REACTIVITY OF SUBSTITUTED N-AMINOPYRIDINIUM SALTS AND THEIR BENZOLOGUES. A NOVEL APPROACH TO s-TRIAZOLO[1,5-a]QUINOLINIUM AND s-TRIAZOLO[5,1-a]ISOQUINOLINIUM DERIVATIVES

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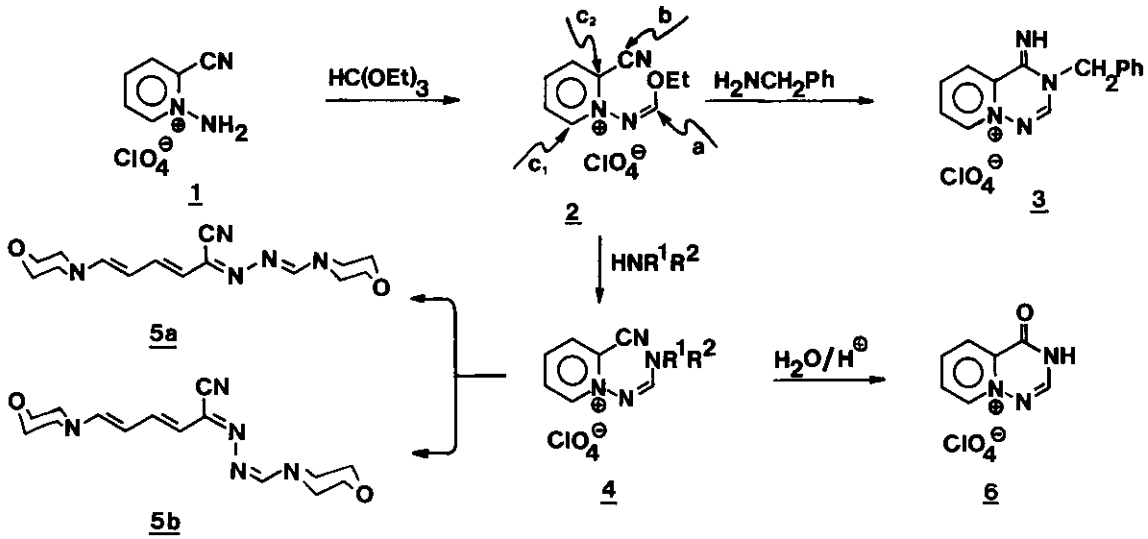
Abstract —— The reaction of 1-amino-2-cyanopyridinium perchlorate (1) with triethyl orthoformate gave an ethyl iminoformate derivative (2) which resulted in formation of a 1-iminopyrido-as-triazinium salt (3) in reaction with primary amine, and a formamidino derivative (4) with secondary amine. The reaction of the latter compound (4) with morpholine gave 2,3-diaza-1,3,5,7-octatetraene (5). The two benzologues of 1, N-aminoquinolinium (9) and N-aminoisoquinolinium (19) gave ethyl iminoformates (10 and 20) and formamidines (14 and 23). In reactions with primary amines these compounds led to s-triazolo[1,5-a]quinolinium (16) and [5,1-a]isoquinolinium (25) salts, respectively.

N-Aminopyridinium salts are precursors in numerous heterocyclic synthesis, and their chemistry has widely been studied.[1] N-Aminopyridinium derivatives react with both nucleophilic[2,3] and electrophilic reagents.[4-8]
Recently,[9] we reported on the reactivity of 2-substituted N-aminopyridinium salts and their benzologues. We have found that the free N-amino moiety can be deprotonated easily by a base (e.g. nucleophilic reagent) and the dimerization reaction of the intermediate ylide took place rather than the nucleophilic attack of the reagent. This kind of dimerization can be suppressed or eliminated by protection of the N-amino moiety.
It has been found that the N-amino group can be condensed with orthoesters and pyrazolo[1,5-a]pyridines[10] or pyrido[2,1-f]-as-triazinium salts[11] can be synthesized from appropriately substituted derivatives. In this work, we studied the reaction of 1-amino-2-cyanopyridinium perchlorate (1) and its benzologues (9, 10) with triethyl orthoformate in order to synthesize derivatives with protected N-amino function (2, 10, 20) and thereby to eliminate the possibility of the un-

desired dimerization reaction.



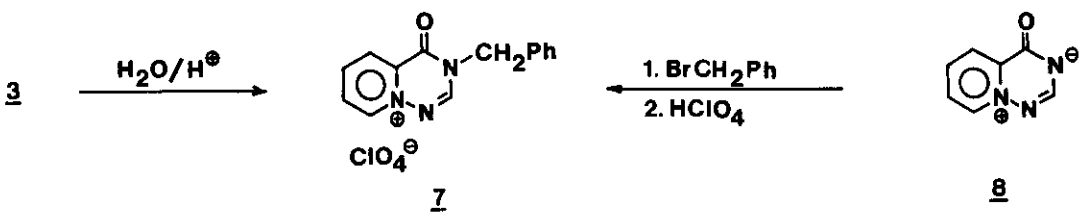
Scheme 1

The compound 2 is a good target of nucleophilic reagents and can be attacked (i) at the carbon atom of iminoformyl group (route a); (ii) at the carbon atom of the cyano group (route b); and (iii) at the α- or α'-carbon atoms of the positively charged pyridine ring (route c_1 and c_2).

The reaction of 2 with secondary amine (e.g. morpholine) gave a formamidine derivative 4a (route a). The structure of 4a was confirmed by its spectral data and an independent synthesis: the condensation of 1 with N-formylmorpholine and thionyl chloride gave the same compound (4a). The use of dimethylformamide, instead of N-formylmorpholine afforded an N,N-dimethylformamidine derivative. The nucleophilic attack of a second morpholine molecule took place at the C-atom of the pyridine ring of 4a (route c_1), and after an electrocyclic ring opening,[12] the 2,3-diaza-1,3,5,7-octatetraenes 5 were isolated.[13] On the basis of its ^{1}H-nmr spectrum the product was proved to be a mixture of isomers 5a and 5b in about 2:1 ratio.

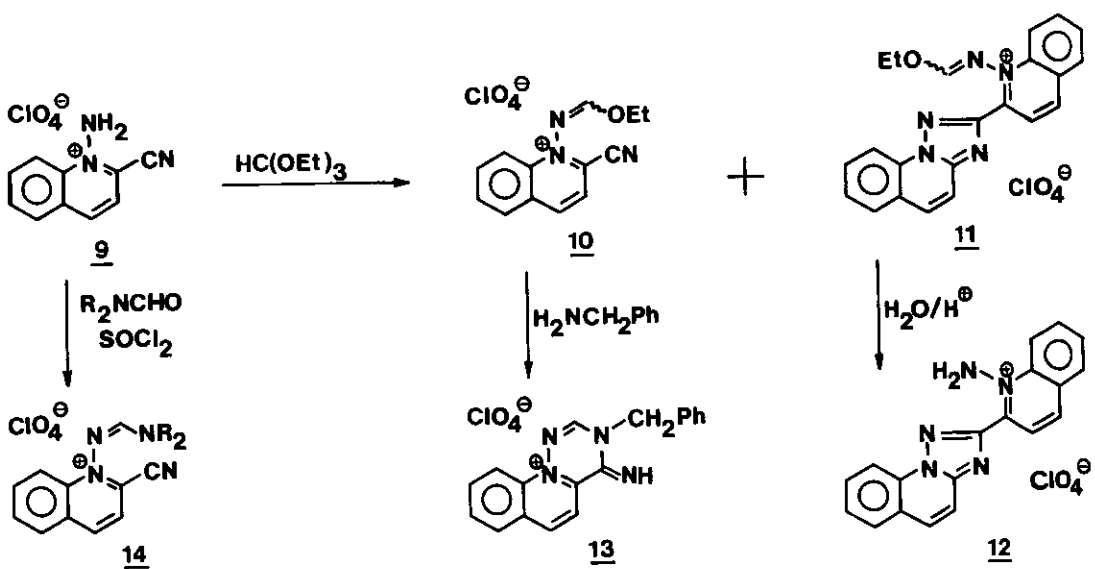
Acidic hydrolysis of the imino ether 2 (reflux in conc. HCl) gave the starting material 1, whereas under the same conditions formamidine 4a yielded 1(2H)-oxo-pyrido[2,1-f]-as-triazinium salt (6).[14] Its formation can be explained by the fact that the formamidine part of compound 4a has an enhanced stability compared

