Synthesis and Properties of Tetrazolium-*N*-phenacylides. Part 2[1]

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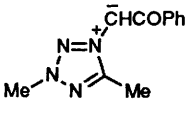
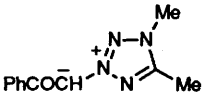
Various 1-alkyl-5-methyl-1*H*-tetrazolium-4-phenacylides **3** (homologues of **C**) have been prepared, acylated and (thio)carbamoylated. The unstable ylide **C** has been acylated *in situ*.

Several years ago we set out to prepare tetrazolium-*N*-phenacylides such as **A**–**C**.[1] The synthetic route we followed was the general one of Kröhnke,[2] *i.e.* treatment of the corresponding tetrazolium salts with an excess of potassium carbonate in the cold. While compounds **A** and **B** were obtained as reasonably stable solids, the isomer **C** was an oil that decomposed on isolation. The instability of the latter is a consequence of poor resonance interaction between the carbanionoid lone pair and the electron-attracting heterocycle.[1] We subsequently concentrated on higher homologues of **C**; preliminary experiments[3] with the tetrazolium salt **2g** (which gave **3g**) had suggested that ylides of that kind should be less elusive species. This was borne



A



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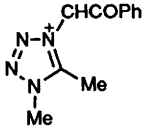
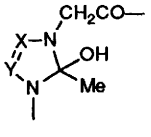
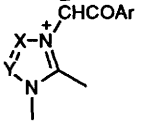


C



D



E

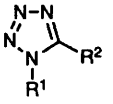
out by base treatment of various tetrazolium salts *e.g.* **2c–f, h, i** [all provided by phenacylation of the tetrazoles **1**(*cf.* refs 1 and 4)]. As in the case of **3g**,[3] the respective ylides **3c–f, h, i** could be easily separated from the reaction mixtures. In addition, the methyltetrazolium salts **2a, b** having bromo- and nitro-substituted phenacyl functions proved suitable candidates, while efforts to isolate ylides derived from salts bearing bulkier groups on tetrazole carbon (*e.g.* **2k** and **2l**) remained unrewarded.

The ylides **3** are colourless or yellow solids (**3b, i**). Their stability depends on the *N*-substituent: derivatives having smaller groups began to decompose soon after isolation, their analytical data are therefore only approximate. An essential feature observed throughout is the presence of crystal water which apparently serves to stabilise the negative charge. Attempts to remove the water by drying agents or even handling of the hydrated ylides in aprotic solvents resulted in fast decomposition.[3b] On addition of acid, the starting tetrazolium ions in **2** were regenerated. This, in conjunction with the analytical composition found (1 mol crystal water), would also hold for a structural unit such as **D** (X = Y = N)[5] and a tetrazolium hydroxide (**2**: OH in place of X), respectively. However, spectroscopic evidence is clearly in favour of the phenacylide function: (i) the IR spectra of solid **3**, in the range ν 1400–1600 cm^{-1}, closely resemble those of the ylides **A** and **B** which are known to crystallise in anhydrous form;[1] (ii) the ^1H and ^{13}C NMR spectra exhibit distinct $\bar{C}H$ signals (in general δ_H 6.4–6.5, δ_C *ca.* 87.0); these appear at higher field with respect to **B** (δ_H 7.2, δ_C 96.2), but are in the region of the ylide **A** (δ_H 6.45, δ_C 87.4; all spectra taken in MeOH); (iii) the UV spectra of **3** display an intense absorption at *ca.* 300 nm and at 350 nm in the case of the nitro-substituted derivatives [recorded in NaOH (0.1 mol dm^{-3})]. This matches known values of the iso-π-electronic moiety **E** (X = N, Y = CMe; X = CH, Y = N).[5a,6] Since the electron-withdrawing force of the tetrazolium ring in **C** is weaker than in **A** and **B**,[1] the (negative) solvatochromism typical of the 'ylide band'[7] is more pronounced than with **A** and **B**. This could be demonstrated by using protic solvents of different polarity (see Experimental section: **3c**); yet, a full range study of the phenomenon as has been performed with **A** and **B**[1] was vitiated by the sensitivity of **3** towards solvents of aprotic character.

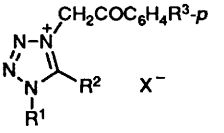
As expected, the ylides **3** show appreciable reactivity towards electrophiles. Treatment of **3e** and **3g** with benzoic anhydride gave the dibenzoylmethylides **4c** and **4d**. A congener of this type, *viz.* a diformylmethylide, has recently been prepared in a different manner and reported to be 'not very stable'.[8] In contrast, the ylides **4c, d** did not decompose even on prolonged storage. The long wavelength UV absorption of these diacylmethylides lacks the strong (negative) solvatochromism observed with the starting ylides **3** (see Experimental section: **4c**).[6] Phenyl isocyanate and isothiocyanate, respectively, smoothly converted **3g** and **3f** into the carbamoylated ylides **4e** and **4f**. From **3g**, carbon disulfide and methyl iodide in the presence of base the ketene thioacetal **5** was obtained (*cf.* refs. 2*c* and 9). This kind of transformation had failed with the ylides **A** and **B** because of lack of reactivity.[3b] Attempts to alkylate the ylides **3**, *e.g.* **3c** or **3g**, only left intractable tars.

Since the 'parent' ylide **C** is not isolable, it has been treated *in situ*. Thus, treatment of the salt **2m** with acetic and benzoic anhydrides in the presence of base afforded the stable ylides **4a** and **4b**. In the first case, minor quantities of the 1*H*-pyrrolotetrazoles **6a** and **6b**† were separated as by-products (identified spectroscopically and by comparison with samples obtained from acetic anhydride and the salts **7a** and **7b**, respectively). Structural type and mode of formation of the major component **6a** refer to certain acetylpyrrolo[1,2-*a*]-benzimidazoles[10a] and an acetylpyrrolo[2,1-*c*]-1,2,4-triazole.[10b] However, this formal analogy does not include the long known direct synthesis of acetylpyrrolo[2,1-*b*]thiazoles because in that case also the carbonyl carbon of the phenacyl group is involved in pyrrole ring closing.[11] Further work on compounds **6** which represent a novel class of aromatic azapentalenes[12] is in progress.

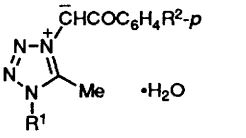
† Work concerning compound **6b** was carried out by D. Decker.



