1,2,3-Triazolium-1-oxide, -1-imide and 1-methanide Hetero-1,3,5-triene Equilibrium: *Ab Initio* Calculations. A New Base Induced Ring Expansion of 1-Alkyl-1,2,3-triazolium Salts to 2,3-Dihydro-1,2,4-triazines and 1-Aminoimidazoles *via* the 1,2,5-Triazahexa-1,3,5-triene System. Azolium 1,3-Dipoles

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Treatment of substituted 1-methyl- and 1-trimethylsilylmethyl-1,2,3-triazolium salts with ethoxide and caesium fluoride respectively gave substituted 2,3-dihydro-1,2,4-triazines and 1-aminoimidazoles *via* 1,2,5-triazahexa-1,3,5-triene intermediates. Expected isomeric 1,2,3-triazolium-1-methanide 1,3-dipoles were not detected and *ab initio* calculations suggested that they are thermodynamically unfavoured. *Ab initio* calculations on the equilibrium between the acyclic hetero-1,3,5-triene system and the cyclic forms of 1,2,3-triazolium-1-oxide, -1-imide and -1-methanide are reported. X-ray crystal structures are described for 2,5,6-triphenyl-2,3-dihydro-1,2,4-triazine **6a** and 1-(*p*-nitroanilino)-4,5-diphenylimidazole **11c**.

The importance of the electrocyclic reactions[1] of the 1,3,5-trienes has led to major interest[2] in the behaviour of the general hetero-1,3,5-triene system of which there are a wide range of structural variations.[2,3] Many of the possible hetero-1,3,5-triene systems have not yet been described and in the nitrogen series examples of the acyclic 1,2,5-triaza-1,3,5-hexatriene system **3'** have not been generated although benzo-derivatives are known with the heteroene moieties as *ortho*-substituents and the 3–4 bond as part of an aromatic ring. Cyclisations of some hetero-1,3,5-trienes[4] give rise to normal 5-membered heterocycles (Scheme 1) and a number of these systems are better known in their heterocyclic ring forms. Recently we described wide

A **B**

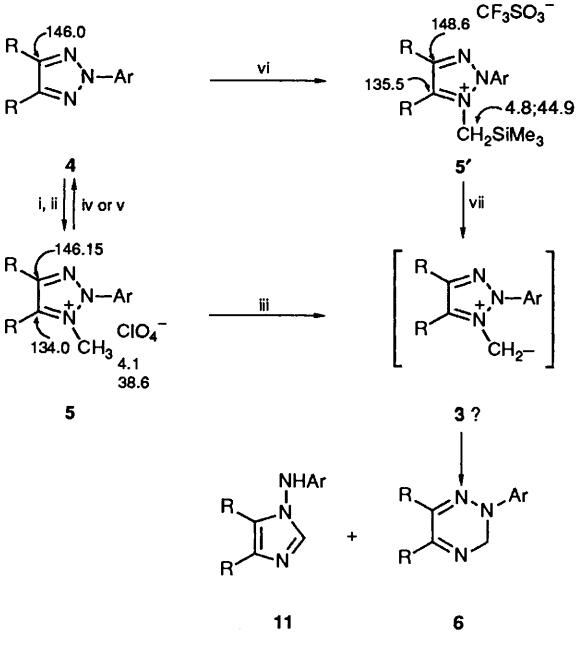
1'; X = NR **1**; X = NR
2'; X = O **2**; X = O
3'; X = CH_2 **3**; X = CH_2

Scheme 1

synthetic applications for the 1,2,3-triazolium imides[5,6] **1** and 1,2,3-triazolium oxides[7] **2** as 1,3-dipoles. The synthetic scope of the systems **1** and **2** prompted a search for the analogous 1,2,3-triazolium methanide 1,3-dipole **3**. Each of the systems **1**–**3** is potentially in equilibrium with the acyclic conjugated triene forms **1'**–**3'** which show no 1,3-dipolar cycloaddition reactions.[8] Herein we describe[9] the generation and behaviour of the system **3**/**3'**.

