSO	MeI	31	69	

[a] Dimethylimidazolidinone, see text.

Table 2 Effect of leaving group on the alkylation of **8**

Substrate	Solvent	Alkylating agent	Yield (%) 5	4	3
8	THF	MEI	100	0	0
8	THF	MeOTs[a]	2	16	82
8	DMSO	MeI	75	12	13
8	DMSO	MeBr	14	26	60
8	DMSO	EtI	43	14	43
8	DMSO	EtBr	13	24	63
8	DMI[b]	MeI	25	31	44
8	DMI[b]	MeOTs	0	0	100

[a] Methyl toluene-*p*-sulphonate. [b] Dimethylimidazolidinone.

Table 3 Effect of electrophilic centre on the alkylation of **8**

Substrate	Solvent	Alkylating agent	Yield (%) 5	4	3
8	DMSO	MeI	75	12	13
8	DMSO	EtI	43	14	43
8	DMSO	MeBr	14	26	60
8	DMSO	EtBr	13	24	63
8	DMSO	Pr^{i}Br	0	10	90

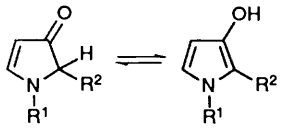
Table 4 Effect of substrate structure on *C*- *vs.* *O*-alkylation of 3-hydroxypyrroles **1**

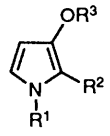
Substrate	Solvent	Alkylating agent	Yield (%) 5	4	3
7	DMSO	MeI	50	17	33
8	DMSO	MeI	75	12	13
9	DMSO	MeI	31	69	
10	DMSO	MeI	77	23	
11	DMSO	MeI	63	37	
12	DMSO	MeI	54	46	

solution*—either by ^{13}C NMR or by low temperature (−55 °C) ^1H NMR using [$^2H_8$]THF as solvent—were unsuccessful, it was clear that a species with the *chemical* properties expected of the anion **2** was being generated. Indeed, quenching of the above DMSO solution derived from the 3-hydroxy-1-phenylpyrrole **8** with excess of iodomethane, gave a mixture of *O*- and *C*-alkylation products **3**–**5** (R^1 = Ph, R^2 = Me) in 1:1:6 ratio. These compounds were readily identified by characteristic peaks in the range δ_H 5.0–9.0 in the NMR spectrum of the mixture. Thus the alkoxypyrroles **3** and **4** show three double doublets and two doublets respectively in the region δ_H 6.0–7.0,[9] whereas the 1*H*-pyrrol-3(2*H*)-one **5** shows a characteristic[10] pair of doublets at δ_H 5.4 and 8.1.

Since **2** is behaving as an ambident anion, the factors influencing *O*- and *C*-alkylation of such enolates were next investigated by a series of small-scale comparative experiments using an excess of base and of alkylating agent (see Experimental section). HSAB theory predicts[11] that *O*-alkylation should be favoured by: (*a*), a polar solvent; (*b*), a 'hard' leaving group in the alkylating agent; and (*c*), a highly substituted alkylating agent, and so each of these factors was varied in turn (Tables 1–3), generally using 3-hydroxy-1-phenylpyrrole as the standard substrate. In addition, a survey of the effect of pyrrole structure on the alkylation was carried out (Table 4).

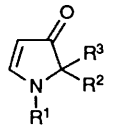
As expected, alkylation of **8** with iodomethane using a solvent of increased polarity resulted in a substantial reduction in the amount of *C*,*C*-dialkylation product **5** and an increase in the amount of *C*,*O*- and *O*-alkylation (**4** and **5**) (Table 1). The use



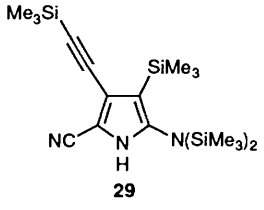


7 R^1 = Bu^t, R^2 = H
8 R^1 = Ph, R^2 = H
9 R^1 = CH_2Ph, R^2 = Ph
10 R^1 = Ph, R^2 = Me
11 R^1 = R^2 = Ph
12 R^1 = Me, R^2 = Ph
13 R^1 = Bu^t, R^2 = Ph

14 R^1 = Ph, R^2 = H, R^3 = Me
15 R^1 = Ph, R^2 = H, R^3 = Et
16 R^1 = Ph, R^2 = H, R^3 = CH_2Ph
17 R^1 = Bu^t, R^2 = H, R^3 = Me
18 R^1 = Bu^t, R^2 = H, R^3 = Et
19 R^1 = Ph, R^2 = R^3 = Me
20 R^1 = R^3 = Me, R^2 = Ph
21 R^1 = Et, R^2 = R^3 = Me
22 R^1 = Bu^t, R^2 = Ph, R^3 = Me
27 R^1 = CH_2Ph, R^2 = Ph, R^3 = Me
28 R^1 = R^2 = Ph, R^3 = Me



23 R^1 = Bu^t, R^2 = R^3 = Me
24 R^1 = Ph, R^2 = R^3 = Me
25 R^1 = CH_2Ph, R^2 = Ph, R^3 = Me
26 R^1 = R^2 = Me, R^2 = Ph



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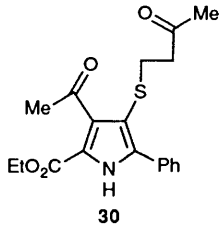

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of dimethylimidazolidinone (DMI), a highly polar solvent recommended as a general replacement for HMPA,[12] was particularly effective in promoting *O*-alkylation and resulted in some 44% of alkoxypyrrole **3** (R^1 = Ph, R^2 = Me). Conversely, relatively non-polar solvents (*e.g.* THF) give high proportions of *C*,*C*-dialkylated product **5**. Similar trends are found when Scheme 1 is entered at the intermediate stage **6** using a 1,2-disubstituted hydroxypyrrole substrate, *e.g.* **9** (Table 1): clearly such substrates can only give products **4** and **5**.

* An EPR study, for which we are grateful to Dr. J. C. Walton (University of St Andrews), confirmed the absence of stable free radicals in these solutions.

