1-Chloro-2-azapropenylium and 1-Chloro-2,4-diazabutenylium Salts. Intermediates For The Synthesis of Pyrido[1,2-*a*]-1,3,5-triazinium Salts

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1-Chloro-1,3-bis(dimethylamino)-3-phenyl-2-azaprop-2-en-1-ylium perchlorate obtained from the reaction of phosphorus oxychloride-*N*,*N*-dimethylbenzamide complex and dimethylcyanamide reacts with 2-amino-4-methylpyridine to yield 8-methyl-4-dimethylamino-2-phenylpyrido[1,2-*a*]-1,3,5-triazinium perchlorate (**8**). The structure is established by X-ray crystallography. Various suitably substituted pyridines react similarly to afford the corresponding pyrido[1,2-*a*]-1,3,5-triazinium salts. The intermediates obtained from several secondary amides give identical products when treated with the same pyridines. The limitations of this procedure are investigated.

J. Heterocyclic Chem., **29**, 1551 (1992).

Compounds in which 1,3,5-triazinium rings are fused to other rings have been known for a long time. They are broadly divided into bridged and condensed types. In 1979 Antus-Ercenyi *et al.* [1] prepared pyrido[1,2-*a*]-1,3,5-triazinium perchlorate **2** by the reaction of iminium chlorides such as **1** with 2-aminopyridine as shown.

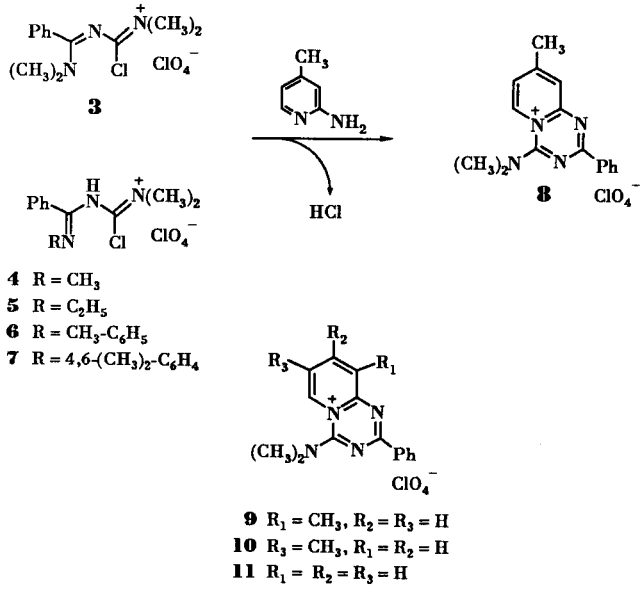
1-Chloro-2-azaiminium or 1-chloro-2,4-diazaiminium salts from the reaction of dimethylcyanamide with phosphorus oxychloride-tertiary amide complexes [2,3] or phosphorus oxychloride-secondary amide complexes [3,4], respectively, have been reported to be successfully used in the synthesis of heteroaromatic compounds of various ring sizes. The present work describes experiments to prepare condensed 1,3,5-triazinium salts from such intermediates.

We found that salt **3** reacted with a variety of nitrogen heterocycles, in which the α-carbon bears an amino group, *e.g.* 2-aminopyridine and 2-aminobenzimidazole. When **3** was allowed to react with 2-amino-4-methylpyridine in refluxing acetonitrile, a compound was obtained in *ca.* 30% yield, whose elemental analysis, spectral characteristics and X-ray crystal structure determination indicated that it was **8**. The reaction involves a sequence of condensation, cyclization and elimination of an amine to the fully conjugated pyrido[1,2-*a*]-1,3,5-triazinium perchlorate as shown.

The data of the X-ray crystallography of **8** are presented in Tables I-IV and Figures 1 and 2.

