The Protecting–Directing Role of the Trityl Group in Syntheses of Pyrrole Derivatives: Efficient Preparations of 1-*H*-Pyrrole-3-carboxylic Acid and 3-Acyl-, 3-Amino-, and 3-Bromo-1-tritylpyrroles

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Trifluoroacetylation, formylation, and bromination of 1-tritylpyrrole occur regioselectively at the 3-position in high yields. Quantitative hydrolysis of the 3-trifluoroacetyl derivative and removal of the trityl group from the resulting acid with sodium in liquid ammonia furnishes a new, short, high-yielding synthesis of the simple 1-*H*-pyrrole-3-carboxylic acid. 1-Tritylpyrrole-3-carboxylic acid has been converted efficiently into 3-aminopyrroles *via* Curtius rearrangement of the derived azide: 3-amino-1-tritylpyrrole appears to exist in solution exclusively as its imino-Δ^4-pyrroline tautomer. 1-*H*-3-t-Butyloxycarbonylamino-pyrrole undergoes trifluoroacetylation regioselectively at the 2-position. Metallation of 1-tritylpyrrole with butyl-lithium in hexamethylphosphoric triamide gives rise to the unexpected products 9-phenyl-fluorene, 1-methoxycarbonylpyrrole and methyl triphenylmethylacetate (after work-up of the lithio-intermediates with carbon dioxide and methylation of the resulting acids).

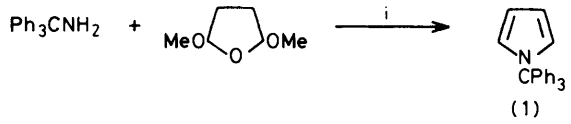
The mechanism proposed for the reductive cleavage of the trityl group in 1-tritylpyrrole is supported by the results of cyclic voltammetry experiments.

Despite the extensive chemical studies [1a–f] of pyrrole and its derivatives and of polypyrrole systems, simple 1-*H*-3-substituted pyrroles remain a class of compound about which relatively little is known. This is due principally to the far from trivial problems posed by their synthesis and the often low stability of these deceptively simple compounds.

With few exceptions, *viz.* nitration [2a,b] and nitrosation,[3] electrophilic substitution of pyrrole occurs preferentially at an α-(2-)position.[4] Two strategies involving modification of the pyrrole nucleus, which overcome this high level of regioselectivity, are available. Firstly, electrophilic substitution of pyrrole derivatives bearing an electron-withdrawing group at the 2-position gives rise to mixtures of 2,5- and 2,4-disubstituted products (in which the latter may predominate [5a–f]). In some cases,[5a,c,d,f] subsequent removal of the 2-substituent (from the 2,4-isomer) yields the simple 1-*H*-3-substituted pyrroles: a good example of this may be found in the recent work of Anderson [6] who has synthesised 3-acetyl- and 3-methoxycarbonyl-pyrroles in 54 and 35% overall yields, respectively. Secondly, pyrroles bearing large 1-substituents undergo directed substitution to the β-positions. For example, formylation [7] and trifluoroacetylation [8] of 1-t-butylpyrrole afford the 2- and 3-isomers in ratios of 1 : 13 and 1 : 9 respectively, in high yields. In addition, β-metallation of 1-alkylpyrroles with alkyl-lithium reagents has been observed.[9a–c] This second approach has hitherto not been applied to the syntheses of 1-*H*-3-substituted pyrroles since the 1-alkyl substituents cannot be removed.

Approaches to 1-*H*-3-substituted pyrroles in which ring construction methodology is employed are generally not very efficient: [10a–e] for example, the most efficient synthesis of pyrrole-3-carboxylic acid was achieved in three stages in 36% overall yield.[11]

In the work presented here we have adopted the second strategy, utilising the trityl (triphenylmethyl) substituent both as a bulky directing group and as a protecting group for the pyrrole nitrogen. The group is simple to introduce, allows a high level of β-regioselectivity and is easily removed under conditions compatible with both the integrity of the pyrrole ring and the carboxy-functionality. The synthetic utility of this new approach to the synthesis of 3-substituted pyrroles with an *N*-hydrogen has been explored through the preparation of a range of hitherto unknown pyrrole derivatives. To our knowledge, the only previous attempt to use this approach was by Anderson [12] who employed the benzyl group. Nitration and bromination of 1-benzylpyrrole gave moderate yields of 3-substituted pyrroles (together with other isomers) although the selectivity for reaction at the 3-position under Vilsmeier–Haack conditions was poor: the idea was abandoned when attempts to remove the benzyl group by catalytic hydrogenation failed.



(1)

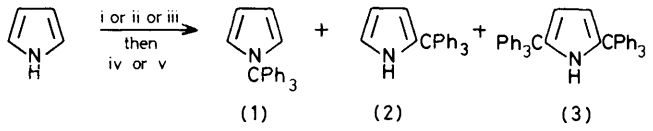
Scheme 1. Preparation of 1-tritylpyrrole by a modified Clauson–Kaas procedure. *Reagents:* i, AcOH, C_6H_6

In the discussion of the results which follows, the preparation and some simple chemistry (formylation, trifluoroacetylation, metallation, and bromination) of 1-tritylpyrrole are presented in section A, the methods for the removal of the trityl group are elaborated in section B, and the application of the methodology to the syntheses of 3-aminopyrrole and its derivatives are described in section C.

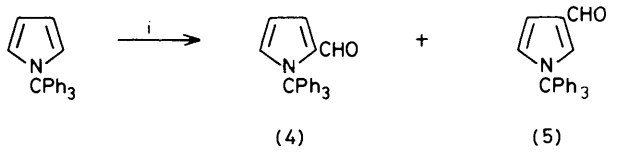
Results and Discussion

(*A*) *Preparation and Chemistry of* 1-*Tritylpyrrole*.—1-Tritylpyrrole (1) may be prepared by the modified Clauson–Kaas method (Scheme 1): tritylamine (which is prepared from the inexpensive trityl chloride by reaction with liquid ammonia) when allowed to react with 2,5-dimethoxytetrahydrofuran in acetic acid and boiling benzene during 16 h furnishes compound (1) in moderate yield (the use of benzene as solvent allows a reduction in the amount of acetic acid required, so that polymerisation side reactions are minimised, and causes the 1-tritylpyrrole to crystallise from the reaction mixture as it is formed). The previous synthesis [13] of (1) required extraordinarily long reaction times.

Alternatively the preparation of 1-tritylpyrrole may be approached *via* alkylation of the pyrrole anion (Scheme 2).



Scheme 2. Tritylation of the pyrrole anion. *Reagents:* i, Bu^{n}Li, hexane; ii, TlOEt, hexane; iii, KH, DME; iv, Ph_3CCl; v, $Ph_3C^+SbCl_6^-$



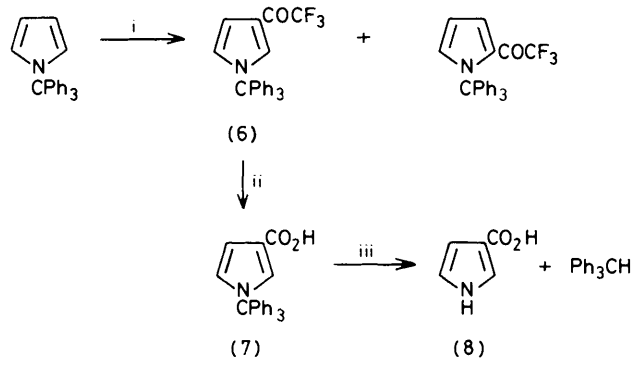
Scheme 3. Vilsmeier formylation of 1-tritylpyrrole. *Reagents:* i, DMF + $POCl_3$ in $ClCH_2CH_2Cl$

The choice of counter cation and solvent is important. Thus, with lithium and tetrahydrofuran (THF) or thallium and hexane, alkylation with trityl chloride gives mixtures of *N*- and *C*-alkylated products; only with potassium and 1,2-dimethoxyethane (DME), in which the metal–pyrrole bond should be essentially ionic, is clean *N*-alkylation observed. The novel 2,5-ditritylpyrrole (3) is obtained from the reaction of potassio-pyrrole in DME with trityl hexachloroantimonate in 7% yield. Compared with the Clauson–Kaas method, the alkylation approach seems inferior in that it suffers from low product yields and the isolation of the product is difficult.

