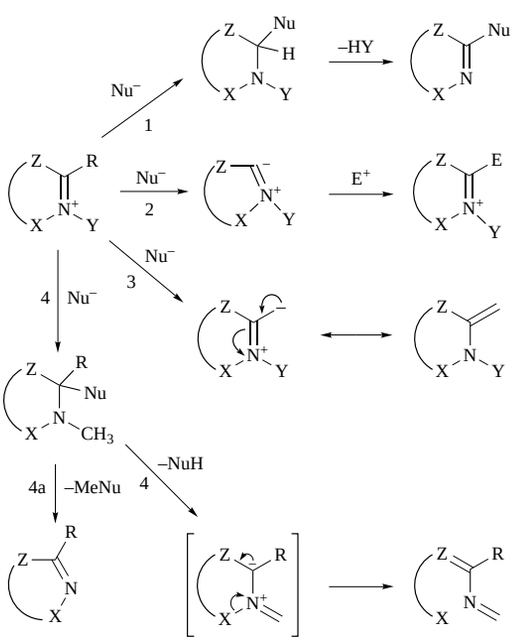
Ring expansions of *N*-methyl-1,2,5-oxadiazolium and 1,2,3-triazolium perchlorate salts with bases to six-membered azines: direct detection of an addition intermediate in an addition–elimination mechanism and a degradation of 1,2,5-oxadiazolium salts to α-cyano nitrones

Richard N. Butler,* Elaine C. McKenna, John M. McMahon, Karen M. Daly, Desmond Cunningham and Patrick McArdle

Chemistry Department, University College Galway, Ireland

Reactions of 2-methyl-1,2,5-oxadiazolium perchlorate salts and 1-methyl-2-aryl-1,2,3-triazolium perchlorate salts with the bases KCN, NaOEt, KOBu^t, LiNPr$^i_2$ give ring expansions to substituted 1,2,5-oxadiazines and 1,2,4-triazines. With cyanide as base the reactions follow an addition–elimination pathway and in two cases the addition intermediate has been isolated or directly detected by low-temperature NMR spectroscopy. The oxadiazolium system with cyanide also gives a useful new route to α-cyano nitrones *via* a ring degradation which competes with ring expansion. The reactions with KOBu^t and LiNPr$^i_2$ do not involve an addition of the base to the azolium salt. Reactions have been monitored by ^{13}C NMR spectroscopy by using $^{13}CN^-$. An X-ray crystal structure is reported for (*E*)-*N*-(α-cyanobenzylidene)methylamine *N*-oxide.

The reactions of azolium salts with bases have attracted wide interest in the past and recently.[1–14] For azolium systems containing ring C–H bonds removal of a ring proton may give rise to an internal azolium ylide[1,2] or an isoelectronic stable azole carbene system[3–5] depending on the nature of the azolium substrate (Scheme 1, path 2). These options are not available with fully substituted azolium salts. With such systems the base may (i) add to the iminium site giving an intermediate which may undergo an elimination or alternatively a fragmentation causing opening and destruction of the azole ring[6,7] or (ii) attack an activated exocyclic α-CH bond giving ultimately substitution at this site.[8] With azolium *N*-alkoxides nucleophilic addition at an unsubstituted iminium carbon may be followed by elimination of the *N*-alkoxy group as an alcohol (Scheme 1, path 1; Y = RO). Alternatively proton loss from the iminium carbon may be followed by electrophilic attack at this site *via* the azolium ylide (Scheme 1, path 2).[8,9] This type of reaction has been widely used for electrophilic substitution with higher azoles, particularly the tetrazoles.[10–14] The range of possible alternative pathways has been classified by Begtrup.[9] One of the rarest pathways is generation of an exocyclic double bond at an azole ring carbon by α-proton loss (Scheme 1, path 3). In the present work[15] we have observed a previously undetected pathway comparable to path 3 in which an addition–elimination process abstracts the α-CH of an *N*-methyl substituent thereby generating a double bond exocyclic to a ring nitrogen (Scheme 1, path 4). This leads ultimately to a ring expansion of the azole to an azine. A combined loss of the *N*-methyl group and the adjacent bonded nucleophile (Scheme 1, path 4a) may also occur leading to the parent unquaternised azole.



