Generation and trapping of a 1,2,3-Triazolium 1-Unsubstituted Methanide. A Carbon Analogue of the Azole *N*-Oxide: Routes to Pyrrolo[1,2-*c*][1,2,3]triazoles and Substituted 1-Aminopyrroles

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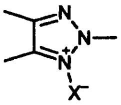
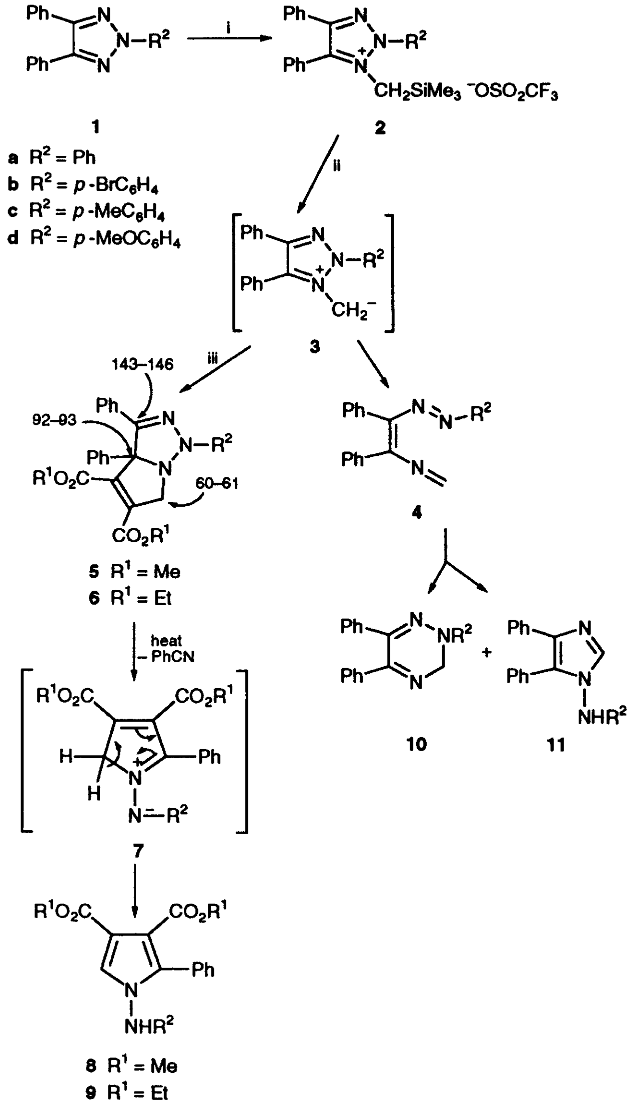
Trapping of the first azole *N*-unsubstituted methanide species, a carbon analogue of the ubiquitous azole *N*-oxide system is described; new synthetic routes to pyrrolo[1,2-*c*][1,2,3]triazoles and 1-aminopyrroles have resulted.

The wide synthetic scope of the cycloaddition–rearrangement reactions of 1,2,3-triazolium-1-aminide and -1-oxide systems **A**[1,2] and **B**[3,4] prompted a search for the analogous triazolium methanide species **C**. Despite the ubiquitous nature of the general azole *N*-oxide structure of type **B**, the unsubstituted carbon analogue **C** is unknown among the azoles, but systems containing two stabilising electron withdrawing groups, C=O or C≡N, bonded to the C^- atom are known[5–9] among the lower azoles. Previous attempts to trap the species **C** from the likely precursor **2** gave **10** and **11** *via* electrocyclisations in the intermediate **4**.[10] A key observation proved to be the high lability of the Me_3Si group of **2** when it was found that **10** and **11** were appearing during the alkylation before the isolation of the alkyl triazolium salt **2**. We now report the trapping of **3**, the first full carbon analogue of an azole *N*-oxide. It provides a synthetic route to the pyrrolo[1,2-*c*][1,2,3]triazole ring systems **5** and **6** and through these a new route to substituted 1-aminopyrroles **8** and **9** has been opened.