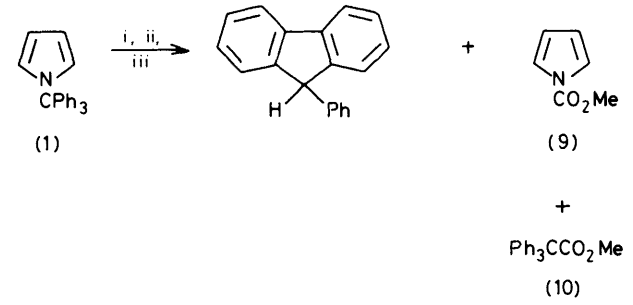
Vilsmeier–Haack formylation of 1-tritylpyrrole under forcing conditions gives the 2-formyl-(4) and 3-formylpyrroles (5) in the ratio 1 : 2.8 in 100% total yield (Scheme 3). The level of regioselectivity for substitution at the 3-position is surprisingly poor compared with that observed in the formylation of 1-t-butylpyrrole.[7] Improvements in the ratio of the aldehydes (4) and (5) may be achieved by variation of the Vilsmeier electrophile; a change of the formamide alkyl group from methyl to n-butyl results in a small decrease in the 2- : 3-aldehyde ratio. A much greater effect is observed with the adduct of *N*,*N*-dimethylformamide (DMF) and triphenylphosphinyl bromide perbromide which gives the aldehydes (4) and (5) in the ratio 1 : 6.7.*

The trifluoroacetylation of 1-tritylpyrrole with trifluoroacetic anhydride has proved to be highly regioselective for the 3-position; only a trace of the 2-trifluoroacetyl product can be detected by n.m.r. spectroscopy and the 3-trifluoroacetyl derivative (6) may be isolated in pure form by simple recrystallisation in 89% yield (Scheme 4). Subsequent treatment with aqueous ethanolic sodium hydroxide converts the trifluoroacetylpyrrole (6) into 1-tritylpyrrole-3-carboxylic acid (7) which may be isolated quantitatively after recrystallisation. Reductive cleavage of the trityl group (*vide* section B) with sodium and methanol in liquid ammonia affords pyrrole-3-carboxylic acid (8) in 90% yield after purification. (Clearly the acid may be separated from the triphenylmethane co-product by simple base extraction.) Thus, the synthesis of the simple 1-*H*-pyrrole-3-carboxylic acid (8) is achieved in three steps, in 80% overall yield, from the readily prepared 1-tritylpyrrole (1).

As an extension of our metallation studies of 1-alkyl-[9a–c] and 1-trialkylsilyl-pyrroles,[14] the behaviour of 1-tritylpyrrole towards n-butyl-lithium has been similarly investigated. 1-Tritylpyrrole fails to metallate with Bu^{n}Li in hexane or ether



Scheme 4. Transformation of 1-tritylpyrrole into pyrrole-3-carboxylic acid. *Reagents:* i, $(CF_3CO)_2O$; ii, NaOH, MeOH, H_2O then H_3O^+; iii, Na, MeOH, liq. NH_3

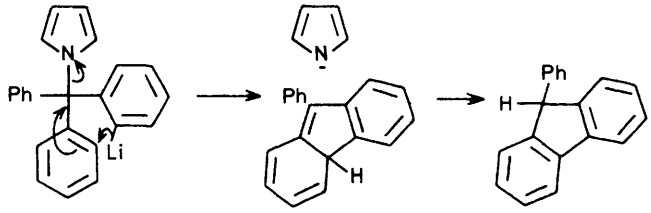


Scheme 5. Metallation of 1-tritylpyrrole. *Reagents:* i, Bu^{n}Li, HMPA; ii, CO_2 then H_3O^+; iii, CH_2N_2

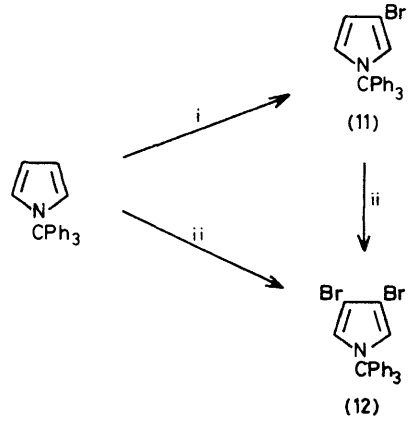
in the presence of the complexing agent *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), presumably because of the insolubility of the pyrrole in these media. With hexamethylphosphoric triamide (HMPA) as solvent, the metallation of 1-tritylpyrrole with a large excess of Bu^{n}Li (after quenching of the intermediate anions with carbon dioxide and subsequent methylation of the product acids with diazomethane) gives rise to unexpected products: 9-phenylfluorene in 31% yield; 1-methoxycarbonylpyrrole (9) in 25% yield; methyl triphenylmethylacetate (10) in 60% yield along with trace amounts of unidentified products (Scheme 5). (These yields are calculated from the molar ratios of individual products to starting material.) Trityl methyl ether behaves analogously to the above during metallation:[15] reaction with lithiating agents furnishes 9-phenylfluorene in 20% yield (after quenching with water) and 9-phenylfluorene-9-carboxylic acid (after quenching with carbon dioxide). The similarities between 1-tritylpyrrole and trityl methyl ether are obvious: both contain a possible leaving group, the pyrrole anion or methoxide anion, whose nucleofugicities are probably similar if the pK_a's of the parent acids are any guide. In order for a direct comparison to be made between reactions conducted under similar conditions, metallations of trityl methyl ether have had to be investigated further: treatment of the ether with Bu^{n}Li in HMPA results only in recovery of starting material whereas reaction with Bu^{n}Li in ether gives a mixture of starting material and 9-phenylfluorene in a 2 : 1 ratio.

It seems possible that these reactions may involve radical intermediates (organolithium compounds behave as electron-transfer agents during photolysis [16a,b]). Repetition of these metallations with the exclusion of light shows reduced product yields in all cases. An intense red colour which forms immediately upon the addition of Bu^{n}Li to 1-tritylpyrrole in HMPA

* We are grateful to M. Honan who carried out this experiment.



Scheme 6. Mechanism proposed for the formation of 9-phenylfluorene during the metallation of 1-tritylpyrrole

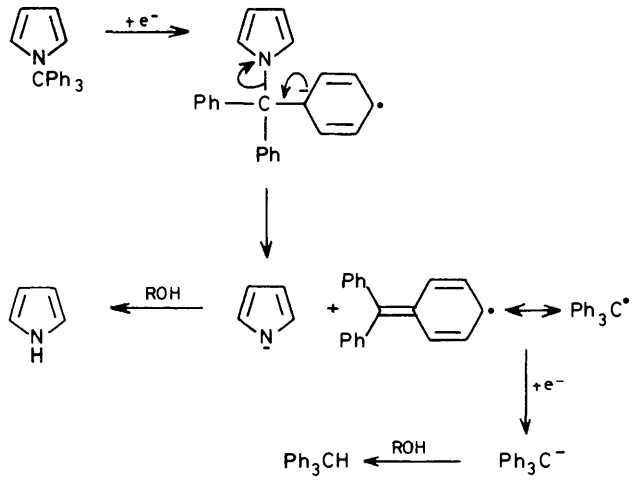


Scheme 7. Bromination of 1-tritylpyrrole. *Reagents:* i, $C_5H_5NBr^+$-Br-, C_5H_5N; ii, Br_2, CH_2Cl_2

is probably due to the trityl anion: separate reactions of triphenylmethane and 9-phenylfluorene with one equivalent of Bu^{n}Li in HMPA give deep red and scarlet coloured solutions, respectively. Subsequent work-up of the solutions of the resulting anions with carbon dioxide followed by ethereal diazomethane solution affords the methyl esters. A further complicating feature is that HMPA has been shown to react with Bu^{n}Li: [17] in the present study we have found that HMPA is metallated by Bu^{n}Li under similar conditions to those employed for the metallation of 1-tritylpyrrole.

Although our experimental metallation data are limited, two types of mechanistic pathway which may operate concurrently seem consistent with the variety of products shown in Scheme 5. (a) Lithiation at a phenyl *ortho*-position in the trityl group and subsequent ring closure across two *ortho*-phenyl positions affords the 9-phenylfluorenyl system (Scheme 6) (this type of mechanism has been proposed in order to rationalise trityl methyl ether metallation products [15]). (b) Reductive cleavage of the trityl group (*via* electron transfer from Bu^{n}Li) should lead to trityl anion and pyrrole anion formation (a mechanism for the cleavage of the N–trityl bond by sodium, liquid ammonia and methanol is given later in this paper).