Results and Discussion

Two approaches were used in an attempt to generate the triazolium methanides **3**; (i) The *N*-methyltriazolium perchlorate salts **5** (Scheme 2) were obtained by heating the parent triazoles **4** at 80 °C in dimethyl sulfate followed by treatment of the concentrated solution with aqueous sodium perchlorate using procedures similar to those developed recently by Moderhack.[10] Basic removal of a proton, if possible, from these salts should give the methanides **3**. (ii) The *N*-trimethylsilylmethyl triazolium trifluoromethylsulfonates **5'** (Scheme 2) were prepared by heating the 1,2,3-triazoles **4** in trimethylsilylmethyl trifluoromethanesulfonate. Treatment of these salts with caesium fluoride in accordance with literature procedures[11,12] should result in desilylation again generating the species **3**.



Scheme 2 *Reagents:* i, Me_2SO_4; ii, $NaClO_4$; iii, NaOEt; iv, BuLi; v, Et_3N; vi, $CF_3SO_3CH_2SiMe_3$; vii, CsF. Some ^1H and ^{13}C NMR shifts shown for R = Ar = Ph

Treatment of the triazolium perchlorate salts **5** with strong nucleophilic bases such as BuLi and Et_3N mainly removed the methyl group and regenerated the triazole **4**. Sodium ethoxide, however, successfully removed a proton and gave good yields of the dihydro-1,2,4-triazines **6** (Scheme 2, Table 2) in an apparent ring expansion of the possible intermediates **3**. When the substituents R were aromatic, the products **6** were accompanied by lesser yields of the *N*-aminoimidazoles **11** (Scheme 3) (Table 2). When the substituents R were methyl groups, the imidazoles

Table 1 Substituted-1-*N*-methyl-1,2,3-triazolium perchlorates

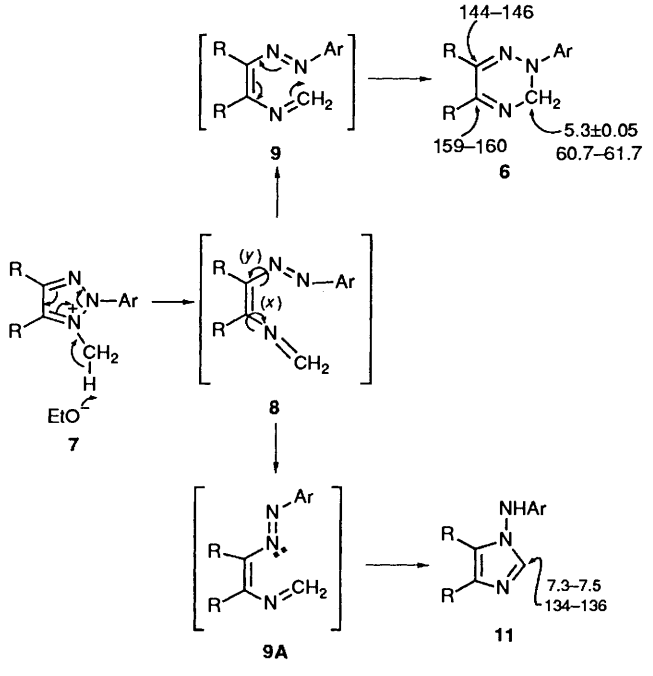
No.		Substrate R	Substrate Ar	Product Cpd	M.p. (°C)	Yield (%)	Microanalysis (%), Found (required) C	H	N
1	**4a**	Ph	Ph	**5a**	210[a]	89	61.0 (61.2)	4.3 (4.4)	10.1 (10.2)
2	**4b**	Ph	*p*-BrC_6H_4	**5b**	218–220[a]	86	51.6 (51.4)	3.3 (3.5)	8.4 (8.6)
3	**4c**	Ph	*p*-$NO_2C_6H_4$	**5c**	178–180[a]	90	55.1 (55.2)	3.6 (3.7)	12.0 (12.3)
4	**4d**	Ph	*p*-MeC_6H_4	**5d**	270–272[a]	80	61.7 (62.0)	4.6 (4.7)	9.8 (9.9)
5	**4e**	Ph	*p*-$MeOC_6H_4$	**5e**	147–149[a]	92	59.8 (59.8)	4.4 (4.5)	9.3 (9.5)
6	**4f**	Me	*p*-BrC_6H_4	**5f**	246–247[a]	83	35.7 (36.0)	3.4 (3.5)	11.3 (11.5)
7	**4g**	Me	*p*-$NO_2C_6H_4$	**5g**	230–232[a]	85	39.5 (39.7)	4.0 (3.9)	16.8 (16.8)
8	**4h**	$(CH_2)_4$	*p*-$NO_2C_6H_4$	**14**	186–188	92	43.3 (43.5)	4.2 (4.2)	15.3 (15.6)

[a] From acetone–ether.