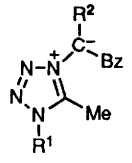
1a $R^1 = R^2 = Me$
b $R^1 = Pr$, $R^2 = Me$
c $R^1 = Pr^i$, $R^2 = Me$
d $R^1 = Bu^i$, $R^2 = Me$
e $R^1 = CH_2Bu^t$, $R^2 = Me$
f $R^1 = c\text{-}C_6H_{11}$, $R^2 = Me$
g $R^1 = Me$, $R^2 = Pr$
h $R^1 = CH_2Bz$, $R^2 = c\text{-}C_6H_{11}$



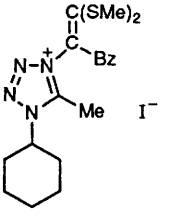
2a $R^1 = R^2 = Me$, $R^3 = Br$, $X = Br$
b $R^1 = R^2 = Me$, $R^3 = NO_2$, $X = Br$
c $R^1 = Pr$, $R^2 = Me$, $R^3 = H$, $X = Br$
d $R^1 = Pr^i$, $R^2 = Me$, $R^3 = H$, $X = Br$
e $R^1 = Bu^i$, $R^2 = Me$, $R^3 = H$, $X = Br$
f $R^1 = CH_2Bu^t$, $R^2 = Me$, $R^3 = H$, $X = Br$
g $R^1 = c\text{-}C_6H_{11}$, $R^2 = Me$, $R^3 = H$, $X = Br$
h $R^1 = c\text{-}C_6H_{11}$, $R^2 = Me$, $R^3 = Br$, $X = Br$
i $R^1 = c\text{-}C_6H_{11}$, $R^2 = Me$, $R^3 = NO_2$, $X = Br$
k $R^1 = Me$, $R^2 = Pr$, $R^3 = H$, $X = ClO_4$
l $R^1 = Me$, $R^2 = c\text{-}C_6H_{11}$, $R^3 = H$, $X = I$
m $R^1 = R^2 = Me$, $R^3 = H$, $X = Br$



3a $R^1 = Me$, $R^2 = Br$
b $R^1 = Me$, $R^2 = NO_2$
c $R^1 = Pr$, $R^2 = H$
d $R^1 = Pr^i$, $R^2 = H$
e $R^1 = Bu^i$, $R^2 = H$
f $R^1 = CH_2Bu^t$, $R^2 = H$
g $R^1 = c\text{-}C_6H_{11}$, $R^2 = H$
h $R^1 = c\text{-}C_6H_{11}$, $R^2 = Br$
i $R^1 = c\text{-}C_6H_{11}$, $R^2 = NO_2$



4a $R^1 = Me$, $R^2 = Ac$
b $R^1 = Me$, $R^2 = Bz$
c $R^1 = Bu^i$, $R^2 = Bz$
d $R^1 = c\text{-}C_6H_{11}$, $R^2 = Bz$
e $R^1 = c\text{-}C_6H_{11}$, $R^2 = CONHPh$
f $R^1 = CH_2Bu^t$, $R^2 = CSNHPh$



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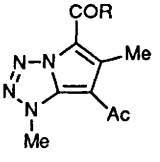
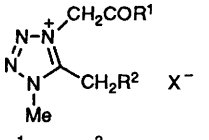


6a R = Ph
b R = Me



7a $R^1 = Ph$, $R^2 = Ac$, $X = BF_4$
b $R^1 = Me$, $R^2 = H$, $X = Br$

Experimental

M.p.s were determined on a Kofler microscope. IR spectra were taken on a Pye-Unicam SP 1100 instrument. ^1H NMR spectra were run on a Varian EM-390 instrument (except for the ylides **3** which were measured with a Bruker AM-400 spectrometer). *J*-Values in Hz. ^{13}C NMR spectra were recorded on a Bruker AM-400 instrument (tetramethylsilane as internal standard throughout). Mass spectra were determined on a Finnigan MAT 8430 instrument. UV spectra were taken with Pye-Unicam SP 8-200 and SP 8-400 spectrophotometers.

Starting 1,5-dialkyltetrazoles **1a**[13] and **1d**, **f**[14] were made by literature procedures, as were **1b**, **c**, **e** and **g** [yield, b.p. or m.p., $\delta_H(CDCl_3)$ of 5-Me or 1-Me] [**1b**, 79%, 75 °C (0.03 Torr)*, 2.60; **1c**, 48%, 120–121 °C (0.1 Torr), 2.60; **1e**, 29%, 88–89 °C (light petroleum) (lit.,[15] 82–83 °C), 2.66; **1g**, 35%, distilled with decomp., 4.0 (quoted δ_H values in accord with ref. 15].

2-(5-Cyclohexyltetrazol-1-yl)acetophenone **1h**.[16]—Anhydrous potassium carbonate (34.6 g, 0.25 mol) was added portionwise to a refluxing solution of 5-cyclohexyltetrazole[17] (76.1 g, 0.5 mol) [m.p. 130–133 °C (water) (lit.,[18] 133–134 °C)] and 2-bromoacetophenone (99.5 g, 0.5 mol) in acetone (500 cm^3). The boiling mixture was stirred for a further 8 h and then poured into cold water (750 cm^3). The solid formed was filtered off and chromatographed on silica gel. Benzene as the first eluent gave the isomeric *2-(5-cyclohexyltetrazol-2-yl)-acetophenone* (51.1 g, 38%), m.p. 76–77 °C (ethyl acetate–light petroleum) (Found: C, 66.8; H, 6.8; N, 20.9. $C_{15}H_{18}N_4O$ requires C, 66.65; H, 6.7; N, 20.7%); ν_{max}(KBr)/cm^{-1} 1710; $\delta_H(CDCl_3)$ 1.0–2.25 [10 H, m, $CH(CH_2)_5$], 2.95 [1 H, m_c, $CH(CH_2)_5$], 6.01 (2 H, s, CH_2CO), 7.3–7.6 (3 H, m, Ph) and 7.8–8.0 (2 H, m, Ph). Subsequent elution with ethyl acetate afforded the product **1h** (43.0 g, 32%), m.p. 116 °C (CH_2Cl_2–light petroleum) (Found: C, 66.7; H, 6.7; N, 20.7. $C_{15}H_{18}N_4O$ requires C, 66.65; H, 6.7; N, 20.7%); ν_{max}(KBr)/cm^{-1} 1705; $\delta_H(CDCl_3)$ 0.9–2.1 [10 H, m, $CH(CH_2)_5$], 2.63 [1 H, m_c, $CH(CH_2)_5$], 5.78 (2 H, s, CH_2CO), 7.4–7.7 (3 H, m, Ph) and 7.9–8.1 (2 H, m, Ph).

1,4,5-Trisubstituted Tetrazolium Salts **2a**–**k**: *General Procedure*.[3b,4]—A solution of the tetrazole **1** (0.01 mol) and (substituted) 2-bromoacetophenone (0.011 mol) in anhydrous nitromethane (15–20 cm^3) was heated to 70–75 °C for the time indicated. The product was isolated by evaporating the solvent under reduced pressure and crystallising the residue from ethanol–ether. In the case of **2k**, aqueous $HClO_4$ (70%; 50 cm^3) was added to the crude bromide dissolved in ethanol; after gentle heating and dilution with water the product was filtered off.