to the iminoformyl group of 2 and the hydrolysis of the CN-group (route b) became a main process allowing an intramolecular cyclization to as-triazine 6.
The reaction of compound 2 with primary amine (e.g. benzylamine) - in contrast to secondary amines - led to 1(2H)-iminopyrido[2,1-f]-as-triazinium salt (3) in an acceptable yield (50%), i.e. an intramolecular cyclization of the probable intermediate 4c (R^1=H, R^2=CH_2Ph) took place.



Scheme 2

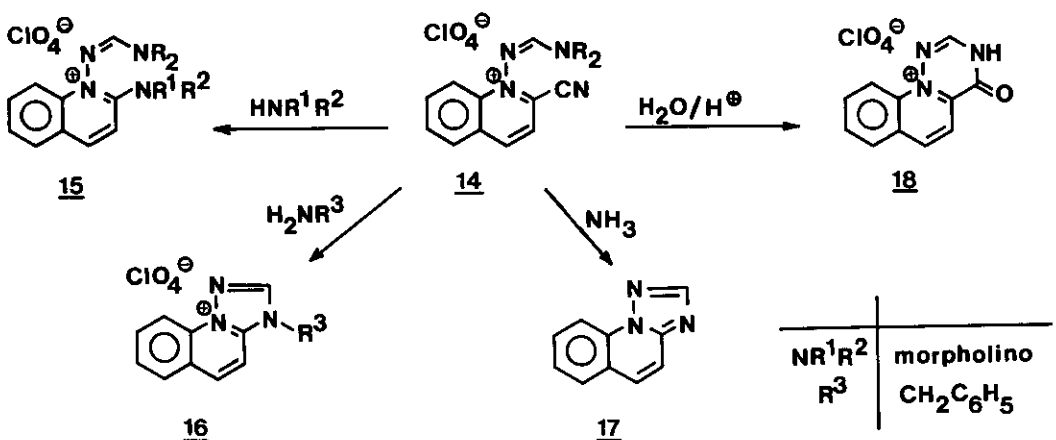
The structure of 3 was supported by the fact that its acidic hydrolysis gave 1(2H)-oxo-2-benzyl derivative (7) which was obtained by benzylation of pyrido-[2,1-f]-as-triazinium-1-olate (8) (available from 6 by base).[14]
Extending the investigation to benzologues we found that 1-amino-2-cyanoquinolinium perchlorate (9) with triethyl orthoformate gave an ethyl iminoformate 10 (37%) similarly to the reaction of N-aminopyridinium derivative but a dimerization reaction also took place and a mixture of dimer 11 was isolated in 19% yield.



Scheme 3

The ^{1}H-nmr spectrum of the ethyl iminoformate (10) showed that the product is a mixture (1:1) of the two corresponding isomers (two triplets of the methyl group in a ratio of 1:1 at 1.68 and 1.37 ppm and a sextet of CH_2 at 4.78 ppm). The spectral evidence, especially the assignment of the proton and the ^{13}C spectra based on homo- and heteronuclear two-dimensional chemical shift correlation experiments,[15,16] made the dimeric structure 11 very likely (see Experimental). A further proof of this structure (11) was provided by its acidic hydrolysis: compound 12a[9] was obtained in 90% yield.

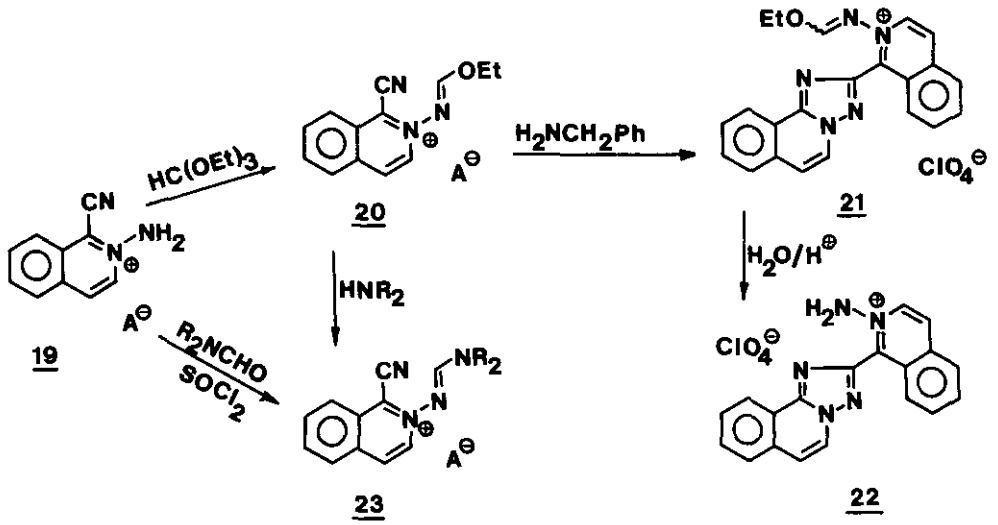
The reaction of the iminoformate 10 with benzylamine gave an iminobenzyl-as-triazinoquinolinium salt (13) in 41% yield similarly to the pyridinium salt. The reaction of 10 with morpholine afforded a complex mixture from which neither formamidine 14a (NR_2=morpholino) nor any other definite products were isolable. The formamidine (14a), however, could be obtained from the reaction of 9 with N-formylmorpholine and thionyl chloride. Using dimethylformamide instead of N-formylmorpholine gave 14b (R=CH_3) in a good yield (80%). The reactivity of formamidine 14 was different from that of pyridinium (4) because its reaction with morpholine afforded 2-morpholinoquinolinium derivative (15), i.e. the substitution of the cyano group of 14 occurred.



Scheme 4

In contrast to the reaction with secondary amines, the reaction of 14 with primary amines presumably involved the initial formation of intermediate 15 (R^1= H, R^2= Subst.) followed by an intramolecular cyclization leading to s-triazolo[1,5-a]-quinolinium salts (16).

When ammonia was used as reagent, s-triazolo[1,5-a]quinoline (17) was obtained. This method is a simple and new synthetic route to prepare s-triazoloquinoline or substituted triazoloquinolinium salts.[17,18] While the acidic hydrolysis of the iminoformate 10 led back to the starting salt 9, the hydrolysis of formimino salt 14 yielded 4(3H)-oxo-as-triazino[1,6-a]quinolinium perchlorate (18) similarly to the pyridinium derivatives.



