Aromatic azapentalenes: 1*H*- and (mesoionic) 2*H*-pyrrolotetrazoles. Part 1. Synthesis and spectral characteristics[1]

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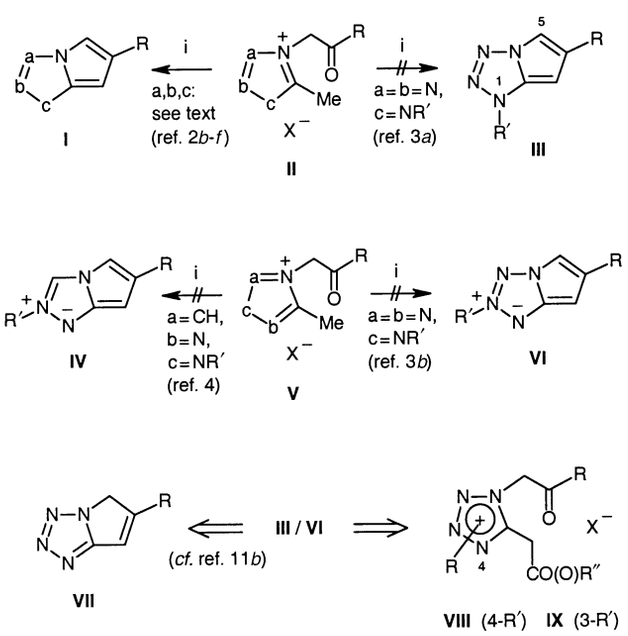
Two separate series of the title systems have been prepared by cyclisation of tetrazolium salts having acylmethyl functions attached to both the ring carbon and the adjacent nitrogen atom (**3**, **4**): (i) working in an acetate buffer led to 7-acyl derivatives (**5**, **6**; Scheme 3), and (ii) treatment with anhydride–base gave 5,7-diacyl compounds by a deviating ring closure mechanism (**11**, **12**; Scheme 4). These materials could be defunctionalised to afford pyrrolotetrazoles (**7**, **8**) which were earlier approached in vain from the respective 5-methyltetrazolium salts (Tschitschibabin reaction). Regarding characterisation data, attention is drawn to the conspicuous spectroscopic differences between the 1*H*- and the 2*H*-system. 2*H*-Pyrrolotetrazoles (**6**, **8**, **12**) represent a novel class of Ramsden's 'type C' heteropentalene mesoions.

Introduction

One of the major and most convenient routes to pyrroloazoles with a bridgehead nitrogen atom (**I**) consists in base-mediated cyclisation of *N*-(acylmethyl)-α-methylazolium ions such as **II** (Scheme 1). This approach—an extension of Tschitschibabin's



Scheme 1 *Reagents and conditions*: i, base, heat.

indolizine synthesis[2a]—includes the preparation of pyrrolo[2,1-*b*]thiazoles (**I**; a = b = CH/CR, c = S), 1*H*-pyrrolo[1,2-*a*]imidazoles (**I**; a = b = CH/CR, c = NR′), 4*H*-pyrrolo[1,2-*a*]benzimidazoles (**I**; ab = CC of benzo, c = NR′), 1*H*-pyrrolo[2,1-*c*][1,2,4]triazoles (**I**; a = CH/CR, b = N, c = NR′) and 1*H*-pyrrolo[1,2-*b*][1,2,4]triazoles (**I**; a = N, b = CR, c = NR′).[2b–f] Surprisingly, application of this method to the corresponding tetrazolium salts (**II**; a = b = N, c = NR′) fails; instead of **III**, imidazolones, dequaternisation products or azide–amide mixtures were found.[3a] In the isomeric azoliums **V**, the methyl group is inactive throughout so as to preclude not only the formation of the (mesoionic) 2*H*-pyrrolotetrazole **VI**[3b] but also that of the analogous 2*H*-pyrrolo[2,1-*c*][1,2,4]triazole **IV**.†[4] These shortcomings drew our attention to tetrazolium salts having an acceptor-substituted methyl group like **VIII** and **IX**. Such species are deprotonated preferably at the *C*-attached side-chain[7] [in contrast to **II** and **V** (a = b = N, c = NR′)[8]] and, hence, should exhibit an enhanced proclivity for ring closure. Earlier observations with appropriately substituted imidazoliums and benzimidazoliums testify to this effect.[9] Since pyrroloazoles **I** bearing an additional acyl or ester group at the pyrrolic half-ring (adjacent to the bridgehead carbon or nitrogen atom) can be easily defunctionalised,[4a,10] the tetrazolium salts **VIII** and **IX** are promising synthons for **III** and **VI**. Another conceivable route to **III** and **VI** constitutes *N*-alkylation of the 5*H*-pyrrolotetrazole **VII**. However, access to the starting bicycle is troublesome[11a] and, as shown by methylation of the 7-methyl congener,[11b] the 2*H*-isomer (type **VI**) is formed only sparingly with an overall low yield.

Results and discussion

Synthesis

As candidates for cyclisation we chose the tetrazolium salts **3a**–**g** and **4a**–**h** (Scheme 2). The derivatives **3e**,**g** and **4a**,**b**,**d**–**h**, like the previously reported **3a**,[7] were made routinely by treatment of the tetrazoles **1c**,**e** and **2a**–**c** with the respective α-bromoketone in the presence of silver tetrafluoroborate (*cf.* ref. 8*a*). The salts **3b**–**d**,**f** resulted smoothly from the reaction of **1f**–**i** with dimethyl sulfate, which constitutes another method applied before;[8a] of the second isomers **4** formed simultaneously, only **4c** was utilised (without separation from **3c**).

Access to the unknown precursors **1f**–**i** and **2a** was also effected by standard procedures, *i.e.* by alkylation of **1b** and **1a**,

† For naming **IV** and **VI** as '2*H*-pyrrolo . . . azole' (instead of using the *Chem. Abstr.* name '2-substituted 1*H*-pyrrolo . . . azolium, inner salt'), *cf.* the established literature practice.[5] From their electronic structure, mesoionic bicycles such as **IV** and **VI**, like the related 2*H*-pyrrolo[1,2-*c*]imidazole[6b,c] and the analogues of ref. 5, belong in Ramsden's classification[6a] to 'type C heteropentalene mesomeric betaines'.

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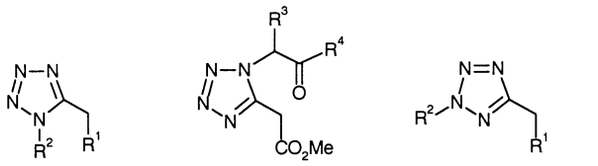
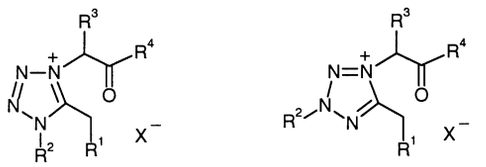


1a R^1 = Ac, R^2 = H
b R^1 = CO_2Me, R^2 = H
c R^1 = Ac, R^2 = Me
d R^1 = H, R^2 = Ph
e R^1 = Ac, R^2 = Ph

1f R^3 = H, R^4 = Ph
g R^3 = Me, R^4 = Ph
h R^3 = H, R^4 = Q
i R^3 = H, R^4 = Me
Q = 4-BrC_6H_4

2a R^1 = Ac, R^2 = Me
b R^1 = CO_2Me, R^2 = Me
c R^1 = Ac, R^2 = Ph



3 **4**

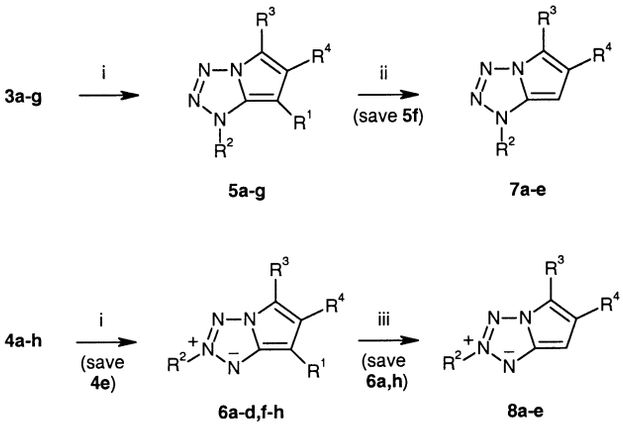
3	R^1	R^2	R^3	R^4	X	4
a	Ac	Me	H	Ph	BF_4	**a**
b	CO_2Me	Me	H	Ph	Z[a]	**b**
c	CO_2Me	Me	Me	Ph	$MeOSO_3$	**c**
d	CO_2Me	Me	H	4-BrC_6H_4	Z[a]	**d**
e	Ac	Me	H	Me	BF_4	**e**
f	CO_2Me	Me	H	Me	Z[a]	**f**
g	Ac	Ph	H	Ph	BF_4	**g**
	Ac	Ph	H	Me	BF_4	**h**

[a] Z = $MeOSO_3$ (with **3**; with **4** from **1**) or BF_4 (with **4** from **2**).

Scheme 2 *Reagents and conditions*: i, $BrCH_2COR^4$–$AgBF_4$, warm; ii, $(MeO)_2SO_2$, rt; iii, $BrCH_2COR^4$–$AgBF_4$ (for **4a**, **b**, **d**, **g**) or ICH_2-COMe–$AgBF_4$ (for **4e**, **f**, **h**), warm.

respectively. To provide the earlier described **1e**,[12a] we more practically condensed **1d** with ethyl acetate in the presence of base (*cf.* ref. 12*b*). The derivative **2c** was advantageously prepared by adoption of the ring transformation process reported for 5-methyl-3-[(nitrophenyl)triazeno)]isoxazoles.[13] However, success with the present phenyl analogue required an inverse protocol for making the starting triazene: here the areneamine, *i.e.* aniline, had to be treated with the diazotised isoxazolamine (instead of reacting benzenediazonium chloride with the isoxazolamine as suggested by the procedure efficient with the nitrophenyl derivatives[13]). Failing this, 1,3-diphenyltriazene was the sole product. We also tried to obtain **2a** in that modified way but could only observe the formation of the corresponding 1,3-bis(isoxazolyl)triazene.