Bromination of 1-tritylpyrrole is highly regioselective: with bromine in methylene dichloride mainly the 3,4-dibromopyrrole (12) is formed whilst monobromination may be achieved with the milder reagent pyridinium bromide perbromide to form 3-bromo-1-tritylpyrrole (11) exclusively in 75% yield (Scheme 7). [Conversion of (11) into (12) aided the structure determination of the bromo-compound (11) by n.m.r. spectrometry.] The stabilising effect of the trityl group upon the pyrrole ring allows regioselective 3-monobromination. In contrast, pyrrole and its derivatives generally give mixtures of polysubstituted products with bromine.[4] Furthermore, the *N*-trityl-bromopyrroles are stable crystalline solids



Scheme 8. Proposed mechanism for the reductive cleavage of the trityl group from the pyrrole nitrogen

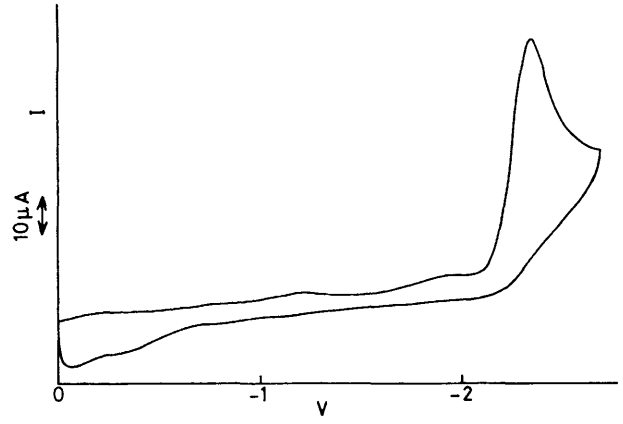


Figure 1. Cyclic voltammogram of 1-tritylpyrrole

whereas 1-*H*-3-bromopyrrole is unknown and 1-*H*-2-bromopyrrole decomposes above 40 °C.[18]

(*B*) *Cleavage of the* N–*Trityl Bond.*—The easy removal of the trityl group from the pyrrole nitrogen under Birch reduction conditions (Scheme 4) may be rationalised by the mechanism shown in Scheme 8. In the first step the transfer of an electron to the trityl group produces a radical anion which decomposes to the pyrrole anion (which is protonated by the alcohol proton donor) and the trityl radical, which is further reduced to the trityl anion and subsequently protonated. In keeping with this mechanism, two moles of sodium are required for the conversion of the trityl derivative (7) into compound (8) (Scheme 4).

In addition to the chemical removal of the trityl group from pyrrole, the feasibility of an electrochemical method was explored. The conditions for cleavage were studied by cyclic voltammetry.* The cyclic voltammograms of 1-tritylpyrrole (1), 3-bromo-1-tritylpyrrole (11), 1-tritylpyrrole-3-carboxylic acid (7), and 3-trifluoroacetyl-1-tritylpyrrole (6) are shown in Figures 1—4 respectively. The graphs depict the first reductive cycle in which the voltage (*vs.* Ag/Ag$^+$) was scanned at a

* The authors wish to thank Professor V. D. Parker and Dr. D. Bethell for carrying out the cyclic voltammetry experiments at the University of Trondheim, Norway.

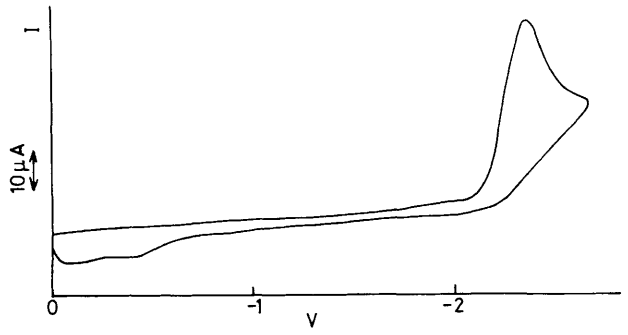


Figure 2. Cyclic voltammogram of 1-trityl-3-bromopyrrole

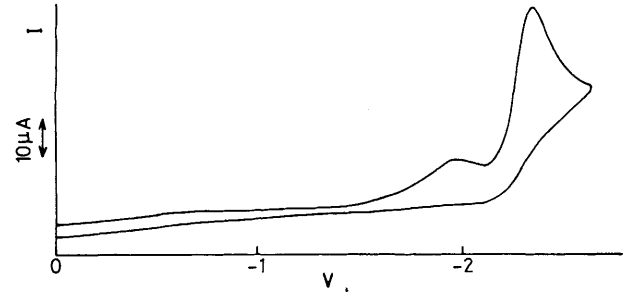


Figure 3. Cyclic voltammogram of 1-tritylpyrrole-3-carboxylic acid

constant rate (along the *x*-axis) from 0 to −2.65 V and then back to 0. The current flow (μA) was measured and is shown on the *y*-axis.

Each of the voltammograms show an irreversible electron addition to the substrate at *ca.* −2.24 V (measured at half the peak height). [These reduction potentials are consistent with the ability of sodium to effect cleavage of the trityl group during the conversion of (7) into (8) (Scheme 4), *i.e.* the standard reduction potential for $Na^+ + e^- \rightleftharpoons Na$ is −2.71 V.] [19] This irreversible reduction process is in accord with the suggested mechanism (Scheme 8), *i.e.* electron addition to the trityl group followed by dissociation to the pyrrole anion and trityl radical which both rapidly undergo further reactions. The second reduction, *viz.* electron addition to the trityl radical, would not be expected to be observed in the first voltage cycle if the trityl radical is reduced more easily than 1-tritylpyrrole. This is borne out in the recently reported [20] reversible one-electron oxidation of the trityl anion to the trityl radical at a potential of −1.12 V. A second reduction peak is observed in the voltammograms of the 3-carboxy- and 3-trifluoroacetyl-derivatives (Figures 3 and 4) at potentials of −1.77 and −1.91 V, respectively. Since carboxylic acids normally require very high potentials for reduction,[21] the second reduction peak of the carboxylic acid is probably due to simple proton reduction. In the trifluoroacetyl case the second peak may be due to carbon–fluorine bond reduction.[21]

In view of these results, it would seem that electrochemical deprotection of 1-tritylpyrrole may be viable if a solvent and electrolyte capable of withstanding the rather large negative potentials required can be utilised on a preparative scale. It is of relevance in this context that the trityl group has been removed by the electroreduction of trityl-protected alcohols, thiols and carboxylic acids at high electrode potentials (2.6 to 2.9 V) [22] but that the group was not removed from tritylamines at voltages up to the discharge potential of the supporting electrolyte.

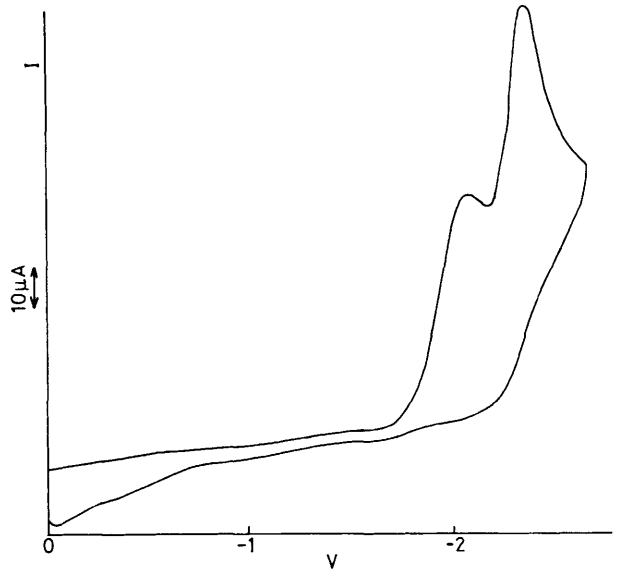


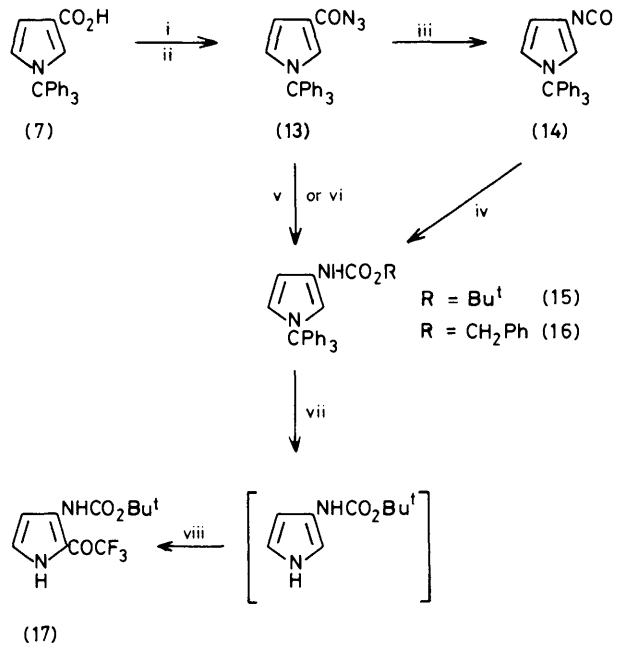
Figure 4. Cyclic voltammogram of 3-trifluoroacetyl-1-tritylpyrrole

Partial cleavage (*ca.* 40% as judged by n.m.r.) of the trityl group from 1-tritylpyrrole (1) may be achieved by palladium-catalysed hydrogenation at one atmosphere pressure in ethyl acetate at 60 °C during 16 h. Further cleavage was not observed over an extended reaction period of 5 days at the same temperature. High-pressure hydrogenation (*e.g.*, 150 atmospheres) may remove the trityl group completely, although such forcing conditions would presumably not be tolerated by other functionalities in a substituted pyrrole. The difficulty of hydrogenolysis is perhaps not surprising in view of the highly crowded nature of the trityl–pyrrole bond.