Table 5 Bond lengths (Å) with standard deviations

N(1)–C(2)	1.406(5)	N(1′)–C(2′)	1.398(5)
N(1)–C(5)	1.372(5)	N(1′)–C(5′)	1.368(5)
N(1)–C(1N)	1.487(5)	N(1′)–C(1N′)	1.494(5)
C(2)–C(3)	1.372(5)	C(2′)–C(3′)	1.371(5)
C(2)–C(1P)	1.515(4)	C(2′)–C(1P′)	1.505(4)
C(3)–C(4)	1.397(5)	C(3′)–C(4′)	1.402(5)
C(3)–O(3)	1.383(4)	C(3′)–O(3′)	1.386(4)
C(4)–C(5)	1.388(5)	C(4′)–C(5′)	1.365(5)
C(1N)–C(11)	1.524(6)	C(1N′)–C(11′)	1.519(6)
C(1N)–C(12)	1.518(6)	C(1N′)–C(12′)	1.516(6)
C(1N)–C(13)	1.525(6)	C(1N′)–C(13′)	1.528(6)
O(3)–C(31)	1.426(5)	O(3′)–C(31′)	1.416(5)

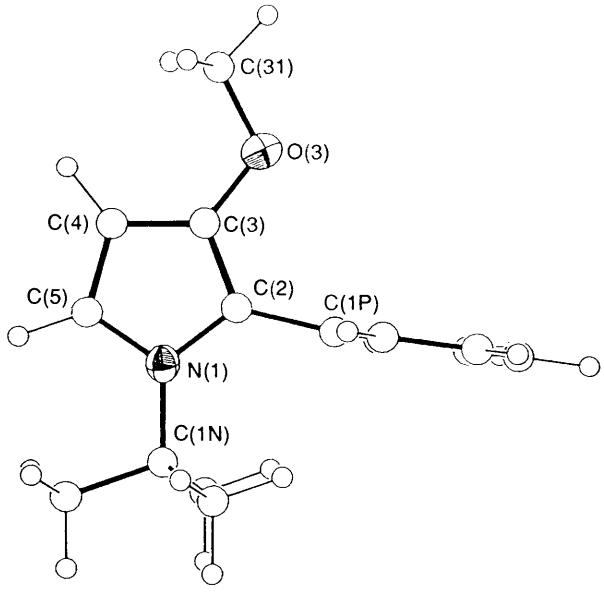

Fig. 1 ORTEP plot of **22** showing crystallographic numbering system

The effect of changing the leaving group of the alkylating agent is shown in Table 2, for the alkylation of **8** in three different solvents. Comparison of the results for bromomethane with iodomethane, or bromoethane with iodoethane in DMSO, shows a marked increase in attack at oxygen in changing from the very soft iodide anion as leaving group. The effect of the toluene-*p*-sulphonate leaving group is more marked even in THF solution, and the combined use of the hard alkylating agent (methyl toluene-*p*-sulphonate) with the highly polar solvent (DMI) results in quantitative and *regiospecific O*-alkylation (Table 2).

Alkylation under neutral conditions using triethyloxonium tetrafluoroborate was also briefly investigated, but the regioselectivity was disappointing: typically the *O*-ethyl material **3** (R^2 = Et) was obtained, contaminated with *ca.* 15% of the *C*,*O*-diethyl product **4** (R^2 = Et).

As expected, increasing the degree of substitution at the site of the leaving group of the alkylating agent causes an increase in *O*-alkylation (Table 3), through the series from methyl to isopropyl. The increase in steric bulk also contributes to the observed regiochemistry, and indeed none of the highly crowded, 2,2-diisopropyl derivative **5** (R^1 = Ph, R^2 = Pr^i) was detected. Changes in the substitution pattern of the substrate also influence the ambident reactivity of the anion generated from **1** or **6** under standard conditions (Table 4), but the effect is rather small. In general terms, the amount of *C*-alkylation is greater in the *N*-aryl examples **8**, **10** and **11** than in the *N*-alkyl series **7**, **9** and **12**.

In applying these preliminary results to preparative alkylations, it is clear that the combination of methyl toluene-*p*-sulphonate and DMI shows the greatest potential as a route to 3-alkoxypyrroles. The procedure proved to be readily adaptable to a larger scale, and the nature of the product was insensitive both to the alkyl toluene-*p*-sulphonate and the substituent pattern of the 3-hydroxypyrrole. Thus alkylation of the *N*-phenyl compound **8** with methyl, ethyl,[13] or even benzyl[13] toluene-*p*-sulphonate allowed isolation of the alkoxy compounds **14** (80%),[2] **15** (65%) and **16** (75%), respectively, with the complete absence of any *C*-alkylated products. The *N*-alkylmethoxypyrrole **17** was also obtained in 80% yield after purification. 1-Aryl-2-alkyl-, 1-alkyl-2-aryl-, and 1,2-dialkylmethoxypyrroles **19** (65%), **20** (90%) and **21** (72%) were isolated with equal facility. No *C*-alkylation was observed in any of these reactions, and we believe that these conditions (described in detail in the Experimental section) represent the best available route to 3-alkoxypyrroles from the 3-hydroxypyrrole–1*H*-pyrrol-3(2*H*)-one system. Taken together with the pyrolysis route to the pyrrolones,[5] this gives a concise 3-step route to simple 1-substituted or 1,2-disubstituted-3-alkoxypyrroles from secondary amines.

Only allyl toluene-*p*-sulphonate gave rise to a small amount (*ca.* 10%) of *C*-alkylation of the *N*-phenyl compound **8**, and this was exacerbated by Claisen rearrangement to a *C*-allyl product on distillation (*cf.* ref. 4).

In general, the *C*,*C*-dialkylated products **5** were found to be readily separable from the alkoxypyrroles **3** and **4** by chromatography on alumina, and so the use of a soft alkylating agent (*e.g.* iodomethane) in either THF or DMSO proved to be acceptable preparatively even when mixtures were obtained. Examples include the formation of the sterically hindered pyrrolone **23** (28%) and the 1-phenyl-2,2-dimethyl compound **24**[5] (from **8** or **10**). The 1-benzyl-2-methyl-2-phenyl derivative **25** (14%) and the 1,2-dimethyl-2-phenyl compound **26** (32%) were both formed unambiguously by this route (from **9** and **12**, respectively): inseparable isomeric mixtures would be expected to result from attempted direct pyrolytic synthesis of the former.[5] From the 2-substituted precursors **9**–**12**, pure samples of the methoxypyrroles **27**, **19**, **28** and **20**, respectively, were also obtained in 30–55% yield, but the toluene-*p*-sulphonate/DMI route to these is clearly preferable if substantial quantities are required.

The 3-alkoxypyrroles were normally oils or low-melting-point solids, (see below, however) which could be stored at −20 °C indefinitely without decomposition, although some discolouration was observed. Although in one case a facile autoxidation took place,[14] this was atypical and 3-alkoxypyrroles can normally be handled at the bench without special precaution. The mass spectra of the 3-alkoxypyrroles (see Experimental section) generally show cleavage of the oxygen substituent as the initial breakdown, though the 1-*tert*-butyl compound **17** first loses isobutene before undergoing the same cleavage as the other derivatives. The NMR spectra of 3-alkoxypyrroles are discussed in Part 11[9] and studies of the chemical reactivity of these systems will be reported in later Parts of this series (*cf.* ref. 6).