Cyclisation of the substrates **3** and **4** was first attempted by heating **3a** with aqueous sodium hydrogencarbonate, *i.e.* by applying the traditional base. The material obtained indeed turned out to be the desired compound **5a**. But as the yield was very poor (< 5%), we repeated the reaction using sodium acetate in acetic acid (the latter for activation of the carbonyl group[14]) (Scheme 3). This modification resulted in a considerable improvement; the method was then applied to both the analogues **3e**,**g** and the ester-functionalised derivatives **3b**–**d**,**f**. Regarding cyclisation of the latter, there was no appreciable change in reactivity. Since the precursors **3b**–**d**,**f** were accompanied by minor quantities of the isomers **4b**–**d**,**f** (X = $MeOSO_3$; *vide supra*), we checked the mother liquor of **5b**,**c** for derivatives **6b**,**c** and found that some were formed, **6c** being isolated in turn (20% yield). This led us to extend the above procedure to the separately prepared salts **4a**,**b**,**d**–**h** (X = BF_4); as expected, all of these (save **4e**) gave the desired pyrrolotetrazoles **6**.



5a-g **7a-e** **6a-d,f-h** **8a-e**

5, 6	R^1	R^2	R^3	R^4	7	8
a	Ac	Me	H	Ph	**a**[a]	
b	CO_2Me	Me	H	Ph	**a**[a]	**a**[a]
c	CO_2Me	Me	Me	Ph	**b**	**b**
d	CO_2Me	Me	H	4-BrC_6H_4	**c**	**c**
e	Ac	Me	H	Me	**d**[a]	
f	CO_2Me	Me	H	Me		**d**[a]
g	Ac	Ph	H	Ph	**e**	**e**
h	Ac	Ph	H	Me		

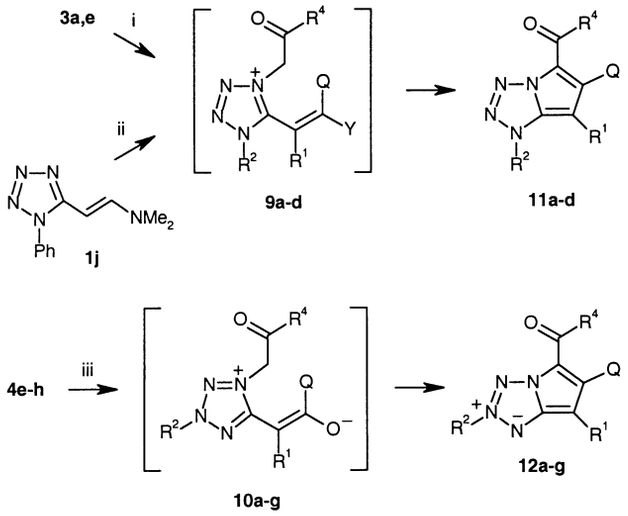
[a] Positioning of compound number is to indicate the preparative route, *e.g.*, **7a** was obtained from both **5a** and **5b**, whereas **8a** was made from **6b** only.

Scheme 3 *Reagents and conditions*: i, NaOAc–AcOH, heat; ii, 6–12 M HCl, heat (with **5c**,**d**: KOH–EtOH; then 12 M HCl, heat); iii, 12 M HCl, heat.

Defunctionalisation of **5** and **6** could be achieved easily with mineral acid (*cf.* refs. 4*a*, 10), but in the case of **5c**,**d** prolonged heating with alkali was required for hydrolysis of the ester group. Regarding the two different routes shown for **7a**, the second approach (**1b**→**1f**→**3b**→**5b**→**7a**) proved altogether the more convenient one.

Cyclisation of **3** and **4** in the presence of an acylating agent leads to the pyrrolotetrazoles **11** and **12** (Scheme 4). This kind of reaction has already been described for the salt **3a** which on treatment with acetic anhydride and triethylamine gave compound **11c** along with some **11d**.[8b] In like manner we now obtained analogous 2*H*-isomers: (i) **12e** from **4f**, (ii) a mixture of **12f** and **12g** from **4g** (in parallel with the finding with **3a**), and (iii) **12g** from **4h**. Formylating agents converted **3e** and **4e**–**h** into the 6-unsubstituted derivatives **11a** and **12a**–**d**, respectively; the corresponding 6-methyl congeners of **12a**–**d** which are conceivable side products were not observed. These cyclisations proceed *via* intermediates such as **9** and **10** (*cf.* refs. 15, 16). Accordingly, the enamine **1j**, after being phenacylated to **9b**, could also be transformed into a derivative of type **11**, albeit in low yield (*cf.* ref. 16*a*).

Formation of the crucial intermediates **9** and **10** will fail if the acylating compound acts as a dehydrating agent (and thereby leads to **5** and **6**). For example, treatment of the salt **3b** (Z = Br) with *N*,*N*-dimethylformamide diethyl acetal (DMF–DEA), instead of generating **9e**, gave rise to the pyrrolotetrazole **5b** (*cf.* ref. 16*b*) (Scheme 5).[17] Likewise, triethyl orthoformate, while suitable for making **11a**, did not convert the salt **4h** into the expected compound **12d** [*via* **10d** (OEt in place of O^-)] but produced a mixture of **6h** and the 5-acetyl



9, 11	(from)	Q	Y	R^1	R^2	R^4	10, 12	(from)
a[a]	(**3e**)	H	OEt	Ac	Me	Me	**a**	(**4e**)
		H		CO_2Me	Me	Me	**b**	(**4f**)
		H		Ac	Ph	Ph	**c**	(**4g**)
		H		Ac	Ph	Me	**d**	(**4h**)
b[a]	(**1j**)	H	NMe_2	H	Ph	Ph		
c	(**3a**)	Me	O^-	Ac	Me	Ph		
d	(**3a**)	Me	O^-	Ac	Me	Me		
		Me		CO_2Me	Me	Me	**e**	(**4f**)
		Me		Ac	Ph	Ph	**f**	(**4g**)
		Me		Ac	Ph	Me	**g**	(**4g,h**)

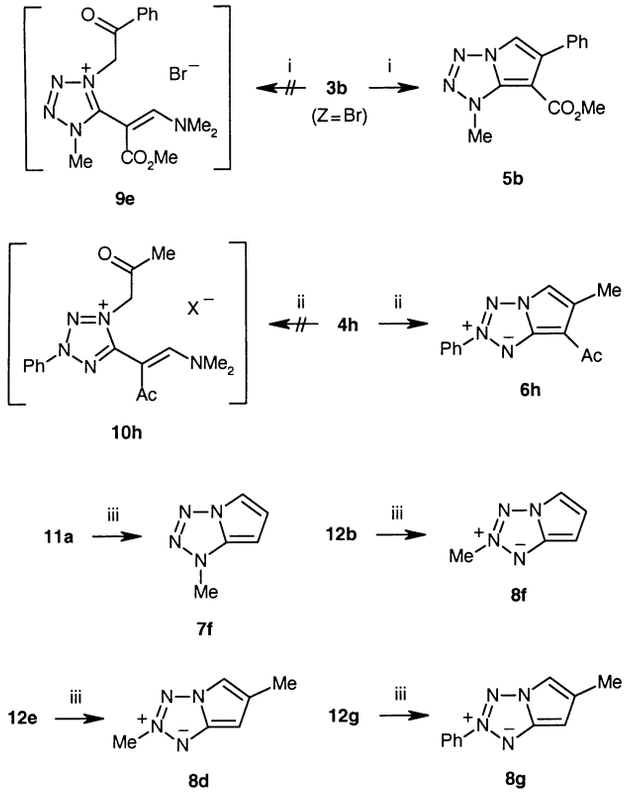
[a] Anion of **9a,b** (BF_4 and Br, respectively) omitted.

Scheme 4 *Reagents and conditions*: i, Ac_2O–Et_3N, heat (with **3a**; *cf.* ref. 8*b*); $HC(OEt)_3$, heat; then base, heat (with **3e**); ii, $BrCH_2COPh$, warm; then NaOAc–AcOH, heat; iii, Ac_2O–Et_3N, heat (with **4f**–**h**); HCOOAc–Et_3N, warm (with **4e**–**h**).

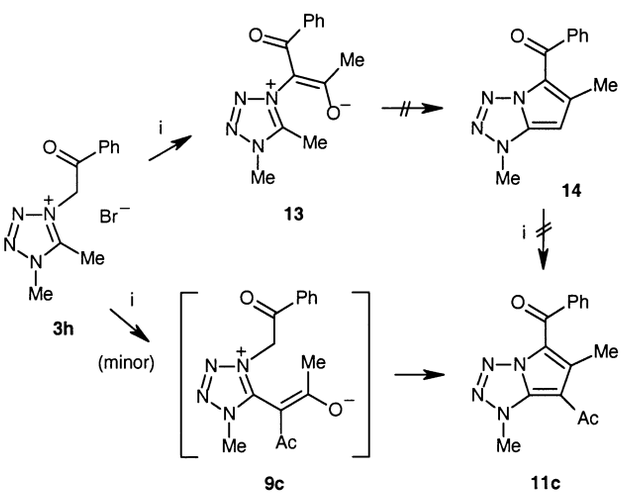
derivative of **8a** (with the latter predominating).[18] Vilsmeier reagent also showed this unwanted behaviour in that it gave rise to **6h** instead of **10h**.[18] Moreover, it may transform acetyl functions into 1-chloro-2-formylvinyl groups; we encountered this trouble in the course of making **11a**.[17]

Removal of the functional groups from the cyclisation products **11** and **12** is partly feasible, rendering **11a** and **12b**,**e**,**g** suitable precursors of the pyrrolotetrazoles **7a** and **8f**,**d**,**g**, respectively (Scheme 5); the low yields of the parent substances **7f** and **8f** reflect the instability typical of azapentalenes which have an unsubstituted pyrrolic half-ring (*cf.* ref. 10*c*). As observed with **12e** and **12g**, defunctionalisation proceeds stepwise, with the group attached to C-5 being removed first.[18] Interestingly, efforts to convert **11b**[17] as well as **12a**,**c**,**d**[18] into the deacylated pyrrolotetrazoles remained unrewarded.

It is well known that diacylpyrroloazoles related to **11** can also be obtained on heating the corresponding *C*-methylazolium salts **II** with an acylating agent and base.[10d,19] In the tetrazole series, however, this reaction does not take place to a considerable extent: treatment of the salt **3h** or its *N*-acetonyl congener with acetic anhydride–triethylamine at elevated temperature gave only small amounts of the expected compounds **11c** (2%)[17] and **11d** (6%).[8b] Minor quantities of these materials (3% and < 1%, respectively)[8b] were also observed as side products during the preparation of the *N*-ylide **13** from the salt **3h**. Regarding the mechanism, there is evidence (from a series of model reactions[17]) that **11c** (Scheme 6) does not arise *via* anhydride-mediated cyclisation of **13** into the benzoyl derivative **14**, followed by acetylation of the latter (as one might suppose in view of the theory advanced in ref. 10*d*), nor does **11d** originate from **11c**. Precursors of these products should be



Scheme 5 *Reagents and conditions*: i, DMF–DEA, heat; ii, DMF–$POCl_3$, rt, then heat; iii, 12 M HCl, heat.