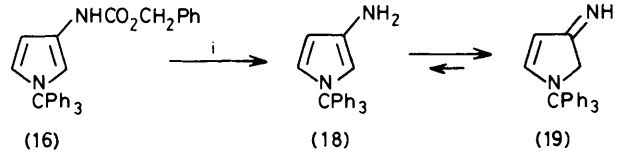
(*C*) 3-*Aminopyrroles*.—Very little is known about the synthesis, chemistry and properties of simple 3-aminopyrroles.[23] These simple molecules are very unstable and have been isolated only in protected form: 1-*H*- and 1-methyl-3-aminopyrroles could not be isolated due to rapid decomposition when their preparation was attempted *via* the catalytic hydrogenation of the corresponding 3-nitropyrroles; [24] Anderson, however, prepared 3-acetamido-1-benzylpyrrole during the reductive acetylation of 1-benzyl-3-nitropyrrole,[12] and Cornforth synthesised 3-acetamidopyrrole (which oxidised rapidly in air) in 10% yield.[25]

We decided to investigate these simple 3-aminopyrroles *via* a route based on our readily prepared 1-tritylpyrrole-3-carboxylic acid (7). Clearly the general stabilising effect that the trityl group has upon the pyrrole nucleus should allow these sensitive 3-aminopyrroles to be studied more easily.

The synthesis of the 3-aminopyrroles is based upon the utility of the Curtius rearrangement through which the amino-group may be created in a protected form and, importantly, under neutral conditions. Thus the acid (7) is converted *via* the acid chloride into the acyl azide (13) with oxalyl chloride followed by sodium azide (Scheme 9) in 90% yield (from the acid). Upon heating of the acyl azide (13) rearrangement occurs smoothly to give the isocyanate (14) and subsequent reaction with t-butyl alcohol affords the t-butyloxycarbonylaminopyrrole (15) in 80% yield. Alternatively, the acyl azide (13) may be converted directly into (15) or the benzyloxycarbonylaminopyrrole (16) in 74 and 89% yields respectively by thermal rearrangement in the presence of the appropriate alcohol.



Scheme 9. Preparations of 3-aminopyrrole derivatives. *Reagents:* i, $(COCl)_2$, C_5H_5N, C_6H_6; ii, NaN_3, dioxan–H_2O; iii, $C_6H_5CH_3$; iv, Bu^tOH; v, Bu^tOH, $C_6H_5CH_3$; vi, $C_6H_5CH_2OH$; vii, Na, MeOH, liq. NH_3; viii, $(CF_3CO)_2O$, C_5H_5N



Scheme 10. Preparation of 3-amino-1-tritylpyrrole (3-imino-1-trityl-Δ^4-pyrroline). *Reagents:* i, NH_4HCO_2, Pd–C, MeOH, H_2O

The protected 3-aminopyrroles (15) and (16) are thus produced very efficiently from 1-tritylpyrrole in 59 and 72% overall yields.

Removal of the trityl group from the butyloxycarbonyl-protected aminopyrrole (15) has been achieved under Birch reducing conditions to yield the unstable 1-*H*-3-t-butyloxycarbonylaminopyrrole which on immediate treatment with trifluoroacetic anhydride reacts regioselectively at the highly activated 2-position to furnish exclusively 3-t-butyloxycarbonylamino-2-trifluoroacetylpyrrole (17).

Although the tautomerism of 2- and 3-hydroxypyrroles with their oxo-forms has been well studied, there is very little knowledge about the analogous amino–imino tautomerism in 2-aminopyrroles [23] and virtually none in 3-aminopyrroles.

The simple 3-amino-1-tritylpyrrole [(18) $\rightleftharpoons$ (19), Scheme 10] may be prepared from the benzyloxycarbonyl-protected precursor (16) by a convenient catalytic transfer hydrogenation method [26] in high yield. The molecule appears to exist exclusively as the 3-imino-1-trityl-Δ^4-pyrroline (19) in solution in $CDCl_3$ as evinced by its ^1H n.m.r. spectra (Figure 5a, $CDCl_3$ only; Figure 5b, $CDCl_3 + D_2O$). Compared with the spectrum of the starting material (16) (Figure 5c) the spectrum of the product is clearly quite different: the 2-ring proton resonance (δ 6.75) has disappeared completely, the 4- and 5-ring proton resonances appear as two three-line multiplets at δ 5.75 and 6.35 respectively and the α-methylene protons appear as a broad signal at δ 2.87. The α-methylene protons and the imine NH (δ 6.10) exchange with D_2O as expected (Figure 5b) leaving the 4- and 5-H ring protons as doublets (*J* 3.0 Hz).

In contrast to the above, M.O. calculations [27] predict that the amino-tautomer is more stable than the imino-tautomer in 2- and 3-aminopyrroles. The only available spectroscopic measurements for these systems have been obtained for 2-aminopyrroles [28a,b] which support the theoretically predicted preference for the amino-tautomer, although one atypical result suggests a preference for the imino-structure.[29] This discrepancy between the theoretical predictions and experimental results may arise from shortcomings in the former (or incorrect interpretations of the latter), a difficult-to-predict effect of the trityl group on the position of tautomeric equilibrium, or from the possible difference in dipole moment between the tautomers (18) and (19) so that solvent interactions (which are not considered in the theoretical analysis) may greatly stabilise the more polar form. The imino-form (19) is probably much more dipolar than the amino-form (18) owing to a significant contribution to the overall ground state by the canonical form (19a) in this vinylogous amidine system. It is of interest, in this connection, that although recent MINDO/3 calculations predict 3-hydroxypyrrole to be more stable than the corresponding pyrrolinone (by 18.8 kJ mol^{-1}), the calculated dipole moment of the latter form (5.19 D) * is much larger than that of the former (2.84 D) so that the equilibrium position should be strongly solvent dependent: [30] the weight of experimental (solution) evidence suggests that 3-hydroxypyrroles exist preferentially as the pyrrolinone tautomers.

In conclusion, the trityl group allows the synthesis of 3-substituted pyrroles which are not readily accessible by traditional methodology. Although generally not very stable, these simple pyrrole derivatives may be handled easily as a result of the stabilising effect of the trityl group. Some of these compounds may be synthetically very useful: the 3-bromopyrrole (11), for example, could be converted by metal-halogen exchange [12] into the 3-lithio-derivative whose synthetic potential is very great.

Experimental

Product purity was checked by thin layer chromatography (t.l.c.) on Merck 10 × 2 cm aluminium-backed plates with a 0.2-mm layer of Kieselgel $60F_{254}$. Preparative thin layer chromatography (p.t.l.c.) was carried out on 100 × 20-cm plates coated with a 1-mm layer of Merck Kieselgel GF_{254}. M.p.s were determined on a Köfler block and are corrected. Microanalyses were performed by the University of Liverpool Micro-Analysis Laboratory under the direction of Mr. D. Newman. ^1H N.m.r. spectra were recorded on a Perkin-Elmer R34 (220 MHz) spectrometer. Tetramethylsilane was used as the internal lock standard. For signals other than singlets (s), doublets (d), triplets (t), quartets (q), and multiplets (m) the number of lines is indicated. ^{13}C N.m.r. spectra were recorded on a Varian XL-100 spectrometer operating at 25.15 MHz for the ^{13}C nucleus in the pulsed F.T. mode. The internal standard was tetramethylsilane. I.r. spectra were recorded on either a Pye Unicam SP1025 or a Perkin-Elmer 125 spectrophotometer. Low resolution mass spectra were recorded on an A.E.I. MS12 spectrometer. The *m/e* value for the molecular ion is followed, in parentheses, by its percentage abundance. High resolution mass spectra were recorded on an A.E.I. MS902 spectrometer. Solvents were dried and distilled prior to use: diethyl ether, dioxan, and 1,2-

* 1 D is 3.3356×10^{-30} C m.