Table 2 Dihydrotriazines and *N*-aminoimidazoles from 1-alkyl-1,2,3-triazolium salts **5**

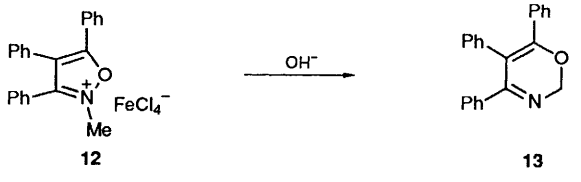
No.	Substrate	Substituents R	Substituents Ar	Products Cpd	M.p.(°C)	Yield[b] (%)	Microanalysis (%), Found (required) C	H	N
1	**5a**	Ph	Ph	**6a**	87–89	73	80.7 (81.0)	5.4 (5.5)	13.5 (13.5)
				11a	153–155	15	80.8 (81.0)	5.3 (5.5)	13.2 (13.5)
2	**5'a**	Ph	Ph	**6a**	87–89	72	80.7 (81.0)	5.4 (5.5)	13.5 (13.5)
				11a	153–155	15	80.8 (81.0)	5.3 (5.5)	13.2 (13.5)
3	**5b**	Ph	*p*-BrC_6H_4	**6b**	104–106	57	64.3 (64.6)	4.3 (4.1)	10.6 (10.8)
				11b	211–213	25	64.7 (64.6)	4.0 (4.1)	10.7 (10.8)
4	**5c**	Ph	*p*-$NO_2C_6H_4$	**6c**	196	45	70.6 (70.8)	4.3 (4.5)	15.6 (15.7)
				11c	279	44	70.5 (70.8)	4.3 (4.5)	15.5 (15.7)
5	**5'c**	Ph	*p*-$NO_2C_6H_4$	**6c**	196	45	70.6 (70.8)	4.3 (4.5)	15.6 (15.7)
				11c	279	45	70.5 (70.8)	4.3 (4.5)	15.5 (15.7)
6	**5d**	Ph	*p*-MeC_6H_4	**6d**	98–100	78	81.0 (81.2)	5.6 (5.9)	12.8 (12.9)
				11d	173–175	10	81.0 (81.2)	5.8 (5.9)	12.7 (12.9)
7	**5e**	Ph	*p*-$MeOC_6H_5$	**6e**	107–109	83	77.8 (77.5)	5.7 (5.6)	12.0 (12.3)
				11e	—[a]	—[a]	—	—	—
8	**5f**	Me	*p*-$NO_2C_6H_4$	**6f**	120–122	5	56.9 (56.9)	5.2 (5.2)	24.3 (24.1)
				11f	223–225	85	56.7 (56.9)	5.3 (5.2)	24.4 (24.1)
9	**5g**	Me	*p*-BrC_6H_4	**6g**	—[a]	—[a]	—	—	—
				11g	153–155	83	49.6 (49.7)	4.7 (4.5)	15.6 (15.8)
10	**14**	—	—	**15**	95–97	75	60.1 (60.5)	5.4 (5.4)	21.5 (21.7)

[a] Trace quantities only were encountered. [b] Product balance was made up by recovered substrate.



Scheme 3 Some ^1H and ^{13}C NMR shift ranges are shown

11 were the main products and were accompanied by low yields of the dihydrotriazines **6** (Table 2). This basic removal of a proton from *N*-methylazolium salts is a synthetically useful process which has not been much explored in the literature. An early example of such a reaction was noted by Kohler and co-workers[13] who deprotonated compound **12** with base but did not realise the ring expanded nature of the product (which was **13**). The structure **13** for the product and the significance of the



reaction was subsequently established by King and Durst.[14] Most of the reported reactions of *N*-alkyl azolium salts with bases have been concerned with removal of aromatic ring protons.[15–17] The basic deprotonation of ring substituted *N*-methylazolium salts is, however, not necessarily a general reaction but depends on the nature of ring since the base can also undergo addition to a ring carbon and cause cleavage of the ring.[18] Desilylation of the salts **5'** readily occurred on treatment with caesium fluoride and the Me_3Si group was so labile that partial desilylation occurred during the alkylation of **4** to give **5** (Scheme 2). The products obtained from the desilylation were again the compounds **6** and **11** and they were obtained in yield ratios which were identical to those obtained from deprotonation of **5** suggesting a common intermediate in both reactions