Scheme 1 R = H for 1,2; R = alkyl for 3; R = aryl for 4

Results and discussion

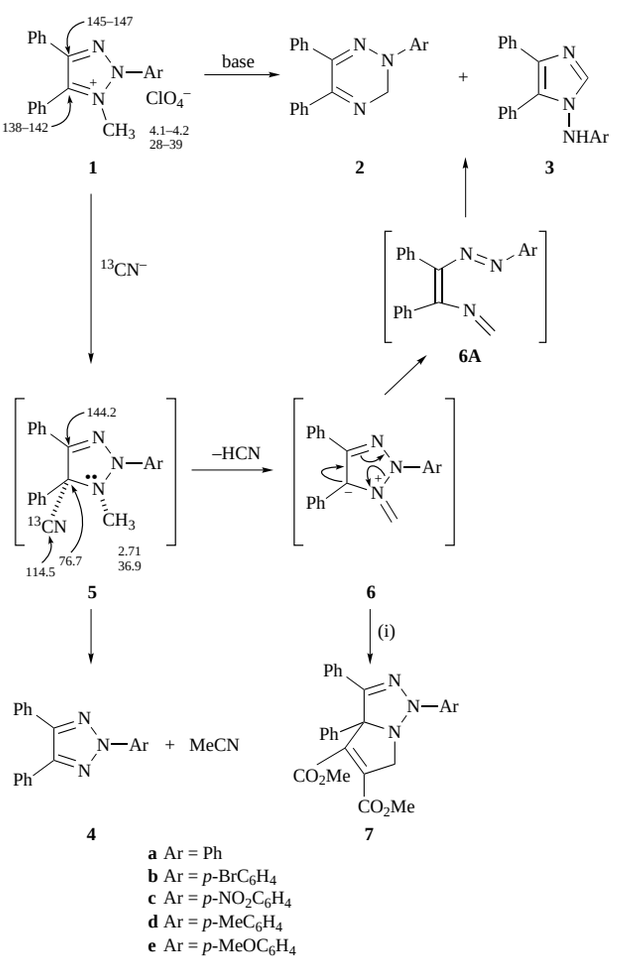
1,2,3-Triazolium salts, 1

Previously, in studies of azolium 1,3-dipoles, we have noted[16] that treatment of the *N*-methyltriazolium salts **1** with ethoxide base in toluene resulted in ring expansion to the triazines **2** along with lesser yields of the imidazoles **3**. No intermediates could be detected in these reactions and it was thought that the process involved a Hoffmann E_2-type proton abstraction from the CH_3 group with concerted ring-opening of the azolium system to give the conjugated triazatriene species **6A** (Scheme 2). This leads on to the products **2** and **3** by competing electrocyclisations.[16] Similar ring expansions of the *N*-methyl-1,2,5-oxadiazolium systems **8** to the oxadiazines **9** (Scheme 3) have now been observed on treatment with bases[15] testifying to the generality of the process. The oxygen analogue of the intermediate **6A** is **12** (Scheme 3). An early example of a ring expansion of this type was found by Kohler and co-workers[17] with an isoxazolium system but they did not recognise the ring-expanded structure of the product and the structure was subsequently established by King and Durst.[18] Similar ring expansions have now been induced by bases such as potassium *tert*-butoxide and lithium diisopropylamide giving products **2** and **3** in yields similar to sodium ethoxide but the efficiency of the reaction (conversion yields) may vary with the base, possibly due to solubility variations (Table 1). With KCN as base the same products **2** and **3** were again formed with **2** as the main product but in this case low yields of the parent triazoles **4** were

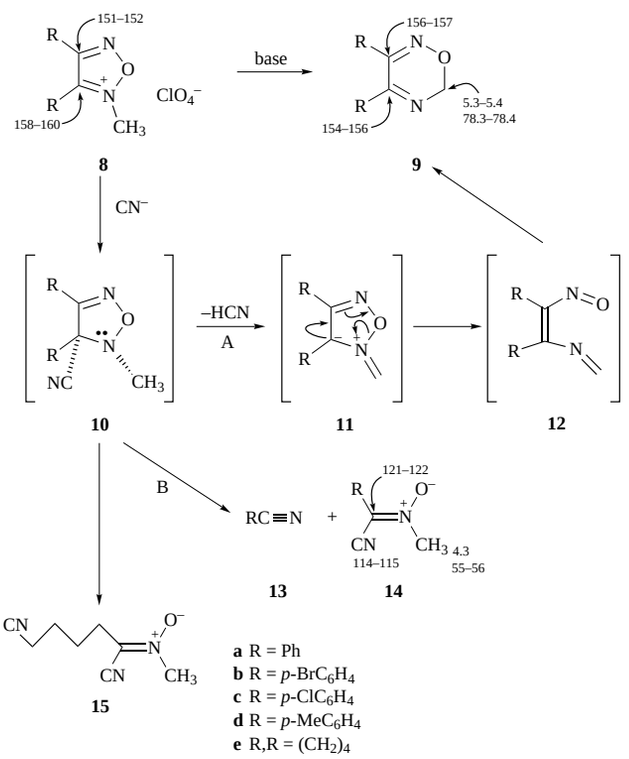
Table 1 Reactions of *N*-methyltriazolium salts **1** with bases[a]