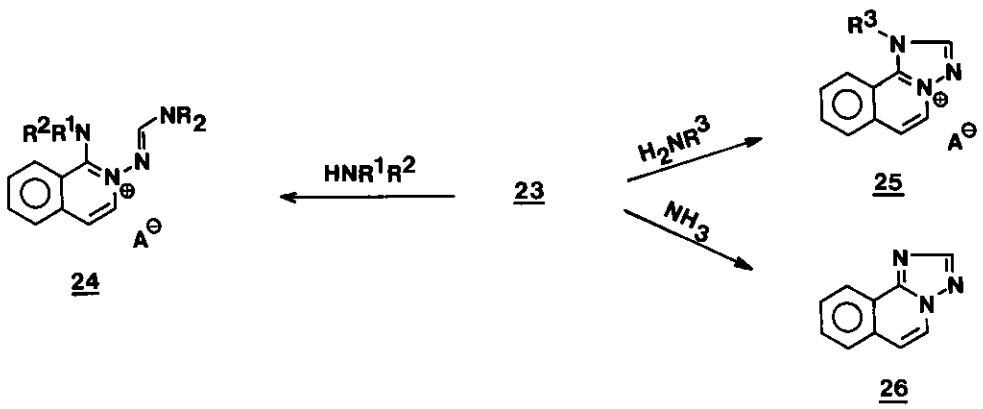
Scheme 5

The other benzologue 2-amino-1-cyanoisoquinolinium tosylate (19) (A=TsO) reacted with triethyl orthoformate to give the corresponding iminoformate derivative 20 (A=TsO). The reaction of 20 with morpholine afforded formamidine 23a (A=TsO, NR_2= morpholino) which was obtained also in one-step from the starting N-amine 19 with N-formylmorpholine and thionyl chloride. Similarly, the reaction of 19 with dimethylformamide and thionyl chloride resulted in the formation of the dimethylamino derivative 23b (R=Me, A=BF_4).

The starting N-amino compound (19) was obtained not only by hydrolysis of 20 but also by acidic treatment of amidine 23 differently from the behaviour of pyridinium or quinolinium derivatives (4 and 14). As a further difference between the two benzologues, the reaction of iminoformate 20 with primary amine (e.g. benzylamine) did not give 1(2H)-imino-as-triazinium salt, but instead dimer 21 was

isolated in 60% yield. Its structure assignment is based on homo- and heteronuclear 2D chemical shift correlation nmr spectra and homonuclear NOE experiments (see Experimental). The acidic hydrolysis of dimer 21 provided a further proof of its structure: compound 22 was obtained in 80% yield.

The unexpected formation of dimer 21 can be explained in a way that, on action of benzylamine, 1-cyanoisoquinoline N-ylide is formed that reacts with a molecule of the starting formimine 20 giving the dimeric product 21. This mechanism is supported by the fact that, in a separate experiment, 1-cyano-2-aminoisoquinoline (19) was deprotonated by triethylamine and reacted with formimine 20 to give the same compound (21) in 64% yield.



Scheme 6

Also in the case of formamidino-1-cyanoisoquinolinium salts (23) the reaction with secondary amines afforded the 1-amino derivatives (24) by substitution of the cyano group.

Finally, the active isoquinolinium compounds (23) reacted with primary amines and ammonia, similarly to the analogous quinolinium salts (14) and s-triazolo[5,1-a]-isoquinolinium salts (25)[18] and the known compound s-triazolo[5,1-a]isoquinoline (26)[19] were obtained in good yields.

EXPERIMENTAL

Melting points were determined by a Büchi apparatus and are uncorrected. Ir spectra were recorded on Specord IR-75 equipment and ^{1}H and ^{13}C nmr spectra on Varian XL-100 and XL-400 instruments at ambient temperature using TMS as internal standard.

2-Cyano-1-[(ethoxymetheno)amino]pyridinium perchlorate (2)

A solution of 1 (1.54 g, 7 mmol) and triethyl orthoformate (3.15 g, 21 mmol) in

dry acetonitrile (35 ml) was refluxed for 2 h. The reaction mixture was cooled, concentrated and the residue was recrystallized from EtOH-AcOEt to give 1.43 g (74%) of colourless crystals, mp 120-121°C; ir (KBr): 3120, 3100, 3070, 3030, 2980, 2940, 1605, 1580, 1490, 1460, 1440, 1320, 1100 cm^{-1}; ^{1}H-nmr (TFA) δ : 9.12 (d, J=5.6 Hz, 1H, H-6); 8.70 (m, 4H, H-3,4,5 and N=CH); 4.68 (q, J=6.8 Hz, 2H, CH_2); 1.57 (t, J=6.8 Hz, 3H, CH_3). Anal. Calcd for $C_9H_{10}N_3O_3$: C, 39.21; H, 3.66; N, 15.24. Found: C, 39.48; H, 3.43; N, 15.15.

2-Cyano-1-[(morpholinometheno)amino]pyridinium perchlorate (4a, NR^1R^2=morpholino) Procedure A. A solution of 2 (2.76 g, 10 mmol) in acetonitrile (30 ml) was stirred at room temperature with morpholine (1 g, 1 ml, 11 mol) for 1 h. Ethyl acetate (50 ml) was added to the reaction mixture and filtered off to give 2.9 g (91%) of analytically pure pale yellow crystals, mp 223-225°C (MeCN-AcOEt); ir (KBr): 3100, 3060, 2980, 2930, 2850, 1620, 1590, 1490, 1430, 1340, 1100 cm^{-1}; ^{1}H-nmr (TFA) δ: 9.04 (d, J=5.8 Hz, 1H, H-6); 8.40 (m, 4H, H-3,4,5 and N=CH); 4.30-3.60 (m, 8H, morpholino). Anal. Calcd for $C_{11}H_{13}ClN_4O_5$: C, 41.72; H, 4.14; N, 17.69. Found: C, 41.98; H, 3.87; N, 17.55. Procedure B: To a solution of N-formylmorpholine (0.57 g, 0.5 ml, 5 mmol) in dry acetonitrile (5 ml), thionyl chloride (0.49 g, 0.3 ml, 4 mmol) was dropped at room temperature, then 1 (0.22 g, 1 mmol) was added to the mixture and was refluxed for 30 min, then cooled and concentrated, then aqueous sodium perchlorate solution was added to the residue. After extraction with nitromethane (3x5 ml), the crude product was recrystallized from acetonitrile–ethyl acetate to give 0.21 g (66%) of 4a; mp 223-225°C. This compound was found to be fully identical with the product obtained by procedure A.

2-Cyano-1-[(dimethylaminometheno)amino]pyridinium perchlorate (4b, R^1=R^2=CH_3) This compound was prepared from 1 (0.22 g, 1 mmol) by the previous method (procedure B), however, instead of N-formylmorpholine, dimethylformamide (0.37 g, 0.30 ml, 5 mmol) was used to give 0.37 g (67%) of pale yellow crystals, mp 213-215°C (MeCN-AcOEt); ir (KBr): 3110, 3090, 3070, 2910, 1620, 1490, 1420, 1330, 1090 cm^{-1}; ^{1}H-nmr (TFA) δ :9.00 (d, J=5.6 Hz, 1H, H-6); 8.35 (m, 4H, H-3,4,5 and N=CH); 3.33 (s, 3H, CH_3); 3.25 (s, 3H, CH_3). Anal. Calcd for $C_9H_{11}ClN_4O_4$: C, 39.36; H, 4.04; N, 20.40. Found: C, 39.60; H, 4.08; N, 20.13.

Hydrolysis of 2. Formation of 1-amino-2-cyanopyridinium perchlorate (1)
A solution of 2 (0.28 g) in conc. HCl (5 ml) was refluxed for 15 min. The reaction mixture was cooled, concentrated and the residue was dissolved in a mixture of MeCN (2 ml) and a few drops of $HClO_4$ (70%). The solution was mixed with AcOEt (10 ml), filtered and the crude product (0.17 g, 77%) was recrystallized from MeCN-AcOEt to give 0.12 g (55%) of colourless crystals, mp 167-170°C. The product was found to be identical with an authentic sample[9] of 1-amino-2-cyanopyridinium perchlorate (1).