1-(4-Bromophenacyl)-4,5-dimethyl-1H-tetrazolium bromide **2a**. Reaction time 4 d; yield 2.35 g (70%), m.p. 170–171 °C [Found: C, 34.3; H, 3.2; N, 14.4. $(C_{11}H_{12}BrN_4O)Br{\cdot}0.5H_2O$ requires C, 34.3; H, 3.4; N, 14.55%]; $\delta_H(CF_3CO_2H)$ 3.05 (3 H, s, 5-Me), 4.46 (3 H, s, 4-Me), 6.52 (2 H, s, CH_2) and 7.79 and 8.02 (4 H, AA′BB′, *J* 9, Ar).

1,5-Dimethyl-4-(4-nitrophenacyl)-1H-tetrazolium bromide **2b**. Reaction time 5 d; yield 1.25 g (35%), m.p. 130–135 °C [Found: C, 36.7; H, 3.9; N, 19.6. $(C_{11}H_{12}N_5O_3)Br{\cdot}H_2O$ requires C, 36.7; H, 3.9; N, 19.4%]; $\delta_H(CF_3CO_2H)$ 3.08 (3 H, s, 5-Me), 4.45 (3 H, s, 1-Me), 6.58 (2 H, s, CH_2) and 8.34 and 8.45 (4 H, AA′BB′, *J* 9, Ar).

5-Methyl-1-phenacyl-4-propyl-1H-tetrazolium bromide **2c**. Reaction time 2–3 d; yield 2.57 g (79%), m.p. 156–157 °C [Found: C, 47.9; H, 5.4; N, 17.2. $(C_{13}H_{17}N_4O)Br$ requires C, 48.0; H, 5.3; N, 17.2%]; $\delta_H(CF_3CO_2H)$ 1.17 (3 H, t, *J* 7, $CH_2CH_2CH_3$), 2.24 (2 H, sext, *J* 7, $CH_2CH_2CH_3$), 3.04 (3 H, s, 5-Me), 4.64 (2 H, t, *J* 7, $CH_2CH_2CH_3$), 6.50 (2 H, s, CH_2CO), 7.45–7.85 (3 H, m, Ph) and 8.0–8.15 (2 H, s, Ph).

* 1 Torr ≈ 133 Pa.

1-*Isopropyl*-5-*methyl*-4-*phenacyl*-1H-*tetrazolium bromide* **2d**. Reaction time 2 d; yield 2.73 g (84%), m.p. 157–158 °C [Found: C, 47.7; H, 5.3; N, 17.05. ($C_{13}H_{17}N_4O$)Br requires C, 48.0; H, 5.3; N, 17.2%]; $\delta_H(CF_3CO_2H)$ 1.87 [6 H, d, *J* 7, $CH(CH_3)_2$], 3.06 (3 H, s, 5-Me), 5.11 [1 H, sept, *J* 7, $CH(CH_3)_2$], 6.50 (2 H, s, CH_2), 7.45–7.85 (3 H, m, Ph) and 8.0–8.15 (2 H, m, Ph).

1-*Isobutyl*-5-*methyl*-4-*phenacyl*-1H-*tetrazolium bromide* **2e**. Reaction time 24 h; yield 2.68 g (79%), m.p. 155 °C [Found: C, 49.6; H, 5.8; N, 16.6. ($C_{14}H_{19}N_4O$)Br requires C, 49.6; H, 5.65; N, 16.5%]; $\delta_H(CF_3CO_2H)$ 1.19 [6 H, d, *J* 7, $CH_2CH(CH_3)_2$], 2.57 [1 H, m$_c$, $CH_2CH(CH_3)_2$], 3.06 (3 H, s, 5-Me), 4.53 [2 H, d, *J* 7, $CH_2CH(CH_3)_2$], 6.52 (2 H, s, CH_2CO), 7.45–7.85 (3 H, m, Ph) and 8.0–8.15 (2 H, m, Ph); $\delta_C(CD_3OH)$ 9.2 (q, 5-Me), 19.6 [q, $CH_2CH(CH_3)_2$], 29.8 [d, $CH_2CH(CH_3)_2$], 57.6, 58.1 [2t, $CH_2CO/CH_2CH(CH_3)_2$], 129.7, 130.2, 136.1 (3d, C-2,3,4 of Ph), 134.3 (s, C-1 of Ph), 155.3 (s, C-5) and 189.8 (s, CO).

5-*Methyl*-1-*neopentyl*-4-*phenacyl*-1H-*tetrazolium bromide* **2f**. Reaction time 24 h; yield 2.26 g (61%), m.p. 145–147 °C [Found: C, 48.6; H, 6.2; N, 15.1. ($C_{15}H_{21}N_4O$)Br·H_2O requires C, 48.5; H, 6.2; N, 15.1%]; $\delta_H(CF_3CO_2H)$ 1.23 [9 H, s, $CH_2C(CH_3)_3$], 3.05 (3 H, s, 5-Me), 4.50 [2 H, s, $CH_2C(CH_3)_3$], 6.53 (2 H, s, CH_2CO), 7.5–7.8 (3 H, m, Ph) and 8.0–8.15 (2 H, m, Ph).

1-*Cyclohexyl*-5-*methyl*-4-*phenacyl*-1H-*tetrazolium bromide* **2g**. Reaction time 5 h; yield 2.74 g (75%), m.p. 182–184 °C [Found: C, 52.5; H, 5.9; N, 15.5. ($C_{16}H_{21}N_4O$)Br requires C, 52.6; H, 5.8; N, 15.3%]; $\delta_H(CF_3CO_2H)$ 1.3–2.5 [10 H, m, $CH(CH_2)_5$], 3.03 (3 H, s, 5-Me), 4.72 [1 H, m$_c$, $CH(CH_2)_5$], 6.52 (2 H, s, CH_2CO), 7.5–7.8 (3 H, m, Ph) and 8.0–8.2 (2 H, m, Ph); $\delta_C(CD_3OH)$ 9.0 (q, 5-Me), 25.57, 25.63, 32.8 [3t, $CH(CH_2)_5$], 57.3 (t, CH_2CO), 62.7 [d, $CH(CH_2)_5$], 129.7, 130.1, 136.1 (3d, C-2,3,4 of Ph), 134.3 (s, C-1 of Ph), 154.3 (s, C-5) and 189.8 (s, CO) (*cf.*[3b,4] hemihydrate of **2g**).

1-(4-*Bromophenacyl*)-4-*cyclohexyl*-5-*methyl*-1H-*tetrazolium bromide* **2h**. Reaction time 30 h; yield 3.60 g (81%), m.p. 197–201 °C [Found: C, 43.25; H, 4.6; N, 12.6. ($C_{16}H_{20}BrN_4O$)Br requires C, 43.3; H, 4.5; N, 12.6%]; $\delta_H(CF_3CO_2H)$ 1.3–2.55 [10 H, m, $CH(CH_2)_5$], 3.03 (3 H, s, 5-Me), 4.70 [1 H, m$_c$, $CH(CH_2)_5$], 6.47 (2 H, s, CH_2CO) and 7.74 and 7.97 (4 H, AA′BB′, *J* 8, Ar).