Scheme 6 *Reagents and conditions*: i, Ac_2O–Et_3N, rt.

the '*C*-ylides' **9c** and **9d** (the latter formally derived from **9c** by benzoyl–acetyl exchange). Indeed, heating of separately prepared **9c** with acetic anhydride and base not only gave the bicycle **11c** but in addition the diacetyl congener **11d** (ratio 1:2).[17] This experiment may likewise illuminate the joint formation of the two pyrrolotetrazoles **12f** and **12g** from the salt **4g** shown in Scheme 4.

Properties

The prepared pyrrolotetrazoles are well crystallised, reasonably stable substances that can be stored for a prolonged period of time. Limitations to storage (even below 0 °C) concern only derivatives devoid of a *C*-attached phenyl, acyl or ester group, *i.e.* the compounds **7d** and **8d**,**g**; especially unstable are the parents **7f** and **8f** (*cf. supra*). The 1*H*-pyrrolotetrazoles are colourless materials (in contrast to the 2*H*-isomers), but should be protected from light, in particular representatives having an

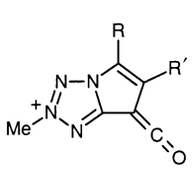
Table 1 Comparison of UV–vis spectra (λ_{max} > 210 nm) of selected pairs of isomeric pyrrolotetrazoles **5**–**6** and **7**–**8** (including fluorescence data of two derivatives of the series **7** and **8**)

Compound	λ_{max} [MeOH]/nm (log ε)	Compound	λ_{max} [MeOH]/nm (log ε)
5a	310 (3.97), 223 (4.27)	**6a**	357 (3.90), 282 (4.23), 220 (4.32)
5b	302 (3.83), 257 (4.34), 220 (4.43)	**6b**[b]	356 (3.97), 267 (4.37), 233 (4.41)
5f	297 (3.47), 263 (3.97), 221 (4.07)	**6f**	350 (3.71), 257 (4.27)
7a	324 (3.45), 268 (4.26), 243 (4.22)	**8a**[b]	377 (3.57), 296 (4.08), 271 (4.23), 245 (4.29)
7a–Ac[a]	326 (4.19), 259 (4.04), 222 (4.10)	**8a**–Ac[c]	323 (4.19), 261 (4.04)
7b	338 (3.34), 2.64 (4.15)	**8b**	392 (3.53), 293 (4.03), 278 (4.07)
7e	342 (3.68), 279 (4.32), 249 (4.41)	**8e**	426 (3.74), 331 (4.32), 254 (4.32)

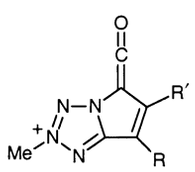
[a] 5-Acetyl-1-methyl-6-phenyl-1*H*-pyrrolo[1,2-*d*]tetrazole (for preparation, see ref. 21). [b] Fluorescence (excitation wavelength 350 nm): λ_{max} 481 [CCl_4]/489 [MeOH] (**6b**); 520 and 495 nm [CCl_4] (**8a**; no fluorescence in MeOH). [c] 5-Acetyl-2-methyl-6-phenyl-2*H*-pyrrolo[1,2-*d*]tetrazole (for preparation, see ref. 21).

unsubstituted 5-position. The 2*H*-isomers, on the whole, are photochemically less sensitive.

In agreement with the properties of related *mesoionic* azapentalenes,[5c,20] the electronic spectra of the 2*H*-pyrrolotetrazoles are characterised by a pronounced bathochromic shift of the longest wavelength compared to that of the 1*H*-isomers (see Table 1; the 5-acetyl derivative is an exception); they also display green or blue fluorescence (*cf.* ref. 6*c*). Within either series common substituent effects become apparent on going (i) from the derivatives **7a/8a** to **7b/8b**, (ii) from **7a/8a** to **5a**,**b**/**6a**,**b**, and (iii) from **7a/8a** to **7e/8e**; the extreme bathochromic shift observed with **8e** reflects the unhindered conjugative interaction of the phenyl group and the heterocycle, which is not possible to that extent with **7e**. Likewise in accord with the literature,[5c,20] the ^{13}C NMR spectra of the 2*H*-derivatives show a marked deshielding of the bridgehead carbon atom compared to the 1*H*-series (Table 2). A salient mass spectrometric feature constitutes intense [M − 15] and [M − 31] peaks observed with the acetyl and ester derivatives of the 2*H*-system (Table 3; *cf.* also ref. 5*c*). These signals can be assigned to the ketenic species **15** and **16**; thus, from the doubly functionalised compound **12b** both **15b** and **16b** arise. The 1*H*-isomers do not



15a R = H, R′ = Ph
b R = Ac, R′ = H



16a R = H, R′ = Ph
b R = CO_2Me, R′ = H

produce fragments of that kind, since here loss of molecular nitrogen from the tetrazolic half-ring predominates. Regarding IR spectra, the ketonic and ester derivatives of either title system exhibit, as known from monocyclic pyrroles, low-frequency carbonyl absorptions; 5-unsubstituted representatives are characterised by a sharp C–H absorption at ≥ 3130 cm^{-1}.

We have shown that the originally desired pyrrolotetrazoles **III** and **VI** (Scheme 1) are readily accessible *via* vicarious cyclisations of acceptor-substituted tetrazolium salts. In the following paper[21] we will report on S_E-reactions of these systems.

Experimental

Mps were determined on a Kofler microscope. IR spectra were taken on Pye-Unicam SP 1100, SP3-200 or Philips PU-9800 FTIR instruments. ^1H NMR spectra were run on a Varian EM-390 or Bruker AM 400 spectrometer (*J*- and *N*-values in Hz); ^{13}C NMR spectra were recorded on a Bruker AM 400 instrument (tetramethylsilane or $CDCl_3$ as internal standard). UV–vis spectra were determined on a Philips PU-8730 spectrometer. Fluorescence spectra were measured on a Kontron SFM 25 instrument. Mass spectra were taken on a Finnigan MAT 8430/8400 machine.

Tetrazoles **1a**,[22] **1b**,[23] **1c**,[7] **1d**,[24] **1j**[25] and **2b**[23] were made by literature procedures, as were the tetrazolium salt **3a**,[7] silver tetrafluoroborate[26] and the precursor of **1a**, *6-methylpyrimidin-4(3H)-one*.[27] **CAUTION**: Regarding preparation of the latter, application of the alternate method described in ref. 28 is strongly discouraged, since we experienced a violent explosion after the reaction mixture had been partly concentrated *in vacuo*!

(1-Phenyl-1*H*-tetrazol-5-yl)acetone 1e

To a solution of potassium *tert*-butoxide (3.36 g, 30 mmol) in anhydrous THF (40 cm^3) were added successively with stirring at 0 °C the 1*H*-tetrazole **1d** (1.60 g, 10 mmol) and ethyl acetate (1.76 g, 20 mmol). The mixture was heated under reflux for 30 min, concentrated to half its volume, diluted with water (20 cm^3) and acidified with 12 M HCl. The product was extracted with dichloromethane and recrystallised from ethanol; yield 1.47 g (73%), mp 101–103 °C (lit.,[12a] 103–104.5 °C); ν_{max}(KBr)/cm^{-1} 1715; δ_H($CDCl_3$) 2.28 (3 H, s), 4.14 (2 H, s), 7.41–7.50 (2 H, m) and 7.54–7.61 (3 H, m); δ_C($CDCl_3$) 30.0 (q), 38.4 (t), 125.1 (2 × d), 130.0 (2 × d), 130.8 (d), 133.5 (s), 149.6 (s) and 200.2 (s).

(Substituted) methyl (1-phenacyl/acetonyl-1*H*-tetrazol-5-yl)-acetates 1f–i. General procedure

To a cooled suspension of the *N*-unsubstituted tetrazole **1b** (2.84 g, 20 mmol) and the respective α-bromoketone (20 mmol) in acetone (20 cm^3) was added dropwise triethylamine (2.02 g, 20 mmol). The mixture was stirred at room temperature for 1 h whereupon the precipitate of triethylammonium bromide was filtered off. The products were isolated from the concentrated filtrate as follows: **1f**–**h** by crystallisation from acetone–diethyl ether; **1i** by column chromatography on silica gel using chloroform–ethyl acetate (4 : 1) as eluent [with the first fraction being the 2*H*-isomer *methyl (2-acetonyl-2H-tetrazol-5-yl)-acetate*].

1f: Yield 1.92 g (37%), mp 103–104 °C (Found: C, 55.4; H, 4.7; N, 21.5. $C_{12}H_{12}N_4O_3$ requires C, 55.4; H, 4.65; N, 21.5%); ν_{max}(KBr)/cm^{-1} 1745 and 1695; δ_H($CDCl_3$) 3.71 (3 H, s), 4.10 (2 H, s), 6.10 (2 H, s), 7.45–7.82 (3 H, m) and 7.95–8.13 (2 H, m); δ_C($CDCl_3$) 29.9 (t), 53.0 (q), 53.6 (t), 128.3 (2 × d), 129.3 (2 × d), 133.5 (s), 135.0 (d), 150.6 (s), 167.4 (s) and 189.5 (s).