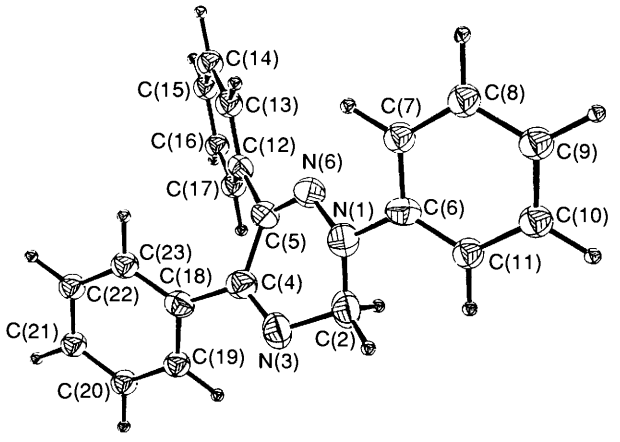


Fig. 1 X-ray crystal structure of **6a**

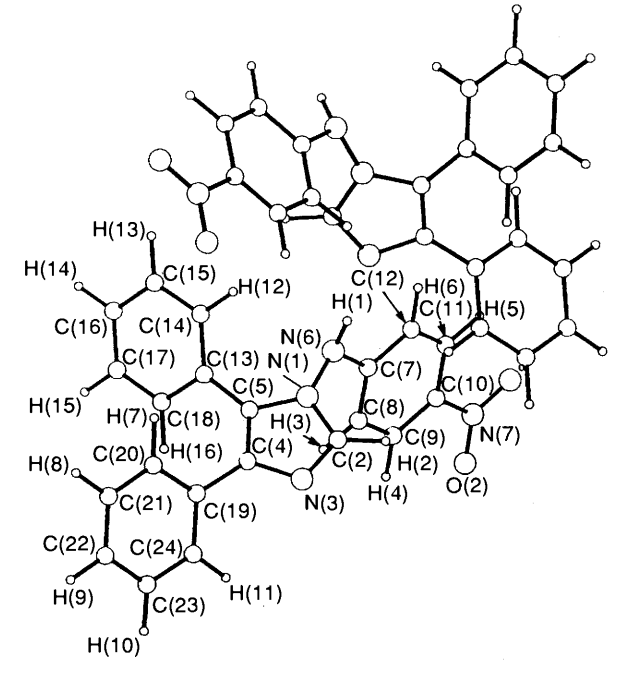


Fig. 2 X-ray crystal structure of **11c**

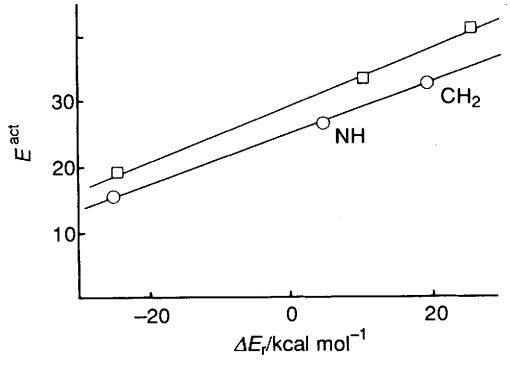


Fig. 3 Plot of activation energy E^{act} *vs.* the reactions energy ΔE_r for the cyclization reactions in Scheme 1; ○ 3-21 g; □ 6-31 g

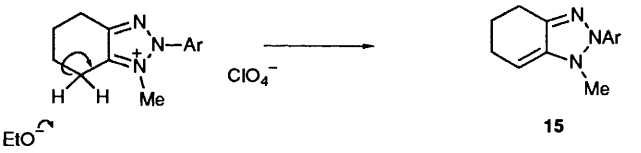
(Table 2, Runs 1,2 and 4,5). The structures of the products were established from microanalyses (Tables 1 and 2), IR, ^{1}H and ^{13}C NMR spectra. Some key NMR shifts are shown in Schemes 2 and 3. The assigned structures were further supported by X-ray crystal structure determinations on the products **6a** (Fig. 1) and **11c** (Fig. 2). In the crystals of compound **11c** there is an intermolecular hydrogen bond between the 1-amino nitrogen,