1-*Cyclohexyl*-5-*methyl*-4-(4-*nitrophenacyl*)-1H-*tetrazolium bromide* **2i**. Reaction time 30 h; yield 3.12 g (76%), m.p. 171–173 °C [Found: C, 46.9; H, 4.9; N, 16.9. ($C_{16}H_{20}N_5O_3$)Br requires C, 46.8; H, 4.9; N, 17.1%]; $\delta_H(CF_3CO_2H)$ 1.25–2.5 [10 H, m, $CH(CH_2)_5$], 3.06 (3 H, s, 5-Me), 4.69 [1 H, m$_c$, $CH(CH_2)_5$], 6.52 (2 H, s, CH_2CO) and 8.28 (4 H, m$_c$, Ar).

1-*Methyl*-4-*phenacyl*-5-*propyl*-1H-*tetrazolium perchlorate* **2k**. Reaction time 3 d; yield 1.07 g (31%), m.p. 143 °C [Found: C, 45.1; H, 5.0; N, 16.2. ($C_{13}H_{17}N_4O$)ClO_4 requires C, 45.3; H, 5.0; N, 16.25%]; $\delta_H(CF_3CO_2H)$ 1.17 (3 H, t, *J* 7, $CH_2CH_2CH_3$), 1.92 (2 H, sext, *J* 7, $CH_2CH_2CH_3$), 3.32 (2 H, t, *J* 7, $CH_2CH_2CH_3$), 4.44 (3 H, s, 1-Me), 6.40 (2 H, s, CH_2CO), 7.45–7.85 (3 H, m, Ph) and 8.0–8.15 (2 H, m, Ph).

5-*Cyclohexyl*-1-*methyl*-4-*phenacyl*-1H-*tetrazolium iodide* **2l**. A suspension of **1h** (11.0 g, 0.04 mol) in MeI (25.0 g, 0.18 mol) was refluxed for 4 d. After storage at room temp. for 24 h, the product (1.90 g, 12%) was filtered off; m.p. 146–148 °C (ethanol) [Found: C, 46.7; H, 5.2; N, 13.5. ($C_{16}H_{21}N_4O$)I requires C, 46.6; H, 5.1; N, 13.6%]; $\delta_H(CF_3CO_2H)$ 1.2–2.4 [10 H, m, $CH(CH_2)_5$], 3.50 [1 H, m$_c$, $CH(CH_2)_5$], 4.54 (3 H, s, 1-Me), 6.61 (2 H, s, CH_2CO), 7.5–7.9 (3 H, m, Ph) and 8.05–8.2 (2 H, m, Ph).

1-*Alkyl*-5-*methyl*-1H-*tetrazolium*-4-*phenacylides* **3a–i**: *General Procedure*.—Addition of potassium carbonate (4.1 g, 0.03 mol) in water (10 cm^3) to the tetrazolium salt **2** (0.01 mol) in the minimum amount of water at 0 °C with vigorous stirring gave immediate separation of the products (in the case of oily precipitates, crystallisation occurred on adding a piece of ice). The mixtures were stirred for a further 30 min at 0 °C, after which the products were filtered off, dried in an air current at ambient temperature and recrystallised from ethanol–water at 0 to −20 °C (unless otherwise stated). On storage, even below 0 °C, the products gradually decomposed. The multiplicity (d) of the ylidic carbon was established by ^1H off-resonance decoupling (not by means of the DEPT pulse technique otherwise applied in this work). An external ^2H lock of CD_3OD or C_6D_6 was used throughout.

1,5-*Dimethyl*-1H-*tetrazolium*-4-(4-*bromophenacylide*) **3a**. Yield 2.72 g (87%), m.p. 50–53 °C (decomp.) (propan-2-ol–water); ν_{max}(KBr)/cm^{-1} 3450br and 1530; λ_{max}[NaOH (0.1 mol dm^{-3}]/nm 300 (log ε 3.89); δ_H(400 MHz; MeOH) 2.78 (3 H, s, 5-Me), 4.25 (3 H, s, 1-Me), 6.45 (1 H, br s, ylidic CH) and 7.53 and 7.69 (4 H, AA′BB′, *J* 7.2, Ar); δ_C(MeOH) 9.3 (q, 5-Me), 36.6 (q, 1-Me), 87.2 (d, ylidic C), 123.7 (s, C-4 of Ar), 129.0, 132.0 (2d, C-2,3 of Ar), 140.2 (s, C-1 of Ar), 151.9 (s, C-5) and 167.6 (s, CO).[19]

1,5-*Dimethyl*-1H-*tetrazolium*-4-(4-*nitrophenacylide*) **3b**. Yield 2.58 g (92%), m.p. 71–77 °C (decomp.); ν_{max}(KBr)/cm^{-1} 3450br and 1555; λ_{max}[NaOH (0.1 mol dm^{-3})]/nm 350 (log ε 3.85); δ_H(400 MHz; MeOH) 2.82 (3 H, s, 5-Me), 4.29 (3 H, s, 1-Me), 6.59 (1 H, br s, ylidic CH) and 7.97 and 8.22 (4 H, AA′BB′, *J* 8.7, Ar); δ_C(MeOH) 9.0 (q, 5-Me), 36.3 (q, 1-Me), 88.8 (d, ylidic C), 123.9, 127.9 (2d, C-2,3 of Ar), 147.5, 149.0 (2s, C-1,4 of Ar), 152.1 (s, C-5) and 166.3 (s, CO).[19]

5-*Methyl*-1-*propyl*-1H-*tetrazolium*-4-*phenacylide* **3c**. Yield 2.07 g (79%), m.p. 62–65 °C (decomp.) (Found: C, 59.45; H, 7.0; N, 21.1. $C_{13}H_{16}N_4O·H_2O$ requires C, 59.5; H, 6.9; N, 21.4%); ν_{max}(KBr)/cm^{-1} 3440br and 1535; λ_{max}[NaOH/NaOMe/NaOEt/NaOPr^i(0.01–0.1 mol dm^{-3})]/nm 299/318/325/330 (log ε 3.80/3.86/3.84/3.86); δ_H(400 MHz; MeOH) 1.07 (3 H, t, *J* 7.4, $CH_2CH_2CH_3$), 2.08 (2 H, sext, *J* 7.4, $CH_2CH_2CH_3$), 2.80 (3 H, s, 5-Me), 4.54 (2 H, t, *J* 7.4, $CH_2CH_2CH_3$), 6.43 (1 H, br s, ylidic CH), 7.30–7.38 (3 H, m, Ph) and 7.70–7.77 (2 H, m, Ph); δ_C(MeOH) 9.4 (q, 5-Me), 11.1 (q, $CH_2CH_2CH_3$), 23.0 (t, $CH_2CH_2CH_3$), 52.6 (t, $CH_2CH_2CH_3$), 87.4 (d, ylidic C), 127.3, 129.1, 130.0 (3d, C-2,3,4 of Ph), 141.4 (s, C-1 of Ph), 151.7 (s, C-5) and 169.3 (s, CO); *m/z* (FAB; glycerol) 489 (2M + H^+, 2%) and 245 ([M + H]$^+$, 100).

