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SYNTHESIS AND NITROGEN ELIMINATION OF 3-ARYLTETRAZOLO(1,5-a)PYRIDINIUM SALTS AND ITS ANGULAR BENZENOLOGUES

Formation of N-arylamino-α-pyridones, -quinolones, -isoquinolones, and phenanthridones[1]

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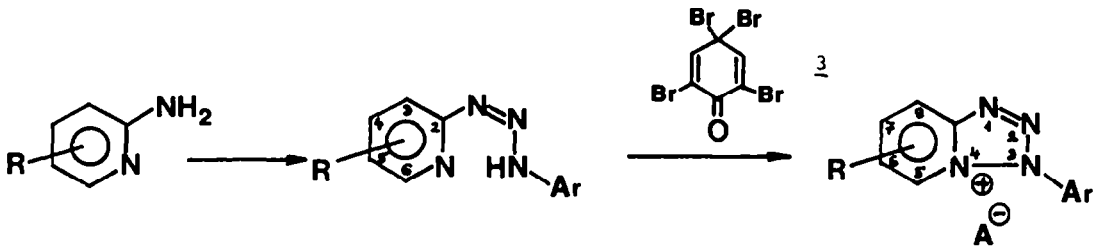
Abstract. - 2-Pyridyl aryltriazenes (2) as well as 1-isoquinolyl-, 2-quinolyl- and 6-phenanthridyltriazenes (6, 9, 12) undergo cyclization in the presence of 2,4,4,6-tribromocyclohexa-2,5-dien-1-one (3) and result in 3-aryltetrazolo(1,5-a)pyridinium salts (4) and its angular benzenologues (7, 10, 13). These new tricyclic (7, 10) and tetracyclic (13) angularly fused tetrazolium salts when treated with tetraalkylammonium hydroxide result in rapid nitrogen elimination under mild conditions and give rise to N-arylaminoisoquinolones, -quinolones and -phenanthridones (14, 15, 16). In the case of the bicyclic tetrazolo(1,5-a)pyridinium salts (4) a nitrogen elimination reaction - analogous to that found with the tricyclic tetrazolium salts - can, however, be observed only by using alkoxides as reagents: thus, tetrazolyldieneethers (18) and N-arylaminopyridones (19) are simultaneously formed.

Earlier we reported[2,3] that reaction of 1-(α-pyridyl)-3-aryltriazenes (2) and 1-(1-isoquinolyl)-3-aryltriazenes (6), prepared from 2-aminopyridines (1) and 1-aminoisoquinoline (5) respectively, with same as above (3) gives 3-aryltetrazolo-(1,5-a)pyridinium (4) and 3-aryl-6-bromotetrazolo(5,1-a)isoquinolinium salts (7).



1 2 4

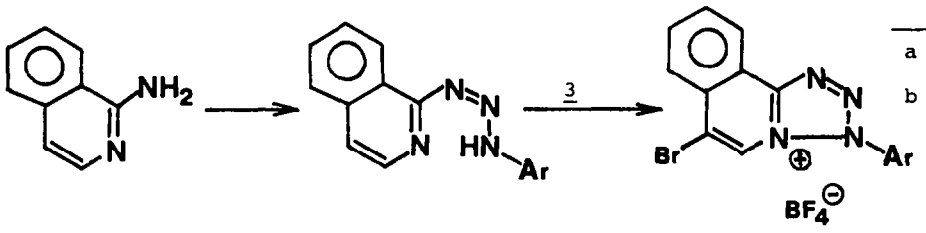
	R	Ar
a	H	C_6H_5
b	H	p-OCH_3-C_6H_4-
c	H	p-Br-C_6H_4-
d	H	p-Cl-C_6H_4-

	R	Ar
e	8-CH_3	p-Cl-C_6H_4-
f	7-CH_3	p-Cl-C_6H_4-
g	6-CH_3	p-Cl-C_6H_4-
h	5-CH_3	p-Cl-C_6H_4-