Table 3 *Ab initio* calculations for (**A**)⟶(**B**) (Scheme 1), H at all sites (kcal mol^{-1})

		X		
	Basis set	O	NH	CH_2
ΔE_r	(3-21G)	−25.33	4.64	19.78
	(G-31G)	−24.47	10.41	26.09
E^a	(3-21G)	15.39	25.91	31.94
	(6-31G)	19.93	33.16	41.18

N(6), and the imidazole N(3) of adjacent molecules. The imidazole ring and the potentially pyramidal 1-amino group are essentially planar.

Mechanisms.—Ab initio *calculations.*—When the reactions described were carried out carefully, at low temperatures, in the presence of favourable dipolarophiles[5–7] such as dimethyl acetylenedicarboxylate and acrylonitrile no cycloadditions or trapping of the species **3** could be achieved. Since **3** should be an excellent 1,3-dipole[5–7] the failure of cycloaddition reactions to occur suggests it may not be present at all. The results of *ab initio* calculations on the equilibrium **A** ⟶ **B** (Scheme 1) are shown in Table 3. The calculations were performed with the 3-21G and 6-31G basis set as provided in the GAUSSIAN86 series of computer programmes.[19] 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**. Fig. 3 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 Postulate[20] 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 observed[8] the equilibrium for the species **1** by low temperature NMR spectroscopic studies. However, the methanides **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. 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 6π-electrocyclic process. Two bond rotations (*x*) and (*y*) can give rise to the intermediates **9A** which are the precursors to the aminoimidazoles **11**. The marked substituent influence on the distribution of the products (Table 2) can be explained qualitatively in the context of the relative ease of the bond rotations (*x*) and (*y*) in the 1,2,5-triaza-1,3,5-triene intermediates **8** (Scheme 3). When the substituents R are aromatic rings it is likely that the aryl group at position C-3 of the triene system will lie in the triene plane allowing for conjugation through the azo-group into the *N*-aryl ring while the other aryl group at position C-4 will then be sterically



14; Ar = *p*-$NO_2C_6H_4$ **15**

Scheme 4

Table 4 Fractional atomic coordinates for **6a**

Atom	*x*	*y*	*z*
N(1)	0.6382(3)	0.2621	0.4497(3)
N(3)	0.6364(3)	0.4059(11)	0.6192(3)
N(6)	0.7493(3)	0.1788(10)	0.4961(3)
C(2)	0.6071(4)	0.4628(11)	0.5051(3)
C(4)	0.7348(4)	0.2955(12)	0.6662(3)
C(5)	0.8016(3)	0.2121(11)	0.6005(3)
C(6)	0.5901(3)	0.2413(11)	0.3344(3)
C(7)	0.6235(3)	0.0490(12)	0.2853(3)
C(8)	0.5811(3)	0.0291(13)	0.1727(3)
C(9)	0.5042(4)	0.2030(12)	0.1091(4)
C(10)	0.4701(4)	0.3933(12)	0.1580(3)
C(11)	0.5132(3)	0.4151(12)	0.2708(3)
C(12)	0.9270(3)	0.1417(11)	0.6462(3)
C(13)	1.0065(3)	0.2810(11)	0.7263(3)
C(14)	1.1248(4)	0.2247(13)	0.7656(4)
C(15)	1.1623(4)	0.0225(12)	0.7247(3)
C(16)	1.0846(4)	−0.1195(12)	0.6456(3)
C(17)	0.9664(4)	−0.0604(12)	0.6052(3)
C(18)	0.7732(3)	0.2499(11)	0.7853(3)
C(19)	0.7410(4)	0.4179(12)	0.8480(3)
C(20)	0.7749(4)	0.3869(13)	0.9593(3)
C(21)	0.8419(4)	0.1893(12)	1.0096(4)
C(22)	0.8719(4)	0.0169(13)	0.9486(3)
C(23)	0.8377(3)	0.0476(13)	0.8371(3)