The procedure has been extended to other 2-aminopyridines. Thus 2-amino-3-methylpyridine, 2-amino-5-methylpyridine, and 2-aminopyridine gave **9**, **10**, and **11** respectively. It was interesting to observe that the azaiminium salts obtained from the secondary amides, **4-7** gave the same product **8**, under similar conditions. The yields were higher but no reason has been suggested for this observation. It was found that the use of more than one molar

Scheme 2



Scheme 1

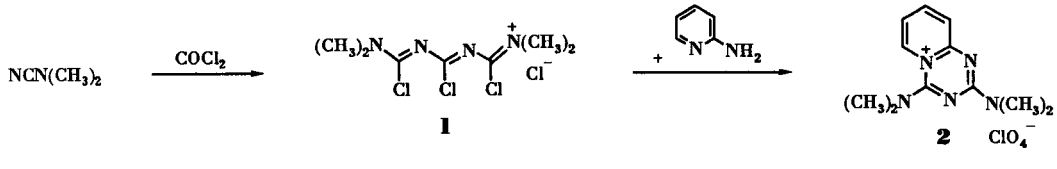


Table I

Summary of the Crystallographic Data for **8**

Compound	$C_{16}H_{17}N_4O_4Cl$
Molecular weight	364.79
space group	P-1 (# 2)
cell constants	
a, Å	7.503(7)
b, Å	10.699(4)
c, Å	11.410(4)
α, deg	72.74(3)
β, deg	79.37(5)
ν, deg	72.89(4)
cell volume, $Å^3$	831.2
molecules/unit cell	2
density (calc), g/cm^3	1.457
radiation	Mo K_α
max crystal dimensions, mm	0.2 x 0.2 x 0.5
scan width, deg	0.8 + 0.34 tanΘ
standard reflections	0 -2 -1, -1 -2 0, 1 0 2
decay of standards, %	0.1 %
reflections measured	2921
2 theta range	4<2Θ<50
observed reflections	898
no parameters varied	227
R	0.062
R_w	0.066

Table II

Positional Parameters and Their Estimated Standard Deviations for **8**

Atom	x	y	z	B($Å^2$)
Cl	0.2724(4)	0.8641(3)	0.8473(3)	4.19(6)
O(1)	0.119(1)	0.8054(8)	0.8849(9)	7.9(3)
O(2)	0.438(1)	0.7622(8)	0.8434(9)	9.5(3)
O(3)	0.251(1)	0.955(1)	0.7318(8)	10.0(4)
O(4)	0.278(1)	0.9326(8)	0.9338(7)	8.5(3)
N(1)	0.5216(9)	0.7778(7)	0.2952(7)	3.3(2)
N(2)	0.577(1)	0.7088(8)	0.5035(7)	4.1(2)
N(3)	0.7089(9)	0.5608(7)	0.3742(7)	3.5(2)
N(4)	0.697(1)	0.6387(8)	0.1649(7)	4.1(2)
C(1)	0.147(2)	1.147(1)	0.359(1)	7.0(4)
C(2)	0.275(1)	1.0122(9)	0.339(1)	4.5(3)
C(3)	0.375(1)	0.9234(9)	0.4309(9)	4.3(3)
C(4)	0.495(1)	0.8010(9)	0.4110(8)	3.7(2)
C(5)	0.672(1)	0.5897(9)	0.4840(8)	3.3(2)
C(6)	0.647(1)	0.6564(8)	0.2783(8)	3.1(2)
C(7)	0.410(1)	0.8688(9)	0.2051(9)	3.9(3)
C(8)	0.287(1)	0.9827(9)	0.2270(9)	4.0(2)
C(9)	0.727(1)	0.746(1)	0.052(1)	5.4(3)
C(10)	0.785(2)	0.500(1)	0.154(1)	6.4(3)
C(11)	0.752(1)	0.4810(9)	0.5896(8)	3.7(2)
C(12)	0.709(1)	0.499(1)	0.7061(9)	4.4(3)
C(13)	0.786(1)	0.394(1)	0.8067(9)	5.6(3)
C(14)	0.908(1)	0.279(1)	0.781(1)	5.5(3)
C(15)	0.953(1)	0.259(1)	0.668(1)	5.1(3)
C(16)	0.875(1)	0.363(1)	0.569(1)	4.7(3)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Table III