Hydrolysis of 4a. Formation of 1(2H)-oxopyrido[2,1-f]-as-triazinium perchlorate (6)
A solution of 4a (0.32 g) in conc. HCl (5 ml) was refluxed for 15 min. The reaction mixture was worked up as in the previous procedure to give 0.15 g (60%) of colourless needles, mp 248-250°C. The product was found to be identical with the authentic sample of 1(2H)-oxopyrido[2,1-f]-as-triazinium perchlorate synthesized earlier by other method.[11]

1(2H)-Imino-2-benzylpyrido[2,1-f]-as-triazinium perchlorate (3)

Into a solution of 2 (1.12 g, 4 mmol) in dry MeCN (20 ml) was dropped a solution of benzylamine (0.43 g, 0.44 ml, 4 mmol) in MeCN (20 ml) in 30 min at room temperature and the mixture was stirred for 2 h, then concentrated. The residue was dissolved in MeCN (2 ml) and $HClO_4$ (4 drops), then the solution was mixed with AcOEt (10 ml). The precipitated crude product (0.75 g) was recrystallized from MeCN-AcOEt to give 0.41 g (30%) of pale yellow crystals, mp 199-202°C; ir (KBr): 3320, 3060, 3020, 2980, 1610, 1550, 1480, 1430, 1400, 1080 cm^{-1}; ^{1}H-nmr (TFA) δ: 9.48 (d, J=6.6 Hz, 2H, H-6,9); 9.11 (t, J=6.6 Hz, 1H, H-8); 8.72 (t, J=6.6 Hz, 1H, H-7); 8.54 (s, 1H, H-3); 7.58 (s, 5H, phenyl); 5.62 (s, 2H, CH_2). Anal. Calcd for $C_{14}H_{13}ClN_4O_4$: C, 49.93; H, 3.98; N, 16.64. Found: C, 49.64; H, 4.04; N, 16.44.

1(2H)-Oxo-2-benzylpyrido[2,1-f]as-triazinium perchlorate (7)

Procedure A. A solution of 3 (0.34 g) in conc. HCl (5 ml) was refluxed for 30 min, then cooled and mixed with 0.2 ml of $HClO_4$ (70%). The mixture was concentrated and the residue was dissolved in H_2O and extracted with $MeNO_2$ (3x5 ml). The residue from the extract was recrystallized from MeCN-AcOEt to give 0.22 g (65%) of colourless crystals, mp 216-218°C, ir (KBr): 3060, 3010, 2950, 1700, 1620, 1550, 1480, 1380, 1100 cm^{-1}; ^{1}H-nmr (TFA) δ: 9.18 (d, J=6.4 Hz, 1H, H-6); 9.06 (d, J=6.6 Hz, 1H, H-9); 8.81 (t, J=6.6 Hz, 1H, H-8); 8.52 (s, 1H, H-3); 8.43 (t, J=6.4 Hz, 1H, H-7); 7.48 (s, 5H, C_6H_5); 5.34 (s, 2H, CH_2). Anal. Calcd for $C_{14}H_{12}ClN_3O_5$: C, 49.79; H, 3.58; N, 12.44. Found: C, 49.86; H, 3.80; N, 12.19. Procedure B: A suspension of pyrido[2,1-f]-as-triazinium-1-olate[14] (8, 0.15 g, 1 mmol) in MeCN (10 ml) was refluxed with benzyl bromide (0.34 g, 0.24 ml, 2 mmol) for 2 h, then was mixed with $HClO_4$ (0.2 ml, 70%) to give 0.31 g (91%) of colourless needles, mp 216-218°C, identical with the compound obtained by the previous procedure (A).

4-Cyano-1,8-dimorpholino-2,3-diaza-1,3,5,7-octatetraene (5)

A solution of 4a (0.32 g, 1 mmol) in morpholine (3 ml, 3 mmol) was stirred at room temperature for 30 min. The excess of morpholine was evaporated in vacuo, the residue was dissolved in $CHCl_3$ (5 ml). The precipitated crystals were filtered off and the mother liquor was worked up by column chromatography (silica gel, eluent: $CHCl_3$). The first yellow fraction was concentrated and the crude product (0.13 g, 43%) was recrystallized from EtOH to give 0.11 g (37%) of yellow prisms, mp 151-153°C; ir (KBr): 3030, 2960, 2900, 2840, 1590, 1490, 1430, 1400, 1350, 1220 cm^{-1}; ^{1}H-nmr: according to the spectrum, the product contains two isomers (5a:5b=2:1). The spectrum of 5a ($CDCl_3$) δ:8.02 (s, 1H, H-1); 6.89 (dd, $J_{5,6}$= 15.5 Hz, $J_{6,7}$=11.0 Hz, 1H, H-6); 6.44 (d, $J_{7,8}$=13.3 Hz, 1H, H-8); 6.12 (d, $J_{5,6}$=15.5 Hz, 1H, H-5); 5.34 (dd, $J_{6,7}$=11.0 Hz, $J_{7,8}$=13.3 Hz, 1H, H-7); 3.73 and 3.12 (m, 16H, morpholine). The spectrum of 5b ($CDCl_3$) δ:8.04 (s, 1H, H-5); 6.90 (dd, $J_{5,6}$= 15.5 Hz, $J_{6,7}$=11.0 Hz, 1H, H-6); 6.74 (d, $J_{5,6}$=15.5 Hz, 1H, H-5); 6.51 (d, $J_{7,8}$= 13.3 Hz, 1H, H-8); 5.33 (dd, $J_{6,7}$=11.0 Hz, $J_{7,8}$=13.3 Hz, 1H, H-7); 3.73 and 3.47 (m, 16H, morpholine). Anal. Calcd for $C_{15}H_{21}N_5O_2$: C, 59.37; H, 6.98; N, 23.09. Found: C, 59.18; H, 6.79; N, 22.78.

Reaction of 9 with triethyl orthoformate. Formation of 2-cyano-1-[(ethoxymetheno)-amino]quinolinium perchlorate (10) and 2-{1-[(ethoxymetheno)amino]quinolin-1-ium-2-yl}-s-triazolo[1,5-a]quinoline perchlorate (11)

