A New Series of Non-classical Type C Heteropentalenes: 2*H*-Pyrrolo[2,1-*c*][1,2,4]triazoles

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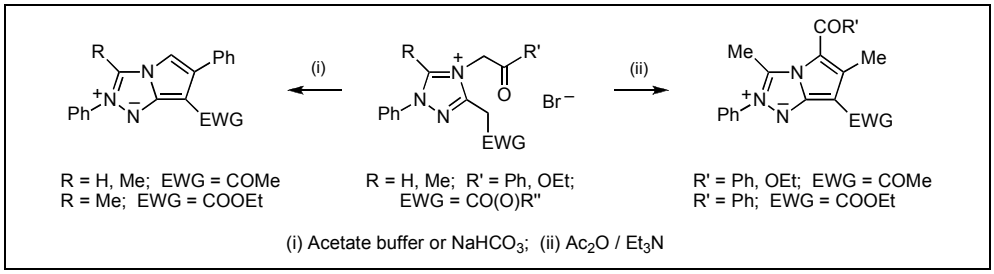
Received July 10, 2006



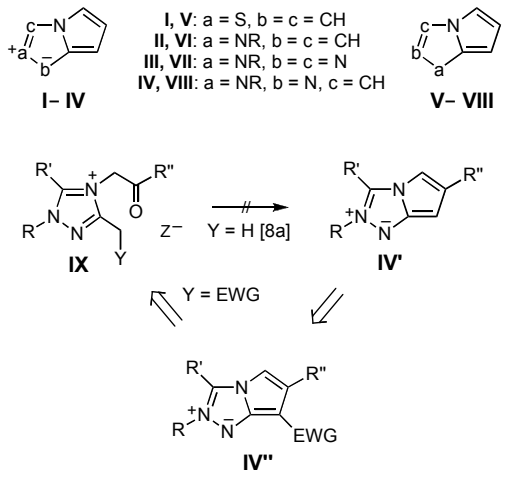
7-Functionalized title compounds **5** are obtained by cyclization of 3-acetonyl- or 3-[(alkoxycarbonyl)-methyl]-4-phenacyl-1,2,4-triazolium salts **2** having methyl at C(5); the process can be effected in an acetate buffer or by base, irrespective of the function at C(3). 5-Unsubstituted salts **2** do not react unless the side chain at C(3) is an acetonyl group. Cyclization of **2** with acetic anhydride–base gives rise to 5,7-difunctionalized compounds **8**; again methyl at C(5) of **2** is compulsory, but here the reaction can be extended to salts having an (alkoxycarbonyl)methyl group at C(4). Regarding defunctionalization, acetyl groups can be split from C(5) only, whereas ester functions are removable also from C(7). Title compounds devoid of acceptor groups (**XIII**) are unstable but can be trapped by electrophilic reagents (DMAD, acetic anhydride, and phenyl isocyanate) to give the derivatives **10** and **12**. The 7-functionalized products **5** are likewise susceptible to S_E-reactions. By comparison, all title compounds appear to be more reactive toward this kind of reagents than the isomeric 1*H*-pyrrolotriazoles (**13**) including 2*H*-pyrrolotetrazoles (**III**). This is consistent with B3LYP-DFT calculations using appropriate models.

J. Heterocyclic Chem., **44**, 393 (2007).

INTRODUCTION

Mesoionic (′non-classical′) heteropentalenes of type C [1] bearing a pyrrolic half-ring were first encountered in 1980; thence studies have developed gradually to include pyrrolo[1,2-*c*]thiazoles (**I**) [2], 2*H*-pyrrolo[1,2-*c*]imidazoles (**II**) [3], and 2*H*-pyrrolotetrazoles (**III**) [4a], *i.e.* the isomers of the ′classical′ systems **V** [5], **VI** [5], and **VII** [4a,6]. Herein we report on the new title series **IV** [7]. Considering the synthetic approach by base-mediated cyclization of *N*-(acylmethyl)-α-methylazolium salts (Tschitschibabin reaction) [5], earlier work has shown that triazolium salts such as **IX** (Y = H) are unsuitable reactants because the 3-methyl group is inactive. As a consequence, salts **IX** having R′ = Me and Y = H led to the isomeric type **VIII** rather than the desired product **IV′**, and representatives **IX** with R′ = H failed to cyclize at all [8a]. Thus we focused on educts **IX** having for Y an activating group (COMe, COOR) to be removed after ring closure. This concept has recently proved fruitful in preparing 2*H*-pyrrolotetrazoles (**III**) [4a]. Nevertheless, starting from **IX** with Y = EWG and R′ = H, one should be aware of possible shortcomings: 5-Unsubstituted 1,2,4-triazolium salts bear an acidic hydrogen at this position [9]; if the electron-withdrawing influence of the acceptor group is too weak, ring deprotonation will be favored over proton loss at the side chain and thus vitiate pyrrole ring closure.

Scheme 1

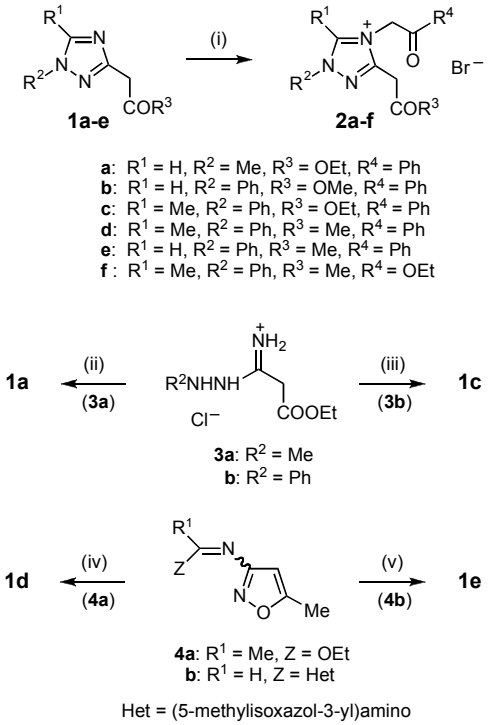


RESULTS AND DISCUSSION

As candidates for cyclization we chose the triazolium salts **2a-f**. These compounds were obtained by quaterniz-

ation of the triazoles **1a-e** with the corresponding alkyl bromide in nitromethane solution [10] (Scheme 2). Access to **1a-e** was effected as follows. Compound **1b** resulted from esterification of the known carboxylic acid [11], whereas the congeners **1a** and **1c** were provided by ring closure of the amidrazones **3a** and **3b** [12] with triethyl orthoformate and acetic anhydride, respectively. Regarding the acetonyltriazoles **1d,e**, the 5-unsubstituted

Scheme 2

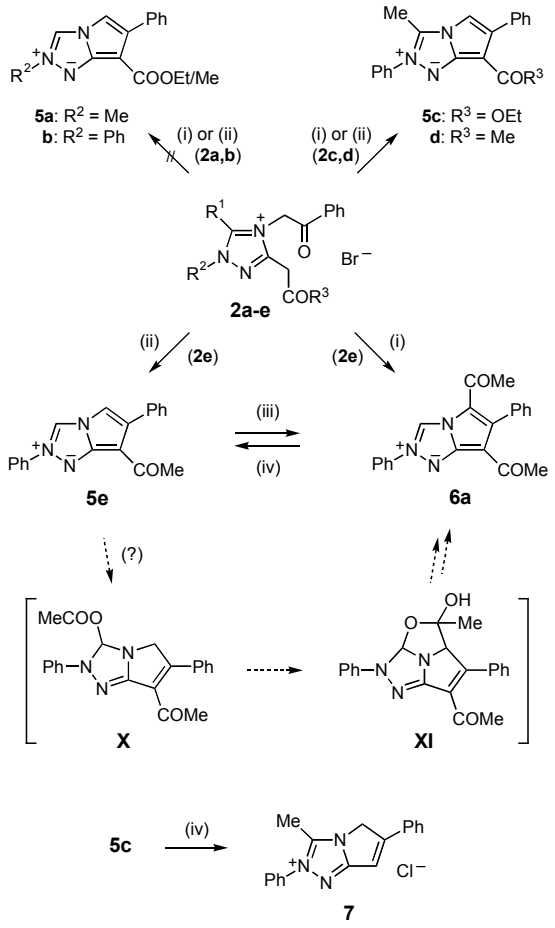


Reagents and conditions: (i) $BrCH_2COPh$, 70 °C, 2 d; or $BrCH_2COOEt$, 70 °C, 24 h (for **2f**); (ii) $CH(OEt)_3$, 80 °C, 1 h; (iii) Ac_2O, 140 °C, 2-3 h; (iv) $PhNH_2$, 60 °C, 8 h; (v) $PhNH_2$, then NaOEt [13]

derivative **1e** was made from the symmetrical *N*,*N*′-bis(isoxazolyl)amidine **4b** by successive treatment with aniline and sodium ethoxide as described earlier [13]. Preparation of **1d**, however, required a modification: Since the homologue of **4b** (Me in place of H) failed to react with aniline, we used the imidate **4a** which on heating with the amine directly produced **1d**.

