

## 1-Chloro-1,3-bis(dimethylamino)-2-azapropenylium Salts: Intermediates for the Synthesis of 1,3,5-Triazines, Pyrimidines, Isoquinolines, Quinazolines, and a 1,3,5-Thiadiazinium Salt

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The title salts, which are formed by the action of dimethylcyanamide on the phosphorus oxychloride complexes of a variety of tertiary amides, are useful precursors of six-membered heteroaromatic compounds: they react with simple amidines to yield 1,3,5-triazines and with *N,N*-dimethylamidines to give pyrimidines; 3-arylmethyl-1-chloro-1,3-bis(dimethylamino)-2-azapropenylium perchlorates form isoquinolines, the related 3-arylamino-1-chloro-1-dimethylamino-2-azapropenylium salts cyclise to quinazolinium salts, and treatment of 1-chloro-1,3-bis(dimethylamino)-3-phenyl-2-azapropenylium perchlorate with potassium thiocyanate results in a rearranged 1,3,5-thiadiazinium salt.

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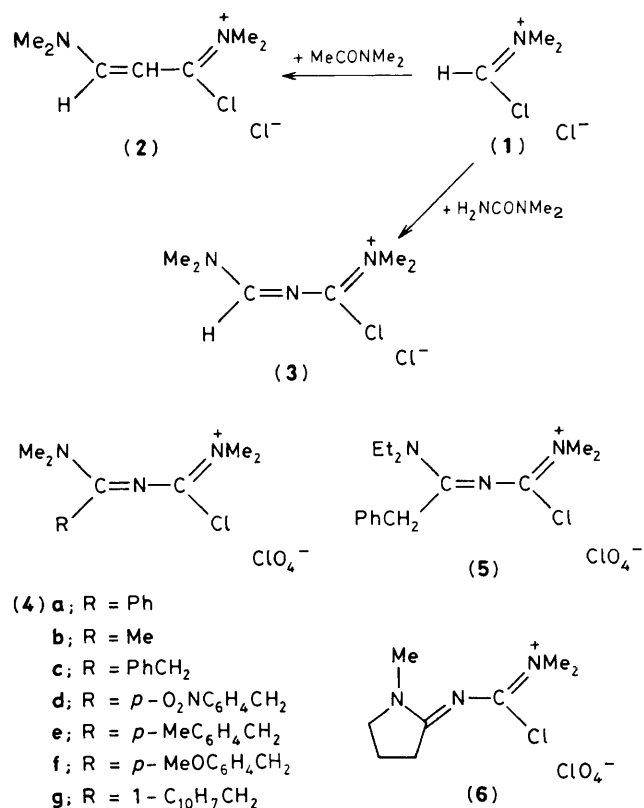
Arnold<sup>1</sup> described the formation of the propenylium salt (**2**) by the action of the Vilsmeier-Haack reagent (**1**) on *N,N*-dimethylacetamide. We have found that *N,N*-dimethylurea reacts similarly, yielding the nitrogen analogue (**3**), which was characterised as the tetraphenylborate, m.p. 167 °C.† The salt

was also obtained when dimethylcyanamide, a synthetic equivalent of the urea, was used. The former reaction is new; the latter has been mentioned briefly,<sup>2</sup> but there have been no reports on the chemistry of the azapropenylium salt.

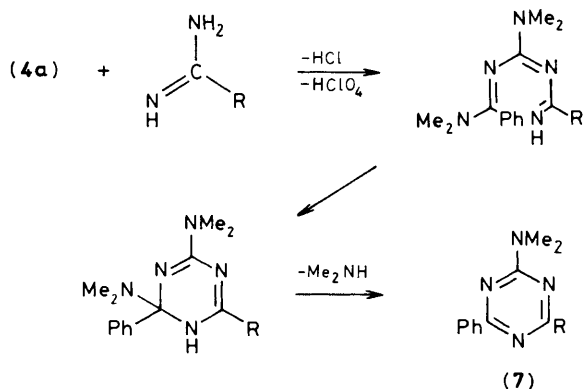
We have considerably extended the range of azapropenylium salts formed by the action of amide-phosphorus oxychloride complexes on dimethylcyanamide. The reactions were conducted in dichloromethane solutions at 10–20 °C and the

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† Satisfactory analytical and spectroscopic data were obtained.