Numbering of system 4

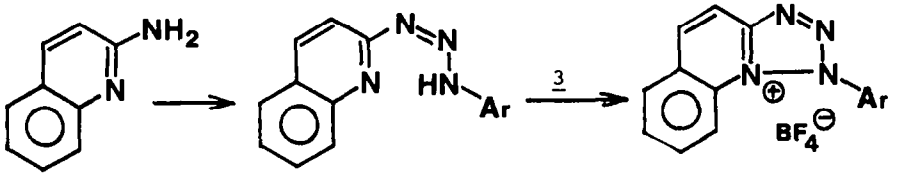
In this paper we give experimental details of the earlier findings, describe the extension of this ring closure for preparation of novel fused tetrazolium systems and discuss the reactivity of the resulting systems in the presence of nucleophilic reagents.

We found that the ring closure leading to tetrazolium salts 4 described for model derivatives can be successfully generalized for preparation of differently substituted derivatives. Reaction of triazenes (2a-h) with reagent 3 in a dichloro methane solution proceeds at 40°C within several minutes and yields an orange-yellow perbromide salt of 4 as the primary product, which can easily be transformed to bromide derivative by treatment with cyclohexene. The closure of the tetrazole ring is well supported - beside the hypsochromic shift of the first UV maxima[2] - by the ^{1}H-NMR spectrum of the positively charged heteroaromatic system (e.g. chemical shift of H-6 in 2a /8.45 ppm/ changes to a value of 9.05 ppm /the same proton in 4a/).



	Ar
a	C_6H_5-
b	p-Br-C_6H_4-

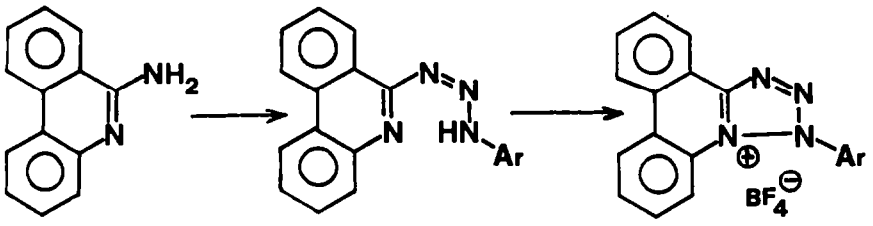
5 6 7



	Ar
a	C_6H_5-
b	p-Cl-C_6H_4-
c	p-CH_3-C_6H_4-
d	p-Br-C_6H_4-
e	3,4-Cl-C_6H_3-

8 9 10

Benzenologues of pyridyltriazenes 2 undergo a similar ring closure with 3 giving angularly fused benzenologues of 4. Thus, treatment of 2-aminoquinoline (8) with diazonium salts gives rise to 1-(2-quinolyl)-3-aryltriazenes which, when reacted with tribromophenol bromine, result in 3-aryl substituted derivatives of the tetrazolo(1,5-a)quinolinium ring system (10). In the case of 1-(1-isoquinolyl)-3-aryltriazines (6), closure of the tetrazole ring is accompanied by bromination of position 4 of the isoquinoline ring as shown by ^{1}H-NMR spectra and elementary analyses. This finding is in agreement with the well known high electrophilic reactivity of this position[5].

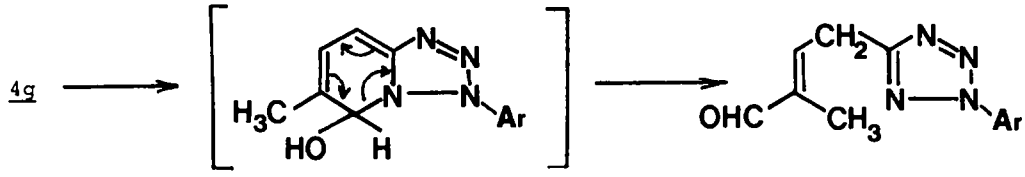


11 12 13

Ar	
a	p-Br-C_6H_4-
b	p-F-C_6H_4-

Formation of triazenes and cyclization to tetrazolium salts was also found with phenanthridine derivatives: 6-aminophenanthridine (11) was first converted to triazene 12 which gave tetrazolo(1,5-f)phenanthridinium salts (13).