A X = NR
B X = O
C X = CH_2



Scheme 1 Some ^{13}C shift ranges shown. *Reagents:* i, trimethylsilylmethyl trifluoromethanesulfonate; ii, CsF; iii, dialkyl acetylenedicarboxylate

After the alkylation of the 1,2,3-triazoles **1** in trimethylsilylmethyl trifluoromethanesulfonate at 100 °C for 5 h, the system was cooled and, without isolation of the alkyl product 2 mol of dialkyl acetylenedicarboxylate in dichloromethane was introduced followed by CsF, using a literature[11,12] procedure, and the mixture stirred at ambient temperature for *ca.* 8 h. After removal of salts, chromatographic separation of the products on a silica gel 60 column (270–400 mesh ASTM) with gradient mixtures of light petroleum (b.p. 40–60 °C)–dichloromethane gave the products **5** or **6** and **10** and **11** (Table 1). Compounds **5** and **6** arise from a direct trapping of the species **3** while **10** and **11** are formed *via* electrocyclisations in **4** from the rapid ring-opening of the triazolium methanide **3** which cannot be completely avoided. If the dipolarophile is added too late or if no dipolarophile is added the products **10** and **11** only are obtained. This is the first example where the fused 5,5-cycloadduct from any azolium ylide type 1,3-dipole did not rearrange or fragment *in situ*. Since the adducts **5** and **6** had been expected to rearrange *in situ* their thermal behaviour in toluene was examined. Heating resulted in extrusion of benzonitrile followed by a rapid 1,3-H migration in **7** giving the 1-aminopyrroles **8** and **9** in 85–90% yields (Table 1) thus providing a new route to 1-aminopyrroles. The intermediate 1,3-dipole **7** was shortlived and was not trapped in cycloaddition reactions with alkyne dipolarophiles. The structures of the products **5**, **6**, **8** and **9** were supported by microanalyses, IR, ^1H and ^{13}C NMR spectra which showed all of the expected signals. The assignments were further supported by X-ray

Table 1 Products

Compound	M.p.[a] (T/°C)	Yield (%)	**10** Yield (%)	**11** Yield (%)	Compound	M.p.[c] (T/°C)	Yield (%)
5a	129–130	50	23.5	8.5	**8a**	158–160	87
5b	142–144	49.5	25	7.5	**8b**	191–193	89
5c	171–173	52.5	21	7.5	**8c**	177–178	92
5d	154–156	47.5	22.5	8	**8d**	152–154	91
6a	123–125	40[b]	9.5	4	**9a**	137–139	93
6b	108–110	39.5[b]	17	4	**9b**	124–126	92
6c	126–128	34[b]	17.5	5	**9c**	118–120	87
6d	124–125	36[b]	16	5	**9d**	122–124	76

[a] From pentane. [b] Low yields (1–3%) of another product, which appears to be isomeric with **6**, were also encountered but the structure could not be characterised to date. [c] From ethanol.

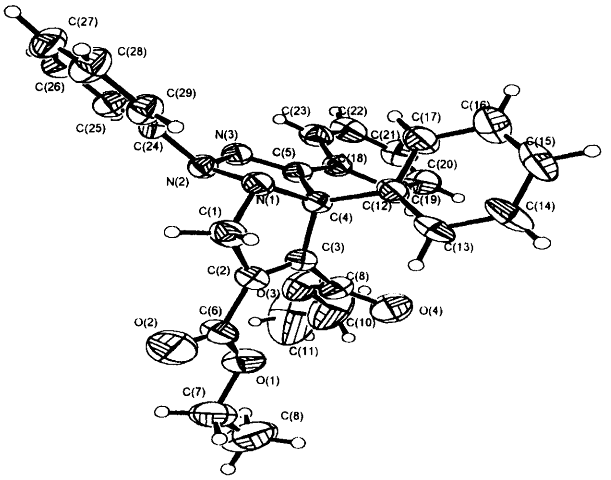


Fig. 1 X-Ray crystal structure of **6a**

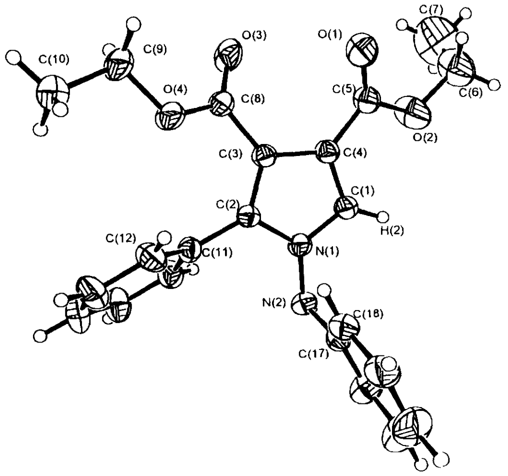


Fig. 2 X-ray crystal structure of **9a**

crystal structure determinations for compounds **6a** and **9a**, Figs. 1 and 2.*

Experimental

The products **5–6** and **8–9** were prepared by the following typical procedures.