There are no structural data in the literature for pyrroles containing only electron donating groups: the few examples available (*e.g.* **29**[15] and **30**[16]) show multiple substitution with bulky and/or electron withdrawing groups. Simple 3-hydroxypyrroles **1** adopt the 1*H*-pyrrol-3(2*H*)-one tautomer in the solid state,[17] but the 3-methoxypyrrole **22**, is a crystalline solid suitable for X-ray structure determination. The results serve as a model for the effect of electron donating substituents in general, and 3-(oxygen-containing) functionality in particular, on the geometry of the pyrrole ring system. Although a 2-aryl

Table 6 Angles (°) with standard deviations

C(2)–N(1)–C(5)	108.0(3)	C(2′)–N(1′)–C(5′)	107.7(3)
C(2)–N(1)–C(1N)	127.4(3)	C(2′)–N(1′)–C(1N′)	127.7(3)
C(5)–N(1)–C(1N)	124.5(3)	C(5′)–N(1′)–C(1N′)	124.4(3)
N(1)–C(2)–C(3)	106.7(3)	N(1′)–C(2′)–C(3′)–	106.4(3)
N(1)–C(2)–C(1P)	129.0(3)	N(1′)–C(2′)–C(1P′)	128.7(3)
C(3)–C(2)–C(1P)	124.3(3)	C(3′)–C(2′)–C(1P′)	125.0(3)
C(2)–C(3)–C(4)	110.0(3)	C(2′)–C(3′)–C(4′)	110.0(3)
C(2)–C(3)–O(3)	121.5(3)	C(2′)–C(3′)–O(3′)	120.9(3)
C(4)–C(3)–O(3)	128.5(3)	C(4′)–C(3′)–O(3′)	129.1(3)
C(3)–C(4)–C(5)	106.0(3)	C(3′)–C(4′)–C(5′)	105.4(3)
N(1)–C(5)–C(4)	109.4(3)	N(1′)–C(5′)–C(4′)	110.5(3)
N(1)–C(1N)–C(11)	110.0(3)	N(1′)–C(1N′)–C(11′)	109.4(3)
N(1)–C(1N)–C(12)	110.3(3)	N(1′)–C(1N′)–C(12′)	108.7(3)
N(1)–C(1N)–C(13)	109.2(3)	N(1′)–C(1N′)–C(13′)	111.1(3)
C(11)–C(1N)–C(12)	108.0(3)	C(11′)–C(1N′)–C(12′)	109.4(3)
C(11)–C(1N)–C(13)	109.1(3)	C(11′)–C(1N′)–C(13′)	107.1(3)
C(12)–C(1N)–C(13)	110.2(3)	C(12′)–C(1N′)–C(13′)	111.1(3)
C(2)–C(1P)–C(2P)	119.85(22)	C(2′)–C(1P′)–C(2P′)	120.39(22)
C(2)–C(1P)–C(6P)	119.90(22)	C(2′)–C(1P′)–C(6P′)	119.41(22)
C(3)–O(3)–C(31)	114.5(3)	C(3′)–O(3′)–C(31′)	115.4(3)

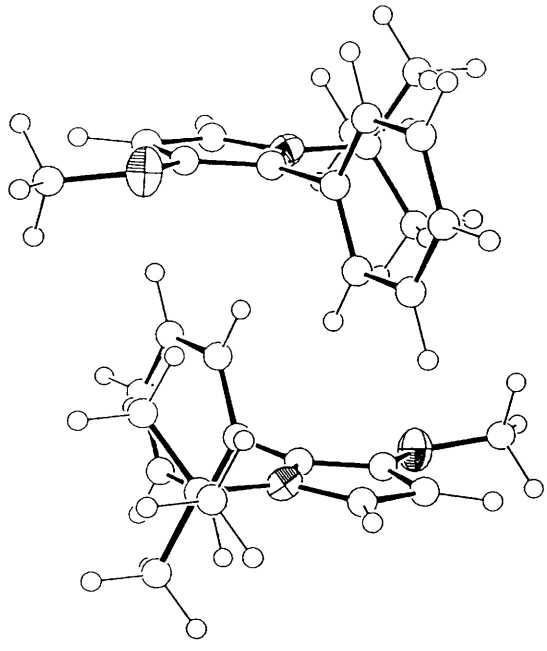

Fig. 2 ORTEP plot showing relative orientation of the two independent molecules of **22**

compound was not our first choice as a 'typical' derivative, we reasoned that the bulky 1-*tert*-butyl group would probably cause the two rings to be orthogonal, and so its conjugative effect on the geometry was likely to be small. The structural parameters of **22** are listed in Tables 5–8 and Fig. 1 is an ORTEP plot showing the crystallographic numbering system. There are two independent molecules in the asymmetric unit and their relative orientation is shown in Fig. 2. Significant differences between the two molecules include a number of the torsion angles associated with the substituents (Table 7) and (marginally) some of the bond angles around the *tert*-butyl group (Table 6): the lengths of the C(4)–C(5) bonds are surprisingly different [0.023(7) Å] in the two molecules (Table 5). In all cases in subsequent discussion, the average value of a given parameter is quoted.

The 5-membered ring of **22** is essentially planar (mean deviation 0.003 Å). The nitrogen atom adopts an approximately trigonal planar configuration [sum of angles around N(1) 359.9°] though the central atom of the *tert*-butyl group [C(1N) and C(1N′)] is displaced by *ca.* 0.064 Å from the ring plane. The two rings are indeed orthogonal with the average angle between the best planes of the two rings being 87.9°. Lack of conjugation between the two rings is confirmed by the C(2)–C(1P) bond length [1.515(4) Å] which is significantly longer than the average inter-ring bond distance in biaryls [1.487(7) Å].[18] The methoxy group lies *s*-*Z* to the 3,4-bond of the pyrrole and is twisted by *ca.* 15° from the plane of the ring. The length of the C(3)–O(3) bond [1.383(4) Å] is close to that of the corresponding parameter in aryl alkyl ethers[18] [1.370(11) Å]. This relatively short value [C–O bonds in dialkyl ethers[18] average 1.416(16) Å] together with the nearly planar configuration of the pyrrole ring and the alkoxy group suggests that electron density from the oxygen atom is indeed being delocalised into the ring, despite the electron rich character of the latter.