Bond Distances in Angstroms for **8**

Cl-O(1)	1.407(9)	N(4)-C(10)	1.46(1)
Cl-O(2)	1.396(8)	C(1)-C(2)	1.53(1)
Cl-O(3)	1.391(9)	C(2)-C(3)	1.36(1)
Cl-O(4)	1.41(1)	C(2)-C(8)	1.38(2)
N(1)-C(4)	1.38(1)	C(3)-C(4)	1.41(1)
N(1)-C(6)	1.40(1)	C(5)-C(11)	1.48(1)
N(1)-C(7)	1.40(1)	C(7)-C(8)	1.35(1)
N(2)-C(4)	1.32(1)	C(11)-C(12)	1.36(1)
N(2)-C(5)	1.33(1)	C(11)-C(16)	1.38(1)
N(3)-C(5)	1.34(1)	C(12)-C(13)	1.42(1)
N(3)-C(6)	1.31(1)	C(13)-C(14)	1.37(1)
N(4)-C(6)	1.33(1)	C(14)-C(15)	1.34(2)
N(4)-C(9)	1.48(1)	C(15)-C(16)	1.40(1)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV

Bond Angles in Degrees for **8**

O(1)-Cl-O(3)	109.2(5)	N(1)-C(4)-C(3)	119.6(8)
O(1)-Cl-O(3)	109.7(6)	N(2)-C(4)-C(3)	119.6(9)
O(1)-Cl-O(4)	108.9(6)	N(2)-C(5)-N(3)	125.1(7)
O(2)-Cl-O(3)	110.5(6)	N(2)-C(5)-C(11)	118.2(9)
O(2)-Cl-O(4)	108.9(6)	N(3)-C(5)-C(11)	116.7(7)
O(3)-Cl-O(4)	109.6(6)	N(1)-C(6)-N(3)	119.6(8)
C(4)-N(1)-C(6)	117.8(7)	N(1)-C(6)-N(4)	119.7(7)
C(4)-N(1)-C(7)	118.7(7)	N(3)-C(6)-N(4)	120.7(7)
C(6)-N(1)-C(7)	123.1(8)	N(1)-C(7)-C(8)	121.0(9)
C(4)-N(2)-C(5)	117.3(9)	C(2)-C(8)-C(7)	120.0(8)
C(5)-N(3)-C(6)	118.12(7)	C(5)-C(11)-C(12)	120.1(8)
C(6)-N(4)-C(9)	125.4(8)	C(5)-C(11)-C(16)	119.4(9)
C(6)-N(4)-C(10)	117.3(7)	C(12)-C(11)-C(16)	120.4(8)
C(9)-N(4)-C(10)	114.6(8)	C(11)-C(12)-C(13)	119.7(9)
C(1)-C(2)-C(3)	120(1)	C(12)-C(13)-C(14)	118(1)
C(1)-C(2)-C(8)	119.6(9)	C(13)-C(14)-C(15)	123.4(9)
C(3)-C(2)-C(8)	120.7(9)	C(14)-C(15)-C(16)	118.4(9)
C(2)-C(3)-C(4)	119(1)	C(11)-C(16)-C(15)	120(1)
N(1)-C(4)-N(2)	120.8(8)		

Numbers in parentheses are estimated standard deviations in the least significant digits.

equivalent of the amino compound led to complications, yielding a product or a mixture of products which could not be isolated in pure form. Many solvents were used in an attempt to improve the yield but the reactions succeeded only in acetonitrile or acetone; the reactions in acetonitrile gave better yields and purer products. The presence of a substituent group, *e.g.* methyl, next to the ring nitrogen atom led to the recovery of the starting salt **3** quantitatively, presumably because of steric hindrance. The reaction also failed when a halogen is present at any position of the nitrogen heterocycle. The presence of a methyl group on the ring, except at the position already mentioned, led to better yields, probably because the ring is thereby activated. There was no appreciable reaction