Attempts to cyclize the salts **2** were started by heating **2a-e** with sodium acetate in acetic acid (*cf.* [4a]). We found that the derivatives **2c,d** readily gave the anticipated products **5c,d** (Scheme 3). However, educts having a free 5-position (**2a,b,e**) either failed to undergo ring closure such as **2a,b** or led to a bicycle that bears an acetyl function also at C(5) (→ **6a**). The first observation shows that the electron-withdrawing force of the ester group is not sufficient to set off ring deprotonation. This can be demonstrated by H/D

Scheme 3



Reagents and conditions: (i) NaOAc / AcOH, 100-110 °C, 1 h; (ii) $NaHCO_3$, 100 °C, 1 h; (iii) AcOH, 100 °C, 20 h; (iv) 12 N HCl, 100 °C, 2 h

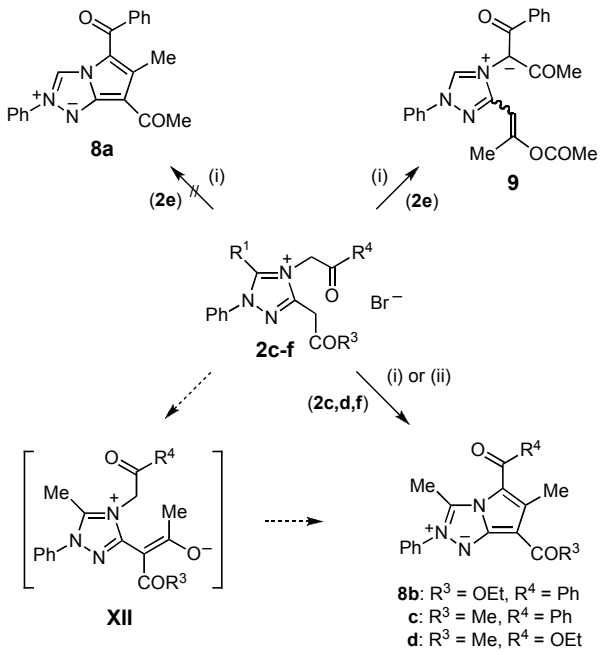
exchange experiments (uncatalyzed): Whereas **2b** exhibits the most active hydrogen at C(5), in the case of **2e** the acetonyl group is preferentially affected. Hence, we repeated cyclization of the latter salt with sodium hydrogencarbonate (conditions of the Tschitschibabin reaction) and thereby could secure the missing compound **5e**. As regards the unexpected formation of **6a**, we tentatively assume that acetic acid protonates C(5) of **5e** giving a cation akin to **7** which, according to the sensitivity of 5-unsubstituted 1,2,4-triazolium ions towards nucleophiles [14], takes up acetate ion to yield the intermediate **X**. This species may cyclize to **XI**. Ensuing dehydration would lead to the tricyclic valence isomer of **6a** [15] which in turn ring-opens. Simply heating of **5e** in acetic acid also gave **6a** [16]. Finally, concerning cyclization of the remainder of **2** with sodium hydrogencarbonate, the salts **2c,d** are reactive too (→ **5c,d**), whereas the 5-unsubstituted representatives **2a** and **2b** under these conditions again turned out to be inert candidates.

Also no bicycle of type **5** was obtained from the salt **2f**: Instead of forming a derivative **5** having an oxygen function at C(6) (*cf.* [17]), **2f** reverted to the triazole **1e** by requaternization [18].

Defunctionalization of the pyrrolotriazoles **5** and **6**, performed with hot mineral acid according to the general practice (*cf.* [4a,8]), proceeded easily as regards the acceptor groups at C(5). However, removing them from C(7), there are limitations: Treatment of the derivatives **5d,e** did no affect the acetyl group and the materials were recovered unchanged; hence, compound **5e** was the sole product from defunctionalization of **6a**. To obtain an acceptor-free bicycle, we resorted to the ester **5c**. In this case, the hydrochloride salt **7** [19] separated directly from the reaction mixture; attempts to isolate the free base **XIII** met with failure and the species had to be trapped by reagents (see later; Scheme 5). This elusive character markedly contrasts with the stability of acceptor-free 2*H*-pyrrolotetrazoles (**III**) [4a] and recalls properties of the 2*H*-pyrrolo[1,2-*c*]imidazole system (**II**) [3a].

In a complementary range of cyclization experiments we sought access to the title class by treating **2** with acetic anhydride in the presence of base, *i.e.* by applying the synthetic principle known from other pyrroloazoles [4,8a,20]. By this procedure the bicycles **8b-d** were obtained from the salts **2c,d**, and **f**, respectively (Scheme 4). The reaction proceeds *via* intermediates such as **XII**; this is inferred from related processes [4a,20b,21,22]. However, for direct observation the species **XII** cyclized too rapidly [23]. The extent of their formation depends on how strongly activation of the C(3)-linked methylene group in **2** exceeds that of the N(4)-linked one. Comparing the educts **2c** and **2f**, the latter is clearly better prepared for attack, since here the relevant side chain at C(3) bears the more efficient activator. Hence the yield of **8d** is nearly twice that of **8b** whereas, conceivably too, that of **8c** holds the mid between them. As a result of the less favored acetylation of the C(3)-linked methylene group of **2c**, the 5-acetyl derivative **6b** arose as a side product of **8b**: Here acetic anhydride simply worked as a dehydrating agent [4a,22b] to form intermediary **5c**, which in turn underwent electrophilic substitution (*cf.* Scheme 5). The salt **2e** having an unsubstituted 5-position could not be cyclized to the derivative **8a** but instead gave the open-chain ylide **9** [24]. Owing to the absence of the electron-releasing methyl group at C(5), activation of the N(4)-linked methylene group of **2e** is obviously too high with respect to the C(3)-linked one. Heating of **9** in methanol slowly produced compound **5e** – a reaction that is comparable to the recently described conversion of similarly functionalized tetrahydroquinolizinium ylides into indolizines [25]. Attempts to transform **9** into the bicycle **8a** by heating the compound with base or by thermolysis remained largely unrewarded [16].