There are some indications that electron withdrawing substituents can cause distortion of the symmetry of the pyrrole ring.[19] In the case of the electron rich pyrrole **22**, the major asymmetry lies in the C–N bonds; although the length of the C(5)–N(1) bond has a typical value,[18] the N(1)–C(2) bond is significantly lengthened. It seems likely that this is due to the steric repulsion between the adjacent phenyl and *tert*-butyl groups rather than any electronic effect. Certainly, the exocyclic bond angles [C(2)–N(1)–C(1N), C(5)–N(1)–C(1N), N(1)–C(2)–C(1P) and C(3)–C(2)–C(1P)] in both molecules show significant distortions consistent with such steric effects. The C–C bond lengths of the five-membered ring of **22** are close to average values reported for the pyrrole ring system.[18] Hence it appears that an electron donating substituent in the 3-position has little effect on any of the bond lengths of the pyrrole ring.

Experimental

^{1}H and ^{13}C NMR spectra were recorded at 80 or 200, and 20 or 50 MHz, respectively, for solutions in [^{2}H]chloroform. *J*-Values are given in Hz.

5-(N-*Benzyl*-N-tert-*butyl*)*aminomethylene*-2,2-*dimethyl*-1,3-*dioxane*-4,6-*dione*.—Prepared by the standard method[5] from 5-methoxymethylene Meldrum's acid and *N*-*tert*-butylbenzylamine in acetonitrile, the 5-(N-*benzyl*-N-tert-*butyl*) *derivative* (99%) had m.p. 180–182 °C (from ethanol) (Found: C, 67.9; H, 7.3; N, 4.4. $C_{18}H_{23}NO_4$ requires C, 68.1; H, 7.25; N, 4.4%); δ_H 8.43 (1 H, s), 7.23–6.99 (5 H, m), 5.20 (2 H, s), 1.53 (9 H, s) and 1.04 (6 H, s); δ_C(2 carbonyls not observed), 154.46, 134.47 (q), 128.58, 127.32, 126.81, 102.39 (q), 86.70 (q), 63.96 (q), 51.44, 28.81 and 25.49; *m*/*z* 317 (M^+, <1%), 259 (100), 203 (79), 202 (46), 175 (30), 174 (35), 159 (20), 158 (78) and 91 (75).

1-tert-*Butyl*-2-*phenyl*-1H-*pyrrol*-3(2H)-*one*.—Flash vacuum pyrolysis[5] of the above Meldrum's acid derivative at 600 °C [inlet temperature 185 °C, pressure 2 × 10^{-4} Torr (mercury diffusion pump), pyrolysis time *ca.* 3 h g^{-1}] gave the 1-tert-*butyl*-2-*phenyl compound* (78%) which was purified by bulb-to-bulb distillation, b.p. 184–186 °C (0.5 Torr) (Found: C, 78.0; H, 8.1; N, 6.45. $C_{14}H_{17}NO$ requires C, 78.1; H, 7.9; N, 6.5%); δ_H 8.19 (1 H, dd, ^3J 3.5 and ^4J 0.4), 7.31–7.17 (5 H, m), 5.11 (1 H, d, ^3J 3.5), 4.52 (1 H, br s) and 1.20 (9 H, s); δ_C 200.90 (q), 165.03, 136.74 (q), 128.53, 127.49, 126.59, 97.81, 68.91, 56.35 (q) and 29.06; *m*/*z* 215 (M^+, 37%), 159 (67), 158 (100), 131 (12), 130 (28), 105 (15), 104 (29), 103 (18), 86 (27), 84 (41) and 77 (34).

Comparative Alkylations.—Sodium hydride (50% dispersion in oil; 45 mg, *ca.* 1 mmol) was washed three times with hexane and was then dried at a vacuum pump. The pyrrolone[5] (0.33 mmol) was dissolved in solvent (4 cm^3) and the prewashed

Table 7 Torsion angles (°) with standard deviations

C(5)-N(1)-C(2)-C(3)	0.4(4)	C(5')-N(1')-C(2')-C(3')	−0.7(4)
C(5)-N(1)-C(2)-C(1P)	179.2(3)	C(5')-N(1')-C(2')-C(1P')	−180.0(3)
C(1N)-N(1)-C(2)-C(3)	177.0(3)	C(1N')-N(1')-C(2')-C(3')	−176.4(3)
C(1N)-N(1)-C(2)-C(1P)	−4.2(6)	C(1N')-N(1')-C(2')-C(1P')	4.3(6)
C(2)-N(1)-C(5)-C(4)	−0.8(4)	C(2')-N(1')-C(5')-C(4')	0.5(4)
C(1N)-N(1)-C(5)-C(4)	−177.5(3)	C(1N')-N(1')-C(5')-C(4')	176.4(3)
C(2)-N(1)-C(1N)-C(11)	178.4(3)	C(2')-N(1')-C(1N')-C(11')	−168.5(3)
C(2)-N(1)-C(1N)-C(12)	59.3(5)	C(2')-N(1')-C(1N')-C(12')	72.1(4)
C(2)-N(1)-C(1N)-C(13)	−62.0(4)	C(2')-N(1')-C(1N')-C(13')	−50.5(5)
C(5)-N(1)-C(1N)-C(11)	−5.5(5)	C(5')-N(1')-C(1N')-C(11')	16.3(5)
C(5)-N(1)-C(1N)-C(12)	−124.6(4)	C(5')-N(1')-C(1N')-C(12')	−103.1(4)
C(5)-N(1)-C(1N)-C(13)	114.1(4)	C(5')-N(1')-C(1N')-C(13')	134.4(4)
N(1)-C(2)-C(3)-C(4)	0.1(4)	N(1')-C(2')-C(3')-C(4')	0.6(4)
N(1)-C(2)-C(3)-O(3)	−179.3(3)	N(1')-C(2')-C(3')-O(3')	179.2(3)
C(1P)-C(2)-C(3)-C(4)	−178.7(3)	C(1P')-C(2')-C(3')-C(4')	180.0(3)
C(1P)-C(2)-C(3)-O(3)	1.8(5)	C(1P')-C(2')-C(3')-O(3')	−1.5(5)
N(1)-C(2)-C(1P)-C(2P)	−90.4(4)	N(1')-C(2')-C(1P')-C(2P')	−95.7(4)
N(1)-C(2)-C(1P)-C(6P)	96.5(4)	N(1')-C(2')-C(1P')-C(6P')	90.2(4)
C(3)-C(2)-C(1P)-C(2P)	88.2(4)	C(3')-C(2')-C(1P')-C(2P')	85.2(4)
C(3)-C(2)-C(1P)-C(6P)	−84.9(4)	C(3')-C(2')-C(1P')-C(6P')	−89.0(4)
C(2)-C(3)-C(4)-C(5)	−0.6(4)	C(2')-C(3')-C(4')-C(5')	−0.4(4)
O(3)-C(3)-C(4)-C(5)	178.8(3)	O(3')-C(3')-C(4')-C(5')	−178.8(3)
C(2)-C(3)-O(3)-C(31)	−168.9(3)	C(2')-C(3')-O(3')-C(31')	163.9(3)
C(4)-C(3)-O(3)-C(31)	11.8(5)	C(4')-C(3')-O(3')-C(31')	−17.8(5)
C(3)-C(4)-C(5)-N(1)	0.8(4)	C(3')-C(4')-C(5')-N(1')	−0.1(4)
C(2)-C(1P)-C(2P)-C(3P)	−173.10(23)	C(2')-C(1P')-C(2P')-C(3P')	−174.07(24)
C(2)-C(1P)-C(6P)-C(5P)	173.10(24)	C(2')-C(1P')-C(6P')-C(5P')	174.13(24)