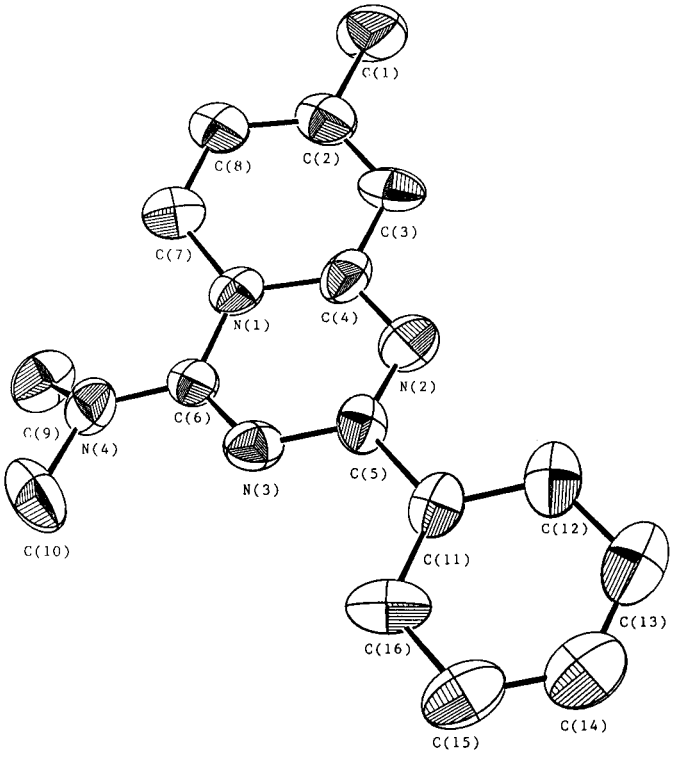


Figure 1. ORTEP plot (50% probability thermal ellipsoids) of the structure of 8 (cation) with the numbering scheme. Hydrogen atoms have been ommited for clarity.

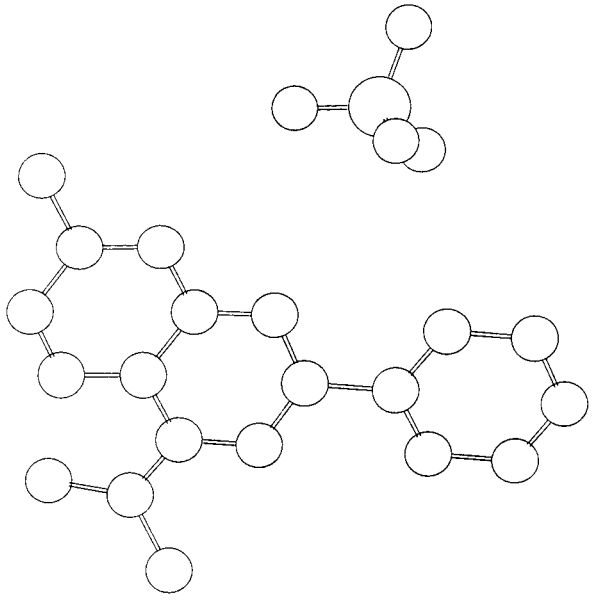


Figure 2. PLUTO plot of the sturcture 8 showing both cation and anion. Hydrogen atoms have been ommited for clarity.

when an extra nitrogen atom is located on the ring. Thus **3** was recovered quantitatively when 4-chloro-2,6-diaminopyrimidine, 4-amino-2,6-dimethylpyrimidine, 2-aminopyrimidine, or 2-aminopyrazine was used. It is noteworthy that when the phenyl group at position 3 of salts **3-7** is replaced by alkyl or arylalkyl group the reaction failed.

EXPERIMENTAL

Melting points were determined with a Gallenkamp electrically heated block and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 298 spectrophotometer, incorporated with a data station, for nujol mulls on sodium chloride plates, unless stated otherwise. The ^{1}H nmr spectra were recorded on a Bruker WM 250 (250 MHz), a Nicolet NT 200 (200 MHz) or a Perkin Elmer R32 (90 MHz) spectrometer. The data are recorded as the chemical shifts in parts per million (ppm) followed by integral, multiplicity and coupling constant (J in Hertz) of the particular proton. Mass spectra were recorded with a micromass 16F, incorporated with a data system Vg 2000, at 35 and 70 electron volts.

Thin-layer chromatography (tlc) was conducted with Merck 60-GF254 precoated silica gel plates. Column chromatography was conducted with Merck Kieslgel 60 (0.0630-0.20 mm grade) silica gel. Preparative tlc was done with 20 x 20 cm (0.1 mm thickness) Merck silica gel 60GF254 plates activated at 110° for 0.5 hour. Drying and/or purification of organic solvents was done as described by Riddick and Bunger [5].