1-*Isopropyl*-5-*methyl*-1H-*tetrazolium*-4-*phenacylide* **3d**. Yield 2.10 g (77%), m.p. 61–63 °C (decomp.) (Found: C, 57.1; H, 7.0; N, 20.4. $C_{13}H_{16}N_4O·1.5H_2O$ requires C, 57.55; H, 7.1; N, 20.65%); ν_{max}(KBr)/cm^{-1} 3420br and 1540; λ_{max}[NaOH (0.1 mol dm^{-3})]/nm 295 (log ε 3.79); δ_H(400 MHz; MeOH) 1.70 [6 H, d, *J* 6.7, $CH(CH_3)_2$], 2.81 (3 H, s, 5-Me), 6.44 (1 H, br s, ylidic CH), 7.33–7.42 (3 H, m, Ph) and 7.75–7.84 (2 H, m, Ph) [$CH(CH_3)_2$ under OH of solvent (4.95)]; δ_C(MeOH) 9.4 (q, 5-Me), 21.7 [q, $CH(CH_3)_2$], 55.6 [d, $CH(CH_3)_2$], 87.0 (d, ylidic C), 127.2, 129.0, 129.9 (3d, C-2,3,4 of Ph), 141.2 (s, C-1 of Ph), 150.9 (s, C-5) and 169.0 (s, CO).

1-*Isobutyl*-5-*methyl*-1H-*tetrazolium*-4-*phenacylide* **3e**. Yield 2.29 g (83%), m.p. 68–70 °C (decomp.) (Found: C, 60.9; H, 7.5; N, 20.2. $C_{14}H_{18}N_4O·H_2O$ requires C, 60.85; H, 7.3; N, 20.3%); ν_{max}(KBr)/cm^{-1} 3390br and 1545; λ_{max}[NaOH (0.1 mol dm^{-3})]/nm 303 (log ε 3.80); δ_H(400 MHz; MeOH) 1.07 [6 H, d, *J* 6.7, $CH_2CH(CH_3)_2$], 2.36 [1 H, m$_c$, $CH_2CH(CH_3)_2$], 2.81 (3 H, s, 5-Me), 4.38 [2 H, d, *J* 7.2, $CH_2CH(CH_3)_2$], 6.45 (1 H, br s, ylidic CH), 7.35–7.42 (3 H, m, Ph) and 7.75–7.83 (2 H, m, Ph); δ_C(MeOH) 9.5 (q, 5-Me), 19.8 [q, $CH_2CH(CH_3)_2$], 29.7 [d, $CH_2CH(CH_3)_2$], 57.6 [t, $CH_2CH(CH_3)_2$], 87.2 (d, ylidic C), 127.3, 129.0, 130.0 (3d, C-2,3,4 of Ph), 141.2 (s, C-1 of Ph), 151.8 (s, C-5) and 168.9 (s, CO).

5-*Methyl*-1-*neopentyl*-1H-*tetrazolium*-4-*phenacylide* **3f**. Yield 2.70 g (93%), m.p. 69–73 °C (decomp.) (Found: C, 62.1; H, 7.8; N, 19.0. $C_{15}H_{20}N_4O·H_2O$ requires C, 62.05; H, 7.6; N, 19.3%); ν_{max}(KBr)/cm^{-1} 3400br and 1540; λ_{max}[NaOH (0.1 mol dm^{-3})]/nm 302 (log ε 3.80); δ_H(400 MHz; MeOH) 1.10 [9 H, s, $CH_2C(CH_3)_3$], 2.83 (3 H, s, 5-Me), 4.41 [2 H, s, $CH_2C(CH_3)_3$],

6.50 (1 H, br s, ylidic CH), 7.36–7.42 (3 H, m, Ph) and 7.75–7.83 (2 H, m, Ph); δ_C(MeOH) 10.2 (q, 5-Me), 27.4 [q, $CH_2C(CH_3)_3$], 34.4 [s, $CH_2C(CH_3)_3$], 61.4 [t, $CH_2C(CH_3)_3$], 87.1 (d, ylidic C), 127.2, 129.0, 130.1 (3d, C-2,3,4 of Ph), 141.0 (s, C-1 of Ph), 152.2 (s, C-5) and 169.3 (s, CO).

1-*Cyclohexyl*-5-*methyl*-1H-*tetrazolium*-4-*phenacylide* **3g**. Yield 2.74 g (91%), m.p. 89–91 °C (decomp.) (lit.,[3b] 87–89 °C) (Found: C, 63.7; H, 7.4; N, 18.4. Calc. for $C_{16}H_{20}N_4O{\cdot}H_2O$: C, 63.6; H, 7.3; N, 18.5%); ν_{max}(KBr)/cm^{-1} 3400br and 1530; λ_{max}[NaOH (0.1 mol dm^{-3})]/nm 296 (log ε 3.82); δ_H(400 MHz; MeOH) 1.30–2.27 [10 H, 5m, $CH(CH_2)_5$], 2.81 (3 H, s, 5-Me), 4.67 [1 H, m$_c$, $CH(CH_2)_5$], 6.40 (1 H, br s, ylidic CH), 7.32–7.39 (3 H, m, Ph) and 7.71–7.79 (2 H, m, Ph); δ_C(MeOH) 9.0 (q, 5-Me), 25.44, 25.46, 32.4 [3t, $CH(CH_2)_5$], 61.4 [d, $CH(CH_2)_5$], 86.7 (d, ylidic C), 127.0, 128,7, 129.6 (3d, C-2,3,4 of Ph), 141.0 (s, C-1 of Ph), 150.7 (s, C-5) and 169.0 (s, CO); *m/z* (FAB; glycerol) 569 (2M + H$^+$, 2%) and 285 (M + H$^+$, 100).