Table 8 Atomic coordinates with esds

Atom	*x*	*y*	*z*
N(1)	−0.175 2(4)	1.143 93(17)	0.628 97(15)
C(2)	−0.133 0(4)	1.113 44(20)	0.560 96(18)
C(3)	0.006 9(4)	1.150 53(22)	0.541 38(18)
C(4)	0.054 5(5)	1.203 70(21)	0.595 34(20)
C(5)	−0.061 5(5)	1.198 85(21)	0.648 73(20)
C(1N)	−0.321 2(5)	1.125 19(23)	0.671 69(19)
C(11)	−0.316 9(6)	1.169 6(3)	0.743 37(21)
C(12)	−0.329 3(5)	1.036 39(25)	0.687 68(25)
C(13)	−0.468 9(5)	1.151 3(3)	0.629 47(22)
C(1P)	−0.217 3(3)	1.050 82(11)	0.515 93(12)
C(2P)	−0.177 3(3)	0.971 44(11)	0.523 67(12)
C(3P)	−0.241 8(3)	0.915 25(11)	0.477 25(12)
C(4P)	−0.346 3(3)	0.938 46(11)	0.423 09(12)
C(5P)	−0.386 4(3)	1.017 81(11)	0.415 36(12)
C(6P)	−0.321 9(3)	1.073 99(11)	0.461 77(12)
O(3)	0.080 8(3)	1.134 45(16)	0.476 24(14)
C(31)	0.238 6(5)	1.166 13(25)	0.469 70(22)
N(1')	0.128 1(4)	0.854 29(17)	0.619 94(15)
C(2')	0.086 5(4)	0.884 69(20)	0.687 59(18)
C(3')	−0.051 8(4)	0.846 58(21)	0.707 52(18)
C(4')	−0.097 5(5)	0.792 02(22)	0.654 02(19)
C(5')	0.015 9(4)	0.798 53(21)	0.601 34(20)
C(1N')	0.273 9(4)	0.873 02(23)	0.576 36(19)
C(11')	0.253 6(6)	0.839 99(25)	0.500 64(20)
C(12')	0.417 5(5)	0.834 1(3)	0.611 79(23)
C(13')	0.297 5(6)	0.963 10(25)	0.569 2(3)
C(1P')	0.170 9(3)	0.947 33(12)	0.731 67(12)
C(2P')	0.278 5(3)	0.925 35(12)	0.785 02(12)
C(3P')	0.344 8(3)	0.982 53(12)	0.829 85(12)
C(4P')	0.303 6(3)	1.061 63(12)	0.821 33(12)
C(5P')	0.196 1(3)	1.083 59(12)	0.767 98(12)
C(6P')	0.129 7(3)	1.026 43(12)	0.723 14(12)
O(3')	−0.124 2(3)	0.862 76(16)	0.773 20(13)
C(31')	−0.284 9(4)	0.836 8(3)	0.779 80(22)

sodium hydride was added in portions while the solution was stirred at room temperature. The alkylating agent was added (3 mmol, except for methyl toluene-*p*-sulphonate, 0.33 mmol) and the reaction mixture was stirred for a further 20 min, except for methyl toluene-*p*-sulphonate which was heated to reflux for 16 h. The mixture was then added to methanol (3 cm^3) and water (10 cm^3) was added. The aqueous solution was extracted with methylene dichloride (3 × 10 cm^3). [The combined organic layers were back extracted with water (3 × 15 cm^3) for reactions in dimethyl sulphoxide.] The organic layer was then dried ($MgSO_4$) and the solvent was removed *in vacuo*. The total residue was then dissolved in [^{2}H]chloroform and the ^{1}H NMR spectrum was obtained. 1,2,2-Trisubstituted 1*H*-pyrrol-3(2*H*)-ones were readily identified by their characteristic pair of doublets at *ca.* δ_H 5.0 and 8.0 due to the 4-H and 5-H, respectively.[10] The corresponding protons appeared as doublets in the range δ_H 5.5–7.0 in the spectra of 1,2-disubstituted 3-alkoxypyrroles, whereas 2-H, 4-H and 5-H of 1-monosubstituted 3-alkoxypyrroles resonate as double doublets in the same chemical shift range.[9] The following 3-alkoxypyrroles, not fully characterised below, were observed and so identified: 1-*tert*-butyl-3-methoxy-2-methyl, δ_H 6.56 (1 H, d) and 5.81 (1 H, d); 3-ethoxy-2-ethyl-1-phenyl, δ_H 6.52 (1 H, d) and 6.04 (1 H, d); 3-isopropoxy-2-isopropyl-1-phenyl, δ_H 6.45 (1 H, d) and 6.02 (1 H, d). Results are shown in Tables 1–4.

Preparative Alkylations.—Method A. Sodium hydride (50% dispersion in oil; 190 mg, *ca.* 4 mmol) was washed three times with light petroleum and then dried at 0.1 Torr. The required pyrrolone[5] (1 mmol) was dissolved in tetrahydrofuran (10 cm^3) and the prewashed sodium hydride was added while the solution was stirred at room temperature. The solution became deep red, and stirring was continued for 10 min before the appropriate alkylating agent (5–10 mmol) was added, and the reaction mixture was stirred for a further 30 min. The colour was discharged during this period. The mixture was then poured into methanol (10 cm^3), and water (20 cm^3) was added. The aqueous solution was extracted with methylene dichloride (3 × 25 cm^3), the combined organic layers were dried ($MgSO_4$) and the solvent was removed *in vacuo*. In some cases this gave a mixture of 3-alkoxypyrrole and 2,2-disubstituted pyrrolone which was separated by column chromatography on alumina using ethyl acetate–hexane (50:50) as eluent. 2-Unsubstituted

examples gave a small amount of *C*-alkylated 3-alkoxypyrroles which were inseparable from the 3-alkoxypyrroles. All products were purified by bulb-to-bulb distillation.