General Procedure for the Preparation of 2,4-Diazabutenylium Perchlorates **3-7**.

Phosphorus oxychloride (12 ml, 130 mmoles) was added slowly to an ice-cold solution of the amide (100 mmoles) and dimethylcyanamide (7.00 g, 100 mmoles) in dichloromethane (40 ml) at such a rate that the temperature did not exceed 15°. The mixture was stirred until the ir spectrum of the reaction mixture no longer showed nitrile absorption due to dimethylcyanamide at 2200 cm^{-1}. The reaction mixture was poured into a mixture of 69-71% perchloric acid (15 ml, *ca* 150 mmoles) and crushed ice. When all the ice had melted the organic layer was separated and the solvent was removed on a rotary evaporator. If the residue was a solid it was collected with the aid of diethyl ether; if it was a gum it was caused to solidify by adding diethyl ether or ethyl acetate.

The following perchlorates were obtained:

1-Chloro-4-methyl-1-dimethylamino-3-phenyl-2,4-diazabut-3-en-1-ylium Perchlorate (**4**).

N-Methylbenzamide (13.52 g, 100 mmoles) gave **4** in 71% yield (23.0 g) after 12 hours reaction time, mp 188-189° from water; ir: ν max 3265 (N-H), 1641 (C=N$^+$), 1602 (C=C), 1098 cm^{-1} (ClO_4^-); ^{1}H nmr (DMSO-d_6): δ 2.90 (1H, br s, NH), 3.35 (3H, s, NMe), 3.57 (6H, s, NMe_2), 7.58-7.83 (5H, m, Ph); ms: m/z 118 (100), 103 (22), 77 (14).

Anal. Calcd. for $C_{11}H_{15}Cl_2N_3O_4$: C, 40.75; H, 4.67; N, 12.96. Found: C, 40.70; H, 4.61; N, 13.10.

1-Chloro-4-ethyl-1-dimethylamino-3-phenyl-2,4-diazabut-3-en-1-ylium Perchlorate (**5**).

N-Ethylbenzamide (14.92 g, 100 mmoles) gave **5** in 71% yield (28.0 g) after 12 hours reaction time, mp 129-130° from water; ir: ν max 3266 (N-H), 1642 (C=N$^+$), 1599, 1581 (C=C), 1104, 1063 cm^{-1} (ClO_4^-); ^{1}H nmr (acetone-d_6): δ 1.40 (3H, t, J = 7.50, 15.00 Hz, C-CH_2), 2.80 (1H, br, NH), 3.57 (6H, s, NMe_2), 3.83 (2H, q, C-CH_2, J = 7.50, 15.00 Hz), 7.61-7.81 (5H, m, Ph); ms: m/z 132

(99), 103 (41), 77 (9), 69 (100).

Anal. Calcd. for $C_{12}H_{17}Cl_2N_3O_4$: C, 42.61; H, 5.08; N, 12.43. Found: C, 42.60; H, 4.97; N, 12.30.

1-Chloro-1-dimethylamino-3-phenyl-4-*p*-tolyl-2,4-diazabut-3-en-1-ylium Perchlorate (**6**).

Benz-*p*-toluidide (21.13 g, 100 mmoles) gave **6** in 88% yield (35.0 g) after 1 month reaction time, mp 201-202° from water; ir: ν max 3327 (N-H), 1624 (C=N$^+$), 1594 (C=C), 1107, 1070 cm^{-1} (ClO_4^-); ^{1}H nmr (DMSO-d_6): δ 2.36 (3H, s, CMe), 3.37 (6H, s, NMe_2), 7.30 (2H, d, Ph), 7.56 (2H, d, Ph), 7.60-7.80 (5H, m, Ph), 12.20 (1H, br, NH); ms: m/z 300 (20), 105 (100), 77 (5).

Anal. Calcd. for $C_{17}H_{19}Cl_2N_3O_4$: C, 51.02; H, 4.79; N, 10.50. Found: C, 51.20; H, 4.73; N, 10.60.

1-Chloro-1-dimethylamino-4-(2,6-dimethylphenyl)-3-phenyl-2,4-diazabut-3-en-1-ylium Perchlorate (**7**).

