Azolium Anions and their Reaction with Electrophilic Reagents

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Summary Anions, produced by deprotonation of various azolium ions with sodium hydride in dimethylformamide, react with electrophiles to give C-, O-, S-, or halogen-substituted azole derivatives.

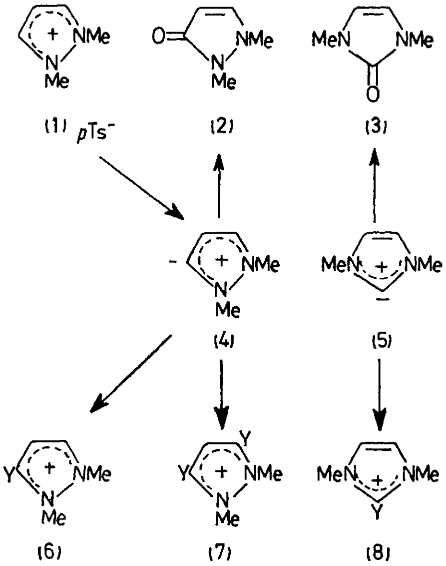
ANIONS derived from acidic azolium ions are reported to yield azole-thiones on reaction with sulphur.[1] We have deprotonated some azolium ions, using NaH in $HCO{\cdot}NMe_2$, and have treated the corresponding anions (**4**, **5**, **11**, and **12**) with a variety of electrophiles, including sulphur.[2] This

TABLE. Products from the reaction of anions derived from azolium salts and various electrophiles

Azolium salts	$MeS{\cdot}SO_3Na$	$Cl_3C{\cdot}CCl_3$	CBr_4	EtI	MeI	Ac_2O	O_2
1,2-dimethylpyrazolium tosylate (**1**)[a]	**7a**[b](85)[c]	[d]	[d]	[d]	mixture	**7g**(95)	**2** (95)
1,3-dimethylimidazolium tosylate	**8a** (*ca.*100)	**8b** (*ca.* 100)	**8c** (*ca.* 100)	**8e** (*ca.* 100)	**8f** (*ca.* 100)	**8g** (50)	**3** (96)
1,2-dimethyl-1,2,3-triazolium chloride	**13a** (36)	**13b** (38)	**13c** (50)	[d]	[d]	**13g** (*ca.*4)	**9** (90)
1,3-dimethyl-1,2,3-triazolium tosylate	**14a** (*ca.* 100)	**14b** (*ca.* 100)	**14c** (80)	**15e** (*ca.* 100)	**14d** (*ca.* 100)	[d]	**10** (33)

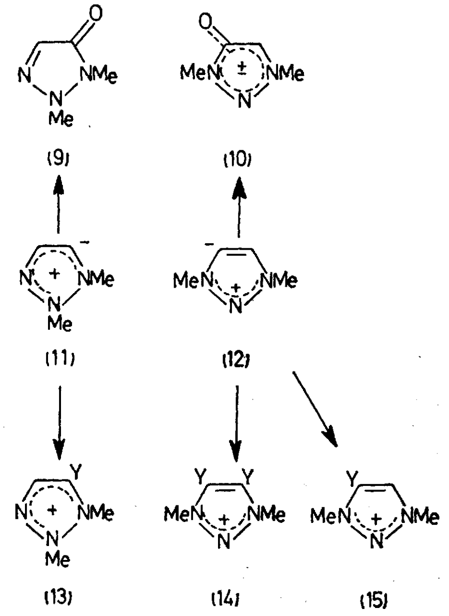
[a] Generally, the azolium salt, NaH (1·2 mol. equiv.), and the solid or liquid electrophile, dissolved in $HCO{\cdot}NMe_2$ at 0° under dry N_2 were kept at 20° for 24—48 h. Oxidations were performed by bubbling oxygen through the solution. [b] (**8a**) and (**2**,**3**,**9**, and **10**) were identical with authentic specimens. The other products were new. Due to contamination with inorganic salt (**8a**), (**8c**); (**13b**), (**13c**), and (**14b**), (**14c**) were identified using their reaction with aqueous base to give known azolones or haloazolones. The remaining products were identified using their ^1H n.m.r. spectra. [c] Figures in parentheses refer to yields determined by ^1H n.m.r. analysis, or, in the case of azolones, by isolation. [d] No conversion.

reaction has proved to be of considerable synthetic versatility (Table).



The anions (**5**) and (**11**) derived from the 1,3-dimethylimidazolium and 1,2-dimethyl-1,2,3-triazolium ions both afforded methylthio-substituted derivatives *viz.* (**8a**) and (**13a**) on reaction with $MeS{\cdot}SO_3Na$. Under identical conditions, the anions (**4**) and (**12**), derived from 1,2-dimethylpyrazolium and 1,3-dimethyl-1,2,3-triazolium ions, yielded the bis-methylthio-substituted derivatives (**7a**) and (**14a**). Reaction with $Cl_3C{\cdot}CCl_3$ or CBr_4 of the anions (**5**) and (**11**) gave the monohalo-substituted products (**8b**—**c**) and (**13b**—**c**) whilst the ion (**12**) yielded the dihalogen derivatives (**14b**—**c**).[8]

Whereas *C*-alkylation of the anions (**4**, **5**, **11**, and **12**) beyond the stage of monoalkylation was never observed when EtI was employed (Table), alkylation with the sterically less demanding MeI resulted in repetitive methylation producing *e.g.* the *CC'*-dimethyl-1,2,3-triazolium salt (**14d**). When neutral resonance structures acquired significance in species resulting from exocyclic deprotonation, side-chain methylation gave *C*-ethyl (**6e**), (**8e**), *C*-isopropyl (**6f**), (**8f**), or, with excess NaH, *CC'*-diethyl (**7e**), *C*-ethyl-*C'*-isopropyl (**7**; Y = Et, Pr^i), and *CC'*-diisopropyl substituted (**7f**) products.



(a; Y = SMe)
(b; Y = Cl)
(c; Y = Br)
(d; Y = Me)
(e; Y = Et)
(f; Y = Pr^i)
(g; Y = Ac)

Ac_2O effected the conversion of the imidazolium and triazolium anions, (**5**) and (**11**), into the *C*-monoacetylated products (**8g**) and (**13g**) whereas the pyrazolium anion (**4**) yielded a *CC'*-diacetyl derivative, (**7g**).

Reaction of the anions (**4**, **5**, **11**, and **12**) with O_2, catalyzed by $CuCl_2$, proceeded smoothly to give the azolones (**2**, **3**, **9**, and **10**).

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[1] H. G. O. Becker, D. Nagel, and H.-J. Timpe, *J. prakt. Chem.*, 1973, **315**, 79, and references cited therein.

[2] M. Begtrup, *J.C.S. Perkin I*, 1975, 507.