1-*Cyclohexyl*-5-*methyl*-1H-*tetrazolium*-4-(4-*bromophenacylide*) **3h**. Yield 3.51 g (92%), m.p. 96–98 °C (decomp.) (Found: C, 50.25; H, 5.6; N, 14.7. $C_{16}H_{19}BrN_4O{\cdot}H_2O$ requires C, 50.4; H, 5.55; N, 14.7%); ν_{max}(KBr)/cm^{-1} 3370br and 1530; λ_{max}[NaOH (0.1 mol dm^{-3})]/nm 299 (log ε 3.91); δ_H(400 MHz; MeOH) 1.32–2.26 [10 H, 5m, $CH(CH_2)_5$], 2.80 (3 H, s, 5-Me), 4.67 [1 H, m$_c$, $CH(CH_2)_5$], 6.43 (1 H, br s, ylidic CH) and 7.51 and 7.67 (4 H, AA′BB′, *J* 8.4, Ar); δ_C(MeOH) 9.0 (q, 5-Me), 25.44, 25.46, 32.4 [3t, $CH(CH_2)_5$], 61.5 [d, $CH(CH_2)_5$], 86.9 (d, ylidic C), 123.5 (s, C-4 of Ar), 128.8, 131.8 (2d, C-2,3 of Ar), 140.2 (s, C-1 of Ar), 150.8 (s, C-5) and 167.6 (s, CO).[19]

1-*Cyclohexyl*-5-*methyl*-1H-*tetrazolium*-4-(4-*nitrophenacylide*) **3i**. Yield 2.88 g (83%), m.p. 83–87 °C (decomp.) (Found: C, 55.4; H, 6.15; N, 19.7. $C_{16}H_{19}N_5O_3{\cdot}H_2O$ requires C, 55.3; H, 6.1; N, 20.2%); ν_{max}(KBr)/cm^{-1} 3440br, 1550 and 1345; λ_{max}[NaOH (0.1 mol dm^{-3})]/nm 349 (log ε 3.86); δ_H(400 MHz; MeOH) 1.35–2.30 [10 H, 5m, $CH(CH_2)_5$], 2.84 (3 H, s, 5-Me), 4.71 [1 H, m$_c$, $CH(CH_2)_5$], 6.56 (1 H, s, ylidic CH) and 7.97 and 8.22 (4 H, AA′BB′, *J* 8.9, Ar); δ_C(MeOH) 9.0 (q, 5-Me), 25.44, 25.47, 32.4 [3t, $CH(CH_2)_5$], 61.6 [d, $CH(CH_2)_5$], 88.6 (d, ylidic C), 123.9, 128.2 (2d, C-2,3 of Ar), 147.6, 149.0 (2s, C-1,4 of Ar), 151.0 (s, C-5) and 166.3 (s, CO).[19]

1,5-*Dimethyl*-1H-*tetrazolium*-4-(α-*acetylphenacylide*) **4a** *and* 4-(α-*Benzoylphenacylide*) **4b**.—Triethylamine (2.02 g, 0.02 mol) was added dropwise to a stirred suspension of the salt **2m** (2.98 g, 0.01 mol; prepared as shown for **2a**–**k**, reaction time 3 d, yield 59%, characterisation data satisfactory[4]) in either acetic anhydride (25.5 g, 0.25 mol) at 20 °C or melted benzoic anhydride (22.6 g, 0.1 mol) at 45 °C. The air-protected mixtures were stirred for a further 48 and 24 h, respectively. Then, in the first case, triethylammonium acetate was filtered off and the filtrate evaporated to dryness while the second reaction mixture, after cooling to 20 °C, was thoroughly washed with ether–light petroleum (1:1). Each residue was crystallised from chloroform–ether to give: (i) the *ylide* **4a** (1.58 g, 61%), m.p. 127–128 °C (decomp.) (Found: C, 60.5; H, 5.6; N, 21.7. $C_{13}H_{14}N_4O_2$ requires C, 60.45; H, 5.5; N, 21.7%); ν_{max}(KBr)/cm^{-1} 1525br; δ_H($CDCl_3$) 1.88 (3 H, s, COMe), 2.58 (3 H, s, 5-Me), 4.05 (3 H, s, 1-Me) and 7.34 (5 H, m$_c$, Ph); δ_C($CDCl_3$) 8.5 (q, 5-Me), 27.8 (q, $COCH_3$), 36.2 (q, 1-Me), 111.5 (s, ylidic C), 127.0, 128.3, 129.2 (3d, C-2,3,4 of Ph), 142.6 (s, C-1 of Ph), 152.4 (s, C-5), 184.5 and 185.7 (2 s, 2 CO); *m/z* (70 eV; 50 °C) 230 (M − 28$^+$, 8%), 188 (100), 146 (5), 118 (33) and 105 (50); and (ii) the *ylide* **4b** (0.50 g, 15%), m.p. 112–115 °C (decomp.) (Found: C, 65.9; H, 5.2; N, 17.1. $C_{18}H_{16}N_4O_2{\cdot}0.5H_2O$ requires C, 65.6; H, 5.2; N, 17.0%); ν_{max}(KBr)/cm^{-1} 3470br and 1505; δ_H($CDCl_3$) 2.41 (1 H, br s, H_2O), 2.67 (3 H, s, 5-Me), 4.03 (3 H, s, 1-Me), 6.75–7.05 (6 H, m, 2 Ph) and 7.15–7.3 (4 H, m, 2 Ph).

1-*Isobutyl*- **4c** *and* -1-*Cyclohexyl*-5-*methyl*-1H-*tetrazolium*-4-(α-*benzoylphenacylide*) **4d**.—A stirred mixture of the ylide **3e** or **3g** (0.01 mol) and benzoic anhydride (5.66 g, 0.025 mol) was kept at 45 °C for 30–45 min. Work-up similar to that for **4b** and recrystallisation (chloroform–ether) gave: (i) the *ylide* **4c** (1.79 g, 49%), m.p. 119–120 °C (decomp.) (Found: C, 69.7; H, 6.1; N, 15.5. $C_{21}H_{22}N_4O_2$ requires C, 69.6; H, 6.1; N, 15.5%); ν_{max}(KBr)/cm^{-1} 1520 and 1505; λ_{max}(H_2O/MeOH/EtOH/$CHCl_3$)/nm 307.5/306.5/309/310 (log ε 4.09/4.19/4.26/4.14); δ_H($CDCl_3$) 0.96 [6 H, d, *J* 7, $CH_2CH(CH_3)_2$], 2.27 [1 H, m$_c$, $CH_2CH(CH_3)_2$], 2.67 (3 H, s, 5-Me), 4.13 [2 H, d, *J* 7, $CH_2CH(CH_3)_2$], 6.75–7.0 (6 H, m, 2 Ph) and 7.15–7.3 (4 H, m, 2 Ph); δ_C($CDCl_3$) 8.8 (q, 5-Me), 19.4 [q, $CH_2CH(CH_3)_2$], 28.9 [d, $CH_2CH(CH_3)_2$], 56.8 [t, $CH_2CH(CH_3)_2$], 110.5 (s, ylidic C), 127.2, 128.5, 129.2 (3d, C-2,3,4 of Ph), 141.0 (s, C-1 of Ph), 152.3 (s, C-5) and 185.3 (s, CO); and (ii) the *ylide* **4d** (1.99 g, 50%), m.p. 127–129 °C (decomp.) (Found: C, 69.6; H, 6.4; N, 13.8. $C_{23}H_{24}N_4O_2{\cdot}0.5H_2O$ requires C, 69.5; H, 6.3; N, 14.1%); ν_{max}(KBr)/cm^{-1} 3640br and 1495; δ_H($CDCl_3$) 1.05–2.25 [10 H, m, $CH(CH_2)_5$], 2.55 (1 H, s, H_2O), 2.63 (3 H, s, 5-Me), 4.30 [1 H, m$_c$, $CH(CH_2)_5$], 6.7–7.0 (6 H, m, 2 Ph) and 7.15–7.3 (4 H, m, 2 Ph); δ_C($CDCl_3$) 8.8 (q, 5-Me), 24.4, 24.7, 31.7 [3t, $CH(CH_2)_5$], 61.2 [d, $CH(CH_2)_5$], 110.6 (s, ylidic C), 127.2, 128.7, 129.4 (3d, C-2,3,4 of Ph), 140.7 (s, C-1 of Ph), 151.5 (s, C-5) and 185.8 (s, CO).