Table 5 Fractional atomic coordinates for **11c**

Atom	*x*	*y*	*z*
O(1)	0.5827(2)	0.2054(3)	−0.1493(1)
O(2)	0.4951(2)	0.0206(3)	−0.1729(2)
N(1)	0.1970(2)	0.1729(2)	0.1678(1)
N(3)	0.1855(2)	−0.0117(2)	0.2452(1)
N(6)	0.2462(2)	0.2743(2)	0.1253(1)
N(7)	0.5108(2)	0.1294(3)	−0.1343(2)
C(4)	0.0793(2)	0.0296(2)	0.2041(2)
C(2)	0.2535(2)	0.0761(3)	0.2214(2)
C(5)	0.0843(2)	0.1441(2)	0.1546(2)
C(7)	0.3106(2)	0.2372(2)	0.0598(2)
C(8)	0.2922(2)	0.1188(3)	0.0102(2)
C(9)	0.3573(2)	0.0843(3)	−0.0536(2)
C(10)	0.4405(2)	0.1674(3)	−0.0683(2)
C(11)	0.4592(2)	0.2858(3)	−0.0211(2)
C(12)	0.3938(2)	0.3214(3)	0.0425(2)
C(19)	−0.0184(2)	−0.0416(2)	0.2245(2)
C(20)	−0.0994(2)	0.0224(3)	0.2612(2)
C(21)	−0.1843(2)	−0.0458(4)	0.2894(2)
C(22)	−0.1916(3)	−0.1787(4)	0.2801(2)
C(23)	−0.1129(3)	−0.2439(3)	0.2411(2)
C(24)	−0.0258(2)	−0.1772(3)	0.2131(2)
C(13)	−0.0025(2)	0.2246(2)	0.0975(2)
C(14)	−0.0082(2)	0.3598(3)	0.1098(2)
C(15)	−0.0941(3)	0.4308(3)	0.0558(2)
C(16)	−0.1724(3)	0.3688(4)	−0.0107(2)
C(17)	−0.1633(3)	0.2363(4)	−0.0230(2)
C(18)	−0.0823(2)	0.1638(3)	0.0303(2)
H(1)	0.2726(26)	0.3417(33)	0.1723(22)

required to twist out of the triene plane. Thus a combination of steric and conjugation effects should enhance the bond rotation (*x*) and inhibit the rotating (*y*) thereby strongly favouring the dihydrotriazine products **6** as observed. When the substituents R are methyl groups conjugation and steric favouring of the *trans*-azo structure as in **9** relative to **9A** can no longer be expected and the bond rotation (*y*) should be enhanced favouring structure **9A** and leading to high yields of the imidazoles **11** as observed. Further support for the Hoffmann type proton abstraction **7** was obtained when an alternative proton source was presented to the ethoxide base as with compound **14** (Scheme 4). In this case proton abstraction occurred at the α-position of the fused cyclohexane moiety giving the product **15** only (Table 2, No. 10).

Table 6 Crystal data for **6a**

Formula	$C_{21}H_{17}N_3$
M (a.m.u.)	311.385
Monoclinic	
Space group	$P2_1$
a(Å)	12.356(1)
b(Å)	5.477(1)
c(Å)	13.194(2)
β(°)	111.69(2)
U(Å^3)	829.59
Z	2
D_c g cm^{-3}	1.25
μ cm^{-1}	0.41
F(000)	328
Radiation Mo-Kα	
graphite monochromator	λ = 0.7093 Å
Diffractometer	Enraf–Nonius CAD4F
Orienting reflections, range	25, 13 < θ < 20°
T/°C	22
Scan method	ω–2θ
Data collection range	2 < 2θ < 48°
No. unique data	1732
Total $I > 2\sigma I$	1054
No. of parameters fitted	141
R^a	5.15%
$R_w{}^b$	4.04%
Largest shift/esd, final cycle	<0.001
Largest positive peak (*e*/Å^3)	0.10
Largest negative peak (*e*/Å^3)	−0.08

^{a} $R = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$. ^{b} $R_w = \{[\Sigma w(|F_o - F_c|)^2]/[\Sigma w(|F_o|)^2]\}^{\frac{1}{2}}$; $w = 0.84/[\sigma F_o)^2]$,