Entry	Substrate	Base (*T*/°C)	Products: yield % (conversion %) **2**	**3**	**4**	**1** (recovered)
1	**1a**	NaOEt	75 (69)	16 (14)	—	(8)
2	**1a**	KCN	33 (8)	31 (7)	35 (10)	(73)
3	**1a**	$KOBu^t$	58 (18)	17 (6)	—	(70)
4	**1a**	$LiNPr^i_2$	84 (69)	16 (13)	—	(18)
5	**1b**	NaOEt	52 (26)	21 (11)	—	(50)
6	**1b**	KCN	38 (13)	35 (12)	22 (17)	(68)
7	**5b**[b]	—	32	20	7	—
8	**1b**	$KOBu^t$	62 (31)	30 (16)	—	(49)
9	**1b**	$LiNPr^i_2$	65 (46)	32 (23)	—	(30)
10	**1c**	NaOEt	50 (24)	42 (20)	—	(54)
11	**1c**	KCN (45)	38 (12)	38 (12)	18 (5)	(66)
12	**1c**	KCN (65)	38 (12)	36 (11)	18 (5)	(67)
13	**5c**	(45)[c]	32	31	30	—
14	**5c**	(65)[c]	49	46	—	—
15	**1c**	$KOBu^t$	45 (23)	36 (19)	—	(49)
16	**1c**	$LiNPr^i_2$	48 (23)	40 (20)	—	(43)
17	**1d**	NaOEt	80 (56)	19 (13)	—	(30)
18	**1d**	KCN	52 (12)	19 (4)	20 (5)	(77)
19	**1d**	$KOBu^t$	67 (40)	24 (14)	—	(40)
20	**1d**	$LiNPr^i_2$	79 (52)	20 (13)	—	(34)
21	**1e**	NaOEt	92 (83)	—[d]	—	(9)
22	**1e**	KCN	30 (9)	23 (7)	19 (6)	(67)

[a] Reactions employed 1.1 mol base in toluene at ambient temperatures except for $LiNPr^i_2$ for which the solvent was dry tetrahydrofuran; reaction 12 h for NaOEt, 24 h for other bases. [b] Generated at −10 °C and warmed to ambient temperatures. [c] Stirred in toluene. [d] Trace quantities only were encountered.



Scheme 2 NMR shift ranges for **1**, $(CD_3)_2SO$ and **5b** in CD_2Cl_2 shown. *Reagent*: (i) $MeO_2CC{\equiv}CCO_2Me$.



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

also formed. The extent of conversion was lower with cyanide ion than with the other bases being in the range 25–40% (Table 1). In the reaction with cyanide ion the intermediates **5** were readily detected. Compound **5c** was a stable solid and was fully characterised. The intermediate **5b** was generated and held in solution at −10 to 5 °C in CD_2Cl_2 and its proton and carbon-13 NMR spectra measured. On warming solutions of the species **5b** and **5c** in toluene they changed into the products **2**, **3** and **4**. This process was followed by ^1H and ^{13}C NMR spectra for solutions in CD_2Cl_2 both for normal substrates and for substrates using carbon-13 labelled cyanide. In all of the reactions of **1** with cyanide ion the parent triazoles **4** were formed by loss of MeCN from **5**. No intermediates could be detected by NMR between **5** and the products **2** and **3** but the species **6** was a likely possibility. The species **6** is a 1,2,3-triazolium-1-methanide 1,3-dipole which we have previously generated by a different

Table 2 Reactions of *N*-methyloxadiazolium salts **8** with bases[a]

			Products				
			9		**13**	**14**	
Entry	Substrate	Base	Mp (*T*/°C)	Yield (%)	Yield (%)	Mp (*T*/°C)	Yield (%)
1	**8a**	NaOEt	116–118[b]	10	72	—	—[f]
2	**8a**	KCN	”	23	68	95–96[e]	62
3	**8a**	$KOBu^t$	”	91	—[d]	—	—
4	**8a**	$LiNPr^i_2$	”	80	—[d]	—	—
5	**8b**	NaOEt	108–110[b]	11	78	—	—[f]
6	**8b**	KCN	”	16	68	131–133[e]	64
7	**8b**	$KOBu^t$	”	86	—[d]	—	—
8	**8b**	$LiNPr^i_2$	”	83	—[d]	—	—
9	**8c**	NaOEt	82–84[b]	9	74	—	—[f]
10	**8c**	KCN	”	18	53	116–117[e]	50
11	**8c**	$KOBu^t$	”	97	—[d]	—	—
12	**8c**	$LiNPr^i_2$	”	80	—[d]	—	—
13	**8d**	NaOEt	93–95[c]	12	81	—	—[f]
14	**8d**	KCN	”	19	50	95–97[e]	63
15	**8d**	$KOBu^t$	”	77	—[d]	—	—
16	**8d**	$LiNPr^i_2$	”	73	—[d]	—	—
17	**8e**	KCN	—	—	—	115–117 (**15**)	83

[a] Reactions with 1.1–1.3 mol base in toluene at ambient temperatures except for $LiNPr^i_2$ for which the solvent was dry tetrahydrofuran. [b] From dichloromethane-hexane. [c] From hexane. [d] Not detected. [e] From dichloromethane–light petroleum (bp 40–60 °C). [f] Intractable oils were encountered.

route.[19] Its presence was confirmed when it was trapped from the intermediate **5b** with dimethyl acetylenedicarboxylate (DMAD). Thus when a solution of **5b**, generated at 0–5 °C in CH_2Cl_2 was treated with DMAD and stirred at ambient temperatures for 48 h the adduct **7b** (28%) was isolated along with products **2b** (40%) and **4b** (12%). The intermediate **6** could not be trapped from any of the reactions with the other bases. Thus cyanide ion reacts with the triazolium salts **1** by an addition–elimination process which is different to the reaction with hard bases although the products are similar.