1-*Cyclohexyl*-5-*methyl*-1H-*tetrazolium*-4-[α-(*phenylcarbamoyl*)*phenacylide*] **4e**.—The ylide **3g** (3.02 g, 0.01 mol) was added portionwise with stirring to neat phenyl isocyanate (11.9 g, 0.1 mol) at 0 °C. After continued stirring for 45 min at 20 °C the mixture was diluted with ether until an oil precipitated which was taken up in chloroform. Addition of ether to the latter caused crystallisation of the product (3.71 g, 88%), m.p. 121–123 °C (decomp.) (Found: C, 65.6; H, 6.4; N, 16.3. $C_{23}H_{25}N_5O_2{\cdot}H_2O$ requires C, 65.5; H, 6.5; N, 16.6%); ν_{max}(KBr)/cm^{-1} 3520, 3450, 1645 and 1520; δ_H[$(CD_3)_2SO$] 1.05–2.3 [10 H, m, $CH(CH_2)_5$], 2.77 (3 H, s, 5-Me), 4.63 [1 H, m$_c$, $CH(CH_2)_5$], 6.7–7.2 (8 H, m, 2 Ph), 7.35–7.55 (2 H, m, Ph) and 12.10 (1 H, s, NH, exch. D_2O); δ_C[$(CD_3)_2SO$] 8.7 (q, 5-Me), 24.07, 24.13, 24.17, 30.6, 31.7 [5t, $CH(CH_2)_5$], 60.1 [d, $CH(CH_2)_5$], 98.0 (s, ylidic C), 118.7, 121.8, 126.0, 128.0, 128.5, 128.8 (6d, C-2,3,4 of 2 Ph), 140.2, 140.9 (2s, C-1 of 2 Ph), 153.0 (s, C-5), 162.8 (s, amidic CO) and 179.6 (s, enolic CO).

5-*Methyl*-1-*neopentyl*-1H-*tetrazolium*-4-[α-(*phenylthiocarbamoyl*)*phenacylide*] **4f**.—In a manner similar to the preparation of **4e**, the ylide **3f** (2.90 g, 0.01 mol) was added to neat phenyl isothiocyanate (13.7 g, 0.1 mol) at 20 °C. Work-up 1 h later as shown above and recrystallisation (chloroform–light petroleum) gave the product (3.55 g, 87%), m.p. 113–114 °C (decomp.) (Found: C, 64.9; H, 6.2; N, 17.1. $C_{22}H_{25}N_5OS$ requires C, 64.8; H, 6.2; N, 17.2%); ν_{max}(KBr)/cm^{-1} 1565 and 1515; δ_H[$(CD_3)_2SO$] 0.83 [9 H, s, $CH_2C(CH_3)_3$], 2.80 (3 H, s, 5-Me), 4.43 [2 H, s, $CH_2C(CH_3)_3$], 7.0–7.4 (8 H, m, 2 Ph), 7.7–7,85 (2 H, m, Ph) and 14.17 (1 H, s, NH, exch. D_2O); δ_C[$(CD_3)_2SO$] 9.5 (q, 5-Me), 26.4 [q, $CH_2C(CH_3)_3$], 33.4 [s, $CH_2C(CH_3)_3$], 59.7 [t, $CH_2C(CH_3)_3$], 108.2 (s, ylidic C), 122.7, 124.3, 125.7, 128.2, 128.4, 128.6 (6d, C-2,3,4 of 2 Ph), 140.3, 140.7 (2s, C-1 of 2 Ph), 155.0 (s, C-5), 179.7 (s, CO) and 184.4 (s, CS).

1-[1-*Benzoyl*-2,2-*bis*(*methylthio*)*vinyl*]-4-*cyclohexyl*-5-*methyl*-1H-*tetrazolium Iodide* **5**.—A solution of potassium carbonate (10.0 g) in water (10 cm^3), followed by carbon disulfide (15 cm^3, *ca.* 0.135 mol) in MeI (18.8 g, 0.13 mol), was added at 0 °C to the salt **2g** (2.56 g, 0.007 mol) in water (10 cm^3). The mixture was vigorously stirred for 24 h at 20 °C and then excess reagents were distilled off. The resultant aqueous solution was extracted with $CHCl_3$ (3 × 25 cm^3) and dried (Na_2SO_4) to give the product (0.40 g, 11%), m.p. 151–152 °C (decomp.)

(ethanol–ether) [Found: C, 44.1; H, 4.9; N, 10.7; S, 12.6. $(C_{19}H_{25}N_4OS_2)I$ requires C, 44.2; H, 4.9; N, 10.85; S, 12.4%]; ν_{max}(KBr)/cm^{-1} 1640; δ_H[$(CD_3)_2SO$] 1.1–2.3 [10 H, m, $CH(CH_2)_5$], 2.43 (3 H, s, SMe), 2.53 (3 H, s, SMe), 3.16 (3 H, s, 5-Me), 4.97 [1 H, m_c, $CH(CH_2)_5$], 7.45–7.7 (3 H, m, Ph) and 7.8–8.0 (2 H, m, Ph).

7-*Acetyl*-5-*benzoyl*-1,6-*dimethyl*-1H-*pyrrolotetrazole* **6a**.—*From* **2m**. The mother liquor of **4a** (*vide supra*) was set aside to allow crystallisation of part of the product (0.05 g), m.p. 210 °C (chloroform–ether) (Found: C, 63.8; H, 5.0; N, 19.0. $C_{15}H_{14}N_4O_2$ requires C, 63.8; H, 5.0; N, 19.85%); ν_{max}(KBr)/cm^{-1} 1645 and 1625; $\delta_H(CDCl_3)$ 2.50, 2.57 (2 × 3 H, 2s, 6-Me/COMe), 4.47 (3 H, s, 1-Me), 7.3–7.5 (3 H, m, Ph) and 7.55–7.7 (2 H, m, Ph); $\delta_C(CDCl_3)$ 15.0 (q, 6-Me), 30.3 (q, $COCH_3$), 37.8 (q, 1-Me), 101.8, 116.8, 137.83, 137.85, 139.2 (5s, quaternary C of pyrrolotetrazole and Ph), 128.4, 128.8, 132.2 (3d, C-2,3,4 of Ph), 184.9 and 191.9 (2s, 2 CO); *m*/*z* (70 eV; 60 °C) 282 (M^+, 99%), 149 (100), 107 (54) and 105 (58). The filtrate was concentrated and chromatographed on silica gel [chloroform–ethyl acetate (9:1) as eluent] to give a second crop of **6a** (0.03 g; total yield 3%) and then an inseparable 1:1 mixture (0.02 g) of **6a** and the pyrrolotetrazole **6b** (TLC, IR, MS).