Table 7 Crystal data for **11c**

Crystal size (mm)	0.25 × 0.33 × 0.30
Formula	$C_{21}H_{16}N_4O_2$
M (a.m.u.)	388.382
Monoclinic	
Space group	$P2_1/n$
a/Å	12.253(3)
b/Å	10.165(2)
c/Å	14.409(3)
β/°	100.80(2)
U/Å^3	1762.9
Z	4
D_c g cm^{-3}	1.46
μ/cm^{-1}	0.52
F(000)	744
Radiation Mo-Kα	
graphite monochromator	λ = 0.7093 Å
Diffractometer	Enraf–Nonius CAD4F
Orienting reflections, range	25, 13 < θ < 20°
T/°C	22
Scan method	ω–2θ
Data collection range	2 < 2θ < 48°
No. unique data	2659
Total $I > 2\sigma I$	1827
No. of parameters fitted	248
R,^{a} $R_w{}^b$	4.92%, 4.81%
Largest shift/esd, final cycle	<0.001
Largest positive peak (*e*/Å^3)	0.07
Largest negative peak (*e*/Å^3)	0.12

^{a} $R = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$. ^{b} $R_w = \{[\Sigma w(|F_o - F_c|)^2]/[\Sigma w(|F_o|)^2]\}^{\frac{1}{2}}$; $w = 1/[(\sigma F_o)^2]$.

Experimental

M.p.s were measured on an Electrothermal apparatus. IR spectra were measured with a Perkin-Elmer 983G spectrophotometer. NMR spectra were measured on a JEOL JNM-GX-270

instrument with tetramethylsilane as internal reference and deuteriochloroform or hexadeuteriodimethyl sulphoxide as solvents, J values are given in Hz. The substrates **4** were prepared by deamination of the corresponding known substituted 1,2,3-triazolium-1-imides **1** with phosphorus trichloride. The reagents used were purchased from Aldrich and all solvents were purified and dried by standard procedures. Microanalyses were measured on a Perkin-Elmer model 240 CHN analyser. The following are typical examples of the reactions summarised in Tables 1 and 2.

N-Methyl-2,4,5-trisubstituted-1,2,3-triazolium Perchlorates **5**.—(No. 7, Table 1). A solution of 2-(*p*-nitrophenyl)-4,5-dimethyl-1,2,3-triazole **4g** (1.0 g, 4.59 mmol) in dimethylsulfate (20 cm^3) was heated to 80 °C, stirred for 8 h, cooled, treated with aqueous sodium perchlorate solution (10 cm^3 containing 0.7 g, 4.98 mmol) and the whole distilled under vacuum until the volume was reduced to 5 cm^3. On addition of ether to the remaining reaction solution 1,4,5-*trimethyl*-2-(p-*nitrophenyl*)-1,2,3-*triazolium perchlorate* **5** separated. M.p. 230–232 °C (from acetone–ether) (1.35 g, 85%); $\delta_H[(CD_3)_2SO]$ 2.5 and 2.6 (2 s, 3 H each, 4- and 5-Me), 4.2 (s, 3 H, NMe) and 8.09 and 8.57 (2 d, J_{AB} 9.0, AA'BB', *p*-$NO_2C_6H_4$); $\delta_C(CDCl_3)$ 9.25 and 10.26 (4- and 5-Me), 37.8 (NMe), 149.7, 125.8, 128.5 and 143.9 (*p*-$NO_2C_6H_4$, C-1', C-2', C-3' and C-4' respectively).

Dihydro-1,2,4-triazines **6** *and 1-Anilinoimidazoles* **11**.—*Compounds* **6a** *and* **11a**. (No. 1, Table 2). A stirred suspension of compound **5a** (1.0 g, 2.4 mmol) in toluene (50 cm^3) was treated with sodium ethoxide (2.7 mmol) and the resulting yellow solution was stirred at ambient temperatures for 12 h, filtered to remove insoluble salts including **5a** (1.5%) and evaporated under reduced pressure. The residue in CH_2Cl_2 (4 cm^3) was placed on a Merck silica gel 60 column (230–400 mesh ASTM) using dichloromethane as eluent for compound **6a**, m.p. 87–89 °C (from dichloromethane), 73% yield; $\delta_H(CDCl_3)$ 5.26 (s, 2 H, CH_2) and 7.1–7.8 (m, 18 H, Ar); δ_C 61.7 (CH_2), 144.2 (C-6), 159.7 (C-5), 143.7, 117.0 and 123.5 (2-NPh, C-1', C-2' and C-4' respectively), 137.0 and 135.3 (5- and 6-C-Ph, C-1's) and 129.9–130.6 (remaining aromatic).