1,2,5-Oxadiazolium salts 8

Treatment of the salts **8** with bases gave the products **9**, **13** and **14**. Interestingly in this case the reactions with ethoxide paralleled those with cyanide. The ring-expanded product **9** alone was obtained in high yield from potassium *tert*-butoxide and lithium diisopropylamide (Scheme 3, Table 2). Mixtures of the products **9**, **13** and **14** were obtained from the reaction with KCN and comparable yields of **9** and **13** were also obtained from the reaction with NaOEt. The expected intermediate **10** from cyanide addition to the oxadiazolium salts could not be directly detected because it was too short-lived. However its presence was clearly signalled by its fragmentation into the products **13** and **14** (path B, Scheme 3) which were the major products. The reaction provides a useful route to α-cyano substituted nitrones **14** which are not readily available. The alternative path A (Scheme 3) from the intermediate **10** was a relatively minor pathway which gave rise to low yields of the products **9**. The oxadiazolium methanide dipole **11**, the analogue of **6**, could not be trapped. Theoretical calculations as well as extensive experimental attempts[15] to generate this dipole have indicated that it is much less stable than **6** and likely to undergo almost spontaneous opening to **12**, the precursor to **9**. In the reactions with ethoxide base, while the products **9** and **13** were obtained in yields similar to those from cyanide (Table 2) the α-ethoxy derivatives of **14** (EtO for CN) were not isolated and only intractable oils were obtained from chromatographic separations. With the substrate **8e**, where the nitrile fragment from the intermediate **10** cannot leave the molecule, the product from the cyanide reaction was the interesting nitrone **15**.

These results suggest that the reactions with cyanide and ethoxide involve additions of the nucleophile at the iminium carbon followed by degradation of the intermediate **10**. With the bases potassium *tert*-butoxide and lithium diisopropylamide steric constraints appear to block this initial addition. No benzonitriles are formed and the yields of the oxadiazines **9** are raised to the range 70–97% (Table 2). In these cases the deprotonation of the *N*-methylazolium salts bypasses the intermediate **10** and probably involves direct E_2 attack by the base at the *N*-methyl group in a Hoffmann-type process.

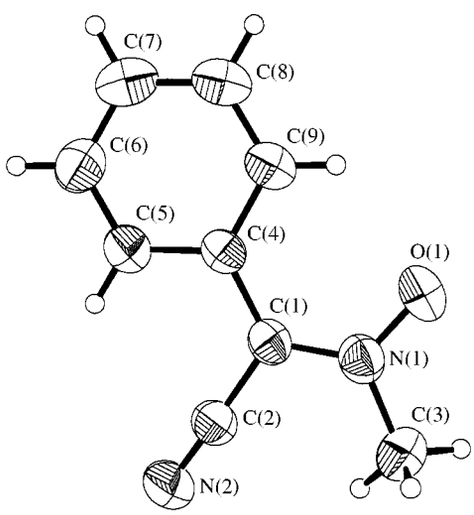


Fig. 1 X-Ray crystal structure of nitrone **14a**

Structure and formation of products

The structures of the products **5**, **9**, **14** and **15** were established from microanalysis, IR, proton and carbon-13 NMR spectra which showed all of the expected signals. Carbon-13 NMR assignments were supported by DEPT and off-resonance decoupled spectra and by the use of C-13 labelled cyano groups for the species **5**. An X-ray crystal structure of **14a** (Fig. 1) confirmed the *E*-configuration with the CN group *cis* to the Me substituent.† The nitrones did not isomerise under the reaction

† Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/129.

conditions and early monitoring of the product mixture showed that the *E*-nitrone only was present in the reaction solution before the work-up. Stereoelectronic studies of the addition of nucleophiles to iminium ions in six-membered rings,[20] including *N*-alkyloxazinium salts,[21] have shown that the developing lone-pair on nitrogen is *trans* to the incoming nucleophile. It is likely that initially in the species **5** and **10** the CN is also *trans* to the lone-pair on the adjacent N-atom and that the products **13** and **14** arise from a rapid 1,3-dipolar cycloreversion in **10**. This cycloreversion did not occur in the intermediates **5** where the stronger conjugated N–NAr bond replaces the N–O bond of **10**. Nitrogen inversions could of course occur in these species but the CN and CH_3 groups are required to be *cis* for elimination of HCN and MeCN from **5**. The products **2**, **3**, **4**, **7b** and **13** are known compounds.[16,19] In the present work these products were identified by comparison with authentic samples.