Benz-2,6-dimethylanilide (22.53 g, 100 mmoles) gave **7** in 88% yield (36.50 g) after 60 hours reaction time, mp 182-183° from acetonitrile; ir: ν max 3221 (N-H), 1631 (C=N$^+$), 1598, 1586 (C=C), 1106, 1064 cm^{-1} (ClO_4^-); ^{1}H nmr (DMSO-d_6): δ 2.29 (6H, s, C-Me x 2), 3.26 (6H, s, NMe_2), 7.25 (3H, m, Ph), 7.67-7.90 (5H, m, Ph), 12.20 (1H, br, NH); ms: m/z 313 (3), 105 (100), 103 (3), 77 (14).

Anal. Calcd. for $C_{18}H_{21}Cl_2N_3O_4$: C, 52.17; H, 5.12; N, 10.14. Found: C, 51.90; H, 5.02; N, 10.10.

General Procedure for the Preparation of Pyrido[1,2-*a*]-1,3,5-Triazinium Perchlorates **8-11**.

The amino-compound (6 mmoles) was added to a solution of 1-chloro-1,3-bis(dimethylamino)-3-phenyl-2-azaprop-2-en-1-ylium perchlorate (2.00 g, 6 mmoles) [2,3] in acetonitrile (20 ml), and the solution was heated under reflux for 1 hour. It was allowed to cool and then poured into a large excess of crushed ice. When all the ice had melted the solid formed was collected.

The following perchlorates were obtained:

8-Methyl-4-dimethylamino-2-phenylpyrido[1,2-*a*]-1,3,5-triazinium Perchlorate (**8**).

2-Amino-4-methylpyridine (0.65 g, 6 mmoles) gave **8** in 32% yield (0.70 g), mp 219-220° from acetonitrile/ethyl acetate or acetic acid; ir: ν max 1629 (C=N$^+$), 1598 (C=C), 1092 cm^{-1} (ClO_4^-); ^{1}H nmr (DMSO-d_6): δ 2.64 (3H, s, C-Me), 3.34 (3H, s, NMe), 3.44 (3H, s, NMe), 7.59-7.74 (4H, m, H-7 & Ph, J = 5.0 Hz), 8.54 (2H, d, Ph, J = 7.5 Hz), 8.70 (1H, d, H-6, J = 5.0 Hz); ms: m/z 264 (100), 249 (51), 103 (20), 77 (21).

Anal. Calcd. for $C_{16}H_{17}ClN_4O_4$: C, 52.67; H, 4.71; N, 15.36. Found: C, 51.90; H, 4.56; N, 15.10.

9-Methyl-4-dimethylamino-2-phenylpyrido[1,2-*a*]-1,3,5-triazinium Perchlorate (**9**).

2-Amino-3-methylpyridine (0.65 g, 6 mmoles) gave **9** in 40% yield (0.85 g), mp 201-202° from acetonitrile/ethyl acetate or acetic acid; ir: ν max 1629 (C=N$^+$), 1600, 1598 (C=C), 1089 cm^{-1} (ClO_4^-); ^{1}H nmr (DMSO-d_6): δ 2.70 (3H, s, C-Me), 3.36 (3H, s, NMe), 3.44 (3H, s, NMe), 7.60-7.78 (4H, m, H-7 & Ph), 8.30 (1H, d, H-8, J = 7.5 Hz), 8.55 (2H, d, Ph, J = 7.5 Hz), 8.66 (1H, d, H-6, J = 7.5 Hz); ms: m/z 264 (100), 249 (64), 103 (16), 77 (17).

Anal. Calcd. for $C_{16}H_{17}ClN_4O_4$: C, 52.67; H, 4.71; N, 15.36. Found: C, 53.00; H, 4.72; N, 15.90.

7-Methyl-4-dimethylamino-2-phenylpyrido[1,2-*a*]-1,3,5-triazinium Perchlorate (**10**).