1g: Yield 1.40 g (26%), mp 78–81 °C (Found: C, 57.0; H, 5.3; N, 20.3. $C_{13}H_{14}N_4O_3$ requires C, 56.9; H, 5.15; N, 20.4%); ν_{max}(KBr)/cm^{-1} 1745 and 1695; δ_H($CDCl_3$) 2.02 (3 H, d, *J* 7.4), 3.63 (3 H, s), 3.94/4.14 (2 H, AB, *J* 17.1), 6.41 (1 H, q, *J* 7.4), 7.52–7.56 (2 H, m), 7.65–7.69 (1 H, m) and 7.96–7.99 (2 H, m); δ_C($CDCl_3$) 17.6 (q), 30.2 (t), 53.0 (q), 59.3 (d), 128.7 (2 × d),

Table 2 Comparison of ^{1}H and ^{13}C NMR data of selected pairs of isomeric pyrrolotetrazoles **5**–**6**, **7**–**8** and **11**–**12**

	δ_H ($CDCl_3$)[a]					δ_C ($CDCl_3$)[a]					
Compound	5-H	6-H	7-H	NMe	Other	C-5	C-6	C-7	C-7a	NMe	Other
5a	7.11			4.54	1.92 (3 H), 7.39–7.46 (5 H, m)	102.5 (d)	134.8[b]	97.6	136.4[b]	37.4 (q)	29.0 (q), 128.1 (d), 128.2 (2 × d), 129.9 (2 × d), 134.7 (C-1 of Ph),[b] 192.0
6a	7.15			4.41	2.46 (3 H), 7.35–7.41 (3 H, m), 7.54–7.57 (2 H, m)	101.1 (d)	138.8	96.5	149.8	41.9 (q)	29.4 (q), 127.84 (2 × d), 127.86 (d), 129.7 (2 × d), 134.3, 189.4
7d	6.99[c]		5.33[d]	3.94	2.27 (3 H)	99.7 (d)	129.8[b]	74.0 (d)	132.9[b]	34.3 (q)	13.5 (q)
8d	6.96[e]		5.69[e]	4.28	2.34 (3 H)	96.1 (d)	133.0	78.9 (d)	146.4	41.0 (q)	13.8 (q)
7f	7.17[f]	6.70[g]	5.49[h]	4.00		99.2 (d)	119.4 (d)	83.1 (d)	129.6	34.4 (q)	
8f	7.14[i]	6.94[j]	5.88[k]	4.33		96.9 (d)	120.6 (d)	78.2 (d)	146.6	41.3 (q)	
11a		7.67		4.57	2.48 (3 H), 2.59 (3 H)	118.6	125.9 (d)	99.8	137.6	37.5 (q)	26.4 (q), 26.7 (q), 184.9, 191.0
12a		7.94		4.62	2.54 (3 H), 2.60 (3 H)	117.5	127.4 (d)	102.1	149.6	42.5 (q)	25.7 (q), 27.7 (q), 184.6, 189.6

[a] Unspecified signals are singlets. [b] Discerned by means of a C,H-COLOC experiment (*cf.* ref. 11*b*). [c] (d, *J* 1.4). [d] (d, *J* 1.4). [e] Coupling not observed. [f] (dd, *J* 2.8, 1.1). [g] (dd, *J* 3.8, 2.8). [h] (dd, *J* 3.8, 1.1). [i] (dd, *J* 2.6, 1.1). [j] (dd, *J* 4.3, 2.6). [k] (dd, *J* 4.3, 1.1).

129.3 (2 × d), 133.5 (s), 134.6 (d), 149.2 (s), 167.2 (s) and 193.4 (s).

1h: Yield 2.15 g (32%), mp 142–146 °C (Found: C, 42.4; H, 3.3; N, 16.4. $C_{12}H_{11}BrN_4O_3$ requires C, 42.5; H, 3.3; N, 16.5%); ν_{max}(KBr)/cm^{-1} 1750 and 1695; δ_H($CDCl_3$) 3.72 (3 H, s), 4.10 (2 H, s), 6.04 (2 H, s) and 7.74/7.91 (4 H, AA′BB′, *N* 8).

1i: Yield 1.03 g (26%), oil; δ_H($CDCl_3$) 2.32 (3 H, s), 3.72 (3 H, s), 4.04 (2 H, s) and 5.43 (2 H, s); δ_C($CDCl_3$) 27.3 (q), 29.8 (t), 53.1 (q), 56.3 (t), 150.1 (s), 167.4 (s) and 198.1 (s).—2*H*-Isomer of **1i**: Yield 0.35 g (9%), oil; δ_H($CDCl_3$) 2.23 (3 H, s), 3.75 (3 H, s), 4.03 (2 H, s) and 5.46 (2 H, s); δ_C($CDCl_3$) 27.1 (q), 31.6 (t), 52.6 (q), 60.9 (t), 160.7 (s), 168.6 (s) and 197.7 (s).

(2-Methyl-2*H*-tetrazol-5-yl)acetone 2a

To a solution of the *N*-unsubstituted tetrazole **1a** (0.99 g, 7.8 mmol) and triethylamine (0.81 g, 8.0 mmol) in acetone (30 cm^3) was added methyl iodide (1.14 g, 8.0 mmol) in the same solvent (*ca*. 15 cm^3). The mixture was heated under reflux for 18 h and then kept at 5–10 °C for 10 h whereupon the triethylammonium iodide was filtered off. The filtrate was concentrated and the residue chromatographed on silica gel using chloroform–diethyl ether (10 : 3) as eluent to afford successively: the product **2a** and its 1*H*-isomer *(1-methyl-1H-tetrazol-5-yl)acetone* **1c** (0.45 g, 41%; identical with the material described in ref. 7). Yield 0.63 g (58%), mp 50 °C (from dichloromethane–diethyl ether) (Found: C, 42.5; H, 5.9; N, 40.3. $C_5H_8N_4O$ requires C, 42.85; H, 5.75; N, 40.0%); ν_{max}(KBr)/cm^{-1} 1721; δ_H($CDCl_3$) 2.29 (3 H, s), 4.05 (2 H, s) and 4.36 (3 H, s); δ_C($CDCl_3$) 29.6 (q), 39.4 (q), 40.3 (t), 160.2 (s) and 202.0 (s).

(2-Phenyl-2*H*-tetrazol-5-yl)acetone 2c

To a vigorously stirred solution of 5-methylisoxazol-3-amine (2.00 g, 20.4 mmol) in 4 M HCl (30 cm^3), cooled below 5 °C, was rapidly added sodium nitrite (1.90 g, 27.5 mmol) in the minimum amount of water. After 45 min the mixture was treated with urea and extracted with dichloromethane (2 × 30 cm^3). The aqueous layer was added to a stirred solution of aniline (1.86 g, 20.0 mmol) in water (50 cm^3) at 5 °C. The yellow precipitate was filtered off 30 min later, dissolved in acetone (50 cm^3) and, after addition of 3 M NH_3 (10 cm^3), heated at 50 °C for 10 min. The mixture was cooled to 5 °C and diluted with water (100 cm^3) whereupon the product precipitated. It was collected by filtration and purified through column chromatography on silica gel using petroleum ether–ethyl acetate (10 : 3) as eluent. Yield 2.31 g (57%), mp 95–96 °C (from petroleum ether–ethyl acetate) (Found: C, 59.2; H, 5.1; N, 27.8. $C_{10}H_{10}N_4O$ requires C, 59.4; H, 5.0; N, 27.7%); ν_{max}(KBr)/cm^{-1} 1710; δ_H($CDCl_3$) 2.33 (3 H, s), 4.15 (2 H, s), 7.47–7.58 (3 H, m) and 8.09–8.13 (2 H, m); δ_C($CDCl_3$) 29.8 (q), 40.6 (t), 119.9 (2 × d), 129.7 (2 × d), 129.8 (d), 136.7 (s), 160.5 (s) and 201.8 (s).

Quaternisation of the 1*H*-tetrazoles 1f–i. General procedure

A mixture of the respective 1*H*-tetrazole **1** (10 mmol) and dimethyl sulfate (6.30 g, 50 mmol) was kept at room temperature for 48 h [in the case of **1h**, the mixture was diluted with chloroform (10 cm^3) and heated under reflux for 1 h prior to treatment as above]. Then the unconsumed reagent was removed by shaking with diethyl ether (4 × 20 cm^3) and the residual oil consisting of an inseparable mixture of *1,4-disubstituted* and *2,4-disubstituted 5-(methoxycarbonylmethyl)tetrazolium methylsulfate* **3b**–**d**,**f** and **4b**–**d**,**f**, respectively, was directly used for cyclisation as shown below.

3b–**4b** (Z = $MeOSO_3$) (7 : 3): δ_H[$(CD_3)_2SO$] 3.69 (2.1 H, s)/3.64 (0.9 H, s), 4.44 (2.1 H, s)/4.80 (0.9 H, s), 4.88 (1.4 H, s)/4.67 (0.6 H, s), 6.76 (1.4 H, s)/6.81 (0.6 H, s), 7.64–7.68 (2 H, m), 7.79–7.82 (1 H, m) and 8.07–8.09 (2 H, m).

3c–**4c** (7 : 3): δ_H[$(CD_3)_2SO$] 1.95 (3 H, d), 3.53 (2.1 H, s)/3.48

Table 3 Comparison of EI mass spectra (significant peaks) of selected isomeric pyrrolotetrazoles **5**–**6** and **7**–**8** (including the spectrum of **12b**)

Compound	*m*/*z* (70 eV)[a] (%)	Compound	*m*/*z* (70 eV)[a] (%)
5a	240 (M^+, 38), 212 (14), 142 (100)	**6a**	240 (M^+, 60), 225[d] (100), 43 (8)
5b	256 (M^+, 47), 225 (2), 196 (81), 142 (100)	**6b**	256 (M^+, 100), 225[d] (44), 43 (32)
7a	198 (M^+, 8), 170 (23), 143 (39), 102 (100)	**8a**	198 (M^+, 66), 102 (68), 43 (100)
7a–Ac[b]	240 (M^+, 37), 169 (100), 43 (11)	**8a**–Ac[c]	240 (M^+, 100), 225[e] (78), 43 (62)
7b	212 (M^+, 28), 184 (29), 143 (26), 102 (100)	**8b**	212 (M^+, 74), 102 (77), 43 (100)
		12b	222 (M^+, 100), 207[f] (84), 191[g] (80), 43 (46)

[a] Ion-source temperature, °C: **5a**, 25; **5b**, 71; **6a**, 100; **6b**, 29; **7a**, 82; **7a**–Ac, 35; **7b**, 20; **8a**, 73; **8a**–Ac, 70; **8b**, 51; **12b**, 80. [b] 5-Acetyl-1-methyl-6-phenyl-1*H*-pyrrolo[1,2-*d*]tetrazole (for preparation, see ref. 21). [c] 5-Acetyl-2-methyl-6-phenyl-2*H*-pyrrolo[1,2-*d*]tetrazole (for preparation, see ref. 21). [d–g] Peaks corresponding to **15a**, **16a**, **15b** and **16b**, respectively.

(0.9 H, s), 4.43 (2.1 H, s)/4.83 (0.9 H, s), 4.96 (1.4 H, s)/4.33 (0.6 H, s), 7.22 (1 H, m), 7.56–7.88 (3 H, m) and 8.10–8.24 (2 H, m).