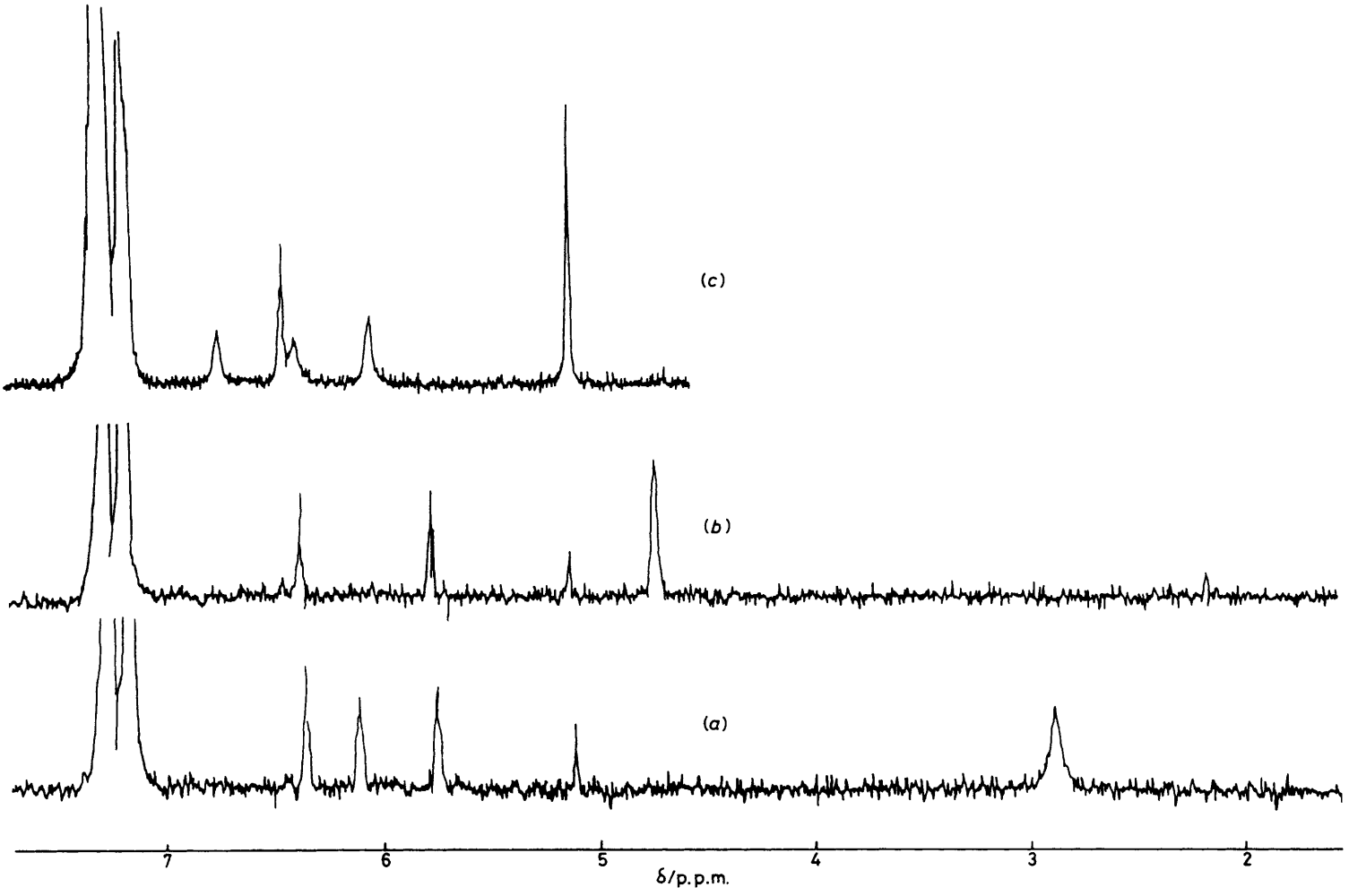
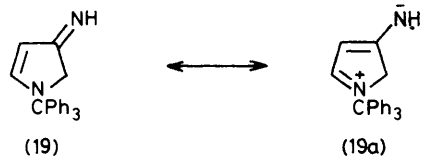


Figure 5. ^{1}H N.m.r. spectra of 3-imino-1-trityl-Δ^4-pyrroline (*a*) in $CDCl_3$ only, and (*b*) with added D_2O, and (*c*) of the benzyloxycarbonyl-protected precursor



(19) (19a)

dimethoxyethane (DME) were distilled from sodium–benzophenone, benzene, and toluene, and light petroleum (b.p. 60—80 °C)–ether from $CaCl_2$, ethyl acetate from $CaSO_4$, acetonitrile from P_2O_5, ethanol from CaO, and *N*,*N*-dimethylformamide (DMF), hexamethyl phosphoric triamide (HMPA) and dimethyl sulphoxide (DMSO) from CaH_2 *in vacuo*. The solvents were usually stored over molecular sieves type 4A.

The concentrations of solutions of commercial Bu^nLi were determined by means of the double-titration method of Jones and Gilman.[31]

Tritylamine.—Trityl chloride (45 g, 0.16 mol) was stirred with liquid NH_3 (*ca.* 1 l) for 6 h. After evaporation of the NH_3 the residue was triturated with Et_2O (600 ml). The extracts were washed with 10% Na_2CO_3, water, and brine, then dried (Na_2SO_4) and evaporated under reduced pressure giving tritylamine (36.7 g, 89%) as an amorphous solid, m.p. 102—104 °C (from EtOAc–hexane) (lit.,[32] 103 °C).

1-*Tritylpyrrole* (1).—Tritylamine (15.0 g, 0.06 mol), 2,5-dimethoxytetrahydrofuran (9.0 g, 0.06 mol) and glacial acetic acid (42 ml) were heated under reflux under N_2 in benzene (90 ml) for 16 h. After the mixture had cooled a brown crystalline solid was filtered off and recrystallised from benzene (and charcoal) giving 1-tritylpyrrole (10.2 g, 55%), as white needles, m.p. 245—246 °C (lit.,[13] 245—246 °C); δ($CDCl_3$) 6.14 (m, 3- and 4-H), 6.61 (m, 2- and 5-H), and 7.16 and 7.29 (m, CPh_3); δ(^{13}C) (CD_2Cl_2) 107.2 (C-3, -4), 123.3 (C-2, -5), 127.3 (C-4′), 127.5 (C-2′, -6′), 129.8 (C-3′, -5′), and 143.6 p.p.m. (C-1′); *m*/*e* 309 (M^+, 3%), 244 (24), 243 (100), 166 (10), 165 (36), and 91 (7).

Attempted Preparation of 1-*Tritylpyrrole by Alkylation of Pyrryl Anion*.—Potassium hydride (as a suspension in oil) (1.5 g, 0.0075 mol) was washed with dry hexane (2 × 5 ml) under N_2 after which dry 1,2-dimethoxyethane (DME) (10 ml) was added. After the slow addition of a solution of pyrrole (0.5 g, 0.0075 mol) in DME (5 ml) the mixture was stirred at room temperature for 0.5 h. A suspension of trityl hexachloroantimonate (4.33 g, 0.0075 mol) prepared from trityl chloride and antimony pentachloride in DME (10 ml) was added and the

mixture stirred under N_2 at room temperature for 1 h. Filtration and evaporation under reduced pressure gave a black oil which contained no pyrrollic compounds.

The material filtered from the reaction mixture was washed with CH_2Cl_2 and the washings were dried ($MgSO_4$) and evaporated under reduced pressure giving 2,5-*ditritylpyrrole* (3) (0.3 g, 7%) as cuboids, m.p. 232—233 °C (from hexane) (Found: C, 91.55; H, 6.0; N, 2.55. $C_{42}H_{33}N$ requires C, 91.42; H, 6.04; N, 2.54%); δ($CDCl_3$) 5.85 (d, *J* 2.8 Hz; 3- and 4-H) and 7.08 and 7.18 (m, CPh_3); δ(^{13}C) (CD_2Cl_2) 60.7 (C-6, -6′), 109.2 (C-3, -5), 126 (C-4′), 127.8 and 130.3 (C-2′, -3′, -5′, -6′), 137.3 (C-2, -4), and 146.1 p.p.m. (C-1′); $\nu_{max.}$ (CCl_4) 3 440, 3 050, 1 490, and 1 444 cm^{-1}; *m/e* 551 (M^+, 6%), 154 (17), 86 (66), 84 (100), and 58 (94).

Formylation of 1-*Tritylpyrrole* (1).—(i) Dry DMF (0.14 g, 0.0016 mol) was added dropwise to phosphoryl chloride (0.25 g, 0.0016 mol) with stirring under N_2 at 0 °C. After 0.5 h, 1-tritylpyrrole (0.5 g, 0.0016 mol) in dry CH_2Cl_2 (15 ml) was added to the mixture which was heated under reflux for 16 h. The mixture was poured into water, basified with Na_2CO_3 and extracted with CH_2Cl_2. The extracts were washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure giving a mixture (0.54 g, 100%) of 2-formyl-1-tritylpyrrole (4) δ($CDCl_3$) 6.29 (4 lines, 4-H), 6.77 (4 lines, 3-H), 7.17 and 7.32 (m, CPh_3 and H-5), and 8.98 (s, CHO), and 3-formyl-1-tritylpyrrole in the ratio 1 : 2.8. Recrystallisation from EtOAc–hexane gave the 3-*formylpyrrole* (5) (0.19 g, 23%) as white needles, m.p. 206—208 °C (Found: C, 85.4; H, 5.75; N, 4.3. $C_{24}H_{19}NO$ requires C, 85.43; H, 5.68; N, 4.15%); δ($CDCl_3$) 6.59 (8 lines, *J* 0.3, 1.7 and 3.2 Hz, 4-H), 6.65 (7 lines, *J* 0.7, 2.4, and 3.2 Hz, 5-H), 7.17 and 7.35 (m, CPh_3 and H-2), and 9.64 (4 lines, *J* 0.3 and 0.7 Hz, CHO); δ(^{13}C) (CD_2Cl_2) 77.5 (C-6), 107.1 (C-4), 125.9 (C-3), 126.4 (C-5), 128.2 (C-2′, -4′, -6′), 130.1 (C-3′, -5′), 131.6 (C-2), 142.8 (C-1′), and 185.2 p.p.m. (CHO); $\nu_{max.}$ (CCl_4) 1 679, 1 490, and 1 118 cm^{-1}; $\nu_{max.}$ (MeCN) 1 670 and 1 118 cm^{-1}; *m/e* (M^+, 2%), 244 (40), 243 (100), 166 (18), 165 (75), and 51 (25).