Scheme 4



Reagents and conditions: (i) Ac_2O / Et_3N, 25 °C, 2 d (for **8b,c**) or 2.5 h (for **9**); (ii) Ac_2O / Et_3N, 130 °C, 1 h (for **8d**)

Table 1. Selected ^{13}C NMR Data of Pyrrolotriazoles [a]

N°	C(5)	C(6)	C(7)	C(7a)
5c	94.6	140.5	82.7	152.7
5e	100.9	138.5	93.1	154.4
6a	115.5	145.4	103.4	152.6
6b	116.4	148.3	91.2	152.5
6c	116.8	146.7	101.9	152.9
8b	115.5	147.1	91.0	153.2
8c	116.0	146.6	100.5	154.1
8d	106.0	146.8	99.1	154.0
10a	114.0	148.6	88.2	153.5

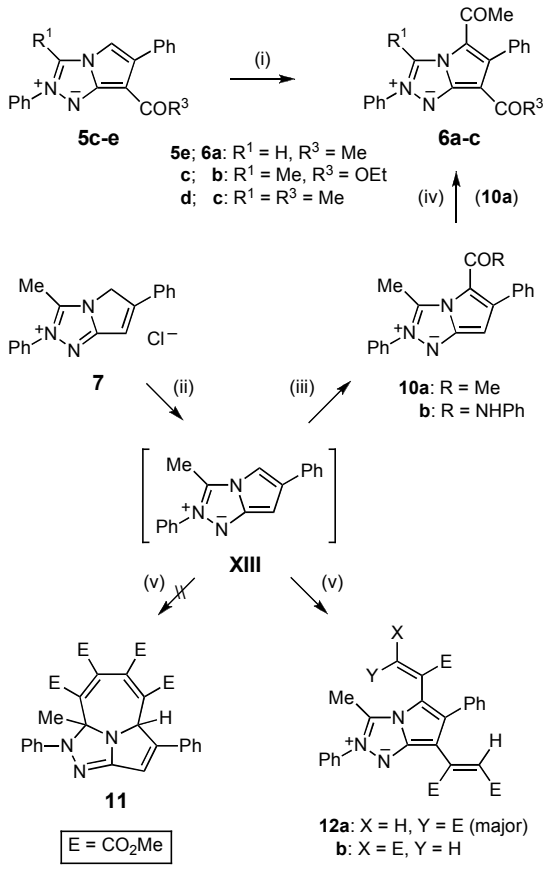
[a] $CDCl_3$ or DMSO-d_6 (**5e**), δ ppm; all signals are singlets except for C(5) of **5c,e** and C(7) of **10a**.

All of the above cyclization products **5**, **6**, and **8** are reliably identifiable by ^{13}C NMR. Diagnostic are the resonances of the pyrrolic carbon atoms since they appear outside the areas typical of the substitutents and of C(3) of the triazole unit. Of particular value is the singlet of the ring junction carbon [C(7a)] which occurs within the narrow range of δ 152–154 ppm (Table 1). As anticipated, this carbon atom absorbs at lower field compared to C(7a) of the isomeric system **VIII** [26]. The same deshielding is observed with 2*H*-pyrrolotetrazoles (**III**) [4a] and other ′non-classical′ type C heteropentalenes [28, 29].

As expected from our experience with the 2*H*-pyrrolotetrazole series (**III**) [4b] and the ample material available on systems **V**–**VII** [30], the new heteropentalenes **5**

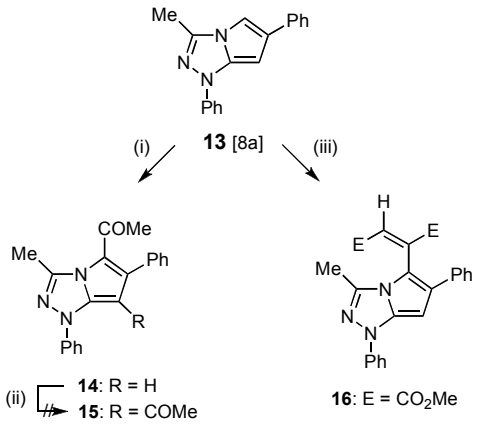
and **XIII** should exhibit appreciable reactivity towards electrophiles. Site of attack should be the pyrrolic half-ring and here, in the case of free 5- and 7-positions, preferentially C(5). This view is consistent with calculations of the π-electron densities (Table 2). From an inspection of these figures it is likewise apparent that the reactivity of the title system (**IV**) should exceed not only that of the 1*H*-isomer (**VIII**) but also that of **III**. These presuppositions are borne out by the following. (i) Treatment of **XIII** with acetic anhydride or phenyl isocyanate led to the 5-functionalized derivatives **10a** and **10b**, respectively (Scheme 5). (ii) Prolonged heating of **10a** with the anhydride introduced a second acetyl group at C(7) to give **6c**. This additional substitution failed not only with the 1*H*-isomer **14** (easily made from **13**; Scheme 6) but also with the 2*H*-pyrrolotetrazole analogue of **10a** (N in place of CMe) [31]. Moreover, while the compounds **5e** and **5d** are readily converted into the diacetyl derivatives **6a** and **6c**, respectively, the tetrazole congener of **5d,e** (N in place of CR^1) could not be induced to undergo further acetylation [4b].

Scheme 5



Reagents and conditions: (i) Ac_2O, 65 °C, 1 h; (ii) DMF / Et_3N; (iii) Ac_2O, 80 °C, 1 h; or PhNCO, 20 °C, 1 h; (iv) Ac_2O, 100 °C, 2 h (for **6c**); (v) DMAD, 65 °C, 1 h

Scheme 6



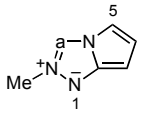
Reagents and conditions: (i) Ac_2O, 65 °C, 1 h; (ii) Ac_2O, 100 °C, 2 h; (iii) DMAD, 65 °C, 1 h

To illustrate the reactivity towards activated multiple bonds, we allowed dimethyl acetylenedicarboxylate (DMAD) to react with the deprotonated salt **7**. From this procedure a 1:2 product was obtained. Considering the behavior of a 2*H*-pyrrolo[1,2-*c*]imidazole derivative (**II**; R = Me) which by virtue of the inherent azomethine ylide moiety yields a 1:2 cycloadduct [3a], the above product might have an analogous constitution (**11**). However, the ^{13}C NMR spectrum revealed that a twofold Michael-type addition had occurred, leading to the 5,7-disubstituted derivative **12a** with *E* and *Z* configurated side chains. The stereochemical assignment was made on the basis of the $^3J_{C(5),H(vinyl)}$ and $^3J_{C(7),H(vinyl)}$ coupling constants (9.6 and 6.4 Hz, respectively), in conjunction with the typically discerned resonances of the β carbon atom of the vinyl groups [32] which appear at δ 123.2 (*E*) and 106.9 (*Z*), respectively. A second stereoisomer (**12b**) could also be detected, albeit in traces ($^3J_{C(5),H(vinyl)}$: 6.2 Hz; $^3J_{C(7),H(vinyl)}$: 6.5 Hz). To compare the above behavior with that of the 1*H*-isomeric class **VIII**, we reacted the derivative **13** under the same conditions. Here we only found the 1:1 product **16**, in parallel to the findings with the pyrrolotetrazole series **III** and **VII** [4b]. This again shows the remarkably high reactivity of the title class **IV**.

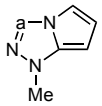
EXPERIMENTAL

Melting points were determined on a Kofler microscope. Elemental analyses were obtained on a Carlo-Erba C-H-N-O Elemental Analyser 1106 or Thermo Quest 1112 Elemental Analyzer (with three compounds optimum values obtained for carbon were within 0.6–0.8 only, although the materials were pure by NMR). The IR spectra were recorded on a Philips PU-9800 FTIR or Thermo Nicolet FT-IR 200 instrument. The NMR spectra were run on a Bruker DRX-400 spectrometer. The UV/VIS spectra were determined on a Philips PU-8730 spectrometer or Jena Specord 200 UV/VIS-Spektrometer. The mass spectra

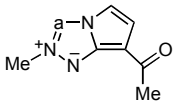
Table 2. Energies and π-Electron Densities of Pyrrolotetrazole and -triazole Models [a]



