

Attempted Generation of Substituted 1,2,3-Triazolium-1-methanides: a New Ring Expansion to 2,3-Dihydro-1,2,4-triazines: *ab initio* Calculations on 1,2,3-Triazolium-1-oxide, -1-imide, and -1-methanide 1,3-Dipoles and a Striking Illustration of the Hammond Principle in the Cyclisation of Hetero-1,3,5-trienes

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Treatment of 1-methyl-1,2,3-triazolium salts with ethoxide gave 2,3-dihydro-1,2,4-triazines *via* 1,2,5-triazahexa-1,3,5-trienes but the expected 1,2,3-triazolium-1-methanide 1,3-dipoles were not detected and *ab initio* calculations suggest that they are thermodynamically unfavoured; the X-ray crystal structure of (6a), a dihydro-1,2,4-triazine, is reported.

Recently we have described some of the wide synthetic applications of 1,2,3-triazolium imides¹⁻³ (1) and 1,2,3-triazolium oxides^{4,5} (2) as 1,3-dipoles. The versatility of these systems in giving extended tandem reactions leading to ready ring expansions prompted us to seek the carbon methanide analogues (3). Such triazolium ylides are unknown but ylides of saturated lower azoles, such as tetrahydropyrazole derivatives, have been recently generated and found to be useful in cycloaddition reactions.⁶⁻⁸

The *N*-methyltriazolium perchlorate salts (5) were obtained by heating the parent triazoles (4) at 80 °C in dimethyl sulphate followed by treatment of the concentrated solution with aqueous sodium perchlorate, using procedures similar to those recently developed by Moderhack.⁹ Basic removal of a proton from these systems (5, R ≠ H)¹⁰ should give the new

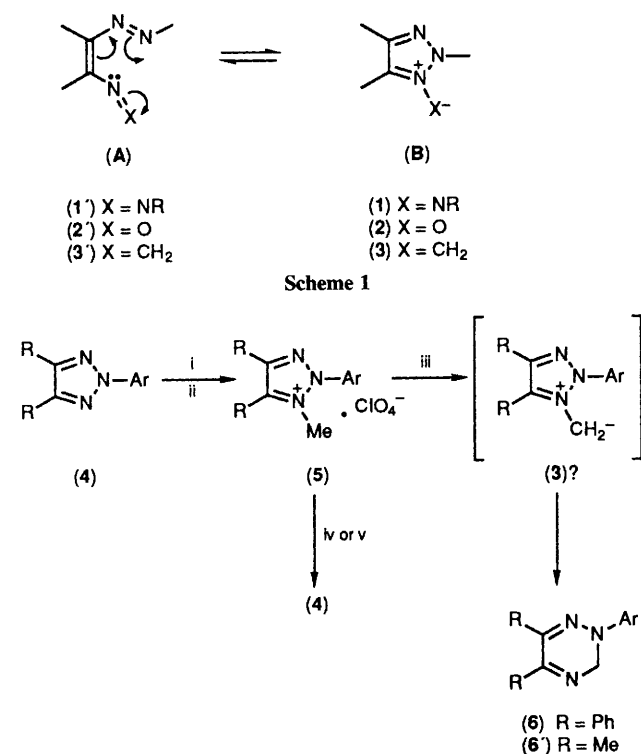
methanides (3). However, some strong nucleophilic bases, *e.g.*, BuⁿLi and Et₃N, mainly removed the methyl group and regenerated the triazole (4) as a good leaving group. Sodium ethoxide did successfully remove a proton and gave good yields of the dihydro-1,2,4-triazines (6) (Scheme 2, Table 1),†

† Typically, a mixture of compound (5a) (1.0 g, 2.4 mmol) in toluene (50 cm³) was stirred at ambient temperature and treated with sodium ethoxide (2.7 mmol). The yellow solution was stirred for 12 h at ambient temperature and evaporated under reduced pressure. Compounds (6a) and (11a) were separated on a Merck silica gel 60 column (230-400 mesh ASTM) using dichloromethane as eluant for compound (6a) and ethyl acetate for (11a). In some cases sodium salts of the products (11) may separate from the toluene before evaporation. Stirring in water will free the product.

Table 1. 1-*N*-Methyl-1,2,3-triazolium deprotonation products.