(ii) Bromine (0.52 g, 3.24 mmol) in CH_2Cl_2 (20 ml) was added at 0 °C under N_2 to triphenylphosphine (0.85 g, 3.24 mmol) and the mixture stirred for 15 min. Dry DMF (0.236 g, 3.24 mmol) and then 1-tritylpyrrole (1.0 g, 3.24 mmol) were added and the mixture was boiled under reflux for 20 h. Saturated, aqueous sodium acetate solution (20 ml) was then added and the mixture boiled under reflux for a further 1 h with vigorous stirring. The aqueous layer was extracted with Et_2O (2 × 50 ml) and the combined extracts washed with 5M-aqueous HCl (2 × 25 ml), H_2O (2 × 50 ml), and brine (50 ml) and dried ($MgSO_4$). Evaporation under reduced pressure afforded yellow crystals (1.45 g), ^1H n.m.r. analysis of which revealed signals due to triphenylphosphine oxide, 1-tritylpyrrole, 2-formyl-1-tritylpyrrole and 3-formyl-1-tritylpyrrole, the last two in the ratio 1 : 6.7. Column chromatography on silica with EtOAc–light petroleum mixtures, and recrystallisation from EtOAc afforded an analytically pure specimen of the 3-formyl derivative (5) (0.2 g).

1-*Trityl*-3-*trifluoroacetylpyrrole* (6).—1-Tritylpyrrole (36.5 g, 0.118 mol) and trifluoroacetic anhydride (18 ml) in dry CH_2Cl_2 (750 ml) were stirred under N_2 at room temperature for 5 h. The mixture was washed with $NaHCO_3$, water and brine, then dried ($MgSO_4$) and evaporated under reduced pressure to give after recrystallisation (from hexane) 1-*trityl*-3-*trifluoroacetylpyrrole* (6) (42.7 g, 89%), m.p. 121.5—122.5 °C (Found: C, 74.25; H, 4.7; N, 3.35. $C_{25}H_{18}F_3NO$ requires C, 74.06; H, 4.48; N, 3.45%); δ($CDCl_3$) 6.55 (4 lines, *J* 2.3 and 3.3 Hz, 5-H), 6.75 (m, 4-H), 7.60 (m, 2-H), and 7.15 and 7.34 (m, CPh_3); δ(^{13}C) (CD_2Cl_2) 77.8 (C-6), 109.8 (C-4), 117 (C-3), 117.1 (CF_3, J_{CF} 291.4 Hz), 126.5 (C-5), 128.4 (C-2′, -4′, -6′), 130.0 (C-3′, -5′), 135.5 (C-2), 142.3 (C-1′), and 175.3 p.p.m. (CO, J_{CF} 35.5 Hz); $\nu_{max.}$ (CCl_4) 3 060, 1 695, 1 191, 1 140, and 1 125 cm^{-1}; $\nu_{max.}$ (MeCN) 1 690, 1 190, 1 150, and 1 125 cm^{-1}; *m/e* 405 (M^+, 2%), 244 (35), 243 (100), 166 (27), and 165 (87).

1-*Tritylpyrrole*-3-*carboxylic Acid* (7).—1-Trityl-3-trifluoroacetylpyrrole (59.5 g, 0.147 mol) and NaOH (96 g) in methanol (450 ml) and water (450 ml) were heated under reflux under N_2 for 6 h. The mixture was acidified with concentrated HCl and extracted with EtOAc (*ca.* 5 l). The extracts were washed with water and brine, then dried ($MgSO_4$) and evaporated under reduced pressure giving after recrystallisation (from toluene) 1-*tritylpyrrole*-3-*carboxylic acid* (7) (52 g, 100%), m.p. 266—268 °C (Found: C, 81.25; H, 5.25; N, 4.25. $C_{24}H_{19}NO_2$ requires C, 81.56; H, 5.42; N, 3.96%); δ($CDCl_3$) 6.56 (3 lines, *J* 2.6 and 3.2 Hz, 5-H), 6.64 (4 lines, *J* 1.9 and 3.2 Hz, 4-H), 7.39 (3 lines, *J* 1.9 and 2.6 Hz, 2-H), and 7.16 and 7.33 (m, CPh_3); $\nu_{max.}$ (KBr) 2 900, 2 550, 1 663, 1 300, 1 205, and 1 100 cm^{-1}; *m/e* 353 (M^+, 3%), 245 (39), 244 (100), 267 (18), 266 (28), and 265 (97).

Pyrrole-3-*carboxylic Acid* (8).—1-Tritylpyrrole-3-carboxylic acid (1.0 g, 0.0028 mol) and methanol (2 ml) were added to liquid NH_3 (*ca.* 150 ml) (distilled from Na). Sodium (*ca.* 1.5 g) was added to the mixture in portions with stirring. After the ammonia had evaporated off, water was cautiously added and the mixture extracted with Et_2O. The aqueous phase was acidified with concentrated HCl then extracted with EtOAc. EtOAc extracts were dried ($MgSO_4$) and evaporated under reduced pressure giving pyrrole-3-carboxylic acid (2.8 g, 90%), as needles, m.p. 145—146 °C (from EtOAc) (lit.,[10b] 148 °C). (Triphenylmethane was recovered from the Et_2O extract quantitatively; its n.m.r. was identical with an authentic sample.)

General Methods for Lithiation Studies.—Reaction of substrate with butyl-lithium in hexane. General method A. The substrate and complexing agent (where required) were placed in a two-necked flask containing a magnetic stirring bar. A condenser was fitted (where required) and the apparatus flushed with dry N_2 before being sealed to the atmosphere with a balloon of N_2 and a septum cap. Bu^nLi dissolved in hexane was injected with a syringe and the mixture was stirred magnetically and the flask heated (where necessary) in an oil-bath.

Reaction of substrate with butyl-lithium in diethyl ether. General method B. A two-necked flask fitted with a condenser (where required) was flushed with dry N_2 and was then sealed with a balloon of dry N_2 and a septum cap. A solution of Bu^nLi in hexane was injected with a syringe. The tap connected to the balloon of N_2 was closed and hexane was removed under reduced pressure through a syringe needle connected to a water-pump whilst the flask was gently warmed. The balloon tap was opened, the flask cooled in a solid CO_2–acetone bath and dry Et_2O was introduced with a syringe. The subsequent use of this solution in lithiation studies was analogous to that employing Bu^nLi in hexane.

Carboxylation of lithio-intermediates. General method C. A continuous stream of dry N_2 was passed through the flask containing the lithio-intermediates. This mixture was poured cautiously on to a slurry of solid CO_2–dry Et_2O with stirring. After the solid CO_2 had evaporated, water was added to dissolve the lithium salts. The aqueous solution was washed with Et_2O (2 × 200 ml), acidified to pH 2 with 2M-HCl, saturated with NaCl, and extracted with EtOAc (4 × 100

ml). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the acids.

Methylation of carboxylic acids. General method D. Diazomethane [33] was generated as a solution in Et_2O from the addition of *N*-nitroso-*N*-methylurea (10 g) to a stirred solution of Et_2O (100 ml) and a solution of KOH (12 g) in H_2O (30 ml) cooled in an ice-bath. After 1 h at 0 °C, the ethereal layer was decanted directly into a stirred solution (or suspension) of the acids in Et_2O, maintained at 0 °C in an ice-bath. The mixture was allowed to attain room temperature and, when the excess of diazomethane had evaporated, the solution was dried ($MgSO_4$), filtered and the filtrate evaporated under reduced pressure to give the crude methyl esters.

Attempted Lithiation of 1-Tritylpyrrole.—(i) 1-Tritylpyrrole (1.0 g, 0.0032 mol) and TMEDA (0.38 g, 0.0032 mol) in hexane (2 ml) were treated at room temperature for 0.5 h with Bu^nLi (2.1 ml, 0.0032 mol) in hexane according to method A. Carboxylation and methylation of the lithio-intermediates (methods C and D) gave methyl pentanoate as the only ester product, and recovered 1-tritylpyrrole.

(ii) Treatment of 1-tritylpyrrole (1.0 g, 0.0033 mol) with Bu^nLi (5 ml, 0.008 mol) and TMEDA (0.95 g, 0.008 mol) in Et_2O (15 ml) under reflux for 1 h (method B) and subsequent carboxylation and methylation (methods C and D) gave only recovered 1-tritylpyrrole.

(iii) 1-Tritylpyrrole (1.0 g, 0.0032 mol) in dry HMPA (75 ml) under N_2 was treated with Bu^nLi (10 ml, 0.015 mol) in hexane at room temperature for 2 h; the mixture became deep red in colour when the Bu^nLi was added. The mixture was poured into a slurry of solid CO_2–Et_2O and after evaporation of the CO_2 the Et_2O extract was washed with water, dried ($MgSO_4$) and evaporated under reduced pressure giving a yellow solid, which was separated by p.t.l.c. [on SiO_2, eluting with chloroform–light petroleum (b.p. 60—80 °C) (1 : 2)] to give three components: (a) 9-phenylfluorene (0.25 g, 31%), m.p. 139—140 °C (lit.,[15] 144.5—145.5 °C); δ($CDCl_3$) 5.06 (s, 9-H), 7.07—7.41 (m, aromatic), and 7.80 (d, aromatic); (b) a yellow oily solid (0.05 g) whose n.m.r. shows signals for a substituted pyrrole, some of component (c) and other unassignable peaks; (c) a white solid (0.03 g), δ($CDCl_3$) 2.90 (6 H, s), 5.46 (1 H, s), 6.67 (2 H, d, *J* 8 Hz), 6.98 (2 H, d, *J* 8 Hz), and 7.12—7.30 (13 H, m).