3d–**4d** (Z = $MeOSO_3$) (6 : 4): δ_H[$(CD_3)_2SO$] 3.73 (1.8 H, s)/3.66 (1.2 H, s), 4.46 (1.8 H, s)/4.82 (1.2 H, s), 4.91 (1.2 H, s)/4.67 (0.8 H, s), 6.79 (1.2 H, s)/6.83 (0.8 H, s), 7.86–8.15 (4 H, AA′BB′).

3f–**4f** (Z = $MeOSO_3$) (6 : 4): δ_H[$(CD_3)_2SO$] 2.35 (3 H, s); 3.73 (3 H, s), 4.41 (1.8 H, s)/4.76 (1.2 H, s), 4.82 (1.2 H, s)/4.57 (0.8 H, s), 6.08 (1.2 H, s)/6.11 (0.8 H, s).

4,5-Diacetonyl-1-methyl-1*H*-tetrazolium tetrafluoroborate 3e

To a solution of the 1*H*-tetrazole **1c** (1.40 g, 10 mmol) in anhydrous nitromethane (20 cm^3) were added successively bromoacetone (i; 1.03 g, 8 mmol) and silver tetrafluoroborate (ii; 0.98 g, 5 mmol). The mixture was warmed at 50–55 °C for a total of 12 d, while fresh reagents (i and ii, amounts as above) were added twice at equal intervals. Filtration of silver bromide followed by concentration of the filtrate *in vacuo* gave an oily residue which, after extraction with boiling diethyl ether, was crystallised from methanol–diethyl ether. Yield 0.93 g (33%), mp 124–127 °C (Found: C, 33.75; H, 4.6; N, 19.6. $[C_8H_{13}N_4O_2]BF_4$ requires C, 33.8; H, 4.6; N, 19.7%); ν_{max}(KBr)/cm^{-1} 1735; δ_H[$(CD_3)_2SO$] 2.31 (6 H, s), 4.30 (3 H, s), 4.88 (2 H, s) and 5.93 (2 H, s); δ_C[$(CD_3)_2SO$] 26.9 (q), 29.9 (q), 36.4 (t), 37.2 (q), 58.1 (t), 150.6 (s), 197.66 (s) and 197.73 (s).

Quaternisation of the 1*H*-tetrazole 1e

To a solution of the 1*H*-tetrazole **1e** (2.02 g, 10 mmol) in anhydrous nitromethane (20 cm^3) were added phenacyl bromide (1.99 g, 10 mmol) and silver tetrafluoroborate (1.95 g, 10 mmol), and the mixture was heated at 70 °C for 7 d. Work-up as detailed with the salt **3e** gave 2.00 g of a crystalline material which, according to NMR (see below), was a 1 : 1 mixture of *5-acetonyl-4-phenacyl-1-phenyl-* **3g** and *5-acetonyl-3-phenacyl-1-phenyl-1H-tetrazolium tetrafluoroborate* **X**. Since separation of the desired component **3g** failed, the mixture was reacted further as such. **3g**–**X** (1 : 1): δ_H[$(CD_3)_2SO$] 2.18 (1.5 H, s)/1.99 (1.5 H, s), 5.37 (1 H, s)/5.09 (1 H, s), 6.62 (1 H, s)/6.81 (1 H, s), 7.60–7.95, 8.14–8.20 (10 H, m).

2,4-Disubstituted 5-acetonyl/(methoxycarbonylmethyl)-2*H*-tetrazolium tetrafluoroborates 4a,b,d–h. General procedure

A mixture of the appropriate 2*H*-tetrazole **2** (10 mmol), the respective α-bromoketone (12 mmol) and silver tetrafluoroborate (2.34 g, 12 mmol) in anhydrous nitromethane (20 cm^3) was stirred at 60 °C for 14 d (**4a**,**g**) or 10 d (**4b**,**d**). In the case of **4e**,**f** and **h**, the reagents [iodoacetone (2.21 g, 12 mmol) and silver tetrafluoroborate (2.34 g, 12 mmol)] were added portionwise at several intervals over a period of 10, 7 and 14 d, respectively. Work-up as above afforded a sticky oil which, after repeated extraction with diethyl ether and acetone–diethyl ether (3 : 8), was crystallised from methanol–chloroform–diethyl ether (attempts to crystallise **4e** failed). Purification was effected by recrystallisation from ethanol–diethyl ether (**4a**,**b**,**d**,**f**), acetone–dichloromethane (**4h**) or ethanol–dichloromethane–diethyl ether (**4g**); analytical figures of **4a**,**f**–**h** were only approximate.

4a: Yield 1.97 g (57%), mp 159–161 °C; ν_{max}(KBr)/cm^{-1} 1726 and 1699; δ_H[$(CD_3)_2SO$] 2.27 (3 H, s), 4.77 (2 H, s), 4.79 (3 H, s), 6.69 (2 H, s), 7.64–7.68 (2 H, m), 7.78–7.82 (1 H, m) and 8.07–8.31 (2 H, m); δ_C[$(CD_3)_2SO$] 29.7 (q), 37.5 (t), 43.8 (q), 56.4 (t), 128.6 (2 × d), 129.0 (2 × d), 133.1 (s), 134.9 (d), 157.2 (s), 188.5 (s) and 199.5 (s).

4b: Yield 2.95 g (81%), mp 123–124 °C (Found: C, 43.2; H, 4.1; N, 15.3. $[C_{13}H_{15}N_4O_3]BF_4$ requires C, 43.1; H, 4.2; N, 15.5%); ν_{max}(KBr)/cm^{-1} 1760 and 1709; δ_H[$(CD_3)_2SO$] 3.65 (3 H, s), 4.67 (2 H, s), 4.80 (3 H, s), 6.81 (2 H, s), 7.65–7.69 (2 H, m), 7.78–7.83 (1 H, m) and 8.07–8.10 (2 H, m); δ_C[$(CD_3)_2SO$] 29.3 (t), 44.0 (q), 52.9 (q), 56.8 (t), 128.7 (2 × d), 129.1 (2 × d), 133.1 (s), 135.0 (d), 156.8 (s), 165.5 (s) and 188.7 (s).

4d: Yield 3.62 g (82%), mp 107–109 °C (Found: C, 35.15; H, 3.2; N, 12.5. $[C_{13}H_{14}BrN_4O_3]BF_4$ requires C, 35.4; H, 3.2; N, 12.7%); ν_{max}(KBr)/cm^{-1} 1737 and 1702; δ_H[$(CD_3)_2SO$] 3.65 (3 H, s), 4.67 (2 H, s), 4.80 (3 H, s), 6.78 (2 H, s) and 7.90/8.00 (4 H, AA′BB′, *N* 8); δ_C[$(CD_3)_2SO$] 29.3 (t), 44.0 (q), 53.0 (q), 56.7 (t), 129.2 (s), 130.6 (2 × d), 132.2 (2 × d), 132.3 (s), 156.8 (s), 165.5 (s) and 188.0 (s).

4e: Yield 1.62 g (57%), dark oil; ν_{max}(neat)/cm^{-1} 1732; δ_H(CF_3CO_2H; external C_6D_6) 2.712 (3 H, s), 2.714 (3 H, s), 4.83 (2 H, s), 4.91 (3 H, s) and 6.04 (2 H, s); δ_C(CF_3CO_2H; external C_6D_6) 26.3 (q), 29.0 (q), 37.9 (t), 43.3 (q), 58.9 (t), 157.3 (s), 200.2 (s) and 204.6 (s).

4f: Yield 1.80 g (60%), mp 145 °C; ν_{max}(KBr)/cm^{-1} 1745; δ_H(CF_3CO_2H; external C_6D_6) 2.58 (3 H, s), 3.94 (3 H, s), 4.46 (2 H, s), 4.74 (3 H, s) and 5.99 (2 H, s); δ_C(CF_3CO_2H; external C_6D_6) 26.2 (q), 30.0 (t), 43.4 (q), 54.4 (q), 59.4 (t), 157.3 (s), 168.1 (s) and 200.8 (s).

4g: Yield 3.26 g (80%), mp 210–211 °C; ν_{max}(KBr)/cm^{-1} 1728 and 1708; δ_H(CF_3CO_2H; external C_6D_6) 2.58 (3 H, s), 4.88 (2 H, s), 6.58 (2 H, s), 7.64–7.68 (2 H, m), 7.75–7.79 (2 H, m), 7.82–7.87 (2 H, m), 8.14–8.15 (2 H, m) and 8.28–8.30 (2 H, m); δ_C(CF_3CO_2H; external C_6H_6) 29.1 (q), 38.6 (t), 57.5 (t), 121.1 (2 × d), 129.0 (2 × d), 129.9 (2 × d), 130.9 (2 × d), 132.4 (s), 134.7 (d), 135.3 (s), 137.1 (d), 157.8 (s), 190.2 (s) and 205.8 (s).

4h: Yield 2.08 g (60%), mp 145 °C; ν_{max}(KBr)/cm^{-1} 1734; δ_H(CF_3CO_2H; external C_6D_6) 2.600 (3 H, s), 2.603 (3 H, s), 4.80 (2 H, s), 6.01 (2 H, s), 7.73–7.77 (2 H, m), 7.81–7.85 (1 H, m) and 8.23–8.26 (2 H, m); δ_C(CF_3CO_2H; external C_6D_6) 26.4 (q), 29.1 (q), 38.4 (t), 59.5 (t), 121.1 (2 × d), 130.9 (2 × d), 134.7 (d), 135.2 (s), 157.4 (s), 201.0 (s) and 205.4 (s).