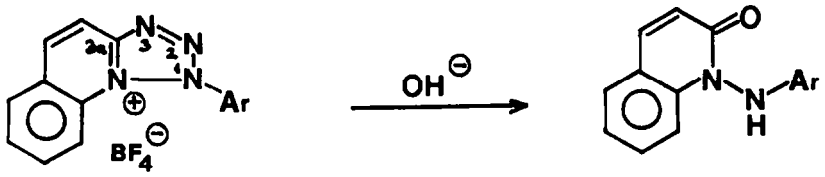
The new bicyclic (4), tricyclic (7, 10) and tetracyclic (13) fused tetrazolium salts proved to be stable compounds both in the crystalline state and in neutral solutions. Under basic conditions, however, tetrazolium salts showed a high tendency to transform and, for example, we have shown recently[6,7] that tetrazolo(1,5-a)pyridinium salts (4) react with amines, alcoholates and thiolates at low temperatures to give tetrazolyldieneamines, -dieneethers and -dienethioethers, respectively. In this study the behaviour of the fused tetrazolium salts in the presence of hydroxide ion was investigated. As reagent, an aqueous solution of tetramethylammonium hydroxide was used.



4g 17

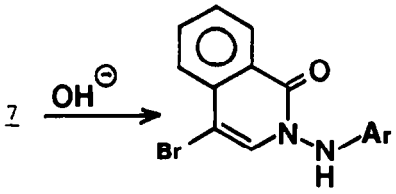
Tetrazolo(1,5-a)pyridinium salts (4) when treated with tetramethylammonium hydroxide (TMAH) solution showed a very rapid decomposition. In the case of most derivatives, however, the dark red reaction mixtures could not be separated to components even by the use of chromatography. As an exception, 6-methyltetrazolo-(1,5-a)pyridinium bromide (4g) gave 3-(2-chlorophenyl)-1-methylcrotonaldehyde (17) as only reaction product in good yield. This reaction can be rationalized by an attack of the hydroxide ion at C-5 followed by retro-electrocyclization (in brackets)[8].

In contrast to the bicyclic system, treatment of the benzofused tetrazolium salts with TMAH resulted in a rapid nitrogen evolution and N-arylaminoquinolones (14), N-arylaminoisoquinolones (15) and N-arylaminophenanthridones (16) precipitated from the reaction mixtures in good yield. Structures of these products

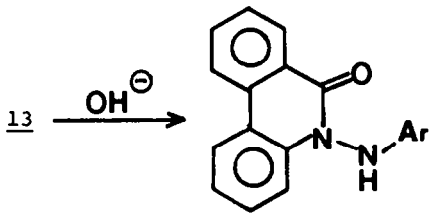


10 14

Ar = p-Br-C_6H_4-



7 15



13 16

are well supported by their mass spectra (M^+ and arylamine fragments) and IR spectra (carbonyl and NH bonds). A possible mechanism for this nitrogen elimination reaction is attack of hydroxide anion at the bridge head carbon atom adjacent to the positive charge (i.e. position 3a in compound 10), withdrawal of a proton from the OH group by the basic medium and fragmentation involving splitting off a nitrogen molecule induced by the lone pair on the oxygen atom (Fig. 1).