Method B. The same procedure as described for Method A was carried out using dimethyl sulphoxide as solvent except that the combined organic extracts were back extracted with water (3 × 50 cm^3) before they were dried, in order to remove the dimethyl sulphoxide.

Method C. The anion was prepared again in the manner of Method A but methyl toluene-*p*-sulphonate (1 mmol) was added as the alkylating agent. The reaction mixture was heated to reflux for 16 h and then cooled and the work-up described in Method A was followed.

Method D. Preparation of 3-Alkoxypyrroles. A solution of the appropriate pyrrolone[5] (1 mmol) in dimethylimidazolidinone (DMI) (3 cm^3) was added under a stream of nitrogen to a stirred suspension of sodium hydride (50%; 144 mg, *ca.* 3 mmol) (prepared as in Method A) in DMI (10 cm^3). A solution of the required alkyl toluene-*p*-sulphonate (1 mmol) in DMI (2 cm^3) was then added dropwise and the stirring was continued at room temperature for 1 h. The reaction mixture was then quenched with ethanol–water (20 cm^3) (1:1) and extracted with ether (3 × 25 cm^3). The combined organic phases were then back-washed with water (3 × 50 cm^3), dried ($MgSO_4$), and the solvent was evaporated under reduced pressure.

Method E. A solution of the pyrrolone (1 mmol) in methylene dichloride (5 cm^3) was treated with a solution of triethyloxonium tetrafluoroborate in methylene dichloride (0.83 mol dm^{-3}, 1.5 cm^3). After the reaction was complete, the mixture was extracted with dilute aqueous sodium hydroxide (1 mol dm^{-3}; 10 cm^3), and the organic layer was dried ($MgSO_4$) and concentrated.

The following pyrrolones were alkylated under these conditions. The method and alkylating agent are given in each case.

1-*Phenyl*-1H-*pyrrol*-3(2H)-*one* (*a*), Method A, iodomethane to give only 2,2-dimethyl-1-phenyl-1*H*-pyrrol-3(2*H*)-one whose ^1H NMR spectrum was identical with that of an authentic sample.[5]

(*b*) Method D, methyl toluene-*p*-sulphonate to give 3-methoxy-1-phenylpyrrole[2] (80%), m.p. 27–29 °C (lit.,[2] 33–34 °C) (Found: C, 76.0; H, 6.45; N, 8.1. Calc. for $C_{11}H_{11}NO$: C, 76.3; H, 6.35; N, 8.1%); δ_H 7.45–7.20 (5 H, m), 6.95 (1 H, dd, ^3J 3.1 and ^4J 2.4), 6.67 (1 H, dd, ^4J 2.0 and 2.4), 6.05 (1 H, dd, ^3J 3.1 and ^4J 2.0) and 3.77 (3 H, s); δ_C 150.75 (q), 140.77 (q), 129.35, 124.82, 119.36, 116.98, 100.78, 100.27 and 57.69; *m/z* 173 (M^+, 100%), 159 (13), 158 (92), 111 (20), 104 (41), 97 (32), 85 (25) and 83 (24).

(*c*) Method D, ethyl toluene-*p*-sulphonate[13] to give 3-*ethoxy*-1-*phenylpyrrole* (65%), b.p. 145–147 °C (0.3 Torr) (Found: C, 77.3; H, 7.2; N, 7.35. $C_{12}H_{13}NO$ requires C, 77.0; H, 6.95; N, 7.5%); δ_H 7.38–7.16 (5 H, m), 6.88 (1 H, dd, ^3J 3.1 and ^4J 2.5), 6.65 (1 H, dd, ^4J 1.9 and 2.5), 6.03 (1 H, dd, ^3J 3.1 and ^4J 1.9), 3.95 (2 H, q, ^3J 7.0) and 1.38 (3 H, t, ^3J 7.0); δ_C 149.50 (q), 140.78 (q), 129.34, 124.77, 119.36, 116.83, 101.42, 100.65, 65.99 and 14.83; *m/z* 187 (M^+, 100%), 159 (46), 158 (93), 104 (33) and 77 (46).

(*d*) Method D, benzyl toluene-*p*-sulphonate[13] to give 3-*benzyloxy*-1-*phenylpyrrole* (75%), m.p. 76–78 °C (from hexane) (Found: C, 81.9; H, 6.0; N, 5.6. $C_{17}H_{15}NO$ requires C, 81.9; H, 6.0; N, 5.6%); δ_H 7.47–7.14 (10 H, m), 6.89 (1 H, dd, ^3J 3.1 and ^4J 2.4), 6.70 (1 H, dd, ^4J 2.4 and 2.1), 6.10 (1 H, dd, ^3J 3.1 and ^4J 2.1) and 4.97 (2 H, s); δ_C 149.57 (q), 140.80 (q), 137.47 (q), 129.38, 128.36, 127.73, 127.48, 124.91, 119.51, 116.90, 102.09, 100.94 and 72.74; *m/z* 249 (M^+, 40%), 158 (100) and 77 (35).

(*e*) Method B, 2-bromopropane to give 3-isopropyloxy-1-phenylpyrrole (68%), (contaminated with a small amount of *O*,*C*-dialkylated product), b.p. 149 °C (0.4 Torr) (Found: C, 75.9; H, 7.55; N, 6.7. Calc. for $C_{13}H_{15}NO$: C, 77.6; H, 7.5; N, 6.95%); δ_H 7.0–7.5 (5 H, m), 6.88 (1 H, dd, ^3J 3.1 and ^4J 2.6), 6.67 (1 H, dd, ^4J 2.6 and 2.0), 6.05 (1 H, dd, ^3J 3.1 and ^4J 2.0), 4.26 (1 H, m) and 1.35 (6 H, d); δ_C 147.79 (q), 140.66 (q), 129.32, 124.74, 119.31, 116.62, 102.98, 101.57, 72.69 and 21.95; *m/z* 201 (M^+, 86%), 186 (21), 160 (27), 159 (100), 158 (41), 130 (35) and 104 (72).