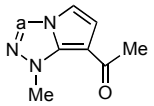
IIIa, IVa



VIIa, VIIIa



IIIb, IVb



VIIb, VIIIb

N°	a	-*E* [b]	E_{rel}	N(1)	N(2)	C/N(3)	N(4)	C(5)	C(6)	C(7)	C(7a)
IIIa	N	413.16130	4.07	1.208	1.430	1.288	1.401	1.189	1.018	1.146	1.104
VIIa	N	413.16778	0.00	1.515	1.158	1.187	1.441	1.161	1.034	1.162	1.114
IVa	CH	397.14195	9.64	1.279	1.447	1.136	1.405	1.226	1.012	1.172	1.082
VIIIa	CH	397.15732	0.00	1.549	1.203	1.064	1.440	1.185	1.031	1.177	1.095
IIIb	N	565.86054	6.42	1.203	1.419	1.258	1.391	1.172	0.973	1.077	1.131
VIIb	N	565.87077	0.00	1.477	1.149	1.174	1.423	1.147	1.038	1.100	1.097
IVb	CH	549.84434	10.87	1.265	1.443	1.098	1.401	1.202	0.966	1.110	1.106
VIIIb	CH	549.86166	0.00	1.502	1.195	1.048	1.430	1.166	1.037	1.108	1.081

[a] Calculated at the B3LYP/6-311+G(d,p) level of theory; all molecules are fully planar; acetyl derivatives shown are lowest energy conformers; [b] *E* in a.u., E_{rel} in kcal/mol.

were taken on a Finnigan MAT 8430 or MAT 90 machine. Chromatography was carried out on silca gel Woelm 63–200 μm.

3-[(Ethoxycarbonyl)methyl]-1-methyl-4-phenacyl-1,2,4-triazolium bromide (2a). Adopting the procedure described in [33], methylhydrazine (4.60 g, 100 mmol) was added with stirring and ice-cooling to a suspension of ethyl 2-(ethoxycarbonyl)acetimidate hydrochloride (19.5 g, 100 mmol) [34] in dry pyridine (50 mL). After 2 hours diethyl ether was added and the mixture was kept overnight at 0–5 °C to allow crystallization of 10.7 g (55%) of 2-(ethoxycarbonyl)-*N*^{2}-methylacetamidrazone hydrochloride (**3a**) [^{1}H NMR ($CDCl_3$; 90 MHz): δ 1.23 (t, *J* = 7 Hz, 3H), 2.52 (s, 3H), 3.84 (s, 2H), 4.12 (q, *J* = 7 Hz, 2H), 11.53 (br s, 1H)]. This material (1.00 g, 6.3 mmol) was dissolved in dry ethanol (25 mL) and, after adding triethyl orthoformate (0.94 g, 6.3 mmol), heated at reflux for 1 hour. The mixture was made alkaline with aqueous sodium carbonate (10%) and extracted with dichloromethane to give 0.88 g (83%) of oily ethyl 1-methyl-1,2,4-triazole-3-carboxylate (**1a**) [^{1}H NMR ($CDCl_3$): δ 1.27 (t, *J* = 7.1 Hz, 3H), 3.78 (s, 2H), 3.88 (s, 3H), 4.19 (q, *J* = 7.1 Hz, 2H), 7.98 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 13.9 (q), 34.4 (t), 35.9 (q), 60.9 (t), 144.1 (d), 158.1 (s), 169.3 (s)]. This material (1.00 g, 5.9 mmol) and 2-bromo-1-phenylethanone (1.20 g, 6 mmol) were dissolved in nitromethane (20 mL) and heated at 70 °C for 48 hours. Concentration *in vacuo* left an oil that on treatment with ethyl acetate–diethyl ether crystallized to afford 1.37 g (63%) of **2a**; mp 199–201 °C (decomp.; ethanol); IR (KBr): $\tilde{\nu}$ 1737, 1711 cm−1; 1H NMR (DMSO-d_6): δ 1.09 (t, *J* = 7.1 Hz, 3H), 4.05 (q, *J* = 7.1 Hz, 2H), 4.20 (s, 3H), 4.38 (s, 2H), 6.25 (s, 2H), 7.62–7.79 (m, 3H), 8.07–8.12 (m, 2H), 10.18 (s, 1H); ^{13}C NMR (DMSO-d_6): δ 13.7 (q), 30.2 (t), 39.0 (q), 53.1 (t), 61.6 (t), 128.4 (d, 2C), 129.0 (d, 2C), 133.4 (s), 134.6 (d), 145.0 (d), 150.7 (s), 166.3 (s), 190.1 (s). *Anal.* Calcd. for $[C_{15}H_{18}N_3O_3]Br$: C, 48.93; H, 4.93; N, 11.41. Found: C, 48.89; H, 4.95; N, 11.20.

3-[(Methoxycarbonyl)methyl]-4-phenacyl-1-phenyl-1,2,4-triazolium bromide (2b). To (1-phenyl-1,2,4-triazol-3-yl)acetic acid (1.00 g, 5 mmol) [11] was added methanol (10 mL) with a drop of concentrated sulfuric acid. The mixture was heated at reflux for 2 hours, then diluted with water and repeatedly extracted with dichloromethane. The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated *in vacuo* to give 0.60 g (59%) of methyl (1-phenyl-1,2,4-triazol-3-yl)acetate (**1b**) [mp 51–54 °C (diethyl ether–light petroleum); IR (KBr): $\tilde{\nu}$ 1750 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.76 (s, 3H), 3.92 (s, 2H), 7.36–7.39 (m, 1H), 7.46–7.50 (m, 2H), 7.64–7.66 (m, 2H), 8.53 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 34.3 (t), 52.3 (q), 119.8 (d, 2C), 128.0 (d), 129.6 (d, 2C), 136.7 (s), 141.1 (d), 158.7 (s), 169.6 (s)]. This material (1.50 g, 6.9 mmol) and 2-bromo-1-phenylethanone (1.65 g, 8.3 mmol) were dissolved in nitromethane (20 mL) and heated at 70 °C for 48 hours. Work-up as described above gave 1.90 g (66%) of **2b**; mp 165 °C (ethyl acetate–acetone); IR (KBr): $\tilde{\nu}$ 1738, 1700 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 3.63 (s, 3H), 4.54 (s, 2H), 6.34 (s, 2H), 7.66–7.83 (m, 6H), 7.97–7.99 (m, 2H), 8.14–8.16 (m, 2H), 11.13 (s, 1H); ^{13}C NMR (DMSO-d_6): δ 30.3 (t), 52.8 (q), 53.5 (t), 120.6 (d, 2C), 128.7 (d, 2C), 129.1 (d, 2C), 130.4 (d, 2C), 130.8 (d), 133.3 (s), 134.6 (s), 134.8 (d), 143.6 (d), 151.5 (s), 166.7 (s), 189.7 (s). *Anal.* Calcd. for $[C_{19}H_{18}N_3O_3]Br$: C, 54.82; H, 4.36; N, 10.09. Found: C, 54.56; H, 4.32; N, 10.00.

3-[(Ethoxycarbonyl)methyl]-5-methyl-4-phenacyl-1-phenyl-1,2,4-triazolium bromide (2c). A mixture of **3b** (1.00 g, 4 mmol) [12] and acetic anhydride (5.00 g, 50 mmol) was heated at reflux until a clear solution had formed (2–3 hours). After addition of water (to allow hydrolysis of unconsumed reagent) it was made alkaline with aqueous sodium carbonate (10%) and extracted several times with dichloromethane. The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo* to afford 0.76 g (78%) of oily ethyl (5-methyl-1-phenyl-1,2,4-triazol-3-yl)acetate (**1c**) [^{1}H NMR ($CDCl_3$): δ 1.21 (t, *J* = 7.1 Hz, 3H), 2.43 (s, 3H), 3.73 (s, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 7.33–7.44 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 13.0 (q), 14.0 (q), 34.3 (t), 61.1 (t), 124.4 (d, 2C), 128.6 (d), 129.2 (d, 2C), 137.1 (s), 152.7 (s), 157.0 (s), 169.4 (s)]. This material (4.90 g, 20 mmol) and 2-bromo-1-phenylethanone (4.20 g, 21 mmol) were dissolved in nitromethane (20 mL) and heated at 70 °C for 48 hours. Work-up as above gave 6.50 g (73%) of **2c**; mp 153 °C (ethanol); IR (KBr): $\tilde{\nu}$ 1718, 1689 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 1.08 (t, *J* = 7.1 Hz, 3H), 2.78 (s, 3H), 4.01 (q, *J* = 7.1 Hz, 2H), 4.47 (s, 2H), 6.33 (s, 2H), 7.66–7.75 (m, 5H), 7.79–7.83 (m, 3H), 8.13–8.15 (m, 2H); ^{13}C NMR (DMSO-d_6): δ 11.2 (q), 13.7 (q), 30.6 (t), 52.3 (t), 61.7 (t), 125.3 (d, 2C), 128.7 (d, 2C), 128.9 (d, 2C), 130.1 (d, 2C), 131.3 (d), 133.8 (s), 134.5 (s), 134.7 (d), 150.2 (s),

154.4 (s), 166.3 (s), 189.7 (s). *Anal*. Calcd. for $[C_{21}H_{22}N_3O_3]Br$: C, 56.77; H, 4.99; N, 9.46. Found: C, 56.06; H, 4.89; N, 9.27 [35].