2-Amino-5-methylpyridine (0.65 g, 6 mmoles) gave **10** in 37% yield (0.75 g), mp 180-181° from acetonitrile/ethyl acetate or acetic acid; ir: ν max 1623 (C=N$^+$), 1599, 1555 (C=C), 1095 cm^{-1} (ClO_4^-); ^{1}H nmr (DMSO-d_6): δ 2.52 (3H, s, C-Me), 3.34 (3H, s, NMe), 3.44 (3H, s, NMe), 7.62-7.73 (3H, m, Ph), 8.02 (1H, d, H-9, J = 10 Hz), 8.35 (1H, d, H-8, J = 10 Hz), 8.51 (2H, d, Ph, J = 7.5 Hz); ms: m/z 264 (80), 249 (50), 103 (20), 77 (100).

Anal. Calcd. for $C_{16}H_{17}ClN_4O_4$: C, 52.67; H, 4.71; N, 15.36. Found: C, 52.67; H, 4.71; N, 15.36.

4-Dimethylamino-2-phenylpyrido[1,2-*a*]-1,3,5-triazinium Perchlorate (**11**).

2-Aminopyridine (0.57 g, 6 mmoles) gave **11** in 29% yield (0.60 g), mp 210-211° from acetonitrile/ethyl acetate or acetic acid; ir: ν max 1627 (C=N$^+$), 1598, 1555 (C=C), 1087 cm^{-1} (ClO_4^-); ^{1}H nmr (DMSO-d_6): δ 3.34 (3H, s, NMe), 3.46 (3H, s, NMe), 7.65-7.75 (4H, m, H-7 & Ph), 8.09 (1H, d, H-9, J = 7.5 Hz), 8.45 (1H, t, H-8, J = 7.0, 15.0 Hz), 8.53 (2H, d, Ph, J = 7.5 Hz); ms: m/z 251 (100), 236 (51), 103 (20), 77 (21).

Anal. Calcd. for $C_{15}H_{15}ClN_4O_4$: C, 51.40; H, 4.32; N, 15.97. Found: C, 50.70; H, 4.24; N, 15.70.

2-Amino-4-methylpyridine gave the same product, *viz.* 8-Methyl-4-dimethylamino-2-phenylpyrido[1,2-*a*]-1,3,5-triazinium perchlorate (**8**) when allowed to react with the following four compounds in the usual way.

1-Chloro-1-dimethylamino-4-methyl-3-phenyl-2,4-diazabut-3-en-1-ylium Perchlorate (**4**) gave **8** in 45% yield (0.98 g). 1-Chloro-1-dimethylamino-4-ethyl-3-phenyl-2,4-diazabut-3-en-1-ylium Perchlorate (**5**) gave **8** in 45% yield (0.98 g).

1-Chloro-1-dimethylamino-3-phenyl-4-*p*-tolyl-2,4-diazabut-3-en-1-ylium perchlorate (**6**) gave **8** in 39% yield (0.84 g).

1-Chloro-1-dimethylamino-4-(2,6-dimethylphenyl)-3-phenyl-2,4-diazabut-3-en-1-ylium perchlorate (**7**) gave **8** in 41% yield (0.88 g).

X-Ray Structure Determination and Refinement.

A transparent pale yellow crystal of **8** was mounted in a thin-walled glass capillary. X-ray intensity data were collected on an Enraf-Nonius CAD4 diffractometer using MoKα radiation and an omega-2-theta technique. Cell parameters and an orientation matrix for data collection were obtained from least-squares refinement using the setting angles of 22 centered reflections. The data were collected at 23±1°. The scan rate varied from 5 to 20°/min in omega. Data were collected to a maximum 2-theta of 50.0°. A total of 2921 reflections were measured. Lorentz and polarization corrections were applied. Linear decay correction were applied. Absorption was neglected.

The structure was solved by direct methods. Hydrogen atoms were calculated at idealized positions and included in the least squares calculation but not refined. The structure was refined in full matrix least squares where the function minimized was $\Sigma W(|F_o|-|F_c|)^2$. Only the 898 reflections having intensities greater than 3 times their standard deviation were used in the refinement. The final cycle of refinement included 227 variables and converged with an unweighted agreement factor of 0.062. Relevant crystallographic data are given in Table I. Final atomic coordinates for non-hydrogen atoms are given in Table II. Bond distances and angle for non-hydrogen atoms are given in Tables III and IV. All calculations were performed on a Micro Vax II using SDP set of programs.

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