Experimental

Mps were measured on an Electrothermal apparatus. IR spectra were measured with a Perkin-Elmer 983G spectrophotometer. NMR spectra were measured on JEOL JNM-GX-270 and JEOL LAMBDA 400 MHz instruments with tetramethylsilane as internal reference and deuteriochloroform or hexadeuteriodimethyl sulfoxide as solvents; *J* values are given in Hz. All carbon-13 NMR assignments were supported by DEPT and off-resonance decoupled spectra and CN signals were confirmed using labelled ^{13}CN groups. Microanalyses were measured on a Perkin-Elmer model 240 CHN analyser. The substrates **8** were prepared by heating the 3,4-diarylfurazans[22] at 80 °C in dimethyl sulfate (2–5 mmol in 5 cm^3) for 48 h and treating the cooled solution with aqueous sodium perchlorate followed by diethyl ether to precipitate the salts which were recrystallised from acetone–diethyl ether: **8a**, mp 140–141 °C (90%) (Found: C, 53.3; H, 3.9; N, 8.2. $C_{15}H_{13}ClN_2O_5$ requires C, 53.5; H, 3.85; N, 8.3%); **8b**, mp 188–190 °C (91%) (Found: C, 36.6; H, 2.35; N, 5.80. $C_{15}H_{11}Br_2ClN_2O_5$ requires C, 36.4; H, 2.20; N, 5.65%); **8c**, mp 174–175 °C (88%) (Found: C, 44.3; H, 2.6; N, 6.6. $C_{15}H_{11}Cl_3N_2O_5$ requires C, 44.4; H, 2.7; N, 6.9%); **8d**, mp 120–122 °C (81%) (Found: C, 56.2; H, 4.5; N, 7.4. $C_{17}H_{17}ClN_2O_5$ requires C, 56.0; H, 4.65; N, 7.7%); **8e**, mp 99–101 °C (76%) (Found: C, 35.4; H, 4.45; N, 11.6. $C_7H_{11}ClN_2O_5$ requires C, 35.25; H, 4.6; N, 11.75%).

Reactions of oxadiazolium salts 8 with bases

The following are typical examples.

LiNPr$^i_2$. A three-necked flask was charged with finely cut lithium (23 mg, 3.26 mmol) followed by pure diisopropylamine (0.36 g, 3.6 mmol) and freshly dried tetrahydrofuran (10 cm^3) and the mixture subjected to sonication and treated dropwise with isoprene (0.12 g, 1.8 mmol). When the lithium had dissolved a solution of compound **8a**, (1 g, 2.97 mmol) in tetrahydrofuran (10 cm^3) was introduced and the mixture was stirred at ambient temperature for 5 min, filtered to remove salts, evaporated under reduced pressure and the residue in dichloromethane (5 cm^3) placed on a column (Merck silica gel 60, 230–400 mesh ASTM) and eluted with CH_2Cl_2–EtOAc (95:5 v/v) to give 3,4-*diphenyl*-6H-1,2,5-*oxadiazine* **9a**, mp 116–118 °C (dichloromethane–hexane) (560 mg, 80%) (Found: C, 76.15; H, 5.2; N, 11.6. $C_{15}H_{12}N_2O$ requires C, 76.3; H, 5.1; N, 11.85%); δ_H($CDCl_3$) 5.28 (s, 2H, CH_2), 7.1–7.3 (10H, m, Ar); δ_C 78.3 (NCH_2), 157.4 (C-3), 156.25 (C-4), 135.1, 128.3, 128.5, 130.4 (C-3-phenyl, C-1′, C-2′, C-3′, C-4′ resp.), 132.1, 127.9, 128.3, 130.1 (C-4-phenyl, C-1′, C-2′, C-3′, C-4′ resp.).

KOBu^t. A solution of **8a** (1 g, 2.97 mmol) in toluene (30 cm^3) was treated with potassium *tert*-butoxide (0.4 g, 3.56 mmol) and the mixture stirred at ambient temperature for 20 h, filtered to remove salts, evaporated and the residue worked up on a column as described to give **9a** (91%).

KCN and NaOEt. (a) A solution of **8a** (0.51 g, 1.5 mmol) in toluene (15 cm^3) was treated with potassium cyanide (0.12 g, 1.8 mmol) and the mixture stirred at ambient temperature for 24 h, filtered to remove salts, evaporated and the residue in dichloromethane (5 cm^3) placed on a column (Merck silica gel 60, 230–400 mesh ASTM). Elution with light petroleum (bp 40–60 °C)–dichloromethane (60:40 v/v) delivered benzonitrile **13a** (68%); using the same eluents in a 20:80 v/v mixture gave (E)-N-(α-*cyanobenzylidene)methylamine* N-*oxide* **14a**, mp 95–96 °C (from dichloromethane–light petroleum, bp 40–60 °C) (150 mg, 62%) (Found: C, 67.4; H, 5.0; N, 17.3. $C_9H_8N_2O$ requires C, 67.5; H, 5.0; N, 17.5%); ν_{max}(Nujol)/cm^{-1} 1570 (C=N), 2214 (C≡N), 1240 (N^+–O^-); δ_H($CDCl_3$) 4.3 (s, 3H, NMe), 7.4 (m, 3H, Ph, H_m, H_p), 8.2–8.3 (m, 2H, Ph, H_o); δ_C 55.8 (NMe), 114.6 (CN), 121.0 (methine C=N), 128.0, 127.4, 128.6, 131.4 (Ph, C-1′, C-2′, C-3′, C-4′ resp.). Compound **9a** (23%) was finally recovered from the column using CH_2Cl_2–EtOAc (95:5 v/v) as eluent. A similar reaction with NaOEt as base gave compound **13a** (72%), **9a** (10%) and intractable oils.