A solution of 9 (2.7 g, 10 mmol) in dry MeCN (50 ml) was refluxed with $HC(OEt)_3$ (4.5 g, 5 ml, 30 mmol) for 2 h. The mixture was cooled, concentrated and the residue was triturated with AcOEt (30 ml) and ether (30 ml). The organic layer was decanted from the resulted gum and the residue was mixed with MeCN (10 ml). The precipitated crystals were filtered off and the crude product (0.48 g) was recrystallized from MeCN to give 0.44 g (19%) of pale yellow crystals of 11; mp 246-248°C, ir (KBr): 3080, 2980, 2920, 1600, 1510, 1440, 1370, 1300, 1100 cm^{-1}. According to the ^1H- and ^{13}C-nmr spectra, the isolated crystals consist of two possible iminoformate isomeres in a ratio of 2:1. The chemical shifts of the minor isomer are given in brackets. ^1H-Nmr (DMSO-d_6) δ : 9.33 [9.34] (d, $J_{3',4'}$=9.0 Hz, H-4'); 9.06 [9.04] (d, $J_{3',4'}$=9.0 Hz, H-3'); 9.05 [8.84] (s, H-iminoformyl); 8.54 (dd, $J_{6,7}$=8.0 Hz, $J_{6,8}$=1.2 Hz, H-6); 8.53 (dd, $J_{8,9}$=7.8 Hz, $J_{7,9}$=1.6 Hz, 1H, H-9); 8.49 [8.69] (dd, $J_{7',8'}$=8.2 Hz, $J_{6',8'}$=1.2 Hz, H-8'); 8.31 (d, $J_{4,5}$=9.0 Hz, 1H, H-5); 8.29 (t, $J_{7,8}$=7.5 Hz, 1H, H-8); 8.22 [8.21] (dd, $J_{5',6'}$=7.8 Hz, $J_{5',7'}$=1.8 Hz, H-5'); 8.11 (t, $J_{6,7}$=8.0 Hz, $J_{7,8}$=7.5 Hz, 1H, H-7); 7.99 [7.97] (t, $J_{6',7'}$=8.0 Hz, $J_{7',8'}$= 8.2 Hz, H-7'); 7.93 (d, $J_{4,5}$=9.0 Hz, 1H, H-4); 7.79 (t, $J_{5',6'}$=7.8 Hz, $J_{6',7'}$= 8.0 Hz, 1H, H-6'); 4.85 [4.46] (q, J=7.4 Hz, CH_2); 1.63 [1.12] (t, J=7.4 Hz, CH_3). ^{13}C-Nmr (DMSO-d_6) δ : 171.90 [165.67] (C-iminoformyl); 155.03 [154.06] (C-2); 148.92 [149.11] (C-3a); 144.02 [144.28] (C-4'); 142.21 [141.47] (C-2'); 138.12 [136.19] (C-8'a); 135.85 [136.23] (C-8); 133.40 [133.26] (C-5); 132.36 [132.50] (C-9a); 131.23 [131.16] (C-7'); 130.73 [130.84] (C-7); 130.00 [129.76] (C-6); 129.62 [129.46] (C-5'); 129.41 [129.46] (C-4'a); 127.41 (C-6'); 123.65 [123.62] (C-5a); 123.58 [123.56] (C-3'); 119.19 [118.65] (C-9); 115.08 [115.76] (C-8'); 114.57 [114.59] (C-4); 66.47 [71.14] (CH_2); 13.84 [14.89] (CH_3). Anal. Calcd for $C_{22}H_{18}ClN_5O_5$: C, 56.48; H, 3.88; N, 14.97. Found: C, 56.72; H, 4.03; N, 14.55. The mother liquor of the crude 11 was concentrated and the residue was triturated with AcOEt. The crystals were filtered off and the crude product (2 g) was recrystallized from MeCN–AcOEt to give 1.2 g (37%) of pale yellow crystals of 10; mp 182-185°C; ir (KBr): 3090, 3050, 2980, 1610, 1500, 1380, 1300, 1080 cm^{-1}; ^1H-nmr (TFA) δ: 9.30 (d, J=8.2 Hz, 1H, H-8); 8.80-8.00 (m, 6H, H-3,4,5,6,7 and N=CH); 4.78 (sext, J=7.4 Hz, 2H, CH_2); 1.68 and 1.37 (two t, J=7.4 Hz, 3H, CH_3 ratio=1:1). Anal. Calcd for $C_{13}H_{12}ClN_3O_5$: C, 47.93; N, 3.71; N, 12.90. Found: C, 48.17; H, 3.92; N, 13.22.

Hydrolysis of 11. Formation of 2-(1-aminoquinolin-1-ium-2-yl)-s-triazolo[1,5-a]-quinoline perchlorate (12)

A solution of 11 (326 mg) in conc. HCl (10 ml) was stirred at room temperature for 3 h, then was concentrated in vacuo. The residue was mixed with H_2O (30 ml) and $HClO_4$ (1 ml of 70% solution), and the mixture was extracted with $MeNO_2$ (3x15 ml). The residue from the extract was recrystallized from MeCN–Et_2O to give 268 mg (93%) of pale yellow needles; mp 288-290°C. The product was found to be fully identical with the authentic sample of 12 obtained by an other way.[9]

2-Benzyl-1(2H)-imino-as-triazino[1,6-a]quinolinium perchlorate (13)

To the stirred solution of 10 (0.33 g, 1 mmol) in dry MeCN (5 ml) was dropped benzylamine (0.11 g, 0.11 ml, 1 mmol) in dry MeCN (5 ml) in 30 min. Stirring was continued for 2 h, then the solvent was evaporated. The residue was mixed with aqueous $NaClO_4$ solution, then was extracted with $MeNO_2$ (3x5 ml). The extract was concentrated and the crude product (0.69 g) was recrystallized from MeCN–Et_2O to give 0.66 (41%) of pale yellow needles; mp 175-177°C; ir (KBr): 3050, 3000, 2980, 1600, 1540, 1430, 1100 cm^{-1}; ^{1}H-nmr (DMSO-d_6) δ: 9.69 (s, 1H, H-3); 8.70 (m, 2H, H-6,9); 8.29 (d, J=8.4 Hz, 1H, H-10); 8.20 (d, J=8.4 Hz, 1H, H-11); 7.43 (m, 3H, H-3',4',5'); 5.92 (s, 2H, CH_2). Anal. Calcd for $C_{18}H_{15}ClN_4O_4$: C, 55.89; H, 3.91; N, 14.49. Found: C, 56.18; H, 4.16; N, 14.33.

2-Cyano-1-[(morpholinometheno)amino]quinolinium perchlorate (14a, NR_2=morpholino)

This compound was prepared by procedure B given for 4a with the modification that instead of 1-amino-2-cyanopyridinium perchlorate (1), 2-cyano-1-aminoquinolinium perchlorate (9, 0.27 g) was used. Pale yellow needles (0.27 g, 74%), mp 244-245°C; ir (KBr): 3070, 3020, 2980, 2910, 2860, 1610, 1570, 1500, 1430, 1370, 1330, 1090 cm^{-1}; ^{1}H-nmr (TFA) δ: 9.12 (d, J=8.4 Hz, 1H, H-8); 8.70-8.10 (m, 6H, H-3,4,5,6,7 and N=CH); 4.50-3.60 (m, 8H, H-morpholino). Anal.Calcd for $C_{15}H_{15}ClN_4O_5$: C, 49.12; H, 4.12; N, 15.28. Found: C, 49.35; H, 4.16; N, 15.25.

2-Cyano-1-[(dimethylaminometheno)amino]quinolinium perchlorate (14b, NR_2=dimethylamino)

This compound was prepared from 9 by the previous method, however, instead of N-formylmorpholine, DMF (0.37 g, 0.39 ml) was used to give 0.26 g (80%) of pale yellow needles; mp 223-224°C, ir (KBr): 3100, 3070, 3020, 2920, 1620, 1570, 1500, 1420, 1360, 1320, 1300, 1090 cm^{-1}: ^{1}H-nmr (TFA) δ: 9.21 (d, J=8.4 Hz, 1H, H-8); 8.70-8.10 (m, 6H, H-3,4,5,6,7 and N=CH); 3.64 and 3.41 (two s, 6H, $N(CH_3)_2$). Anal. Calcd for $C_{13}H_{13}ClN_4O_4$: C, 48.08; H, 4.04; N, 17.25. Found: C, 48.31; H, 3.97; N, 17.46.