7-Functionalised 1*H*- and 2*H*-pyrrolotetrazoles 5a–g and 6a–d,f–h. General procedure

A stirred mixture of the appropriate tetrazolium salt **3** (5 mmol) or **4** (4 mmol) and anhydrous sodium acetate [1.00 g, 12 mmol (with **3**); 2.00 g, 24 mmol (with **4**)] in acetic acid [10.0 g, 167 mmol (with **3**); 20.0 g, 334 mmol (with **4**)] was heated at 100–110 °C for 1 h (**4a**: 2 h); in the case of **3b**–**d**,**f**, the crude material containing **4b**–**d**,**f** was employed. For isolation of the products **5**, the cooled mixture was diluted with water (20 cm^3) and extracted with dichloromethane (3 × 20 cm^3); the combined

organic layers were washed with aqueous sodium carbonate and water, dried and concentrated. The residue was recrystallised from dichloromethane–light petroleum (**5a**), chloroform–diethyl ether (**5b**–**f**) or chloroform–light petroleum (**5g**). To isolate the products **6** (derivatives **a**,**b**,**d**,**f**–**h**), the reaction mixture was neutralised with aqueous sodium carbonate and extracted with dichloromethane (3 × 50 cm^3), and the residue of the combined organic layers was chromatographed on silica gel using chloroform–ethyl acetate (4 : 1) as eluent. To obtain **6c**, the mother liquor of **5c** was concentrated and chromatographed as above. Recrystallisation was effected with dichloromethane–diethyl ether (**6a**), chloroform–diethyl ether (**6b**–**d**), diethyl ether–light petroleum (**6f**), dichloromethane–light petroleum (**6g**) or dichloromethane–diethyl ether–light petroleum (**6h**).

5a: Yield 0.16 g (66%) [from 0.35 g (1 mmol) **3a**], mp 92–94 °C (lit.,[1] 92–94 °C) (Found: C, 64.95; H, 5.1; N, 23.4. $C_{13}H_{12}N_4O$ requires C, 65.0; H, 5.0; N, 23.3%); ν_{max}(KBr)/cm^{-1} 3155 and 1640; for δ_H and δ_C, see Table 2.

5b: Yield 0.73 g (82%; based on 7 : 3 mixture of **3b**–**4b**), mp 128–129 °C (lit.,[1] 128–129 °C) (Found: C, 61.0; H, 4.7; N, 21.9. $C_{13}H_{12}N_4O_2$ requires C, 60.9; H, 4.7; N, 21.9%); for ν_{max}/cm^{-1}, δ_H and δ_C, see ref. 1.

5c: Yield 0.49 g (52%; based on 7 : 3 mixture of **3c**–**4c**), mp 123–125 °C (Found: C, 62.4; H, 5.2; N, 20.7. $C_{14}H_{14}N_4O_2$ requires C, 62.2; H, 5.2; N, 20.7%); ν_{max}(KBr)/cm^{-1} 1713; δ_H($CDCl_3$) 2.39 (3 H, s), 3.65 (3 H, s), 4.39 (3 H, s) and 7.32–7.43 (5 H, m); δ_C($CDCl_3$) 9.1 (q), 36.7 (q), 50.4 (q), 83.0 (s), 111.4 (s), 127.2 (d), 127.6 (2 × d), 130.5 (2 × d), 130.8 (s), 134.0 (s), 134.8 (s) and 163.8 (s).

5d: Yield 0.71 g (64%; based on 6 : 4 mixture of **3d**–**4d**), mp 117–118 °C (lit.,[1] 114–116 °C) (Found: C, 46.6; H, 3.3; N, 16.7. $C_{13}H_{11}BrN_4O_2$ requires C, 46.6; H, 3.3; N, 16.7%); ν_{max}(KBr)/cm^{-1} 3160 and 1680; δ_H($CDCl_3$) 3.72 (3 H, s), 4.40 (3 H, s), 7.16 (1 H, s) and 7.35/7.51 (4 H, AA′BB′, *N* 8.6); δ_C($CDCl_3$) 36.8 (q), 50.7 (q), 83.5 (s), 102.6 (d), 121.9 (s), 130.9 (2 × d), 131.3 (2 × d), 133.0 (s), 134.5 (s), 136.2 (s) and 163.5 (s).

5e: Yield 0.77 g (86%), mp 152–154 °C (lit.,[1] 152–154 °C) (Found: C, 53.8; H, 5.7; N, 31.4. $C_8H_{10}N_4O$ requires C, 53.9; H, 5.7; N, 31.4%); ν_{max}(KBr)/cm^{-1} 3155 and 1630; δ_H($CDCl_3$) 2.42 (3 H, s), 2.44 (3 H, d, *J* 1.0), 4.49 (3 H, s) and 6.96 (1 H, d, *J* 1.0); δ_C($CDCl_3$) 14.9 (q), 29.3 (q), 37.4 (q), 98.0 (s), 102.6 (d), 129.0 (s), 136.9 (s) and 191.1 (s).

5f: Yield 0.33 g (57%), mp 105–108 °C (Found: C, 49.1; H, 5.3; N, 28.9. $C_8H_{10}N_4O_2$ requires C, 49.5; H, 5.2; N, 28.85%); ν_{max}(KBr)/cm^{-1} 3140 and 1685; δ_H($CDCl_3$) 2.39 (3 H, d, *J* 1.1), 3.83 (3 H, s), 4.34 (3 H, s) and 6.96 (1 H, d, *J* 1.1); δ_C($CDCl_3$) 13.4 (q), 36.3 (q), 50.5 (q), 84.5 (s), 102.2 (d), 131.3 (s), 135.8 (s) and 164.3 (s).

5g: Yield 0.62 g (82%; based on 1 : 1 mixture of **3g**–**X**), mp 95–96 °C (lit.,[1] 95–96 °C) (Found: C, 71.45; H, 4.6; N, 18.65. $C_{18}H_{14}N_4O$ requires C, 71.5; H, 4.7; N, 18.5%); ν_{max}(KBr)/cm^{-1} 3155 and 1630; δ_H($CDCl_3$) 1.89 (3 H, s), 7.24 (1 H, s), 7.40–7.45 (5 H, m) and 7.48–7.56 (5 H, m); δ_C($CDCl_3$) 29.4 (q), 98.4 (s), 102.7 (d), 125.7 (2 × d), 128.2 (d), 128.31 (2 × d), 128.33 (2 × d), 129.5 (d), 130.0 (2 × d), 133.7 (s), 134.7 (s), 134.9 (s), 135.4 (s) and 191.0 (s).

6a: Yield 0.10 g (10%), mp 167–169 °C (Found: C, 65.95; H, 5.05; N, 23.3. $C_{13}H_{12}N_4O$ requires C, 65.0; H, 5.0; N, 23.3%); ν_{max}(KBr)/cm^{-1} 3138 and 1630; for δ_H and δ_C, see Table 2.

6b: Yield 0.62 g (60%), mp 145–146 °C (Found: C, 60.6; H, 4.7; N, 21.8. $C_{13}H_{12}N_4O_2$ requires C, 60.9; H, 4.7; N, 21.9%); ν_{max}(KBr)/cm^{-1} 3138 and 1693; δ_H($CDCl_3$) 3.85 (3 H, s), 4.45 (3 H, s), 7.21 (1 H, s), 7.34–7.43 (3 H, m) and 7.60–7.62 (2 H, m); δ_C($CDCl_3$) 41.8 (q), 51.0 (q), 84.8 (s), 100.2 (d), 127.8 (2 × d), 127.9 (d), 129.8 (2 × d), 133.9 (s), 139.7 (s), 148.9 (s) and 163.4 (s).

6c: Yield 0.08 g (20%; based on 7 : 3 mixture of **3c**–**4c**), mp 177–179 °C (Found: C, 62.15; H, 5.5; N, 20.7. $C_{14}H_{14}N_4O_2$ requires C, 62.2; H, 5.2; N, 20.7%); ν_{max}(KBr)/cm^{-1} 1692; δ_H($CDCl_3$) 2.40 (3 H, s), 3.81 (3 H, s), 4.46 (3 H, s) and 7.35–7.44 (5 H, m); δ_C($CDCl_3$) 9.5 (q), 41.8 (q), 50.8 (q), 84.4 (s), 108.9 (s), 127.4 (d), 127.6 (2 × d), 130.5 (2 × d), 133.7 (s), 135.5 (s), 147.1 (s) and 163.5 (s).

6d: Yield 0.80 g (60%), mp 174 °C (Found: C, 46.5; H, 3.25; N, 16.7. $C_{13}H_{11}BrN_4O_2$ requires C, 46.6; H, 3.3; N, 16.7%); ν_{max}(KBr)/cm^{-1} 3142 and 1692; δ_H[$(CD_3)_2SO$] 3.84 (3 H, s), 4.45 (3 H, s), 7.19 (1 H, s) and 7.47/7.52 (4 H, AA′BB′, *N* 8); δ_C[$(CD_3)_2SO$] 41.9 (q), 51.0 (q), 84.7 (s), 100.2 (d), 122.2 (s), 131.0 (2 × d), 131.4 (2 × d), 132.8 (s), 138.4 (s), 149.0 (s) and 163.3 (s).

6f: Yield 0.26 g (33%), mp 104–105 °C (Found: C, 49.4; H, 5.2; N, 28.8. $C_8H_{10}N_4O_2$ requires C, 49.5; H, 5.2; N, 28.85%); ν_{max}(KBr)/cm^{-1} 1688; δ_H($CDCl_3$) 2.55 (3 H, s), 3.90 (3 H, s), 4.43 (3 H, s) and 7.00 (1 H, s); δ_C($CDCl_3$) 13.4 (q), 41.6 (q), 50.8 (q), 85.8 (s), 100.0 (d), 136.4 (s), 148.3 (s) and 164.2 (s).

6g: Yield 0.97 g (80%), mp 161–163 °C (Found: C, 71.1; H, 4.7; N, 18.8. $C_{18}H_{14}N_4O$ requires C, 71.5; H, 4.7; N, 18.5%); ν_{max}(KBr)/cm^{-1} 3097 and 1635; δ_H($CDCl_3$) 2.60 (3 H, s), 7.24 (1 H, s), 7.38–7.44 (3 H, m), 7.55–7.62 (5 H, m) and 8.22–8.24 (2 H, m); δ_C($CDCl_3$) 29.7 (q), 97.0 (s), 101.2 (d), 120.3 (2 × d), 127.9 (2 × d), 128.1 (d), 129.7 (2 × d), 129.8 (2 × d), 130.6 (d), 134.2 (s), 137.2 (s), 140.6 (s), 149.9 (s) and 189.3 (s).

6h: Yield 0.16 g (17%), mp 149–150 °C (Found: C, 64.9; H, 5.1; N, 23.3. $C_{13}H_{12}N_4O$ requires C, 65.0; H, 5.0; N, 23.3%); ν_{max}(KBr)/cm^{-1} 3130 and 1636; δ_H($CDCl_3$) 2.60 (3 H, s), 2.67 (3 H, s), 7.07 (1 H, s), 7.50–7.59 (3 H, m) and 8.13–8.17 (2 H, m); δ_C($CDCl_3$) 14.4 (q), 29.4 (q), 97.9 (s), 101.0 (d), 120.1 (2 × d), 129.8 (2 × d), 130.3 (d), 137.3 (s), 138.3 (s), 149.6 (s) and 190.0 (s).