The aqueous extracts (after CO_2 quenching) were acidified, extracted with EtOAc and the organic extracts were dried ($MgSO_4$), evaporated and treated with diazomethane in the usual manner yielding an off-white solid (0.3 g) which was separated into two components by p.t.l.c. [on SiO_2, eluting with chloroform–light petroleum (b.p. 60—80 °C) (1 : 2)]: (a) 1-methoxycarbonylpyrrole (9) (0.1 g, 25%); δ($CDCl_3$) 4.95 (s, OCH_3), 6.24 (m, 3- and 4-H), and 7.27 (m, 2- and 5-H); and (b) *methyl triphenylmethylacetate* (10) (0.56 g, 60%) as white needles, m.p. 183—185 °C (from hexane) (Found: C, 83.15; H, 6.0. $C_{21}H_{18}O_2$ requires C, 83.42; H, 6.00%); δ($CDCl_3$) 3.78 (s, OCH_3), 7.17 and 7.25 (m, CPh_3); $\nu_{max.}$ (CCl_4) 1 734 and 1 210 cm^{-1}; *m/e* 302 (M^+, 1%), 244 (40), 243 (100), 165 (82), and 78 (15).

(iii) 1-Tritylpyrrole (1.0 g) was treated with Bu^nLi (10 ml) in HMPA (75 ml) (deoxygenated by stirring under a vacuum for 1 h) at room temperature for 2 h ' in the dark '. After quenching with CO_2 as above 1-tritylpyrrole was filtered and the filtrate was extracted with CH_2Cl_2. The combined organic extracts gave, after drying ($MgSO_4$) and evaporation, a small quantity of 1-tritylpyrrole and 9-phenylfluorene in the ratio 2 : 1.

Trityl Methyl Ether.—Sodium (0.6 g, 0.026 mol) was added [illegible] to dry methanol (15 ml) under N_2 until effervescence had ceased. Trityl chloride (5.0 g, 0.018 mol) as a slurry in methanol (25 ml) was added to the mixture and after *ca.* 15 h a solid was filtered off (5 g) which was recrystallised from hexane giving trityl methyl ether (2.8 g, 60%), m.p. 79—80 °C (lit.,[15] 83—84 °C); δ($CDCl_3$) 3.02 (s, OCH_3), 7.23 and 7.45 (m, CPh_3).

Lithiations of Trityl Methyl Ether.—(i) Trityl methyl ether (0.5 g, 0.0018 mol) was treated with Bu^nLi (4.8 ml, 0.0072 mol) in hexane and HMPA (30 ml) under N_2 at room temperature for 2 h giving an intense deep red solution. The mixture was worked up according to methods A, C, and D. Trityl methyl ether (100%) was recovered from the Et_2O extracts.

(ii) Trityl methyl ether (0.4 g, 0.0015 mol) was treated with Bu^nLi (0.006 mol) in Et_2O (3 ml) under reflux under N_2 for 24 h (method B). The mixture was quenched with water and extracted with Et_2O to give, after drying ($MgSO_4$) and evaporation, a yellow solid (0.37 g) which was shown by n.m.r. to be a mixture of trityl methyl ether and 9-phenylfluorene in the ratio 2 : 1.

(iii) The above reaction (ii) was repeated ' in the dark ' to give after work-up, trityl methyl ether and 9-phenylfluorene in the ratio 4 : 1.

Lithiation of 9-Phenylfluorene.—9-Phenylfluorene (0.2 g, 0.0008 mol) in HMPA (5 ml) was treated with Bu^nLi (0.6 ml, 0.0008 mol) in hexane under N_2 at room temperature for 1 h; the mixture immediately became scarlet in colour. It was quenched with solid CO_2–Et_2O, allowed to evaporate overnight, acidified with 5% HCl and extracted with EtOAc. The extracts were evaporated and treated with diazomethane in Et_2O (method D). After drying ($MgSO_4$) and evaporation under reduced pressure of the mixture a solid (0.23 g) was obtained which was shown by n.m.r. to contain 9-phenylfluorene and 9-methoxycarbonyl-9-phenylfluorene [δ($CDCl_3$) 3.94 (s, OCH_3), 7.07, 7.22—7.40 and 7.79 (m, aromatic-H)] in the ratio 5 : 1.

Lithiation of Triphenylmethane.—Triphenylmethane (0.5 g, 0.002 mol) in HMPA (5 ml) was treated with Bu^nLi (1.5 ml, 0.002 mol) in hexane under N_2 at room temperature for 1 h; the mixture immediately became an intense deep red colour. It was treated in a manner analogous to the lithiation of 9-phenylfluorene to give a mixture of triphenylmethane [δ($CDCl_3$) 5.54 (s, Ph_3CH), and 7.10—7.30 (m, CPh_3)] and methyl triphenylmethylacetate in the ratio 1 : 1.

Lithiation of HMPA.—HMPA (30 ml) and Bu^nLi (5 ml, 0.007 mol) were heated at 40 °C for 24 h under N_2; the mixture was dark brown in colour. It was poured into a slurry of solid CO_2–Et_2O, treated with water, extracted with Et_2O, acidified with 5% aqueous HCl and extracted (EtOAc). After evaporation under reduced pressure of EtOAc, the residue was treated with diazomethane to give, after drying and evaporation, a liquid whose n.m.r. spectrum in $CDCl_3$ showed signals at 3.4 (m) and 5.77 (m).

Bromination of 1-Tritylpyrrole.—(i) Pyridinium bromide perbromide (2.1 g, 0.0065 mol) in pyridine (10 ml) was added during 1 h to 1-tritylpyrrole (2.0 g, 0.0065 mol) suspended in pyridine (20 ml) under N_2 at 0 °C. After 18 h, CH_2Cl_2 (75 ml) was added to the mixture and it was then washed with 5% aqueous HCl (3 ×), aqueous $NaHSO_3$, and water. Drying ($MgSO_4$) and evaporation under reduced pressure of the solvent gave a pale red solid (1.9 g) which contained 3-bromo-1-tritylpyrrole (11), m.p. 213—215 °C (from toluene–hexane) (Found: C, 70.8; H, 4.55; N, 3.35. $C_{23}H_{18}BrN$ requires C, 71.00; H, 4.67; N, 3.61%); δ($CDCl_3$) 6.15 (4 lines, 4-H),

6.49 (4 lines, 5-H), 6.60 (4 lines, 2-H), and 7.15 and 7.29 (m, CPh_3); δ(^{13}C) ($CDCl_3$) 95.1 (C-3), 110.2 (C-4), 122.6 (C-2 or -5), 123.8 (C-2 or -5), 127.6 (C-2′, -4′, -6′), 129.8 (C-3′, -5′), and 142.8 p.p.m. (C-1′); $\nu_{max.}$ (KBr) 1 590, 1 484, 1 448, 1 252, 755, and 700 cm^{-1}; *m/e* 389 and 387 (M^+, 3%), 244 (85), 243 (100), and 165 (88).

(ii) Bromine (0.1 g, 0.000 65 mol) in CH_2Cl_2 (2 ml) was added dropwise to 1-tritylpyrrole (0.2 g, 0.000 65 mol) suspended in CH_2Cl_2 (4 ml) under N_2 at 0 °C. The mixture was left for 0.5 h, washed with aqueous $NaHCO_3$, aqueous $NaHSO_3$, water and dried ($MgSO_4$). Evaporation under reduced presure of the solvent gave a white solid (0.17 g) which was shown by n.m.r. to contain a mixture of 3-bromo-1-tritylpyrrole and 3,4-dibromo-1-tritylpyrrole (12) [δ($CDCl_3$) 6.67 (s, 2- and 5-H) and 7.30 (m, CPh_3)].

Cyclic Voltammetry.—This work was carried out for the authors by Drs. V. D. Parker and D. Bethell at the University of Trondheim, Norway.

The conditions used were as follows: generally *ca.* 5 mg of the 3-substituted-1-tritylpyrroles were dissolved in a 0.1M-acetonitrile solution of *N,N,N,N*-tetra-n-butylammonium tetrafluoroborate at 20 °C. The voltage of the Au-working electrode was swept at a rate 500m Vs^{-1} between the limits 0 to −2.5 V and 0 to +2.5 V relative to a Ag/Ag^+ electrode (0.01M in acetonitrile).

No change in the cyclic voltammogram of 1-tritylpyrrole was observed after the addition of alumina to remove residual water (or other proton donors) from the cell solution.