Compound **11a** was subsequently eluted from the column with ethyl acetate, m.p. 153–155 °C (from acetone); 15% yield; $\delta_H(CDCl_3)$ 6.8–7.8 (m, 18 H, Ar), 8.0 (s, 1 H, imidazole 2-CH) and 9.4 (s, 1 H, NH); δ_C 138.2 (imidazole C-2), 128.2, 135.6 (imidazole C-4 and C-5), 130.23 and 134.7 (4- and 5-Ph, C-1's) and 148.0, 111.9 and 120.0 (N-Ph, C-1', C-2' and C-4' respectively) and 125.3–132.3 (remaining aromatic). In some cases sodium salts of the products **11** may separate from the toluene before evaporation. Stirring in water will free the product **11** and also remove any $NaClO_4$ present.

Compounds **6a** *and* **11a**. (No. 2, Table 2). The triazole **4a** (0.01 mol) was stirred at 80 °C for 12 h in trimethylsilylmethyl trifluoromethanesulfonate (2 cm^3). Excess of the reagent was leached out of the oily residue with ether, compound **5'a**; $\delta_H[(CD_3)_2SO]$ 0 ($SiMe_3$), 4.8 (s, CH_2) and 7.5–8.3 (m, 18 H, aromatic); δ_C 44.9 (CH_2), 135.5 (triazole C-5), 148.6 (triazole C-4), 142.4 (2-N-phenyl C-1'), 133.5, 124.7 (4- and 5-Ph, C-1's respectively) and 129.0–130.7 (remaining aromatic).

The sticky residue of **5'a** without further purification owing to the lability of the $SiMe_3$ group was dissolved in dimethyldigol (diethylene glycol dimethyl ether) treated with caesium fluoride (0.01 mol) and the solution stirred at ambient temperature for 2 h, filtered and the solvent evaporated under reduced pressure. The residue was separated on a silica gel column as described to give compounds **6a** (71%) and **11a** (15%). Similar results were obtained when these reactions were carried out in the presence of dimethyl acetylenedicarboxylate and acrylonitrile.

Compound **15**. (No. 10, Table 2). A stirred mixture of **14** (0.50 g, 1.4 mmol) in toluene (30 cm^3) was treated with sodium ethoxide (1.4 mmol) and stirred at ambient temperature for 12 h after which the red solution was filtered to remove salts including recovered **14** (20%), evaporated under reduced pressure and the residue in CH_2Cl_2 (4.0 cm^3) placed on a column of Merck Silica gel 60 which was eluted with dichloromethane to give compound **15**, m.p. 95–97 °C (from light petroleum, b.p. 40–60 °C) (75% yield); $\delta_H(CDCl_3)$ 1.84 (m, 2 H), 2.27 (m, 2 H), 2.63 (m, 2 H) (3 × CH_2), 2.94 (s, 3 H, NMe), 5.07 (t, 1 H, CH=), 7.27 (d, 2 H) and 8.15 (d, 2 H) (J_{AB}, 9.2, AA'BB', *p*-$NO_2C_6H_4$); δ_C 22.1, 23.7 (CH_2), 44.3 (N-Me), 99.0 (CH=), 146.3 and 141.9 (triazole C-4, C-5) and 150.9, 115.3, 125.3 and 146.3 (2-$NC_6H_4NO_2$-*p*, C-1', C-2', C-2' and C-4' respectively).

X-Ray Crystallography.—Crystal data for compounds **6a** and **11c** are given in Tables 4 and 5. The structures were solved by direct methods, SHELX86,[21] and refined by full matrix least squares using SHELX76.[22] Data were corrected for Lorentz and polarization effects but not for absorption. The hydrogen atom attached to N(6) of compound **11c** was located and refined all other hydrogen atoms in **11c** and **6a** were included in calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. The thermal parameters were terms Uij of $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)$.

The atomic scattering factors for non-hydrogen and hydrogen atoms and the anomalous dispersion correction factors for non-hydrogen atoms were taken from the literature.[23,24,25] All calculations were performed on a VAX 8700 computer. The ORTEP program was used to obtain the drawings.[26] Fractional atomic coordinates are given in Tables 6 and 7 Full details of crystal data, fractional atomic coordinates, bond lengths, bond angles, hydrogen coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.*

* For details of the CCDC deposition scheme see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1992, Issue 1.

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