3-Acetonyl-5-methyl-4-phenacyl-1-phenyl-1,2,4-triazolium bromide (2d). A mixture of 5-methylisoxazol-3-amine (3.00 g, 30 mmol) and triethyl orthoacetate (4.90 g, 30 mmol) was heated at reflux for 1.5 hours. *In vacuo* concentration gave 4.90 g (96%) of oily ethyl *N*-(5-methylisoxazol-3-yl)acetimidate (**4a**) [^{1}H NMR ($CDCl_3$): δ 1.32 (t, J = 7.1 Hz, 3H), 2.01 (s, 3H), 2.37 (d, J = 0.8 Hz, 3H), 4.28 (q, J = 7.1 Hz, 2H), 5.68 (d, J = 0.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 12.5 (q), 14.0 (q), 17.9 (q), 62.4 (t), 98.2 (d), 165.7 (s), 166.7 (s), 169.7 (s)]. This material (4.00 g, 24 mmol) was heated with aniline (2.24 g, 24 mmol) at 60 °C for 8 hours. Removal of formed ethanol under reduced pressure left 4.90 g (95%) of oily (5-methyl-1-phenyl-1,2,4-triazol-3-yl)-acetone (**1d**) [^{1}H NMR ($CDCl_3$): δ 2.28 (s, 3H), 2.52 (s, 3H), 3.87 (s, 2H), 7.43–7.46 (m, 3H), 7.49–7.51 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 13.1 (q), 29.6 (q), 43.3 (t), 124.4 (d, 2C), 128.7 (d), 129.3 (d, 2C), 137.1 (s), 152.8 (s), 157.3 (s), 203.8 (s)]. This material (4.30 g, 20 mmol) and 2-bromo-1-phenylethanone (4.80 g, 24 mmol) were dissolved in nitromethane (20 mL) and heated at 70 °C for 48 hours. Work-up as above gave 7.10 g (86%) of **2d**; mp 188 °C (decomp.; ethanol); IR (KBr): $\tilde{\nu}$ 1733, 1693 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 2.26 (s, 3H), 2.78 (s, 3H), 4.67 (s, 2H), 6.27 (s, 2H), 7.64–7.68 (m, 2H), 7.72–7.74 (m, 3H), 7.77–7.83 (m, 3H), 8.15–8.17 (m, 2H); ^{13}C NMR (DMSO-d_6): δ 11.3 (q), 29.7 (q), 39.1 (t), 52.5 (t), 125.2 (d, 2C), 128.8 (d, 2C), 128.9 (d, 2C), 130.1 (d, 2C), 131.2 (d), 133.5 (s), 134.5 (s), 134.6 (d), 151.0 (s), 154.1 (s), 190.0 (s), 201.6 (s). *Anal*. Calcd. for $[C_{20}H_{20}N_3O_2]Br$: C, 57.98; H, 4.87; N, 10.14. Found: C, 58.19; H, 4.56; N, 10.15.

3-Acetonyl-4-phenacyl-1-phenyl-1,2,4-triazolium bromide (2e). A mixture of **1e** (4.02 g, 20 mmol) [13] and 2-bromo-1-phenylethanone (4.80 g, 24 mmol) was heated in nitromethane (20 mL) at 70 °C for 48 hours. Work-up as described above gave 5.20 g (65%) of **2c**; mp 205 °C (decomp.; ethanol); IR (KBr): $\tilde{\nu}$ 1731, 1700 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 2.29 (s, 3H), 4.64 (s, 2H), 6.16 (s, 2H), 7.65–7.83 (m, 6H), 7.95–7.98 (m, 2H), 8.12–8.15 (m, 2H), 10.98 (d, J = 1.5 Hz, 1H); ^{13}C NMR (DMSO-d_6): δ 29.8 (q), 38.8 (t), 53.2 (t), 120.6 (d, 2C), 128.6 (d, 2C), 129.1 (d, 2C), 130.4 (d, 2C), 130.8 (d), 133.3 (s), 134.7 (s), 134.8 (d), 143.5 (d), 152.3 (s), 189.7 (s), 201.5 (s). *Anal*. Calcd. for $[C_{19}H_{18}N_3O_2]Br$: C, 57.01; H, 4.53; N, 10.50. Found: C, 56.57; H, 4.62; N, 10.22.

3-Acetonyl-4-[(ethoxycarbonyl)methyl]-5-methyl-1-phenyl-1,2,4-triazolium bromide (2f). A mixture of **1c** (4.30 g, 20 mmol; material as above) and ethyl bromoacetate (3.30 g, 20 mmol) was heated in nitromethane (20 mL) at 70 °C for 24 hours. Work-up as described above gave 1.00 g (13%) of **2f**; mp 179–181 °C (ethanol); IR (KBr): $\tilde{\nu}$ 1740, 1722 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 1.28 (t, J = 7.1 Hz, 3H), 2.32 (s, 3H), 2.81 (s, 3H), 4.26 (q, J = 7.1 Hz, 2H), 4.64 (s, 2H), 5.43 (s, 2H), 7.71–7.73 (m, 3H), 7.76–7.78 (m, 2H); ^{13}C NMR (DMSO-d_6): δ 11.3 (q), 13.9 (q), 29.7 (q), 38.9 (t), 46.8 (t), 62.2 (t), 125.2 (d, 2C), 130.1 (d, 2C), 131.3 (d), 134.4 (s), 150.7 (s), 154.0 (s), 165.3 (s), 201.6 (s). *Anal*. Calcd. for $[C_{16}H_{20}N_3O_3]Br$: C, 50.27; H, 5.27; N, 10.99. Found: C, 50.14; H, 5.28; N, 10.84.

Ethyl 3-methyl-2,6-diphenyl-2*H*-pyrrolo[2,1-*c*][1,2,4]triazole-7-carboxylate (5c). Procedure (i): A solution of **2c** (0.44 g, 1 mmol) in acetic acid (5.00 g, *ca*. 83 mmol) was heated with anhydrous sodium acetate (0.55 g, 6.7 mmol) for 1 hour at 100–110 °C. After cooling the mixture was made weakly alkaline with aqueous sodium carbonate (10%) and repeatedly extracted with dichloromethane. The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo* to give a residue that was chromatographed on silica gel using dichloromethane–ethyl acetate (4/1) as eluent.

Procedure (ii): To a suspension of **2c** (0.89 g, 2 mmol) in water (20 mL) was added sodium hydrogencarbonate (0.17 g, 2 mmol) and the mixture was heated for 1 hour at 100 °C. After cooling the precipitate was collected by filtration.