1-[(Dimethylaminometheno)amino]-2-morpholinoquinolinium perchlorate (15, R=Me, NR^1R^2=morpholino)

A solution of 14b (0.32 g, 1 mmol) in dry MeCN (5 ml) was stirred at room temperature with morpholine (0.44 g, 0.44 ml, 5 mmol) for 3 h. The mixture was concentrated and the residue was mixed with H_2O (10 ml) and $NaClO_4$ (0.5 g). The crystals were filtered and the crude product (0.23 g) was recrystallized from MeCN–Et_2O to give 0.17 g (45%) of colourless needles; mp 140-142°C, ir (KBr): 3100, 3000, 2960, 2870, 1620, 1570, 1520, 1420, 1100 cm^{-1}; ^{1}H-nmr (TFA) δ: 9.21 (d, J=8.2 Hz, 1H, H-8); 8.58 (d, J=8.8 Hz, 1H, H-4); 8.45 (s, 1H, N=CH); 8.00 (m, 3H, H-5,6,7); 7.59 (d, J=8.8 Hz, 1H, H-3); 4.25 (s, 8H, morpholino); 3.72 and 3.59 (two s, 6H, $N(CH_3)_2$). Anal. Calcd for $C_{16}H_{21}ClN_4O_5$: C, 49.94; H, 5.50; N, 14.56. Found: C, 50.20; H, 5.38; N, 14.70.

1-Benzyl-s-triazolo[1,5-a]quinolinium perchlorate (16, R^3=benzyl)

A solution of 14b (0.32 g, 1 mmol) in dry MeCN (5 ml) was stirred with benzylamine (0.22 g, 0.22 ml, 2 mmol) at room temperature for 2 h. The solvent was evaporated, the residue was triturated with AcOEt and the crude product (0.27 g) was recrys-

tallized from MeCN–Et_2O to give 0.21 g (58%) of colourless crystals; mp 180-182°C; ir (KBr): 3100, 3060, 3000, 2950, 1605, 1540, 1440, 1350, 1090 cm^{-1}; ^{1}H-nmr (TFA) δ: 8.92 (s, 1H, H-2); 8.65 (m, 2H, H-5,9); 8.70-7.80 (m, 4H, H-6,7,8,10); 7.53 (s, 5H, phenyl); 5.76 (s, 2H, CH_2). Anal. Calcd for $C_{17}H_{14}ClN_3O_4$: C, 56.75; H, 3.92; N, 11.68. Found: C, 56.42; H, 4.06; N, 11.91.

s-Triazolo[1,5-a]quinoline (17)

To a stirred solution of 14b (0.32 g, 1 mmol) in MeCN (5 ml) was dropped 25% NH_4OH (0.75 ml, 10 mmol) at room temperature. Stirring was continued for 24 h, then the solvent was evaporated and the residue was mixed with H_2O (10 ml) and extracted with Et_2O (3x5 ml). After evaporation the residue was recrystallized from cyclohexane to give 90 mg (54%) of pale yellow needles; mp 97-99°C; ir (KBr): 3080, 1610, 1550, 1520, 1440, 1390, 1300 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ: 8.55 (d, J=8.4 Hz, 1H, H-5); 8.40 (s, 1H, H-2); 8.10-7.40 (m, 5H, H-6,7,8,9,10). Anal. Calcd for $C_{10}H_7N_3$: C, 70.99; H, 4.17; N, 24.84. Found: C, 70.86; H, 3.96; N, 24.98.

Hydrolysis of 10. Formation of 1-amino-2-cyanoquinolinium perchlorate (9)

A solution of 10 (0.16 g) in 35% HCl (2.5 ml) was stirred at room temperature for 2 h. The mixture was evaporated and the residue was dissolved in H_2O (15 ml), mixed with 70% $HClO_4$ (0.2 ml) and extracted with $MeNO_2$ (3x5 ml). The extract was evaporated and the crude product (83 mg) was recrystallized from MeCN–AcOEt to give 72 mg (53%) of colourless crystals; mp 188-190°C. The product was identical with the authentic sample[9] of 9.

Hydrolysis of 14b. Formation of 4(3H)-oxo-as-triazino[1,6-a]quinolinium perchlorate (18)

A solution of 14b (0.32 g) in 35% HCl (5 ml) was refluxed for 30 min, then it was mixed with 70% $HClO_4$ (0.2 ml), cooled and the crystals were filtered off. The crude product (0.23 g) was recrystallized from MeCN–AcOEt to give 0.21 g (70%) of colourless needles; mp 290-293°C; ir (KBr): 3070, 3000, 2800, 2660, 2600, 1730, 1620, 1590, 1560, 1510, 1480, 1420, 1320, 1100 cm^{-1}; ^{1}H-nmr (TFA) δ: 9.40 (d, J=8.4 Hz, 1H, H-6); 9.32 (d, J=8.8 Hz, 1H, H-10); 9.00 (d, J=8.8 Hz, 1H, H-11); 8.92 (s, 1H, H-3); 8.70-8.10 (m, 3H, H-7,8,9). Anal. Calcd for $C_{11}H_8ClN_3O_5$: C, 44.39; H, 2.71; N, 14.12. Found: C, 44.20; H, 2.86; N, 14.04.

Reaction of 19 with triethyl orthoformate. Formation of 1-cyano-2-[(ethoxymetheno)-amino]isoquinolinium tosylate (20)

A suspension of 19 (17 g, 50 mmol) in dry MeCN (250 ml) was refluxed with $HC(OEt)_3$ (22.2 g, 25.0 ml, 150 mmol) for 2 h. The reaction mixture was cooled, concentrated to 25 ml, then AcOEt (50 ml) was added and the precipitate was filtered off. The crude product was recrystallized from dry MeCN to give 10.2 g (51%) of pale yellow needles; mp 159-162°C; ir (KBr): 3040, 3020, 2960, 2920, 1620, 1600, 1580, 1440, 1180 cm^{-1}; ^{1}H-nmr (TFA) δ: 9.00-8.65 (m, 3H, H-3,4 and N=CH); 8.60-8.20 (m, 4H, H-5,6,7,8); 7.86 (d, J=9.0 Hz, 2H, H-2',6'); 7.32 (d, J=9.0 Hz, 2H, H-3',5'); 4.73 (q, J=6.4 Hz, 2H, CH_2); 2.42 (s, 3H, CH_3-tosyl); 1.59 (t, J=6.4 Hz, 3H, CH_3). Anal. Calcd for $C_{20}H_{19}N_3O_4S$: C, 60.44; H, 4.82; N, 10.57. Found: C, 60.25; H, 5.03; N, 10.34.

2-{2-[(Ethoxymetheno)amino]isoquinolin-2-ium-1-yl}-s-triazolo[5,1-a]isoquinoline perchlorate (21, A=ClO_4)