From **7a**. Triethylamine (0.20 g, 0.002 mol) was added to a stirred suspension of the salt **7a**[20] (0.69 g, 0.002 mol) in acetic anhydride (5 cm^3). The clear solution formed was stirred at 110 °C for 20 min and then at 130 °C for 40 min. Evaporation of the excess of reagent left a brown oil which was shaken with benzene–water [50 cm^3; (4:1)]. The benzene phase was dried (Na_2SO_4) and concentrated to 5–10 cm^3. On addition of ether most of the product (0.07 g) crystallised (data as above). The filtrate was chromatographed as before to afford a second crop of **6a** (0.01 g; total yield 14%) and then a trace amount of **6b** that could not be purified.

5,7-*Diacetyl*-1,6-*dimethyl*-1H-*pyrrolotetrazole* **6b**.—In a way similar to the latter procedure for **6a**, triethylamine (1.5 cm^3, *ca.* 0.01 mol) and the salt **7b**[4] (0.94 g, 0.004 mol) were heated in acetic anhydride (20 cm^3) to 90–100 °C for 2 h. The cooled mixture was diluted with water (40–50 cm^3) and extracted with toluene (3 × 20 cm^3). The combined organic layers were washed with aqueous sodium carbonate, dried (Na_2SO_4) and concentrated. The residue was recrystallised (chloroform–ether) to give the product (0.05 g, 6%), m.p. 130–131 °C (Found: C, 54.6; H, 5.5; N, 25.5. $C_{10}H_{12}N_4O_2$ requires C, 54.5; H, 5.5; N, 25.4%); ν_{max}(KBr)/cm^{-1} 1645; $\delta_H(CDCl_3)$ 2.51 (3 H, s, 6-Me), 2.74, 2.85 (2 × 3 H, 2s, 2 COMe) and 4.53 (3 H, s, 1-Me); $\delta_C(CDCl_3)$ 14.0 (q, 6-Me), 30.4, 30.8 (2q, 2 $COCH_3$), 38.1 (q, 1-Me), 102.0, 117.0, 137.3, 138.5 (4s, quaternary C of pyrrolotetrazole), 187.4 and 192.2 (2s, 2 CO); *m*/*z* (70 eV; 30 °C) 220 (M^+, 76%), 149 (100) and 107 (53).

References

1 Part 1, D. Moderhack and A. Lembcke, *J. Chem. Soc., Perkin Trans. 1*, 1986, 1157 (see also p. 2009).
2 (*a*) F. Kröhnke, *Ber. Dtsch. Chem. Ges.*, 1935, **68**, 1117; (*b*) C. A. Henrick, E. Ritchie and W. C. Taylor, *Aust. J. Chem.*, 1967, **20**, 2441; (*c*) A. R. Katritzky and D. Moderhack, *J. Chem. Soc., Perkin Trans. 1*, 1976, 909.
3 (*a*) D. Moderhack, unpublished work 1979; (*b*) A. Lembcke, Dissertation, Technische Universität Braunschweig (Germany), 1985.
4 D. Moderhack and A. Lembcke, *Chem.-Ztg.*, 1985, **109**, 432.
5 Compounds of this type have been observed in the related 1,2,4-triazole series (**D**: X = N, Y = CMe): (*a*) H. G. O. Becker, H. D. Steinleitner and H.-J. Timpe, *Synthesis*, 1973, 414; (*b*) F. S. Babichev and V. A. Kovtunenko, *Ukr. Khim. Zh.* (*Russ. Ed.*), 1975, **41**, 252.
6 *Cf.* H.-J. Timpe, V. Schröder and R. Worschech, *Rev. Roum. Chem.*, 1980, **25**, 407.
7 E. M. Kosower and B. G. Ramsey, *J. Am. Chem. Soc.*, 1959, **81**, 856.
8 V. Král, V. V. Semenov, M. I. Kanishchev, Z. Arnold, S. A. Shevelev and A. A. Fainzilberg, *Collect. Czech. Chem. Commun.*, 1988, **53**, 1519.
9 F. Kröhnke and K. Gerlach, *Chem. Ber.*, 1962, **95**, 1108; F. Kröhnke, K. Gerlach and K.-E. Schnalke, *Chem. Ber.*, 1962, **95**, 1118.
10 (*a*) V. A. Kovtunenko and F. S. Babichev, *Ukr. Khim. Zh.* (*Russ. Ed.*), 1972, **38**, 1244; (*b*) F. S. Babichev, V. A. Kovtunenko and L. N. Didenko, *Ukr. Khim. Zh.* (*Russ. Ed.*), 1974, **40**, 245.
11 B. B. Molloy, D. H. Reid and F. S. Skelton, *J. Chem. Soc.*, 1965, 65.
12 For definition of this term see: J. Elguero, R. M. Claramunt and A. J. H. Summers, *Adv. Heterocycl. Chem.*, 1978, **22**, 183.
13 F. E. Condon, R. Waldman, N. Kundu and J. P. Trivedi, *Org. Prep. Proced. Int.*, 1974, **6**, 135.
14 E. K. Harvill, R. M. Herbst, E. C. Schreiner and C. W. Roberts, *J. Org. Chem.*, 1950, **15**, 662.
15 K. Nishiyama and A. Watanabe, *Chem. Lett.*, 1984, 455.
16 *Cf.* P. Yates, R. G. F. Giles and D. G. Farnum, *Can. J. Chem.*, 1969, **47**, 3997.
17 *Cf.* W. G. Finnegan, R. A. Henry and R. Lofquist, *J. Am. Chem. Soc.*, 1958, **80**, 3908.
18 J. S. Mihina and R. M. Herbst, *J. Org. Chem.*, 1950, **15**, 1082.
19 For 'reverse substituent effect' exerted by Br and NO_2 ligands on δ_C(CO) of compounds **3a**, **b**, **h**, **i** *cf.* H. H. Vogt and R. Gompper, *Chem. Ber.*, 1981, **114**, 2884.
20 D. Moderhack and D.-O. Bode, *Chem.-Ztg.*, 1991, **115**, 331.

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