Defunctionalised 1*H*- and 2*H*-pyrrolotetrazoles 7a–f and 8a–g. General procedure

The appropriate pyrrolotetrazole **5**, **6**, **11** or **12** (2 mmol; with **5a** 1 mmol, with **11a** 2.5 mmol) was heated under reflux as detailed below: **5a**,**e** in 6 M HCl (15 and 10 cm^3, respectively; 1 h); **5b** in 12 M HCl (10 cm^3; 4 h); **5c**,**d** in potassium hydroxide–ethanol (1.00 g, 9 cm^3; 20 h), followed by neutralisation with 12 M HCl and heating after addition of further 12 M HCl (10 cm^3; 0.5 h); **5g** in 12 M HCl–ethanol (1 : 1) (20 cm^3; 1 h); **6b**–**d**,**f** in 12 M HCl (10 cm^3; 2 h); **6g** in 12 M HCl (10 cm^3; 1.5 h); **11a** in 12 M HCl (10 cm^3; 2.5 h); **12b** in 12 M HCl (10 cm^3; 1 h); **12e** in 12 M HCl (10 cm^3; 5.5 h); **12g** in 12 M HCl (10 cm^3; 2 h). The cooled reaction mixture was neutralised with sodium carbonate (or hydrogencarbonate), in the case of **8** after dilution with water (20 cm^3); then **8e** was filtered off, while the remaining products **7** and **8** were extracted with dichloromethane (3 × 30 cm^3). Recrystallisation (after possible filtration over a short column of silica gel) was effected with chloroform (**7a**,**e**), chloroform–light petroleum (**7b**), dimethylformamide–water (**7c**), ethanol (*picrate* of **7d**), chloroform–diethyl ether (**8a**), dichloromethane–diethyl ether–light petroleum (**8b**,**d**) or dichloromethane–diethyl ether (**8c**,**e**). The derivatives **7f**, **8f** and **8g** were purified by sublimation (45–50, 60–70 and 40 °C, respectively; 25 Pa). Analytical figures of **7d**,**f** and **8f** were only approximate.

7a: Yield 0.13 g (66%) (from **5a**) and 0.30 g (76%) (from **5b**), mp 140–142 °C (lit.,[1] 140–142 °C) (Found: C, 66.6; H, 5.1; N, 28.2. $C_{11}H_{10}N_4$ requires C, 66.65; H, 5.1; N, 28.3%); for ν_{max}/cm^{-1}, δ_H and δ_C, see ref. 1.

7b: Yield 0.36 g (85%), mp 86–88 °C (Found: C, 68.25; H, 5.9; N, 26.35. $C_{12}H_{12}N_4$ requires C, 67.9; H, 5.7; N, 26.4%); δ_H($CDCl_3$) 2.64 (3 H, s), 3.99 (3 H, s), 5.60 (1 H, s), 7.26–7.30 (1 H, m), 7.39–7.43 (2 H, m) and 7.47–7.50 (2 H, m); δ_C($CDCl_3$) 10.0 (q), 34.4 (q), 71.5 (d), 107.5 (s), 126.4 (d), 128.3 (2 × d), 128.5 (2 × d), 130.4 (s), 131.3 (s) and 136.5 (s).

7c: Yield 0.32 g (58%), mp 201–203 °C (lit.,[1] 201–203 °C) (Found: C, 47.6; H, 3.2; N, 20.1. $C_{11}H_9BrN_4$ requires C, 47.7; H,

3.3; N, 20.2%); ν_{max}(KBr)/cm^{-1} 3150; δ_H[$(CD_3)_2SO$] 4.06 (3 H, s), 6.10 (1 H, d, *J* 1.4), 7.57/7.64 (4 H, AA′BB′, *N* 8.6) and 7.96 (1 H, d, *J* 1.4).

7d: Yield 0.18 g (66%), oil (mp < 0 °C) (lit.,[1] oil); ν_{max}(neat)/cm^{-1} 3141; for δ_H and δ_C, see Table 2. *Picrate*: mp 102–104 °C (Found: C, 39.5; H, 3.1; N, 26.9. $[C_6H_9N_4]C_6H_2N_3O_7$ requires C, 39.5; H, 3.0; N, 26.8%).

7e: Yield 0.42 g (81%), mp 127–129 °C (lit.,[1] 127–129 °C) (Found: C, 73.8; H, 4.4; N, 21.7. $C_{16}H_{12}N_4$ requires C, 73.8; N, 4.65; N, 21.5%); ν_{max}(KBr)/cm^{-1} 3140; δ_H($CDCl_3$) 6.13 (1 H, d, *J* 1.4), 7.25–7.41 (4 H, m), 7.50–7.62 (4 H, m), 7.52 (1 H, d, *J* 1.4) and 7.72–7.80 (2 H, m); δ_C($CDCl_3$) 75.4 (d), 98.5 (d), 117.3 (2 × d), 126.1 (2 × d), 126.7 (d), 127.2 (d), 128.8 (2 × d), 129.6 (s), 129.8 (2 × d), 134.6 (s), 135.1 (s) and 135.9 (s).

7f: Yield 0.02 g (7%), mp 34–35 °C; ν_{max}(KBr)/cm^{-1} 3135; for δ_H and δ_C, see Table 2.

8a: Yield 0.39 g (98%), mp 129–131 °C (Found: C, 66.2; H, 5.2; N, 28.2. $C_{11}H_{10}N_4$ requires C, 66.7; H, 5.1; N, 28.3%); ν_{max}(KBr)/cm^{-1} 3144; δ_H($CDCl_3$) 4.25 (3 H, s), 6.17 (1 H, d, *J* 1.2), 7.20–7.26 (1 H, m), 7.34–7.39 (2 H, m), 7.42 (1 H, d, *J* 1.2) and 7.62–7.64 (2 H, m); δ_C($CDCl_3$) 41.2 (q), 76.2 (d), 94.2 (d), 126.3 (2 × d), 127.0 (d), 128.7 (2 × d), 135.6 (s), 136.7 (s) and 147.0 (s).

8b: Yield 0.34 g (80%), mp 90–91 °C (Found: C, 67.8; H, 5.7; N, 26.4. $C_{12}H_{12}N_4$ requires C, 67.9; H, 5.7; N, 26.4%); δ_H($CDCl_3$) 2.61 (3 H, s), 4.32 (3 H, s), 6.00 (1 H, s), 7.26–7.31 (1 H, m), 7.38–7.43 (2 H, m) and 7.51–7.54 (2 H, m); δ_C($CDCl_3$) 10.5 (q), 41.2 (q), 77.0 (d), 103.3 (s), 126.5 (d), 128.5 (2 × d), 128.6 (2 × d), 133.9 (s), 136.7 (s) and 144.4 (s).

8c: Yield 0.55 g (99%), mp 212–214 °C (Found: C, 47.5; H, 3.3; N, 20.1. $C_{11}H_9BrN_4$ requires C, 47.7; H, 3.3; N, 20.2%); ν_{max}(KBr)/cm^{-1} 3142; δ_H[$(CD_3)_2SO$] 4.40 (3 H, s), 6.32 (1 H, s), 7.57/7.70 (4 H, AA′BB′, *N* 8) and 7.94 (1 H, s); δ_C[$(CD_3)_2SO$] 41.6 (q), 75.6 (d), 94.8 (d), 119.8 (s), 127.8 (2 × d), 131.6 (2 × d), 134.0 (s), 134.6 (s) and 146.4 (s).

8d: Yield 0.20 g (73%) (from **6f**) and 0.27 g (99%) (from **12e**), mp 39–40 °C (Found: C, 52.8; H, 6.1; N, 41.0. $C_6H_8N_4$ requires C, 52.9; H, 5.9; N, 41.15%); ν_{max}(KBr)/cm^{-1} 3123; for δ_H and δ_C, see Table 2.

8e: Yield 0.51 g (98%), mp 198–199 °C (Found: C, 73.4; H, 4.8; N, 21.5. $C_{16}H_{12}N_4$ requires C, 73.8; N, 4.65; N, 21.5%); ν_{max}(KBr)/cm^{-1} 3133; δ_H($CDCl_3$) 6.31 (1 H, d, *J* 1.2), 7.28–7.33 (1 H, m), 7.40–7.50 (3 H, m), 7.53–7.58 (3 H, m), 7.68–7.72 (2 H, m) and 8.15–8.18 (2 H, m); δ_C($CDCl_3$) 77.3 (d), 94.3 (d), 119.9 (2 × d), 126.4 (2 × d), 127.3 (d), 128.8 (2 × d), 129.50 (d), 129.54 (2 × d), 135.4 (s), 137.9 (s), 138.7 (s) and 147.3 (s).

8f: Yield 0.04 g (15%), mp 36–38 °C; ν_{max}(KBr)/cm^{-1} 3132; for δ_H and δ_C, see Table 2.

8g: Yield 0.39 g (98%), mp 86–88 °C (Found: C, 66.6; H, 5.1; N, 28.0. $C_{11}H_{10}N_4$ requires C, 66.7; H, 5.1; N, 28.3%); δ_H($CDCl_3$) 2.39 (3 H, s), 5.83 (1 H, s), 7.06 (1 H, s), 7.44–7.47 (1 H, m), 7.51–7.56 (2 H, m) and 8.12–8.14 (2 H, m); δ_C($CDCl_3$) 14.0 (q), 80.1 (d), 96.2 (d), 119.8 (2 × d), 129.2 (d), 129.5 (2 × d), 135.5 (s), 138.2 (s) and 146.8 (s).

1-Methyl-4-phenacyl-1*H*-tetrazolium-5-(α-acetylacetonylide) 9c

Triethylamine (0.6 cm^3, 4 mmol) was added dropwise to a suspension of the tetrazolium salt **3a** (0.69 g, 2 mmol) in acetic anhydride (10 cm^3) and the mixture was stirred at 20 °C for 4 h. After dilution with water (20 cm^3) to allow hydrolysis of the unconsumed reagent, it was concentrated *in vacuo* to half its volume and extracted with dichloromethane (3 × 20 cm^3) to afford the product. Yield 0.27 g (45%), mp 134–137 °C (from dichloromethane–diethyl ether) (Found: C, 60.1; H, 5.4; N, 18.7. $C_{15}H_{16}N_4O_3$ requires C, 60.0; H, 5.4; N, 18.7%); δ_H($CDCl_3$) 2.33 (6 H, s), 3.99 (3 H, s), 5.87 (2 H, s), 7.51–7.55 (2 H, m), 7.65–7.69 (1 H, m) and 7.93–7.95 (2 H, m); δ_C($CDCl_3$) 29.9 (2 × q), 37.1 (q), 56.0 (t), 93.7 (s), 128.2 (2 × d), 129.1 (2 × d), 133.7 (s), 134.7 (d), 156.9 (s), 188.0 (s) and 189.5 (2 × s).

