Formation of 1,2,4-Triazinium 1-Imides from 4-Aryl-1-azido-1,3-bis(dimethylamino)-2-azabutenylium Salts: Heterocyclic *N*-Imides lacking Exocyclic Stabilisation

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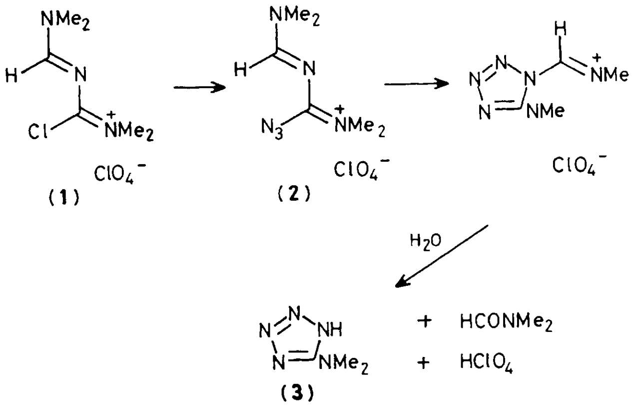
Treatment of 4-aryl-1-azido-1,3-bis(dimethylamino)-2-azabutenylium perchlorates (**5**) with sodium hydroxide yields stable 6-aryl-3,5-bis(dimethylamino)-1,2,4-triazinium 1-imides (**8**), in which the exocyclic nitrogen atom bears only hydrogen.

While investigating the chemistry of the recently reported[1] 1-chloro-1,3-bis(dimethylamino)-2-azapropenylium salts we found that they react with sodium azide to yield azido salts, which undergo further transformations. Thus the parent compound (**1**) gives the known[2] 5-dimethylaminotetrazole (**3**) by spontaneous cyclisation of the intermediate azide (**2**) and subsequent hydrolysis (Scheme 1). In contrast, the phenylmethyl analogue (**4a**) yields the stable azido perchlorate (**5a**) (90%), m.p. 121 °C (decomp.).† This salt loses the elements of perchloric acid by the action of sodium hydroxide to give a pale-yellow base, m.p. 107—109 °C (decomp.)† in 78% yield, which was evidently not the tetrazole (**7a**), since its ^{1}H n.m.r. spectrum lacked a signal due to an olefinic proton and its i.r. spectrum exhibited NH absorption. The structure was solved by *X*-ray analysis,‡ which showed it to be the 1,2,4-triazinium imide (**8a**). The analogues (**8b—d**), m.p. (decomp.) 107, 104.5, and 120.5 °C,† respectively, were obtained in 34—90% yields from the appropriate arylazabutenylium salts (**4b—d**).

We suggest that the triazinium imides are formed by an unprecedented 6π-electrocyclisation of intermediate 1-azido-2-azabutadienes (**6**) onto the central nitrogen atom of the azide group, followed by prototropy (see Scheme 2). The imides are to our knowledge the first stable members of the class of heterocyclic *N*-imides, in which the formal negative charge on the exocyclic nitrogen atom is not delocalised over an adjacent group as, for instance, in pyridinium 1-nitroimide.[3]

Indeed, the *X*-ray structure of compound (**8a**) (see Figure 1) suggests that the *N*-imide canonical form (**8**) does not represent these compounds satisfactorily. The bond lengths, in particular the short exocyclic N=N distance and the long



Scheme 1

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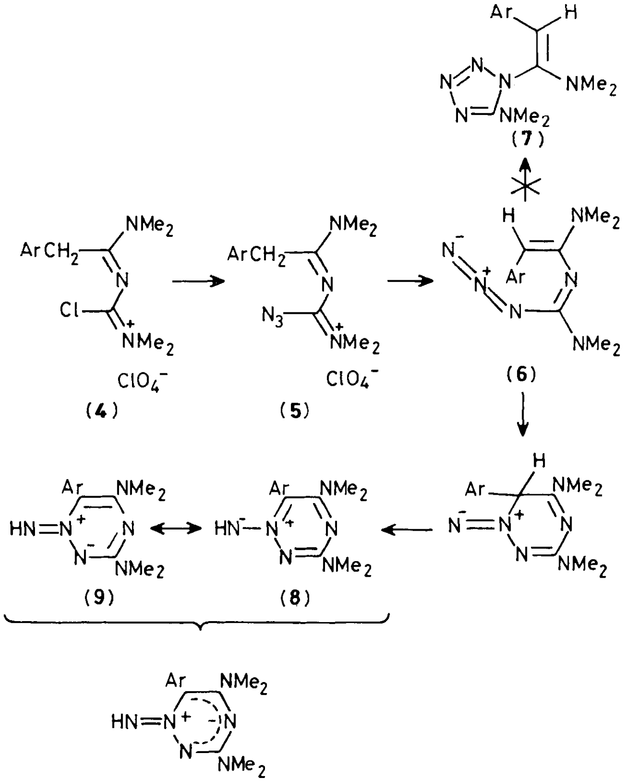
† Satisfactory analytical and spectroscopic data were obtained.

‡ *Crystal data:* (**8a**), $C_{13}H_{18}N_6$, orthorhombic, space group $P\,2_12_12$, $a = 15.095(3)$, $b = 16.333(3)$, $c = 5.643(1)$ Å, $U = 1391.3(5)$ Å^3, $Z = 4$, $D_x = 1.233$ Mg m^{-3}, Cu-K_α radiation, $\lambda = 1.54178$ Å, $\mu = 5.60$ cm^{-1}, $F(000) = 552$, $T = 293(1)$ K, $R = 0.043$ for 2525 independent reflections.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



a; Ar = Ph
b; Ar = p-MeC$_6$H$_4$
c; Ar = p-MeOC$_6$H$_4$
d; Ar = p-ClC$_6$H$_4$

Scheme 2

endocyclic N(1)–N(2) and N(1)–C(6) bonds, together with the intermediate distances between the other ring atoms, indicate that forms such as (**9**) make important contributions; the molecules are best represented by the expression (**10**). This is in marked contrast to the structure of pyridinium 1-nitroimide, which possesses a long exocyclic bond of 1.421 Å, emanating from the pyridine nitrogen atom, and whose endocyclic bonds (C–C 1.366—1.387 and C–N 1.340, 1.350 Å) are intermediate between single and double bonds.[3]

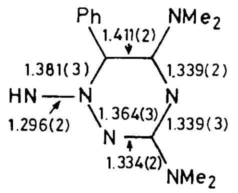


Figure 1. Endocyclic bond lengths and the exocyclic N=N distance (Å) in the triazinium imide (**8a**).

In order to obtain information about the structure of the imide (**8a**) in solution, we determined its ^{15}N n.m.r. spectrum. The spectrum was recorded for a chloroform solution on a Bruker WH-400 instrument at 40.6 MHz at 24 °C with aqueous ammonium nitrate as external standard. Six ^{15}N resonances were observed: two high-field signals at 41.1 and 43.8 p.p.m., assigned to the nitrogen atoms of the dimethylamino groups, and four downfield signals at 291.6 [N(1)], 168.9 [N(2)], 221.8 [N(4)], and 218.5 p.p.m. (imide nitrogen). These assignments are based on a comparison with the spectra of known compounds and analysis of nuclear Overhauser enhancement effects.[4] The chemical shifts do not correlate with those of aromatic triazines,[4] which suggests that the molecule is best represented by (**10**), indicating substantial zwitterionic character within the ring, in solution as well as in the solid phase.

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