3-*Azidocarbonyl*-1-*tritylpyrrole* (13).—1-Tritylpyrrole-3-carboxylic acid (6.9 g, 0.0196 mol), oxalyl chloride (2.5 ml, 0.028 mol), pyridine (1 ml) and benzene (120 ml) were heated under reflux under N_2 for 4 h. Evaporation under reduced pressure gave 3-chlorocarbonyl-1-tritylpyrrole (pure by spectroscopic analysis), δ($CDCl_3$) 6.62 (m, 4- and 5-H), 7.27 and 7.34 (m, CPh_3), and 7.50 (3 lines, 2-H); δ(^{13}C) (CD_2Cl_2) 111.0 (C-4), 119.0 (C-3), 126.4 (C-5), 128.4 (C-2′, -4′, -6′), 130.0 (C-3′, -5′), 132.5 (C-2), and 142.3 p.p.m. (C-1′); $\nu_{max.}$ (CCl_4) 3 050, 1 753, 1 505, 1 495, 1 460, 1 304, and 1 140 cm^{-1}.

The unpurified acid chloride was stirred overnight at room temperature with sodium azide (1.3 g, 0.0196 mol), dioxan (150 ml) and water (150 ml). The mixture was treated with water and extracted with CH_2Cl_2. CH_2Cl_2 was removed by evaporation under reduced pressure and water added slowly to release a solid which was filtered and dried *in vacuo* to give the azide (13) (6.5 g, 90% from the acid), δ($CDCl_3$) 6.53 (4 lines, *J* 2.3 and 3.1 Hz, 5-H), 6.60 (4 lines, *J* 1.8 and 3.1 Hz, 4-H), 7.15 and 7.30 (m, CPh_3) and 7.38 (4 lines, *J* 1.8 and 2.2 Hz, 2-H); δ(^{13}C) ($CDCl_3$) 109.2 (C-4), 116.3 (C-3), 125.5 (C-5), 127.9 (C-2′, -4′, -6′), 129.2 (C-2), 129.8 (C-3′, -5′), and 142.3 p.p.m. (C-1′); $\nu_{max.}$ (CCl_4) 2 120, 1 689, 1 189, and 1 130 cm^{-1}; $\nu_{max.}$ (MeCN) 2 126, 1 683, 1 190, and 1 130 cm^{-1}.

3-*Isocyanato*-1-*tritylpyrrole* (14).—Unpurified 3-azidocarbonyl-1-tritylpyrrole was heated under reflux for 3 h in dry toluene. Evaporation under reduced pressure of the solvent gave the isocyanate (14), δ($CDCl_3$) 5.98 (3 lines, 4-H), 6.45 (m, 2- and 5-H), 7.15 and 7.30 (m, CPh_3); $\nu_{max.}$ (CCl_4) 2 280 and 1 680 cm^{-1}.

3-t-*Butyloxycarbonylamino*-1-*tritylpyrrole* (15).—(i) The isocyanate (14) (0.49 g, 0.001 45 mol) was heated under reflux in t-butyl alcohol (50 ml) for 3 h under N_2. Subsequent evaporation under reduced pressure gave a brown residue which was dissolved in CH_2Cl_2, filtered and evaporated under reduced pressure giving the *urethane* (15) (0.49 g, 80%).

(ii) The crude azide (13) (1.0 g, 0.002 65 mol) was heated under reflux under N_2 for 3 h with t-butyl alcohol (2 g) and toluene (50 ml). The mixture was evaporated under reduced pressure giving the *urethane* (15) (0.83 g, 74%) as needles, m.p. 215—218 °C (from toluene–hexane) (Found: C, 79.4; H, 6.85; N, 6.5. $C_{28}H_{28}N_2O_2$ requires C, 79.21; H, 6.65; N, 6.60%); δ($CDCl_3$) 1.41 (s, Bu^t), 6.05 (br, 4-H), 6.18 (br, NH), 6.45 (3 lines, 5-H), 6.64 (br, 2-H), and 7.18 and 7.28 (m, CPh_3); $\nu_{max.}$ ($CHCl_3$) 3 435, 2 960, 1 708, and 1 150 cm^{-1}; *m/e* 424 (M^+, <1%), 243 (35), 165 (53), 91 (19), and 57 (100).

Birch Reduction of 3-t-*Butyloxycarbonylamino*-1-*trityl-pyrrole and Subsequent Trifluoroacetylation.*—(i) Sodium (0.1 g, 0.004 mol) was added in portions to the urethane (15) (0.5 g, 0.0012 mol) and methanol (0.1 g, 0.003 mol) suspended in liquid NH_3 (50 ml) (distilled from sodium). The NH_3 was evaporated in a stream of dry N_2 leaving a white solid to which were added CH_2Cl_2 (25 ml) and pyridine (0.6 g, 0.0076 mol). The mixture was cooled to 0 °C under N_2, treated with trifluoroacetic anhydride (0.0036 mol) and stirred for 2 h, and then water was added. The organic layer was washed with water, dried ($MgSO_4$) and evaporated under reduced pressure. The crude mixture was separated by p.t.l.c. (on SiO_2, two elutions with $CHCl_3$) to give three components; (*a*) triphenylmethane (0.2 g, 68%); (*b*) 3-t-butyloxycarbonylaminopyrrole (0.05 g, 23%), δ(CD_2Cl_2) 1.45 (s, Bu^t), 5.98 (m, 4-H), 6.50 (br, N*H*CO_2Bu^t), 6.57 (m, 5-H), 6.85 (br; 2-H), and 8.45 (br, 1-H); and (c) 3-t-butyloxycarbonylamino-2-trifluoroacetylpyrrole (17) (0.12 g, 36%) as cuboids, m.p. 161.5—162.5 °C (sublimed), δ(CD_2Cl_2) 1.50 (s, Bu^t), 6.94 (3 lines, *J* 1.8 and 3.0 Hz, 4-H), 7.10 (3 lines, *J* 3.0 and 3.5 Hz; 5-H), 8.85 (br, 1-H), and 9.12 (br, N*H*CO_2Bu^t); $\nu_{max.}$ ($CHCl_3$) 3 468, 3 340, 1 725, 1 635, 1 568, 1 339, and 1 145 cm^{-1}; *m/e* 278.0886 (M^+, 5%) ($C_{11}H_{13}F_3N_2O_3$ requires 278.0878), 149 (54), 91 (42), 59 (66), 58 (100), and 57 (70).

(ii) The above procedure was repeated except that after NH_3 was evaporated from the reaction mixture, CH_2Cl_2 was added and the mixture was filtered (to remove NaOMe). The filtrate was then trifluoroacetylated in the presence of pyridine, as above, to give a mixture (by n.m.r.) of triphenylmethane and the 2-trifluoroacetyl derivative (17) (*ca.* 80%) only.

3-*Benzyloxycarbonylamino*-1-*tritylpyrrole* (16).—3-Azidocarbonyl-1-tritylpyrrole (2.0 g, 0.005 mol) was heated under N_2 at 110—120 °C with benzyl alcohol (25 ml) for 3 h. The mixture was evaporated under reduced pressure to give the urethane (16) (1.8 g, 89%), m.p. 178—180 °C (from benzene–hexane); δ($CDCl_3$) 5.11 (s, CH_2), 6.04 (br, 4-H), 6.37 (b, NH), 6.45 (4 lines, 5-H), 6.75 (br, 2-H), and 7.19—7.26 (m, CPh_3 and CH_2*Ph*); δ(^{13}C) (CD_2Cl_2) 66.9 (CH_2), 100.9 (C-4), 113.0 (C-2), 121.9 (C-5), 122.9 (C-3), 127.4, 127.9, 128.6, 130.1, and 143.7 p.p.m. (Ph); $\nu_{max.}$ (CCl_4) 3 450, 1 746, 1 200, and 1 135 cm^{-1}; *m/e* 454 (M^+, 3%), 244 (30), 243 (100), 155 (56), 91 (74), and 74 (36).

Catalytic Transfer Hydrogenation of 3-*Benzyloxycarbonyl-amino*-1-*tritylpyrrole.*—3-Benzyloxycarbonylamino-1-tritylpyrrole (0.2 g, 0.000 22 mol) and ammonium formate (0.081 g, 0.0012 mol) were dissolved in methanol (4 ml) and water (0.5 ml), 10% Pd–C (0.04 g) was added, and the mixture was stirred vigorously under N_2 at room temperature for 1 h. The mixture was filtered through Celite and evaporated under reduced pressure to give 3-imino-1-trityl-Δ^4-pyrroline (19) (0.043 g, 61%); δ($CDCl_3$) 2.87 (br, CH_2), 5.75 (4 lines, *J* 2.1

and 2.8 Hz, 4-H), 6.11 (3 lines, *J* 2.1 Hz, NH), 6.35 (3 lines, *J* 2.8 Hz, 5-H), and 7.17 and 7.27 (m, CPh_3); δ($CDCl_3$ + D_2O) 5.75 (d, *J* 3.0 Hz, 4-H), 6.35 (d, *J* 3.0 Hz, 5-H), and 7.17 and 7.27 (m, CPh_3).

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