5c: Yield from (i) and (ii): 0.12 g (35%) and 0.58 g (47%), respectively; mp 158 °C (ethanol); IR (KBr): $\tilde{\nu}$ 1658 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.26 (t, J = 7.1 Hz, 3H), 2.66 (s, 3H), 4.26 (q, J = 7.1 Hz, 2H), 6.50 (s, 1H), 7.29–7.36 (m, 3H), 7.47–7.58 (m, 7H); ^{13}C NMR ($CDCl_3$): δ 10.1 (q), 14.7 (q), 58.3 (t), 82.7 (s), 96.4 (d), 125.2 (d, 2C), 127.1 (d), 127.3 (d, 2C), 129.3 (d, 2C), 129.5 (d, 2C), 129.7 (d), 129.8 (s), 135.0 (s), 136.6 (s), 140.5 (s), 152.7 (s), 164.0 (s); UV (MeOH): λ (log ε) 221 (4.31), 253 (4.43), 274 (4.26), 348 (3.84) nm; MS (m/z, %): 345 (M$^+$, 48), 118 (100). *Anal*. Calcd. for $C_{21}H_{19}N_3O_2$: C, 73.03; H, 5.54; N, 12.17. Found: C, 72.62; H, 5.43; N, 11.90.

7-Acetyl-3-methyl-2,6-diphenyl-2*H*-pyrrolo[2,1-*c*][1,2,4]-triazole (5d). Procedure (i): A solution of **2d** (1.00 g, 2.4 mmol) in acetic acid (10.0 g, *ca*. 170 mmol) was heated with anhydrous sodium acetate (1.10 g, 13.4 mmol) as above and worked up accordingly.

Procedure (ii): To a suspension of **2d** (4.00 g, 9.7 mmol) in water (20 mL) was added sodium hydrogencarbonate (0.90 g, 10.7 mmol) and the mixture was stirred at 25 °C for 3 days, whereupon the solid was filtred off.

5d: Yield from (i) and (ii): 0.24 g (32%) and 2.90 g (95%), respectively; mp 231 °C (decomp.; ethanol); IR (KBr): $\tilde{\nu}$ 3122, 1588 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.48 (s, 3H), 2.73 (s, 3H), 6.58 (s, 1H), 7.30–7.36 (m, 4H), 7.56–7.59 (m, 6H); ^{13}C NMR: spectrum not available because of poor solubility; UV (MeOH): λ (log ε) 222 (4.40), 257 (4.28), 295 (4.10), 351 (4.15) nm; MS (m/z, %): 315 (M$^+$, 65), 300 (90), 77 (100). *Anal*. Calcd. for $C_{20}H_{17}N_3O$: C, 76.19; H, 5.43; N, 13.32. Found: C, 75.72; H, 5.48; N, 13.15.

7-Acetyl-2,6-diphenyl-2*H*-pyrrolo[2,1-*c*][1,2,4]triazole (5e). To a suspension of **2e** (0.80 g, 2 mmol) in water (20 mL) was added sodium hydrogencarbonate (0.17 g, 2 mmol) and the mixture was heated at 100 °C for 1 hour; the solid formed was collected by filtration.

5e: Yield: 0.57 g (89%); mp 217 °C (decomp.; ethanol); IR (KBr): $\tilde{\nu}$ 3118, 1589 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 2.47 (s, 3H), 7.13 (s, 1H), 7.30–7.37 (m, 3H), 7.53–7.57 (m, 3H), 7.64–7.68 (m, 2H), 8.00–8.03 (m, 2H); ^{13}C NMR (DMSO-d_6): δ 29.4 (q), 93.1 (s), 100.9 (d), 120.5 (d, 2C), 123.3 (d), 126.9 (d), 127.3 (d, 2C), 129.1 (d), 129.3 (d, 2C), 129.8 (d, 2C), 135.1 (s), 137.0 (s), 138.5 (s), 154.4 (s), 185.4 (s); UV (MeOH): λ (log ε) 226 (4.34), 263 (4.28), 295 (4.38), 360 (3.93) nm; MS (m/z, %): 301 (M$^+$, 85), 286 (100). *Anal*. Calcd. for $C_{19}H_{15}N_3O \cdot H_2O$: C, 71.46; H, 5.37; N, 13.16. Found: C, 71.23; H, 5.44; N, 13.03.

5,7-Diacetyl-2,6-diphenyl-2*H*-pyrrolo[2,1-*c*][1,2,4]triazole (6a). Procedure (i): A solution of **2e** (0.40 g, 1 mmol) in acetic acid (10.0 g, *ca*. 83 mmol) was heated with anhydrous sodium acetate (0.55 g, 6.7 mmol) as described above for **5c** [procedure (i)] and worked up accordingly.

Procedure (ii): A mixture of **5e** (0.30 g, 1 mmol) and acetic anhydride (5.00 g, 50 mmol) was stirred at 65 °C for 1 hour. The cooled solution was diluted with water (10 mL) to allow hydrolysis of unconsumed reagent and neutralized with aqueous sodium carbonate (20%); then the solid was filtered off.

6a: Yield from (i) and (ii): 0.12 g (35%) and 0.19 g (55%), respectively; mp 209 °C (decomp.; ethanol); IR (KBr): $\tilde{\nu}$ 1646, 1610 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.80 (s, 3H), 2.24 (s, 3H), 7.41–7.62 (m, 8H), 7.91–7.94 (m, 2H), 10.14 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 26.7 (q), 29.6 (q), 103.4 (s), 115.5 (s), 121.0 (d, 2C), 124.6 (d), 128.4 (d, 2C), 128.5 (d), 129.0 (d, 2C), 129.8 (d), 130.0 (d, 2C), 134.8 (s), 136.9 (s), 145.4 (s), 152.6 (s), 186.0 (s), 190.8 (s); UV (MeOH): λ (log ε) 265 (4.53), 368 (4.43) nm; MS (m/z, %): 343 (M^+, 60), 328 (100). *Anal.* Calcd. for $C_{21}H_{17}N_3O_2$: C, 73.45; H, 4.99; N, 12.24. Found: C, 73.20; H, 4.91; N, 11.91.

Ethyl 5-acetyl-3-methyl-2,6-diphenyl-2*H*-pyrrolo[2,1-*c*]-[1,2,4]triazole-7-carboxylate (6b). Following the above procedure (ii), **5c** (0.35 g, 1 mmol) was heated with acetic anhydride (5.00 g, 50 mmol) and the mixture was worked up accordingly.

6b: Yield: 0.26 g (67%); mp 192–194 °C (ethanol); IR (KBr): $\tilde{\nu}$ 1685 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.05 (t, J = 7.1 Hz, 3H), 1.74 (s, 3H), 3.15 (s, 3H), 4.12 (q, J = 7.1 Hz, 2H), 7.36–7.38 (m, 2H), 7.42–7.45 (m, 3H), 7.58–7.59 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.1 (q), 14.5 (q), 28.2 (q), 59.2 (t), 91.2 (s), 116.4 (s), 126.2 (d, 2C), 127.8 (d, 2C), 127.9 (d), 129.0 (d, 2C), 129.5 (d, 2C), 130.3 (d), 135.7 (s), 136.7 (s), 137.8 (s), 148.3 (s), 152.5 (s), 163.1 (s), 185.0 (s). *Anal.* Calcd. for $C_{23}H_{21}N_3O_3$: C, 71.30; H, 5.46; N, 10.85. Found: C, 71.03; H, 5.53; N, 10.62.

5,7-Diacetyl-3-methyl-2,6-diphenyl-2*H*-pyrrolo[2,1-*c*][1,2,4]-triazole (6c). Procedure (i): Compound **5d** (0.31 g, 1 mmol) was heated with acetic anhydride (5.00 g, 50 mmol) according to the above procedure (ii) for **6a**. The cooled mixture was diluted with water (10 mL) and, after hydrolysis of unconsumed reagent, neutralized with aqueous sodium carbonate (20%) to be followed by repeated extractions with dichloromethane. The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo* and the residue was chromatographed on silica gel using dichloromethane–ethyl acetate (4/1) as eluent.

Procedure (ii): A stirred mixture of **10a** (0.10 g, 0.3 mmol; for preparation, see below) and acetic anhydride (3.00 g, 30 mmol) was heated at 100 °C for 2 hours. Work-up was performed as with (i).