Reaction of the ylide 9c with acetic anhydride–base

A suspension of **9c** (0.50 g, 1.7 mmol) in acetic anhydride (10 cm^3) and triethylamine (0.3 cm^3, 2.2 mmol) was heated at 100–110 °C for 1 h and then cooled to room temperature. Hydrolysis by addition of water (20 cm^3) and extraction with dichloromethane (3 × 20 cm^3) gave a residue whose ^{1}H NMR spectrum showed a 3 : 4 mixture of *7-acetyl-5-benzoyl-* **11c** and *5,7-diacetyl-1,6-dimethyl-1H-pyrrolo[1,2-d]tetrazole* **11d** (identified by comparison with authentic samples[8b]). Fractional crystallisation from chloroform–diethyl ether afforded 0.04 g (8%) **11c** and 0.06 g (16%) **11d** (mps and spectroscopic data consistent with ref. 8*b*).

5,7-Diacetyl-1-methyl-1*H*-pyrrolo[1,2-*d*]tetrazole 11a

The finely powdered tetrazolium salt **3e** (0.57 g, 2 mmol) was heated with triethyl orthoformate (3.00 g, 20 mmol) in anhydrous ethanol (3 cm^3) under reflux for 5 h. Concentration *in vacuo* gave a sticky brown oil which was taken up with pyridine (10 cm^3) and piperidine (1 cm^3) and again heated under reflux for 1 h. After evaporation of the volatiles the product was isolated by chromatography [silica gel; chloroform–diethyl ether (4 : 1) as eluent] and crystallisation from chloroform–diethyl ether. Yield 0.17 g (41%), mp 178–180 °C (Found: C, 52.4; H, 4.9; N, 27.0. $C_9H_{10}N_4O_2$ requires C, 52.4; H, 4.9; N, 27.2%); ν_{max}(KBr)/cm^{-1} 3100 and 1650; for δ_H and δ_C, see Table 2.

5-Benzoyl-1-phenyl-1*H*-pyrrolo[1,2-*d*]tetrazole 11b

The 1*H*-tetrazole **1j** (2.15 g, 10 mmol) and phenacyl bromide (2.39 g, 12 mmol) were warmed in nitromethane (20 cm^3) at 50–55 °C for 3 d. After removal of the solvent under reduced pressure and repeated extraction of the residual mass with diethyl ether, acetic acid (20.0 g, 334 mmol) and anhydrous sodium acetate (2.00 g, 24 mmol) were added and the mixture was heated at 100–110 °C for 1 h. Work-up as described for the 1*H*-pyrrolotetrazoles **5** left a material which was chromatographed on silica gel [chloroform–ethyl acetate (4 : 1) as eluent] and recrystallised from chloroform–diethyl ether. Yield 0.17 g (6%), mp 171–172 °C (Found: C, 70.5; H, 4.1; N, 19.4. $C_{17}H_{12}N_4O$ requires C, 70.8; H, 4.2; N, 19.4%); ν_{max}(KBr)/cm^{-1} 3130 and 1615; δ_H($CDCl_3$) 6.08 (1 H, d, *J* 4.5), 7.37 (1 H, d, *J* 4.5), 7.41–7.60 (6 H, m) and 7.80–7.89 (4 H, m); δ_C($CDCl_3$) 81.7 (d), 117.9 (s), 118.5 (2 × d), 128.2 (d), 128.3 (2 × d), 128.8 (2 × d), 129.6 (d), 130.1 (2 × d), 131.5 (d), 134.4 (s), 134.9 (s), 138.8 (s) and 181.8 (s).

5,7-Functionalised 2*H*-pyrrolotetrazoles 12a–g. General procedure

The appropriate tetrazolium salt **4** (4 mmol) was dissolved or suspended in acetic formic anhydride (i; 10–20 cm^3) and acetic anhydride (ii; 20–30 cm^3), respectively. After cautious addition of triethylamine (1.5 cm^3, *ca*. 11 mmol) the mixture was heated with stirring for 2 h at 60–65 °C (i) or 90–100 °C (ii). Work-up for **12a**–**d**: the cooled reaction mixture was diluted with water (20–30 cm^3), made weakly alkaline with sodium hydrogencarbonate and extracted with dichloromethane (3 × 50 cm^3). The products were isolated by flash chromatography on silica gel (40–63 μm) using dichloromethane–diethyl ether (10 : 3) as eluent and recrystallised from dichloromethane–light petroleum (**12a**–**c**) or dichloromethane–diethyl ether (**12d**). Work-up for **12e**–**g**: Dilution with water (60 cm^3) to allow hydrolysis of the anhydride, followed by addition of sodium carbonate (until pH 8) and extraction with dichloromethane (3 × 50 cm^3) gave crude materials which were purified on silica gel [chloroform–ethyl acetate (4 : 1) as eluent] and recrystallised from dichloro-

methane–light petroleum. Analytical figures of **12a** were only approximate.

12a: Yield 0.31 g (39%), mp 233–234 °C; ν_{max}(KBr)/cm^{-1} 3090 and 1644; for δ_H and δ_C, see Table 2.

12b: Yield 0.28 g (32%), mp 186–188 °C (Found: C, 48.4; H, 4.5; N, 25.2. $C_9H_{10}N_4O_3$ requires C, 48.6; H, 4.5; N, 25.2%); ν_{max}(KBr)/cm^{-1} 3104, 1718 and 1647; δ_H($CDCl_3$) 2.53 (3 H, s), 3.94 (3 H, s), 4.61 (3 H, s) and 7.98 (1 H, s); δ_C($CDCl_3$) 25.6 (q), 42.4 (q), 51.6 (q), 91.7 (s), 117.1 (s), 128.9 (s), 149.3 (s), 162.6 (s) and 184.3 (s).

12c: Yield 1.27 g (96%), mp 220–221 °C (Found C, 68.6; H, 4.2; N, 16.8. $C_{19}H_{14}N_4O_2$ requires C, 69.1; H, 4.3; N, 17.0%); ν_{max}(KBr)/cm^{-1} 3069, 1661 and 1625; δ_H($CDCl_3$) 2.68 (3 H, s), 7.51–7.59 (2 H, m), 7.61–7.66 (4 H, m), 7.90–7.92 (2 H, m), 7.99 (1 H, s) and 8.35–8.37 (2 H, m); δ_C($CDCl_3$) 28.2 (q), 103.0 (s), 116.9 (s), 120.9 (2 × d), 128.6 (2 × d), 128.7 (2 × d), 129.9 (2 × d), 130.7 (d), 131.4 (d), 132.1 (d), 136.9 (s), 137.8 (s), 150.2 (s), 182.1 (s) and 189.7 (s).

12d: Yield 0.32 g (29%), mp 211–212 °C (Found: C, 60.1; H, 4.35; N, 20.0. $C_{14}H_{12}N_4O_2$·0.5 H_2O requires C, 60.6; H, 4.7; N, 20.2%); ν_{max}(KBr)/cm^{-1} 3090 and 1639; δ_H($CDCl_3$) 2.58 (3 H, s), 2.68 (3 H, s), 7.61–7.66 (3 H, m), 8.05 (1 H, s) and 8.32–8.35 (2 H, m); δ_C($CDCl_3$) 26.0 (q), 28.1 (q), 102.5 (s), 117.5 (s), 120.9 (2 × d), 128.5 (d), 129.9 (2 × d), 131.4 (d), 136.8 (s), 149.7 (s), 184.6 (s) and 189.6 (s).

12e: Yield 0.62 g (66%), mp 212–213 °C (Found: C, 50.6; H, 5.2; N, 23.6. $C_{10}H_{12}N_4O_3$ requires C, 50.8; H, 5.1; N, 23.7%); ν_{max}(KBr)/cm^{-1} 1703; δ_H($CDCl_3$) 2.60 (3 H, s), 2.87 (3 H, s), 3.92 (3 H, s) and 4.57 (3 H, s); δ_C($CDCl_3$) 13.3 (q), 29.8 (q), 42.3 (q), 51.2 (q), 90.9 (s), 116.7 (s), 143.8 (s), 148.9 (s), 163.4 (s) and 185.3 (s).

12f: Yield 0.19 g (14%), mp 236 °C (Found: C, 69.7; H, 4.6; N, 16.0. $C_{20}H_{16}N_4O_2$ requires C, 69.75; H, 4.7; N, 16.3%); ν_{max}(KBr)/cm^{-1} 1649 and 1623; δ_H($CDCl_3$) 2.54 (3 H, s), 2.76 (3 H, s), 7.48–7.52 (2 H, m), 7.57–7.64 (4 H, m), 7.70–7.72 (2 H, m) and 8.24–8.26 (2 H, m); δ_C($CDCl_3$) 15.2 (q), 30.4 (q), 100.8 (s), 116.4 (s), 120.5 (2 × d), 128.4 (2 × d), 128.5 (2 × d), 129.9 (2 × d), 131.1 (d), 131.9 (d), 136.9 (s), 139.4 (s), 144.6 (s), 150.6 (s), 184.7 (s) and 191.0 (s).

12g: Yield 0.19 g (17%) (from **4g**) and 0.65 g (58%) (from **4h**), mp 259 °C (Found: C, 63.8; H, 5.0; N, 19.7. $C_{15}H_{14}N_4O_2$ requires C, 63.8; H, 5.0; N, 19.85%); ν_{max}(KBr)/cm^{-1} 1657 and 1644; δ_H($CDCl_3$) 2.71 (3 H, s), 2.73 (3 H, s), 2.99 (3 H, s), 7.59–7.67 (3 H, m) and 8.25–8.28 (2 H, m); δ_C($CDCl_3$) 13.9 (q), 30.1 (q), 30.5 (q), 100.9 (s), 116.8 (s), 120.4 (2 × d), 129.9 (2 × d), 131.1 (d), 136.9 (s), 145.0 (s), 149.9 (s), 185.9 (s) and 191.2 (s).

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