(b) A solution of **8e** (0.61 g, 2.55 mmol) in dry dichloromethane (25 cm^3) was treated with potassium cyanide (0.2 g, 3.07 mmol), stirred at ambient temperature for 2 h, filtered to remove salts, evaporated under reduced pressure and the residue crystallised from methanol to give (E)-(1,5-*dicyanopentylidene*)*methylamine* N-*oxide* **15**, mp 115–117 °C (MeOH) (0.3 g, 83%) (Found: C, 58.1; H, 6.8; N, 25.3. $C_8H_{11}N_3O$ requires C, 58.2; H, 6.65; N, 25.45%); ν_{max}(Nujol)/cm^{-1} 1634 (C=N), 2202, 2246 (two CN); δ_H($CDCl_3$) 1.75–1.77 (m, 4H), 2.42–2.45 (m, 2H), 2.59 (m, 2H) [$(CH_2)_4CN$], 4.07 (s, 3H, NMe); δ_C 16.4, 23.5, 23.6, 27.4 (4-cyanobutyl, C-4, C-3, C-2, C-1 resp.), 52.9 (NMe), 113.9 (α-CN), 118.9 (4-cyanobutyl, CN), 123.5 (methine C=N).

Reactions of the triazolium salts 1 with bases

The following are typical examples.

KCN; intermediates 5. (a) A suspension of 1-methyl-2-(*p*-bromophenyl)-4,5-diphenyl-1,2,3-triazolium perchlorate **1b** (0.16 g, 0.3 mmol) in CD_2Cl_2 (1.5 cm^3) was treated with KCN (0.09 g, 1.4 mmol), stirred at 0 °C for 24 h, then filtered to remove salts and unreacted **1b**. The NMR spectra of the yellow solution (Solution A) measured at −20 °C showed that it contained pure 1-*methyl*-2-(p-*bromophenyl*)-4,5-*diphenyl*-5-*cyano*-2,5-*dihydro*-1H-1,2,3-*triazole* **5b**, δ_H 2.71 (s, 3H, NMe), 7.26–7.33 (m), 7.47–7.51 (m) (8H, 5-Ph, 4-Ph, $H_{m,p}$, 5-Ph, H_o), 7.38 and 7.56 (ABq, 4H, J_{AB}, 8.7, 2-NC_6H_4Br-*p*, AA′BB′); 7.67–7.69 (m, 2H, 4-Ph, H_o); δ_C 36.9 (NMe), 76.7 (C-5), 114.5 (CN), 144.2 (C-4), 145.0, 113.9, 123.5, 119.5 (2-NC_6H_4Br-*p*, C-1′, C-2′, C-3′, C-4′ resp.), 135.3, 134.3 (5-Ph, 4-Ph, C-1′), 130.8, 130.5 (5-Ph, 4-Ph, C-4′), 127.4, 129.1, 129.7, 132.5 (remaining Ph, CH). Solution (A) was stirred at ambient temperature for 24 h, placed on a silica gel-60 column (230–400 mesh ASTM) and eluted with dichloromethane to give **4b** (7%), **2b** (32%) and eluted with EtOAc to give **3b** (20%). When a solution (A) (prepared from 0.30 g, 0.6 mmol, **1b** in CH_2Cl_2, 5 cm^3) was first treated with DMAD (0.1 cm^3) in CH_2Cl_2 (10 cm^3) at 0 °C prior to stirring at ambient temperature and worked up as described eluting initially with gradient mixtures of light petroleum (bp 40–60 °C)–dichloromethane (9:1 to 7:3 v/v) gave the following products: **4b** (15%), **7b** (27%), mp 142–144 °C (lit.,[19] mp 142–144 °C), **2b** (32%) and **3b** (<4%) and some intractable oils [a crude unstable sample of **5b**, mp 37–40 °C (Found: C, 63.8; H, 4.0; N, 12.2. $C_{22}H_{17}BrN_4$ requires C, 63.3; H, 4.1; N, 13.4%) was isolated by treating a toluene solution with Et_2O at −5 °C but the compound was best kept in solution] (Table 1, entries 6,7).