6c: Yield from (i) and (ii): 0.17 g (48%) and 0.09 g (80%), respectively; mp 236–238 °C (ethanol); IR (KBr): $\tilde{\nu}$ 1640, 1617 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.73 (s, 3H), 2.12 (s, 3H), 3.14 (s, 3H), 7.38–7.41 (m, 2H), 7.46–7.49 (m, 3H), 7.58–7.60 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.5 (q), 28.3 (q), 29.5 (q), 101.9 (s), 116.8 (s), 126.1 (d, 2C), 128.34 (d), 128.35 (d, 2C), 128.9 (d, 2C), 129.6 (d, 2C), 130.4 (d), 135.7 (s), 136.6 (s), 137.9 (s), 146.7 (s), 152.9 (s), 185.7 (s), 190.4 (s); UV (MeOH): λ (log ε) 203 (4.48), 366 (4.49) nm; MS (m/z, %): 357 (M^+, 50), 342 (100). *Anal.* Calcd. for $C_{22}H_{19}N_3O_2$: C, 73.93; H, 5.36; N, 11.76. Found: C, 73.15; H, 5.50; N, 11.41 [35].

3-Methyl-2,6-diphenyl-5*H*-pyrrolo[2,1-*c*][1,2,4]triazolium chloride (7). To **5c** (0.35 g, 1 mmol) was added 12 N HCl (10 mL) and the mixture was heated at 100 °C for 2 hours. On neutralization with aqueous sodium carbonate (10%) the product precipitated and was collected by filtration.

7: Yield: 0.09 g (29%); mp 184 °C (ethanol); IR (KBr): $\tilde{\nu}$ 3045, 1611 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.85 (s, 3H), 5.73 (s, 2H), 7.56–7.59 (m, 3H), 7.70–7.78 (m, 6H), 7.87–7.88 (m, 2H); ^{13}C NMR (DMSO-d_6): δ 11.2 (q), 52.3 (t), 108.9 (d), 125.1 (d, 2C), 126.9 (d, 2C), 129.2 (d, 2C), 130.0 (d, 2C), 130.7 (s), 130.9 (d), 131.2 (d), 135.2 (s), 149.5 (s), 157.5 (s), 160.9 (s). *Anal.* Calcd. for $[C_{18}H_{16}N_3]Cl \cdot H_2O$: C, 65.95; H, 5.53; N, 12.82. Found: C, 65.51; H, 5.52; N, 12.53.

Ethyl 5-benzoyl-3,6-dimethyl-2-phenyl-2*H*-pyrrolo[2,1-*c*]-[1,2,4]triazole-7-carboxylate (8b). To a solution of **2c** (0.74 g, 1.7 mmol) in acetic anhydride (15 mL) was added triethylamine (0.8 mL, 5.6 mmol) and stirred for 2 days at room temperature. Then the mixture was diluted with water (20 mL) to allow hydrolysis of unconsumed reagent and repeatedly extracted with dichloromethane. The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo* to afford a solid that, according to ^1H NMR, consisted of a 3:1 mixture of **8b** and **6b**. On treatment with methanol (20 mL) the latter component (data as above) was separated from **8b**.

8b: Yield: 0.16 g (25%); mp 198 °C (methanol); IR (KBr): $\tilde{\nu}$ 1671 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.36 (t, J = 7.1 Hz, 3H), 2.24 (s, 3H), 3.03 (s, 3H), 4.36 (q, J = 7.1 Hz, 2H), 7.45–7.49 (m, 2H), 7.52–7.60 (m, 6H), 7.72–7.74 (m, 2H); ^{13}C NMR ($CDCl_3$): 13.6 (q), 14.7 (q), 15.1 (q), 59.5 (t), 91.0 (s), 115.5 (s), 126.1 (d, 2C), 128.4 (d, 2C), 128.9 (d, 2C), 129.6 (d, 2C), 130.3 (d), 131.4 (d), 136.7 (s), 136.9 (s), 141.0 (s), 147.1 (s), 153.2 (s), 164.1 (s), 183.1 (s); UV (MeOH): λ (log ε) 202 (4.51), 237 (4.43), 368 (4.33) nm. *Anal.* Calcd. for $C_{23}H_{21}N_3O_3$: C, 71.30; H, 5.46; N, 10.85. Found: C, 71.14; H, 5.46; N, 10.78.

7-Acetyl-5-benzoyl-3,6-dimethyl-2-phenyl-2*H*-pyrrolo[2,1-*c*][1,2,4]triazole (8c). A mixture of **2d** (0.83 g, 2 mmol), acetic anhydride (15 mL), and triethylamine (0.8 mL, 5.6 mmol) was treated and worked up accordingly to give a residue that was chromatographed on silica gel using dichloromethane–ethyl acetate (4/1) as eluent.

8c: Yield: 0.21 g (29%); mp 238–239 °C (decomp.; ethanol); IR (KBr): $\tilde{\nu}$ 1619, 1594 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.28 (s, 3H), 2.63 (s, 3H), 2.99 (s, 3H), 7.45–7.49 (m, 2H), 7.53–7.62 (m, 6H), 7.73–7.75 (m, 2H); ^{13}C NMR ($CDCl_3$): 13.5 (q), 15.6 (q), 30.6 (q), 100.5 (s), 116.0 (s), 125.8 (d, 2C), 128.4 (d, 2C), 129.0 (d, 2C), 129.8 (d, 2C), 130.4 (d), 131.7 (d), 136.5 (s), 137.0 (s), 140.6 (s), 146.6 (s), 154.1 (s), 183.9 (s), 191.5 (s); UV (MeOH): λ (log ε) 239 (4.36), 379 (4.35) nm; MS (m/z, %): 357 (M^+, 100), 342 (81). *Anal.* Calcd. for $C_{22}H_{19}N_3O_2 \cdot ½\ H_2O$: C, 72.12; H, 5.50; N, 11.47. Found: C, 72.39; H, 5.20; N, 11.41.

Ethyl 7-acetyl-3,6-dimethyl-2-phenyl-2*H*-pyrrolo[2,1-*c*]-[1,2,4]triazole-5-carboxylate (8d). To a solution of **2f** (0.38 g, 1 mmol) in acetic anhydride (15 mL) was added at 120 °C triethylamine (0.2 mL, 1.4 mmol) and the mixture was heated at 130 °C for 1 hour. On addition of water (20 mL) to the cooled solution the product began to precipitate and was collected by filtration.

8d: Yield: 0.13 g (40%); mp 213 °C (ethanol); IR (KBr): $\tilde{\nu}$ 1685 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.40 (t, J = 7.1 Hz, 3H), 2.59 (s, 3H), 2.87 (s, 3H), 3.05 (s, 3H), 4.34 (q, J = 7.1 Hz, 2H), 7.55–7.61 (m, 5H); ^{13}C NMR ($CDCl_3$): 13.6 (q), 14.0 (q), 14.5 (q), 30.6 (q), 60.0 (t), 99.1 (s), 106.0 (s), 126.0 (d, 2C), 129.7 (d, 2C), 130.4 (d), 136.0 (s), 136.7 (s), 146.8 (s), 154.0 (s), 161.7 (s), 191.2 (s). *Anal.* Calcd. for $C_{18}H_{19}N_3O_3$: C, 66.45; H, 5.89; N, 12.91. Found: C, 66.23; H, 5.88; N, 12.94.

5-Acetyl-3-methyl-2,6-diphenyl-2*H*-pyrrolo[2,1-*c*][1,2,4]-triazole (10a). In analogy to the method of ref. [36], dimethylformamide (10 mL) was added to **7** (0.31 g, 1 mmol), followed by acetic anhydride (0.11 g, 1.1 mmol) and triethylamine (0.10 g, 1 mmol). The mixture was stirred at 80 °C for 1 hour and poured into water (30 mL). The solid formed was filtered off.