Run	Substrate (R)	Compound	M.p./ °C	Yield/ %	Compound	M.p./ °C	Yield/ %
1	(5a) (Ph)	(6a)	87—89 ^a	73	(11a)	153—155 ^b	15
2	(5b) (Ph)	(6b)	104—106 ^b	57	(11b)	211—213 ^a	25
3	(5c) (Ph)	(6c)	196 ^a	45	(11c)	279 ^b	44
4	(5d) (Ph)	(6d)	98—100 ^a	78	(11d)	173—175 ^a	10
5	(5'b) (Me)	(6'b)	—	—	(11'b)	153—155 ^b	83
6	(5'c) (Me)	(6'c)	120—122 ^a	5	(11'c)	223—225 ^b	85

^a From dichloromane. ^b From acetone.



Scheme 2. Reagents: i, Me₂SO₄; ii, NaClO₄; iii, NaOEt; iv, BuLi; v, Et₃N.

in an apparent ring expansion of the species (3). However, careful attempts at low temperatures to achieve 1,3-dipolar cycloadditions from the species (3) with favourable dipolarophiles¹⁻³ such as dimethyl acetylenedicarboxylate and acrylonitrile failed.

The results of *ab initio* calculations on the equilibrium (A) \rightleftharpoons (B) (Scheme 1) are shown in Table 2. The calculations were performed with the 3-21G basis set as provided in the GAUSSIAN86 series of computer programmes.¹¹ Analytical gradient methods were employed to verify equilibrium or transition state structures. The cyclic structures (B) (Scheme 1) were found to be planar, while the terminal =NH group in (A) (Scheme 1) was found to be *ca.* 50° out of the plane formed by the other atoms in (A). Figure 1 shows a plot of the activation energy E^a vs. the reaction energy ΔE_r for the cyclization reactions in Scheme 1. The plot is remarkably linear over a difference in ΔE_r of 50 kcal mol⁻¹ (1 kcal = 4.184 kJ) and gives a striking confirmation of Hammond's Postulate¹² and its extensions in the case of these hetero-1,3,5-triene systems. The triazolium oxides (2B) are strongly favoured in the cyclic form while the imides (1B) are borderline. We have previously directly observed¹³ the equilibrium for the species (1) by low temperature NMR studies. However, the methan-

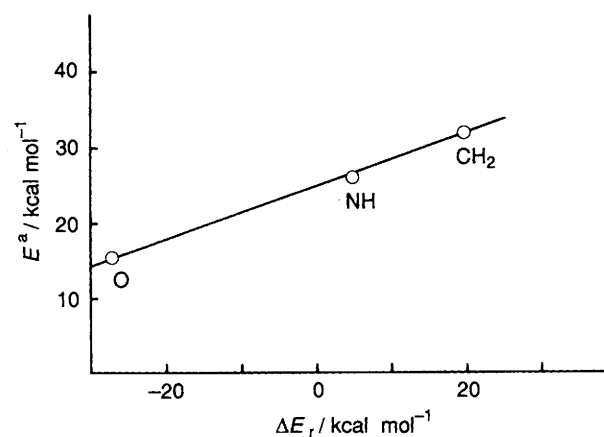
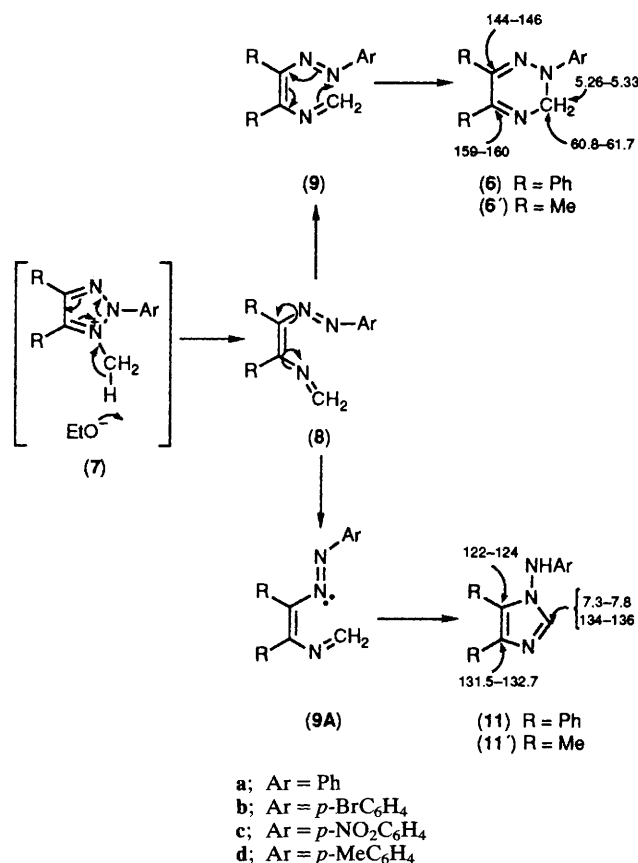
**Figure 1****Scheme 3.** Some ¹H and ¹³C NMR shift (δ) ranges are shown.