Procedure A: To a stirred suspension of 20 (0.4 g, 1 mmol) in dry MeCN (10 ml) was slowly dropped a solution of benzylamine (0.11 g, 0.11 ml, 1 mmol) in dry MeCN (10 ml) in 30 min. Stirring was continued for 16 h, the reaction mixture was evaporated, the residue was mixed with H_2O (10 ml) and $NaClO_4$ (1.0 g) and was extracted with $MeNO_2$ (3x5 ml). The residue from the extract (0.18 g) was recrystallized from MeCN–AcOEt to give 0.14 g (60%) of pale yellow needles; mp 188-191°C; ir (KBr): 3070, 2980, 2920, 1640, 1600, 1560, 1510, 1440, 1370, 1080 cm^{-1}. According to the ^1H- and ^{13}C-nmr spectra, the isolated crystals contained two possible iminoformate isomers in a ratio of 3:2. Chemical shifts of the minor isomer are given in brackets. ^1H-Nmr (DMSO-d_6) δ: 8.94 [8.05] (s, H-iminoformyl); 8.86 (d, $J_{3',4'}$=6.8 Hz, 1H, H-3'); 8.72 (d, $J_{3',4'}$=6.8 Hz, 1H, H-4'); 8.63 (d, $J_{5,6}$=7.1 Hz, 1H, H-5); 8.61 [8.63] (dd, $J_{9,10}$=7.2 Hz, $J_{8,10}$=1.0 Hz, H-10); 8.43 [8.36] (dd, $J_{7',8'}$=8.1 Hz, $J_{6',8'}$=1.0 Hz, H-8'); 8.41 [8.40] (dd, $J_{5',6'}$=7.2 Hz, $J_{5',7'}$=1.2 Hz, H-5'); 8.22 (t, $J_{5',6'}$=7.2 Hz, $J_{6',7'}$=7.8 Hz, 1H, H-6'); 8.07 (d, $J_{7,8}$=7.8 Hz, 1H, H-7); 8.02 (t, $J_{5',7'}$=7.8 Hz, $J_{7',8'}$=8.1 Hz, 1H, H-7'); 7.90 (t, $J_{7,8}$=7.8 Hz, $J_{8,9}$=7.5 Hz, 1H, H-8); 7.86 (t, $J_{8,9}$=7.5 Hz, $J_{9,10}$=7.2 Hz, 1H, H-9); 7.68 [7.66] (d, $J_{5,6}$=7.1 Hz, H-6); 4.28 [4.60] (q, J=6.8 Hz, CH_2); 1.23 [1.45] (t, J=6.8 Hz, CH_3). ^{13}C-nmr (DMSO-d_6) δ: 169.26 [162.89] (C-iminoformyl); 151.80 [151.39] (C-2); 149.45 [149.55] (C-10b); 143.91 [143.55] (C-1'); 136.63 [136.47] (C-4'a); 135.71 [135.79] (C-6'); 133.56 [133.43] (C-3'); 131.81 [131.58] (C-7'); 131.08 [131.03] (C-6a); 130.75 [130.64] (C-8); 129.06 [129.00] (C-8'); 128.86 [128.77] (C-9); 127.56 [127.43] (C-5'); 127.37 [127.31] (C-7); 124.08 [123.96] (C-10); 123.48 [123.56] (C-5); 121.04 [121.11] (C-10a); 116.44 [116.25] (C-6); 66.10 [71.78] (CH_2); 13.02 [14.61] (CH_3). Anal. Calcd for $C_{22}H_{18}ClN_5O_5$: C, 56.48; H, 3.88; N, 14.97. Found: C, 56,14; H, 4.17; N, 14.56. Procedure B: To a stirred suspension of 19 (0.17 g, 0.5 mmol) and 20 (0.2 g, 0.5 mmol) in dry MeCN (20 ml) was dropped a solution of Et_3N (0.05 g, 0.069 ml, 0.5 mmol) in dry MeCN (10 ml). After being stirred at room temperature for 20 h, the solution was evaporated to dryness, the residue was mixed with H_2O (20 ml) and $NaClO_4$ (2 g), then was extracted with $MeNO_2$ (3x10 ml) and the extract was worked up as usual to give 0.15 g (64%) of pale yellow needles; mp 187-190°C. The product was identical with that of obtained by procedure A.

Hydrolysis of 21. Formation of 2-(2-aminoisoquinolin-2-ium-yl)-s-triazolo[5,1-a]-isoquinoline perchlorate (22)

Compound 21 (100 mg) was hydrolysed in conc. HCl (3 ml) according to the procedure given for the analogous quinoline derivative (11) to give 22[9] (72 mg, 82%).

1-Cyano-2-[(morpholinometheno)amino]isoquinolinium perchlorate (23a, NR_2=morpholino, A=ClO_4)

Procedure A: A solution of 20 (0.4 g, 1 mmol) in MeCN (5 ml) was stirred with morpholine (0.1 g, 0.1 ml, 1.1 mmol) at room temperature for 1 h. Ethyl acetate was added and the crude product was filtered off and recrystallized from MeCN-DMF to give 0.34 g (77%) of pale yellow crystals; mp 221-224°C. The compound was a

tosylate salt (23a, A=TsO) and was converted to a perchlorate salt (23a, A=ClO_4) by treating with aqueous $NaClO_4$ solution. Yellow crystals; mp 211-213°C (MeCN-AcOEt); ir (KBr): 3160, 3140, 3100, 2920, 2860, 1630, 1590, 1550, 1100 cm^{-1}; ^{1}H-nmr (TFA) δ : 8.89 (d, J=6.8 Hz, 1H, H-3)); 8.71 (d, J=6.8 Hz, 1H, H-4)); 8.63 (s, 1H, N=CH); 8.50-8.10 (m, 4H, H-5,6,7,8); 4.40-3.70 (m, 8H, morpholino). Anal. Calcd for $C_{15}H_{15}ClN_4O_5$: C, 49.12; H, 4.12; N, 15.28. Found: C, 49.38; N, 4.17; N, 15.18. Procedure B: Compound 23a can be prepared by procedure B given for the synthesis of 4a with the modification that 1-cyanoisoquinolinium tosylate (19, 0.34 g) was used instead of 1-amino-2-cyanopyridinium perchlorate (1). Yellow crystals (0.26 g, 72%); mp 210-213°C (MeCN-AcOEt). The product was found to be identical with that of obtained by procedure A.

1-Cyano-2-[(dimethylaminometheno)amino]isoquinolinium tetrafluoroborate (23b, NR_2=dimethylamino, NR^1R^2=morpholino, A=BF_4)
This compound was prepared from 19 (9.34 g) according to the previous method (B) with the difference that DMF (0.37 g, 5 mmol) and $NaBF_4$ were used instead of N-formylmorpholine and $NaClO_4$, respectively. Pale yellow crystals (0.24 g, 77%) were obtained; mp 193-195°C; ir (KBr): 3080, 3050, 3010, 2910, 1630, 1590, 1550, 1420, 1100 cm^{-1}; ^{1}H-nmr (TFA) δ : 8.83 (d, J=6.8 Hz, 1H, H-3); 8.64 (d, J=6.8 Hz, 1H, H-4); 8.60-8.10 (m, 5H, H-5,6,7,8 and N=CH); 3.38 and 3.35 (two s, 6H, $N(CH_3)_2$). Anal. Calcd for $C_{13}H_{13}BF_4N_4$: C, 50.03; H, 4.20; N, 17.95. Found: C, 50.24; H, 4.17; N, 17.70.

1-Morpholino-2-[(morpholinometheno)amino]isoquinolinium perchlorate (24a, NR_2=NR^1R^2=morpholino, A=ClO_4)
A suspension of 23a (A=TsO, 0.66 g, 1.5 mmol) in MeCN (15 ml) was stirred with morpholine (0.66 g, 0.66 ml, 7.5 mmol) at room temperature for 30 min, then was bring to boiling for 5 min, cooled and evaporated. The residue was dissolved in H_2O (7 ml) and was mixed with $HClO_4$ (0.5 ml, 70%) and filtered off. After recrystallization from MeCN-AcOEt 0.59 g (92%) of pale yellow crystals were obtained; mp 253-256°C, ir (KBr): 3180, 2960, 2920, 2860, 1630, 1610, 1560, 1520, 1430, 1100 cm^{-1}; ^{1}H-nmr (TFA)) δ : 8.51 (m, 2H, H-8 and N=CH); 8.30-8.00 (m, 3H, H-5,6,7); 7.95 (d, J= 7.6 Hz, 1H, H-3); 7.81 (d, J=7.6 Hz, 1H, H-4); 4.40-3.70 (m, 16H, morpholino). Anal. Calcd for $C_{18}H_{23}ClN_4O_6$: C, 50.65; H, 5.43; N, 13.13. Found: C, 50.81; H, 5.56; N, 13.14.