10a: Yield: 0.20 g (63%); mp 149–153 °C (acetone–water); IR (KBr): $\tilde{\nu}$ 1604 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.85 (s, 3H), 3.23 (s, 3H), 5.82 (s, 1H), 7.39–7.46 (m, 5H), 7.53–7.59 (m, 5H); ^{13}C NMR ($CDCl_3$): 14.9 (q), 27.9 (q), 88.2 (d), 114.0 (s), 126.1 (d,

2C), 128.2 (d), 128.3 (d, 2C), 129.7 (d, 2C), 129.9 (d, 2C), 130.4 (d), 137.4 (s), 137.5 (s), 137.7 (s), 148.6 (s), 153.5 (s), 181.6 (s). *Anal.* Calcd. for $C_{20}H_{17}N_3O$: C, 76.17; H, 5.43; N, 13.32. Found: C, 75.44; H, 5.37; N, 13.07 [35].

3-Methyl-2,6-diphenyl-2*H*-pyrrolo[2,1-*c*][1,2,4]triazole-5-carbanilide (10b). In analogy to the method of ref. [36], dimethylformamide (10 mL) was added to **7** (0.31 g, 1 mmol), followed by phenyl isocyanate (0.12 g, 1 mmol) and triethylamine (0.10 g, 1 mmol). The mixture was stirred at room temperature for 1 hour and poured into water (30 mL). The solid formed was filtered off.

10b: Yield: 0.27 g (67%); mp 179–181 °C (acetone–water); IR (KBr): $\tilde{\nu}$ 3402, 1647 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.21 (s, 3H), 5.80 (s, 1H), 6.93–6.99 (m, 2H), 7.07–7.09 (m, 2H), 7.16–7.20 (m, 2H), 7.50–7.60 (m, 10H); ^{13}C NMR ($CDCl_3$): 14.1 (q), 83.7 (d), 103.4 (s), 118.8 (d, 2C), 122.5 (d), 125.8 (d, 2C), 128.5 (d), 128.8 (d, 2C), 128.9 (d, 2C), 129.6 (d, 2C), 129.7 (d, 2C), 130.0 (d), 134.5 (s), 136.4 (s), 137.3 (s), 139.0 (s), 143.1 (s), 152.5 (s), 158.7 (s). *Anal.* Calcd. for $C_{25}H_{20}N_4O \cdot ½\ H_2O$: C, 74.80; H, 5.27; N, 13.96. Found: C, 75.10; H, 5.10; N, 13.69.

Reaction of 3-methyl-2,6-diphenyl-5*H*-pyrrolo[2,1-*c*][1,2,4]-triazolium chloride (7) with dimethyl acetylenedicarboxylate (DMAD). To **7** (0.31 g, 1 mmol) was added, successively, methanol (20 mL), triethylamine (0.10 g, 1 mmol), and DMAD (0.50 g, 3.5 mmol), and the mixture was stirred at 80 °C (bath) for 1 hour. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel using dichloromethane–ethyl acetate (1/2) as eluent to give 0.16 g of a dark red, viscous oil containing dimethyl 5-[(*E*)-1,2-bis(methoxycarbonyl)vinyl]-3-methyl-2,6-diphenyl-2*H*-pyrrolo[2,1-*c*][1,2,4]triazole-7-maleate (**12a**) and a trace of tetramethyl 3-methyl-2,6-diphenyl-2*H*-pyrrolo[2,1-*c*][1,2,4]triazole-5,7-dimaleate (**12b**); attempts to separate the components failed.

12a: IR (neat): $\tilde{\nu}$ 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.46 (s, 3H), 3.23 (s, 3H), 3.41 (s, 3H), 3.645 (s, 3H), 3.649 (s, 3H), 6.44 (s, 1H), 6.60 (s, 1H), 7.25–7.35 (m, 5H), 7.57–7.60 (m, 5H); ^{13}C NMR ($CDCl_3$): 11.3 (q), 51.0 (q), 51.6 (q), 51.9 (q), 52.8 (q), 91.6 (s, $^3J_{C,H}$ = 6.4 Hz), 106.7 (s, $^3J_{C,H}$ = 9.5 Hz), 106.9 (d), 123.2 (d), 125.6 (d, 2C), 127.4 (d, 2C), 127.9 (d), 129.7 (d, 2C), 130.3 (d), 131.1 (d, 2C), 132.0 (s), 132.8 (s), 134.1 (s), 136.5 (s), 140.4 (s), 143.3 (s), 151.2 (s), 165.4 (s), 167.2 (s), 167.4 (s), 168.0 (s).

12b: ^{1}H NMR ($CDCl_3$): δ 5.64 (s, 1H), 6.40 (s, 1H); ^{13}C NMR ($CDCl_3$): 93.4 (s, $^3J_{C,H}$ = 6.5 Hz), 108.0 (s, $^3J_{C,H}$ = 6.2 Hz).

5-Acetyl-3-methyl-1,6-diphenyl-1*H*-pyrrolo[2,1-*c*][1,2,4]-triazole (14). A mixture of **13** (0.27 g, 1 mmol) [8a] and acetic anhydride (5.00 g, 50 mmol) was stirred at 65 °C for 1 hour. The cooled solution was diluted with water (10 mL) to allow hydrolysis of unconsumed reagent and neutralized with aqueous sodium carbonate (20%). Repeated extraction with dichloromethane gave a material that was chromatographed on silica gel using dichloromethane–ethyl acetate (1/1) as eluent.

14: Yield: 0.08 g (25%); mp 118 °C (ethanol); IR (KBr): $\tilde{\nu}$ 1626, 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.92 (s, 3H), 2.97 (s, 3H), 5.97 (s, 1H), 7.18–7.23 (m, 1H), 7.41–7.46 (m, 7H), 7.64–7.67 (m, 2H); ^{13}C NMR ($CDCl_3$): 15.2 (q), 28.6 (q), 86.6 (d), 116.6 (s), 117.1 (d, 2C), 125.1 (d), 128.1 (d), 128.2 (d, 2C), 129.45 (d, 2C), 129.46 (d, 2C), 136.7 (s), 138.0 (s), 141.7 (s), 142.4 (s), 144.5 (s), 185.3 (s). *Anal.* Calcd. for $C_{20}H_{17}N_3O$: C, 76.17; H, 5.43; N, 13.32. Found: C, 76.16; H, 5.43; N, 13.23.

Dimethyl 3-methyl-1,6-diphenyl-1*H*-pyrrolo[2,1-*c*][1,2,4]-triazole-5-fumarate (16). To **13** (0.27 g, 1 mmol) [8a] was added, successively, methanol (20 mL) and dimethyl acetylenedicarboxylate (DMAD; 0.50 g, 3.5 mmol), and the mixture was stirred at 80 °C (bath) for 1 hour. The solvent was removed *in vacuo* and the residue was recrystallized.

16: Yield: 0.15 g (36%); mp 82–85 °C (ethanol–water); IR (KBr): $\tilde{\nu}$ 1729, 1712 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.37 (s, 3H), 3.53 (s, 3H), 3.54 (s, 3H), 6.14 (s, 1H), 6.93 (s, 1H), 7.14–7.18 (m, 1H), 7.24–7.28 (m, 1H), 7.32–7.39 (m, 4H), 7.43–7.48 (m, 2H), 7.66–7.69 (m, 2H); ^{13}C NMR ($CDCl_3$): 11.9 (q), 51.8 (q), 52.9 (q), 82.2 (d), 104.8 (s), 116.1 (d, 2C), 123.9 (d), 126.9 (d), 127.1 (d), 128.3 (d, 2C), 128.4 (d, 2C), 129.4 (d, 2C), 134.3 (s), 136.0 (s), 136.9 (s), 138.1 (s), 138.7 (s), 139.3 (s), 165.2 (s), 167.3 (s). *Anal.* Calcd. for $C_{24}H_{21}N_3O_4$: C, 69.39; H, 5.10; N, 10.11. Found: C, 69.39; H, 5.11; N, 9.86.

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