Table 2. *Ab initio* 3-21G calculations for (A) → (B) (Scheme 1), H at all sites (kcal mol⁻¹).

ΔE_r E^a	X		
	O	NH	CH ₂
	-27.33	4.64	19.78
	15.39	25.91	31.94

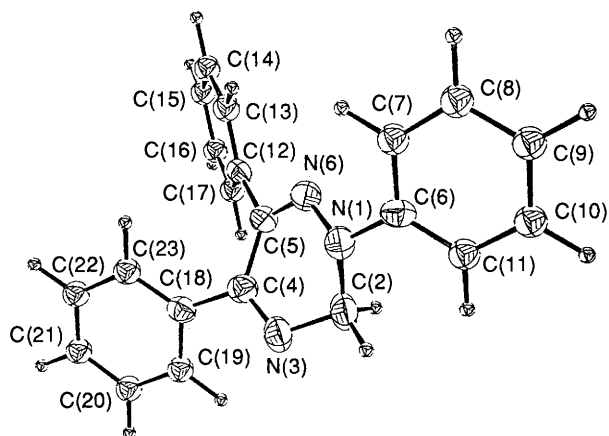


Figure 2. X-Ray crystal structure of compound (6a).

ides (3) are the reverse of the oxides and the acyclic form (3'A) is strongly favoured thermodynamically. Thus the species (3B) is thermodynamically unfavoured and was probably not formed at all, thereby explaining the failure to detect 1,3-dipolar cycloadditions which should be highly favourable.¹⁻⁵ Proton abstraction from the compounds (5) gives an *E*₂-Hoffmann-degradation type transition state (7) (Scheme 3), generating the 1,2,5-triaza-1,3,5-hexatriazenes (8) as key intermediates, which give the main products (6) through a bond rotation to (9) followed by a 6 π -electrocyclic process. The other possible products from the intermediates (9), the 1-anilinoimidazoles (11) were obtained in low yields in the parent reaction (Table 1, run 1).

Substituent effects such as those of electron-withdrawing groups in the *N*-aryl ring were found to orient the reaction towards the products (11) (Table 1, runs 1-3) and with methyl groups in place of conjugated phenyl groups on the carbons the products (11) were dominant (Table 1). The structures of the products were established from ¹H and ¹³C NMR spectra, which showed all of the expected signals.

All of the compounds gave satisfactory microanalyses. An X-ray crystal structure (Figure 2) was determined for compound (6a) to confirm the ring expanded structure.‡

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‡ *Crystal data* for (6a): monoclinic, space group *P*2₁, *a* = 12.356(1), *b* = 5.477(1), *c* = 13.194(2) Å, β = 111.69(2)°, *Z* = 2, *U* = 829.59, μ = 0.41 cm⁻¹, 1732 unique reflections measured of which 1054 were observed with *I* > 2 σ (*I*) using a CAD4 diffractometer and Mo-*K* α radiation, 2 θ_{max} = 48°. The structure was solved by direct methods, SHELX86,¹⁴ and refined with 126 variable parameters using SHELX76.¹⁵ After full-matrix refinement, *R* = 5.15% and *R*_w = 4.04%. The maximum and minimum excursions in the final *F*_o - *F*_c difference map were 0.10 and -0.08 e Å⁻³.¹⁶ The ORTEP program was used to obtain the drawing.¹⁶ Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.