Preparation of Pyrrolo[1,2-c][1,2,3]*triazole* **5a**.—A solution of **1a** (0.50 g, 1.68 mmol) in trimethylsilylmethyl trifluoromethanesulfonate (0.44 cm^3, 2.02 mmol) was heated to 100 °C and stirred for 5 h, cooled to ambient temperature, and then treated with dry dichloromethane (20 cm^3) and dimethyl acetylenedicarboxylate (0.41 cm^3, 3.36 mmol) followed by CsF (0.38 g, 2.52 mmol) and the mixture stirred at ambient temperature for 8 h. The solution was filtered to remove insoluble salts and the solvent removed under reduced pressure. The residue in dichloromethane (3 cm^3) was placed on a silica gel-60 column (230–400 mesh ASTM) and the product **5a** was eluted using a gradient mixture of light petroleum (b.p. 40–60 °C)–dichloromethane (1:0–1:1.5 v/v), m.p. 129–130 °C (from pentane) (50%) (Found: C, 71.4; H, 5.2; N, 9.1. $C_{27}H_{23}N_3O_4$ requires: C, 71.5; H, 5.1; N, 9.3%); ν_{max}(Nujol)/cm^{-1} 1735 and 1724 (ester C=O); δ_H(CDCl$_3$) 3.3 (s, 3 H, OMe), 3.8 (s, 3 H, OMe), 4.2 (s, 2 H, CH$_2$N) and 7.1–7.6 (m, ArH); δ_C 52.2 and 52.4 (OMe), 60.8 (CH$_2$N), 165.6 and 162.6 (ester C=O), 146.3, 143.4, 142.1, 139.0 and 135.6 and 130.2 (quaternary C), 92.0 (bridgehead C), 129.4, 128.9, 128.7, 128.3, 127.7, 127.2, 126.7, 123.2 and 117.5 (aromatic CH). The other products recovered from the column were **10a** (24%), **11a** (9%), **1a** (5%) and some intractable resins.

Preparation of 1-*Aminopyrrole* **8**.—A solution of **5a** (150 mg, 0.331 mmol) in dry toluene (10 cm^3) was stirred under reflux for 46 h, cooled and then the solvent removed under reduced pressure. The residue was crystallized from EtOH giving compound **8a** (87%), m.p. 158–160 °C (from EtOH) (Found: C, 68.3; H, 5.1; N, 7.8. $C_{20}H_{18}N_2O_4$ requires C, 68.6; H, 5.2; N, 8.0%); ν_{max}(Nujol)/cm^{-1} 3318 (NH) and 1719 and 1694 (ester C=O); δ_H([$^2H_6$]DMSO) 3.65 (s, 3 H, OMe), 3.77 (s, 3 H, OMe), 7.70 (s, 1 H, pyrrole 5-H), 9.54 (s, 1 H, NH), 6.48 (d, 2 H, H$_{ortho}$ N-Ph) and 6.8–7.5 (m, Ar-H); δ_C 51.5 and 51.8 (MeO), 165.2 and 162.9 (ester C=O), 147.7, 135.5, 129.3, 113.7 and 112.5 (quaternary C), 120.2 (pyrrole C-5), 129.5, 129.2, 128.5, 128.4, 128.0 and 127.8 (aromatic CH).

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* Crystal data for **6a**, $C_{22}H_{22}N_2O_4$. Monoclinic, a = 8.706(2), b = 13.191(2), c = 17.818(2) Å, α = 90, β = 100.88, γ = 90.07°, Z = 4, space group $P2_1/n$, 6949 reflections observed with $I > 2\sigma(I)$ using a CAD4F diffractometer and Mo-Kα radiation; $2\theta_{max}$ = 63.94°. The structure was solved using SHELX 86 and refined with 259 variable parameters using SHELXL 93. After full matrix refinement; R_1 = 7.10 and wR_2 = 22.2. The maximum and minimum excursions in the final F_o–F_c difference map were 0.784 and −0.537 e Å^{-3}. The ORTEP program was used to obtain the drawings.

Crystal data for **9a**, $C_{29}H_{27}N_3O_4$. Triclinic, a = 9.4784(10), b = 11.5639(10), c = 12.8436(10) Å, α = 80.414(8), β = 68.821(8), γ = 78.283(8°), Z = 2, space group P_1, 8061 reflections observed $I > 2\sigma(I)$ using a CAD4F diffractometer and Mo-Kα radiation; $2\theta_{max}$ = 59.94°. The structure was solved using SHELX 86 and refined with 330 variable parameters using SHELXL 93. After full matrix refinement; R_1 = 7.04 and wR_2 = 22.20. The maximum and minimum excursions in the final F_o–F_c difference map were 0.553 and −0.333 e Å^{-3}. The ORTEP program was used to obtain the drawings.

Atomic coordinates, bond lengths and angles, and thermal parameters for compounds **6a** and **9a** have been deposited at the Cambridge Crystallography Data Centre. For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1994, Issue 1.

Acknowledgements

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