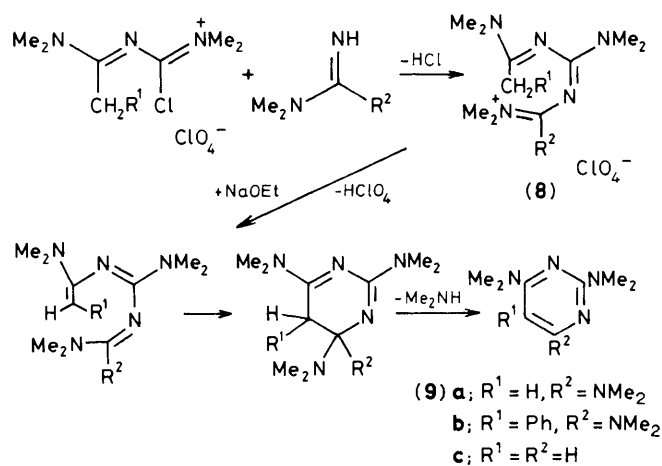
- (4) a; R = Ph  
 b; R = Me  
 c; R = PhCH<sub>2</sub>  
 d; R = *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>  
 e; R = *p*-MeC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>  
 f; R = *p*-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>  
 g; R = 1-C<sub>10</sub>H<sub>7</sub>CH<sub>2</sub>



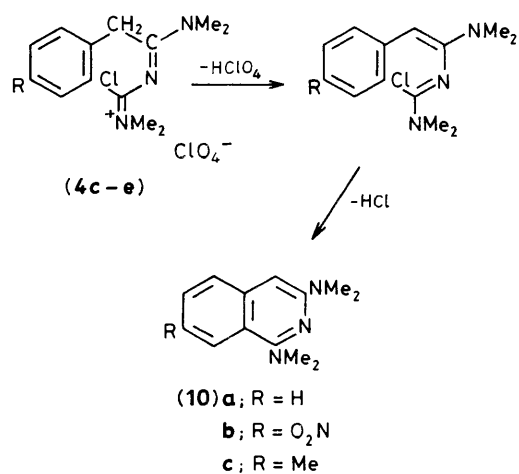
- a; R = Ph  
 b; R = NH<sub>2</sub>  
 c; R = pyrrolidino  
 d; R = SMe

Scheme 1

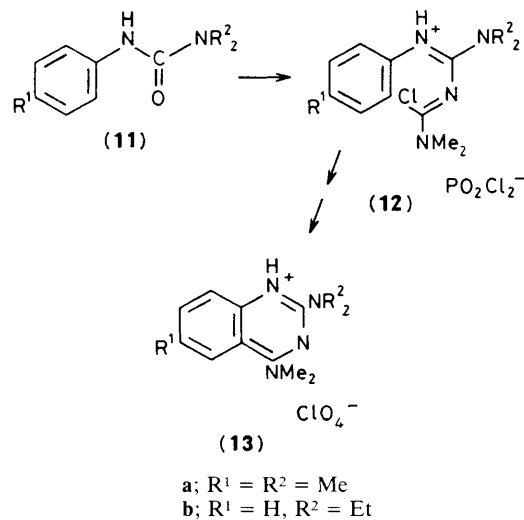
products were isolated as perchlorates by adding aqueous perchloric acid, when i.r. spectroscopy indicated that all the cyanamide had been consumed (0.5–48 h). The salts (4a–g), m.p. 161, 162, 118, 120, 76, 88, and 115 °C,<sup>†</sup> respectively, were obtained in 60–94% yields from the appropriate *N,N*-dimethylamides. *N,N*-Diethylphenylacetamide and *N*-methylpyrrolidin-2-one gave the perchlorates (5) (91%), m.p. 95 °C,<sup>†</sup> and (6) (74%), m.p. 99 °C,<sup>†</sup> respectively. The azapropenylium perchlorates are stable colourless solids [the nitro-derivative (4d) is orange]; their i.r. spectra show characteristic C=N<sup>+</sup> absorptions at *ca.* 1650 cm<sup>-1</sup> and the <sup>1</sup>H n.m.r. spectra of the bis(dimethylamino) compounds exhibit four singlets due to the protons of the methyl groups. The salts