1-tert-*Butyl*-1H-*pyrrol*-3(2H)-*one*. (*a*) Method B, iodomethane to give 1-tert-*butyl*-2,2-*dimethyl*-1H-*pyrrol*-3(2H)-*one* (28%, after chromatography), m.p. 114–115 °C (from hexane) (Found: C, 72.1; H, 10.2; N, 8.1. $C_{10}H_{17}NO$ requires C, 71.85; H, 10.2; N, 8.4%); δ_H 7.99 (1 H, d, ^3J 3.5), 5.03 (1 H, d, ^3J 3.5), 1.40 (9 H, s) and 1.34 (6 H, s); δ_C 204.68(q), 161.05, 94.34, 69.56 (q), 57.05 (q), 30.77 and 24.52; *m/z* 167 (M^+, 24%), 152 (10), 111 (26), 110 (100), 83 (20), 82 (27), 68 (12) and 57 (31); together with some 1-*tert*-butyl-3-methoxypyrrole (see below) and 1-*tert*-butyl-3-methoxy-2-methylpyrrole, identified by ^1H NMR spectroscopy (see above) and GC–MS.

(*b*) Method D, methyl toluene-*p*-sulphonate to give 1-tert-*butyl*-3-*methoxypyrrole* (80%) b.p. 150–152 °C (0.4 Torr) (Found: C, 69.7; H, 10.0; N, 9.1 $C_9H_{15}NO{\cdot}0.1H_2O$ requires C, 69.8; H, 9.85; N, 9.05%) (analysed consistently as partial hydrate); δ_H 6.58 (1 H, dd, ^3J 3.0 and ^4J 2.7), 6.38 (1 H, dd, ^4J 2.1 and 2.7), 5.82 (1 H, dd, ^3J 3.0 and ^4J 2.1), 3.71 (3 H, s) and 1.48 (9 H, s); δ_C 148.39 (q), 114.99, 99.77, 95.83, 57.61, 54.45 (q) and 30.25; *m/z* 153 (M^+, 42%), 97 (100) and 70 (10).

(*c*) Method E, to give a 68% yield of mixture, b.p. 83 °C (0.3 Torr), consisting of 85% of 1-*tert*-butyl-3-ethoxypyrrole, δ_H 6.54 (1 H, dd, ^3J 3.0 and ^4J 2.6), 6.36 (1 H, dd, ^4J 2.0 and 2.6), 5.78 (1 H, dd, ^3J 3.0 and ^4J 2.0), 3.87 (2 H, q), 1.45 (9 H, s) and 1.33 (3 H, t); δ_C 147.29 (q), 114.79, 100.53, 96.45, 65.78, 54.30 (q), 30.22 and 14.90: together with 15% of 1-*tert*-butyl-3-ethoxy-3-ethylpyrrole tentatively identified by characteristic ^1H NMR resonances, δ_H 6.45 (1 H, d) and 5.67 (1 H, d).

2-*Methyl*-1-*phenyl*-1H-*pyrrol*-3(2H)-*one*. (*a*), Method A, iodomethane to give 2,2-dimethyl-1-phenyl-1*H*-pyrrol-3(2*H*)-one (85%), whose GLC retention time and NMR spectra were identical with those of an authentic sample.[5]

(*b*) Method D, methyl toluene-*p*-sulphonate to give 3-*methoxy*-2-*methyl*-1-*phenylpyrrole* (65%), b.p. 116–118 °C (0.4 Torr) (Found: C, 76.8; H, 7.05; N, 7.35. $C_{12}H_{13}NO$ requires C, 77.0; H, 6.95; N, 7.5%); δ_H 7.50–7.25 (5 H, m), 6.60 (1 H, d, ^3J 3.2), 6.07 (1 H, d, ^3J 3.2), 3.80 (3 H, s) and 2.14 (3 H, s); δ_C 145.43 (q), 140.48 (q), 128.82, 126.26, 125.05, 116.84, 113.02 (q), 97.24, 58.77 and 8.95; *m/z* 187 (M^+, 77%), 172 (100), 104 (9) and 77 (33): the same product was obtained in 34% yield using Method C.

1,2-*Diphenyl*-1H-*pyrrol*-3(2H)-*one*. Method B, iodomethane to give a mixture of 2-*methyl*-1,2-*diphenyl*-1H-*pyrrol*-3(2H)-*one* (48% after chromatography), m.p. 104–106 °C (from cyclohexane) (Found: C, 79.4; H, 6.25; N, 5.3. $C_{17}H_{15}NO{\cdot}0.5\ H^2O$ requires C, 79.05; H, 6.2; N, 5.45%); δ_H 8.57 (1 H, d, ^3J 3.7), 6.8–7.5 (10 H, m), 5.44 (1 H, d, ^3J 3.7) and 1.75 (3 H, s); δ_C (C-2 quaternary not observed—possibly superimposed on solvent peaks) 203.50 (q), 159.16, 133.73 (q), 129.33, 128.89, 128.06 (q), 127.66, 125.23, 123.95, 118.33, 99.36 and 20.32; *m/z* 249 (M^+, 46%), 220 (38), 206 (17), 180 (29), 105 (42) and 77 (100); and 3-*methoxy*-1,2-*diphenylpyrrole* (43%, after chromatography), m.p. 68–69 °C (from toluene) (Found: C, 81.9; H, 6.2; N, 5.3. $C_{17}H_{15}NO$ requires C, 81.95; H, 6.0; N, 5.6%); δ_H 6.8–7.5 (10 H, m), 6.73 (1 H, d, ^3J 3.2), 6.19 (1 H, d, ^3J 3.2) and 3.82 (3 H, s); δ_C 146.93 (q), 140.54 (q), 129.34 (q), 128.73 (two peaks superimposed), 127.61, 125.96, 125.28, 124.94, 120.43, 116.91 (q), 97.29 and 58.18; *m/z* 249 (M^+, 100%), 234 (71) and 77 (95).

1-*Methyl*-2-*phenyl*-1H-*pyrrol*-3(2H)-*one*. (*a*) Method B, iodomethane to give a mixture of 1,2-*dimethyl*-2-*phenyl*-1H-pyrrol-3(2H)-*one* (32%, after chromatography), m.p. 81–82 °C

(from toluene) (Found: C, 74.95; H, 7.0; N, 7.15. $C_{12}H_{13}NO$·0.5-H_2O requires C, 74.6; H, 7.1; N, 7.25%); δ_H 7.87 (1 H, d, ^3J 3.3), 7.1–7.5 (5 H, m), 5.05 (1 H, d, ^3J 3.3), 2.94 (3 H, s) and 1.64 (3 H, s); δ_C 203.67 (q), 164.80, 139.49 (q), 128.64, 127.57, 125.60, 94.47, 67.45 (q), 32.58 and 19.34; *m/z* 187 (M^+, 100%), 158 (91) and 118 (50), together with 3-methoxy-1-methyl-2-phenylpyrrole (see below) in 38% yield after chromatography.