2-[(Dimethylaminometheno)amino]-1-morpholinoisoquinolinium tetrafluoroborate (24b, NR_2=dimethylamino, NR^1R^2=morpholino, A=BF_4)
A solution of 21b (R=Me, A=BF_4, 9.36 g, 30 mmol) in MeCN (100 ml) was stirred with morpholine (13.1 g, 13.1 ml, 150 mmol) at room temperature for 2 h, then was evaporated to dryness and the residue was dissolved in H_2O (50 ml). The solution was mixed with $NaBF_4$ (10 g) and filtered off. After recrystallization from MeCN–AcOEt, 7.3 g (65%) of pale yellow crystals were obtained; mp 137-139°C; ir (KBr): 3050, 3010, 2950, 2910, 2850, 1630, 1550, 1510, 1480, 1430, 1080 cm^{-1}; ^{1}H-nmr (TFA) δ : 8.64 (s, 1H, N=CH); 8.57 (d, J=8.0 Hz, 1H, H-8); 8.30-8.00 (m, 3H, H-5,6,7); 7.99 (d, J=7.6 Hz, 1H, H-3); 7.81 (d, J=7.6 Hz, 1H, H-4); 4.60-3.90 (m, 8H, morpholino); 3.61 (s, 6H, $N(CH_3)_2$). Anal. Calcd for $C_{16}H_{21}BF_4N_4O$: C, 51.63; H, 5.69; N, 15.05. Found: C, 51.89; H, 5.65; N, 14.90.

Synthesis of 1-substituted s-triazolo[5,1-a]isoquinolinium salts (25a-c)

General procedure: A solution of 23a,b (1 mmol) in dry MeCN (5 ml) was stirred with appropriate primary amine (2 mmol) at room temperature for 1 h, then was evaporated to dryness and the residue was triturated with AcOEt (5 ml). The crystals were filtered off and recrystallized from MeCN–AcOEt to give the product.

1-Benzyl-s-triazolo[5,1-a]isoquinolinium tosylate (25a, A=TsO)

The compound was prepared according to the general procedure from 23a (NR_2 = morpholino, A=TsO, 0.44 g) and benzylamine (0.22 g). Yield: 0.30 g (70%), colourless crystals; mp 192-195°C (MeCN–AcOEt); ir (KBr): 3110, 3080, 3040, 2920, 1640, 1550, 1490, 1455, 1200 cm^{-1}; ^{1}H-nmr (TFA) δ : 8.79 (s, 1H, H-2); 8.73 (m, 2H, H-5,10); 8.40-8.00 (m, 4H, H-6,7,8,9); 7.85 (d, J=9.0 Hz, 2H, H-2',6'-tosyl); 7.54 (s, 5H, C_6H_6); 7.29 (d, J=9.0 Hz, 2H, H-3',5'-tosyl); 6.17 (s, 2H, CH_2); 2.44 (s, 3H, CH_3-tosyl). Anal. Calcd for $C_{24}H_{21}N_3O_3S$: C, 66.80; H, 4.91; N, 9.74. Found: C, 66.94; H, 4.86; N, 9.62.

1-(2-Hydroxyethyl)-s-triazolo[5,1-a]isoquinolinium tetrafluoroborate (25b, A=BF_4)

Procedure A: This compound was prepared using the general procedure, from 23b (R=Me, A=BF_4, 0.31 g) and ethanolamine (0.12 g). Yield: 0.21 g (70%), colourless needles; mp 167-170°C (MeCN–AcOEt); ir (KBr): 3270, 3100, 3070, 3050, 3040, 2930, 2870, 2800, 1640, 1540, 1460, 1440, 1400, 1080 cm^{-1}; ^{1}H-nmr (TFA) δ : 9.15 (s, 1H, H-2); 8.74 (m, 2H, H-5,10); 8.29 (m, 3H, H-7,8,9); 8.06 (d, J=7.2 Hz, 1H, H-6); 5.60-4.40 (m, 4H, CH_2-CH_2). Anal. Calcd for $C_{12}H_{12}BF_4N_3O$: C, 47.87; H, 4.02; N, 13.96. Found: C, 47.95; H, 4.08; N, 13.84.

Procedure B. According to the general procedure the reaction of 23a (NR_2 = morpholino, A=TsO, 0.44 g) and ethanolamine (0.12 g) gave the tosylate salt (24b, 0.30 g, 77%); mp 176-178°C. This compound was converted to tetrafluoroborate salt which was identical with the product obtained by procedure A.

1-(3-Dimethylaminopropyl)-s-triazolo[5,1-a]isoquinolinium tetrafluoroborate (25c, A=BF_4)

This compound was prepared using the general procedure, from 23b (12.5 g, 40 mmol) and 3-dimethylaminopropylamine (8.16 g, 80 mmol). Yield: 11.3 g (82%), yellow prisms; mp 121-123°C (MeCN–AcOEt); ir (KBr):3050, 2940, 2860, 2820, 2770, 1640, 1540, 1460, 1080 cm^{-1}; ^{1}H-nmr (TFA) δ : 9.18 (s, 1H, H-2); 8.76 (m, 2H, H-5,10); 8.32 (m, 3H, H-7,8,9); 8.09 (d, J=7.4 Hz, 1H, H-6); 5.20 (t, J=7.2 Hz, 2H, 1'-CH_2); 3.71 (m, 1H, 3'-CH_2); 3.23 and 3.05 (two s, 6H, $N(CH_3)_2$); 2,90 (t, J=6.8 Hz, 2H, 2'-CH_2). Anal. Calcd for $C_{15}H_{19}BF_4N_4$: C, 52.65; H, 5.60; N, 16.38. Found: C, 52.81; H, 5.71; N, 16.23.

s-Triazolo[5,1-a]isoquinoline (26)

To a solution of 23b (R=Me, A=BF_4, 0.31 g) in MeCN (5 ml) was dropped slowly 25% NH_4OH (0.75 ml, 10 mmol). After stirring for 24 h at room temperature, the residue was recrystallized from cyclohexane to give 0.12 g (71%) of colourless needles; mp 99-100°C. (Lit.,[19] mp 95-96.5°C).

Hydrolysis of 20 (A=TsO). Formation of 2-amino-1-cyanoisoquinolinium perchlorate (19, A=ClO_4)

A solution of 20 (0.40 g) in conc. HCl (5 ml) was refluxed for 1o min, then was cooled, mixed with 70% $HClO_4$ (0.5 ml) and evaporated to dryness. The residue was dissolved in MeCN (2.4 ml), mixed with AcOEt (10 ml) and the precipitate was recrystallized from MeCN–AcOEt. Yield: 0.17 g (63%) of pale yellow crystals; mp 196-197°C; ir (KBr): 3230, 3100, 3000, 1590, 1420, 1390, 1340, 1080 cm^{-1}; ^{1}H-nmr (TFA) δ : 8.98 (d, J=6.6 Hz, 1H, H-3); 8.69 (d, J=6.6 Hz, 1H, H-4); 8.65 (d, J=8.0 Hz, 1H, H-8); 8.40 (m, 3H, H-5,6,7). Anal. Calcd for $C_{10}H_8ClN_3O_4$: C, 44.54; H, 2.99; N, 15.58. Found: C, 44.63; H, 3.07; N, 15.43.

Hydrolysis of 23b. Formation of 2-amino-1-cyanoisoquinolinium perchlorate (19)

A solution of 23b (0.31 g) in conc. HCl (5 ml) was refluxed for 30 min. The reaction mixture was worked up as given in the previous procedure to give the same product (19, A=ClO_4) as above (0.15 g, 56%); mp 195-197°C.

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