(b) A mixture of **1c** (0.3 g, 0.7 mmol) in toluene (3 cm^3) was treated with K^{13}CN (0.2 g, 3.1 mmol), stirred at ambient temperatures under a nitrogen atmosphere for 24 h, filtered to remove salts and unreacted **1c** (47%), cooled at 0 °C and treated with light petroleum (bp 40–60 °C) causing separation of 1-*methyl*-2-(p-*nitrophenyl*)-4,5-*diphenyl*-5-*cyano*-2,5-*dihydro*-1H-

Table 3 Crystal data for **14a**

Empirical formula	$C_9H_8N_2O$
M	160.17
T/K	293(2)
λ/Å	0.710 69
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 6.5967(6) Å
	b = 9.1775(12) Å; β = 101.084(9)°
	c = 13.793(2) Å
V/Å^3	819.5(2)
Z	4
D_c	1.298 Mg m^{-3}
Absorption coefficient	0.88 mm^{-1}
F(000)	336
Crystal size	0.24 × 0.15 × 0.09 mm
θ range for data collection	2.68 to 31.93°
Index ranges	$-7 \leqslant h \leqslant 7$; $0 \leqslant k \leqslant 10$; $0 \leqslant l \leqslant 14$
Reflections collected	2203
Independent reflections	2077 [R(int) = 0.0494]
Reflections observed (>2σ)	944
Refinement method	Full matrix least-squares on F^2
Data/restraints/parameters	2077/0/110
Goodness-of-fit F^2	0.901
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0581 wR_2 = 0.1571
R indices (all data)	R_1 = 0.1233 wR_2 = 0.1855
Largest diff. peak and hole	0.173 and −0.163 e Å^{-3}

R indices; $R_1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$ (based on F), $wR_2 = \{[\Sigma_w(|F_o^2 - F_c^2|)^2]/[\Sigma_w(F_o^2)^2]\}^{\frac{1}{2}}$ (based on F^2) $w = 1/[(\sigma F_o)^2 + (0.2866*P)^2]$ $P = (\text{Max}\ (F_o^2,0) + 2*F_c^2)/3$ Goodness-of-fit = $[\Sigma_w(F_o^2 - F_c^2)^2/(N_{\text{obs}} - N_{\text{parameters}})]^{\frac{1}{2}}$.

1,2,3-*triazole* **5c**, mp 102–104 °C (from toluene–light petroleum, bp 40–60 °C at ambient temperature) (0.12 g, 48% conversion) (Found: C, 69.4; H, 4.6; N, 18.4. $C_{22}H_{17}N_5O_2$ requires C, 68.9; H, 4.4; N, 18.3%); $\delta_H(CD_2Cl_2)$ 2.90 (s, 3H, NMe), 7.68 and 8.22 (ABq, J_{AB} 8.3, AA′BB′, p-$NO_2C_6H_4$), 7.34–7.54 (m, 10H, 2 × Ph); δ_C 40.4 (NMe), 76.1 (d, $J_{C-^{13}CN}$, 79.4), (C-5), 114.6 (CN), 144.2 (C-4), 148.9, 116.4, 125.7, 142.9 (2-$NC_6H_4NO_2$-*p*, C-1′, C-2′, C-3′, C-4′ resp.), 135.7, 127.4, 129.8, 131.1 and 135.7, 127.8, 129.2, 130.5 (4- and 5-Ph, C-1′, C-2′, C-3′, C-4′). When a toluene solution of the salt **1c** was heated with KCN or when a toluene solution of **5c** was heated separately similar mixtures of the known[16] compounds **2c**, **3c** and **4c** were obtained (Table 1, entries 11–14).

(c) A mixture of 1-methyl-2-(*p*-tolyl)-4,5-diphenyl-1,2,3-triazolium perchlorate **1d** (0.3 g, 0.7 mmol) in toluene (15 cm^3) was treated with KCN (0.06 g, 0.9 mmol), stirred at ambient temperatures for 24 h, filtered to remove salts and unreacted **1d** (77%), evaporated under reduced pressure and the residue in CH_2Cl_2 (3 cm^3) placed on a silica gel-60 column (230–400 mesh ASTM) and eluted with CH_2Cl_2 to give **4d** (0.01 g, 5%) followed by **2d** (0.028 g, 12%), mp 98–100 °C (lit.,[16] mp 98–100 °C). Elution with EtOAc gave **3d** (0.01 g, 4%, mp 173–174 °C (lit.,[16] mp 173–175 °C) (Table 1, entry 18).

LiN^{i}Pr$_2$. A three-necked flask was charged with finely cut lithium (36 mg, 5.14 mmol) followed by pure diisopropylamine (0.8 cm^3, 5.71 mmol) and dry tetrahydrofuran (20 cm^3) and the mixture subjected to sonication and treated dropwise with isoprene at 10 °C giving a light yellow solution which was added to a mixture of **1a** (1.0 g, 2.43 mmol) in dry tetrahydrofuran (20 cm^3) and stirred at ambient temperature for 24 h, filtered to remove salts and unreacted **1a** (18%) and the filtrate partitioned between water (150 cm^3) and chloroform (50 cm^3). The aqueous extract was further extracted with chloroform (2 × 50 cm^3) and the combined extract dried over anhydrous magnesium sulfate and evaporated giving a residue which, in CH_2Cl_2 (4 cm^3), was placed on a silica gel column (270–400 mesh ASTM) and eluted first with CH_2Cl_2 to give **2a** (0.52 g, 69%) followed by EtOAc to give compound **3a** (0.1 g, 13%) (Table 1, entry 4).