(*b*) Method D, methyl toluene-*p*-sulphonate to give 3-*methoxy*-1-*methyl*-2-*phenylpyrrole* (90%), b.p. 113–115 °C (0.1 Torr) (Found: C, 77.1; H, 7.15; N, 7.45. $C_{12}H_{13}NO$ requires C, 77.0; H, 6.95; N, 7.5%); δ_H 7.45–7.27 (5 H, m), 6.51 (1 H, d, ^3J 3.1), 6.01 (1 H, d, ^3J 3.1), 3.77 (3 H, s) and 3.60 (3 H, s); δ_C 145.09 (q), 130.95 (q), 128.76, 127.81, 125.68, 119.29, 117.73 (q), 94.89, 57.95 and 34.91; *m/z* 187 (M^+, 70%), 172 (100), 144 (30), 131 (20), 118 (25) and 103 (25).

1-*Benzyl*-2-*phenyl*-1H-*pyrrol*-3(2H)-*one*. Method B, iodomethane to give a mixture of 1-*benzyl*-2-*methyl*-2-*phenyl*-1H-*pyrrol*-3(2H)-*one* (14%, after chromatography), m.p. 66.5–68 °C (from toluene) (Found: C, 82.1; H, 6.55; N, 5.4. $C_{18}H_{17}NO$ requires C, 82.15; H, 6.45; N, 5.3%); δ_H 7.78 (1 H, d, ^3J 3.4), 7.0–7.4 (10 H, m), 5.03 (1 H, d, ^3J 3.4), 4.32 (1 H, d, ^2J 14.2), 4.19 (1 H, d, ^2J 14.2) and 1.59 (3 H, s); δ_C 203.53 (q), 163.56, 136.48 (q), 134.87 (q), 128.45, 128.41, 128.32, 127.81, 127.49, 125.66, 94.80, 71.96 (q), 49.59 and 19.57; *m/z* 263 (M^+, 20%), 211 (10), 134 (14), 127 (31), 99 (60) and 91 (100), together with 1-*benzyl*-3-*methoxy*-2-*phenylpyrrole* (54%, after chromatography), m.p. 33–34 °C (from toluene) (Found: C, 81.6; H, 6.55; N, 5.3. $C_{18}H_{17}NO$ requires C, 82.15; H, 6.45; N, 5.3%); δ_H 7.2–7.75 (10 H, m), 6.78 (1 H, d, ^3J 3.1), 6.38 (1 H, d, ^3J 3.1), 5.25 (2 H, s) and 3.99 (3 H, s); δ_C 145.22 (q), 138.30 (q), 130.94 (q), 129.01, 128.03, 127.74, 126.74, 126.06, 125.85, 118.84, 118.03 (q), 96.05, 57.85 and 50.49; *m/z* 263 (M^+, 22%), 211 (11), 137 (30), 99 (66) and 91 (100).

1-*Ethyl*-2-*methyl*-1H-*pyrrol*-3(2H)-*one*. Method D, methyl toluene-*p*-sulphonate, to give 1-*ethyl*-3-*methoxy*-2-*methylpyrrole* (72%), b.p. 150–152 °C (1 Torr) (Found: C, 69.0; H, 9.6; N, 10.2. $C_8H_{13}NO$ requires C, 69.1; H, 9.35; N, 10.1%); δ_H 6.35 (1 H, d, ^3J 3.2), 5.85 (1 H, d, ^3J 3.2), 3.75 (2 H, q, ^3J 7.2), 3.72 (3 H, s), 2.12 (3 H, s) and 1.31 (3 H, t, ^3J 7.2); δ_C 144.05 (q), 114.35, 112.10 (q), 95.20, 58.80, 41.40, 16.00 and 7.55; *m/z* 139 (M^+, 42%), 124 (100), 110 (60) and 97 (30).

1-tert-*Butyl*-2-*phenyl*-1H-*pyrrol*-3(2H)-*one*. Method D, methyl toluene-*p*-sulphonate, to give 1-tert-*butyl*-3-*methoxy*-2-*phenylpyrrole* (75%), m.p. 81–82 °C (from isopropyl alcohol) (Found: C, 77.9; H, 8.55; N, 6.0. $C_{15}H_{19}NO$·0.125 H_2O requires C, 77.8; H, 8.3; N, 6.05%); δ_H 7.41–7.38 (5 H, m), 6.73 (1 H, d, ^3J 3.3), 5.98 (1 H, d, ^3J 3.3), 3.67 (3 H, s) and 1.43 (9 H, s); δ_C 146.52 (q), 134.71 (q), 132.75, 127.47, 127.32, 118.65 (q), 114.75, 94.28, 58.60, 56.95 (q) and 31.36; *m/z* 229 (M^+, 50%), 173 (90), 158 (100), 130 (15) and 103 (20).

Crystal Data.—$C_{15}H_{19}NO$, M = 229.32. Orthorhombic, space group $P2_12_12_1$, a = 8.3523(9), b = 16.7518(21), c = 18.543(3) Å, V = 2594.5 Å^3 [from 2θ values of 14 reflections measured at $\pm\omega$ (2θ = 24–26°, $\bar{\lambda}$ = 0.710 73 Å)], Z = 8, D_{calc} = 1.174 g cm^{-3}, T = 173 ± 0.1 K, colourless columnar crystal, 0.65 × 0.17 × 0.14 mm, μ = 0.07 mm^{-1}, $F(000)$ = 992.

Data Collection and Processing.—Stoë STADI-4 four-circle diffractometer equipped with Oxford Cryosystems low-temperature device,[20] graphite-monochromated Mo-K_α X-radiation, T = 173 K, ω-2θ scans using the learnt-profile method,[21] 1951 unique data ($2\theta_{max}$ 45°, h 0 ⟶ 8, k 0 ⟶ 18, l 0 ⟶ 19) of which 1585 with $F \geqslant 6\sigma(F)$ were used in all calculations. No significant crystal decay or movement was observed.

Structure Solution and Refinement.—Automatic direct methods[22] located the positions of all non-hydrogen atoms which were then refined (by least-squares on F[23]) with anisotropic thermal parameters. The phenyl ring was refined as an idealised group with D_{6h} symmetry and H atoms were included at fixed, calculated positions. At final convergence R, R_w = 0.0367, 0.0494 respectively, S = 1.209 for 284 refined parameters and the final ΔF synthesis showed no peak above 0.16 eÅ^{-3}. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,447\,F^2$ gave satisfactory agreement analyses and in the final cycle $(\Delta/\sigma)_{max}$ was 0.014.

Atomic scattering factors were inlaid,[23] molecular geometry calculations utilised CALC[24] and Fig. 1 was produced by ORTEPII.[25]

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