Scheme 2



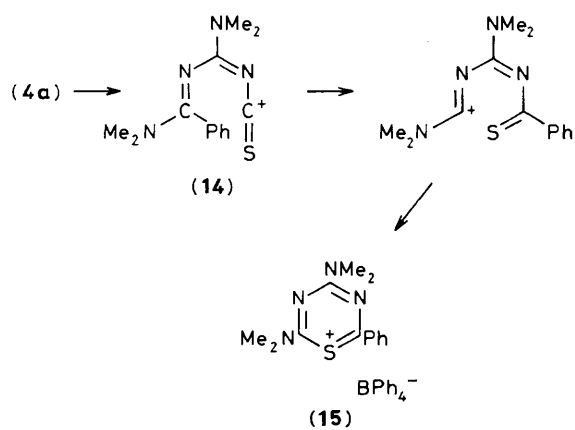
Scheme 3



Scheme 4

are useful reagents for the synthesis of a variety of six-membered heteroaromatic compounds.

The phenyl derivative (4a) reacts with amidines to yield the 1,3,5-triazines (7a–d) in 20–90% yields, m.p. 173, 166, 117,



Scheme 5

and 112 °C,<sup>‡</sup> respectively, which result from successive condensation, electrocyclicisation, and elimination of dimethylamine (Scheme 1). Pyrimidines (**9**) are formed from *N,N*-dimethylamidines and 3-methyl- or 3-phenylmethylazapropenylium salts *via* isolable acyclic iminium perchlorates (**8**) (see Scheme 2). Thus *N,N,N',N'*-tetramethylguanidine and the salts (**4b**) and (**4c**) gave the pyrimidines (**9a**) (45%), m.p. 142 °C,<sup>‡</sup> and (**9b**) (55%), m.p. 109 °C,<sup>‡</sup> respectively, and the known<sup>3</sup> 2,6-bis(dimethylamino)pyrimidine (**9c**) was obtained (30%) from (**4b**) and *N,N*-dimethylformamidine. Treatment of the arylmethylazapropenylium perchlorates (**4c–e**) with sodium carbonate resulted in the novel 1,3-bis(dimethylamino)isoquinolines (**10a–c**), m.p. 40, 171, and

61 °C,<sup>‡</sup> respectively, in excellent yields (Scheme 3); the naphthyl compound (**4g**) similarly gave 2,4-bis(dimethylamino)benzo[*f*]isoquinoline (98%), m.p. 91 °C.<sup>‡</sup> The salts (**12**), formed from the arylureas (**11a, b**), phosphorus oxychloride, and dimethylcyanamide, cyclise spontaneously to quinazolinium salts, which were characterised as the perchlorates (**13a, b**) (*ca.* 40%), m.p. 259 and 151 °C,<sup>‡</sup> respectively (see Scheme 4).

Finally, we report that 1-chloro-1,3-bis(dimethylamino)-3-phenyl-2-azapropenylium perchlorate (**4a**) reacts with potassium thiocyanate to yield a rearranged product, which was isolated as the tetraphenylborate (61%), m.p. 216 °C.<sup>‡</sup> *X*-Ray analysis<sup>‡</sup> showed it to be the 1,3,5-thiadiazinium salt (**15**).<sup>4</sup> We suggest that it is produced by a [1,5] sigmatropic shift of the phenyl group in the initially formed isothiocyanate cation (**14**) (Scheme 5).

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## References

- 1 Z. Arnold, *Collect. Czech. Chem. Commun.*, 1961, **26**, 3051.
- 2 C. Jutz, *Adv. Org. Chem.*, 1976, **9** (Pt. 1), 317.
- 3 R. Gompper and U. Heinemann, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 297.
- 4 The corresponding perchlorate was obtained by a different method by H. Hartmann, J. Liebscher, and P. Czerney, Ger. (East) Patent 138,208 (1979) (*Chem. Abstr.*, 1980, **92**, 128 973).

<sup>‡</sup> Details of the *X*-ray analysis will be published elsewhere.