The reactions with potassium *tert*-butoxide were similar to those with sodium ethoxide.[16]

X-Ray crystal structure determination of compound 14a

Crystal data are given in Table 3. The structure was solved by direct methods, SHELX-86,[23] and refined by full matrix least squares using SHELX-93.[24] SHELX operations were rendered paperless using ORTEX which was also used to obtain the drawings.[25] Data were corrected for Lorentz and polarization effects but not for absorption. Hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. The non-hydrogen atoms were refined anisotropically. All calculations were performed on a Silicon Graphics R4000 computer.

Acknowledgements

E. C. McK., J. M. McM. and K. M. D. acknowledge grants from the Irish Government Science Agency, FORBAIRT.

References

1 M. Begtrup and K. V. Poulsen, *Acta Chem. Scand.*, 1971, **25**, 2087; M. Begtrup and P. A. Kristensen, *Acta. Chem. Scand.*, 1969, **23**, 2733.
2 M. Begtrup, *Acta Chem. Scand.*, 1971, **25**, 249; *J. Chem. Soc., Chem. Commun.*, 1975, 334.
3 A. J. Arduengo III, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361.
4 A. J. Arduengo III, H. V. R. Dias, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1992, **114**, 5530.
5 D. Enders, K. Breuer, G. Raabe, J. Runsink, J. H. Teles, J.-P. Melder, K. Ebel and S. Brode, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1021.
6 R. N. Butler, H. A. Gavin, D. Cunningham, and P. McArdle, *J. Chem. Res.* (*S*), 1994, 12.
7 R. N. Butler, J. P. Duffy, E. P. NiBhradaigh, P. McArdle and D. Cunningham, *J. Chem. Res.* (*S*), 1994, 216.
8 M. Begtrup and P. Vedso, *J. Chem. Soc., Perkin Trans. 1*, 1992, 2555.
9 M. Begtrup, *Heterocycles*, 1992, **33**, 1129.
10 R. Weiss and R. H. Lowack, *Angew Chem., Int. Ed. Engl.*, 1991, **30**, 1162.
11 S. Araki, Y. Wanibe, F. Uno, A. Morikawa, K. Yamamoto, K. Chiba and Y. Butsugan, *Chem. Ber.*, 1993, **126**, 1149.
12 V. P. Karavai and P. N. Gaponik, *Khim Geterotsikl. Soedin.*, 1991, 66 (*Chem. Abstr.*, 1991, **115**, 71 484).
13 R. H. Lowack and R. Weiss, *J. Am. Chem. Soc.*, 1990, **112**, 333.
14 P. N. Gaponik, Yu. V. Grigor'ev and A. O. Koren, *Khim. Geterotsikl. Soedin.*, 1988, 1699 (*Chem. Abstr.*, 1989, **111**, 194 674).
15 A part of the present work on oxadiazoles has been published in a preliminary communication; R. N. Butler, K. M. Daly, J. M. McMahon and L. A. Burke, *J. Chem. Soc., Perkin Trans. 1*, 1995, 1083.
16 R. N. Butler, J. P. Duffy, D. Cunningham and P. McArdle, *J. Chem. Soc., Perkin Trans. 1*, 1992, 147.
17 E. P. Kohler and A. H. Blatt, *J. Am. Chem. Soc.*, 1928, **50**, 1217; E. P. Kohler and N. K. Richtmeyer, *J. Am. Chem. Soc.*, 1928, **50**, 3092; E. P. Kohler and W. F. Bruce, *J. Am. Chem. Soc.*, 1931, **53**, 644.
18 J. F. King and T. Durst, *Can. J. Chem.*, 1962, **40**, 882.
19 R. N. Butler, P. D. McDonald, P. McArdle and D. Cunningham, *J. Chem. Soc., Perkin Trans. 1*, 1996, 1617.
20 P. Deslongchamps in *Stereoelectronic Effects in Organic Chemistry*, Pergammon Press, Oxford, 1983, pp. 211–221 and 291–300.
21 M. Petrzilka, D. Felix and A. Eschenmoser, *Helv. Chim. Acta*, 1973, **56**, 2950.
22 A. J. Boulton, P. Hadjimihalakis, A. R. Katritzky and A. Majid Hamid, *J. Chem. Soc. C*, 1969, 1901.
23 G. M. Sheldrick, *Acta. Crystallogr., Sect. A*, 1990, **46**, 467.
24 G. M. Sheldrick, SHELXL-93 a computer program for crystal structure determination, University of Gottingen, 1993.
25 P. McArdle, *J. Appl. Crystallogr.*, 1995, **28**, 65.

Paper 7/01233K
Received 21*st February* 1997
Accepted 19*th May* 1997