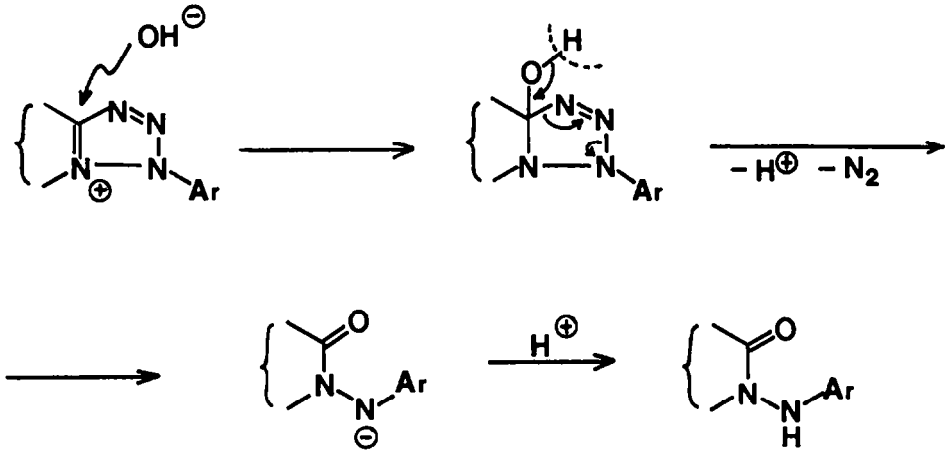
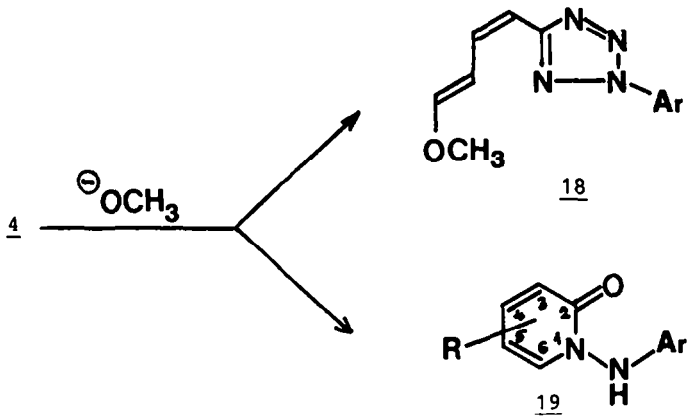


Fig. 1. Proposed mechanism of formation of fused N-arylaminopyridones

It is interesting to note that a detailed investigation of the reactivity of the tetrazolo(1,5-a)pyridinium system towards nucleophiles allowed observation of the above nitrogen elimination process in that case also. Earlier we published[7] that reaction of tetrazolium salts 4 with alcoholates proved to be suitable method



	R
a	H
b	4-CH_3
c	5-CH_3

for synthesis of tetrazolyl dieneethers. A thorough work up of reaction mixture obtained from 4a and sodium methoxide led, however, to isolation of N-p-chloroanilinopyridone (19a) in poor yield. The yield of this by-product proved to be strongly dependent on substitution of the pyridine ring and was found, interestingly, to be as high as 72 per cent in the case of compound 4g. Reaction of 4 with alcoholates to yield N-arylaminopyridones probably proceeds through an intermediate bearing methoxy group which must undergo de-methylation to result in the observed nitrogen elimination. Comparison of these results with those found recently by us[7] show that while tetrazolo(1,5-a)pyridinium system (4) shows ambident reactivity with nucleophiles (i.e. can be attacked at both positions 5 and 8a by nucleophiles), the tricyclic and tetracyclic angularly fused compounds react regiospecifically only at the bridge head carbon atom adjacent to the positively charged nitrogen.

Further studies of this facile nitrogen elimination and of the reactivity of fused tetrazolium salts with different types of nucleophiles are in progress.

EXPERIMENTAL PART

Melting points were determined by a Büchi apparatus and are uncorrected. NMR spectra were obtained by a Varian XL-100 spectrometer, IR spectra were recorded on a Unicam SP-200, UV spectra on a Unicam SP-800 equipment.

1-(α-Pyridyl)-3-aryltriazenes (2)

A solution of 2-aminopyridine derivative (1) (0.27 mol) in water (1500 ml) at -2°C was treated with a diazonium salt solution obtained from the appropriate aniline derivative (0.28 mol) in 10 per cent hydrochloric acid (220 ml). The mixture was then treated with an excess of potassium hydrogen carbonate, stirred for 5 h at this temperature and stored finally in a refrigerator for an additional 15 h. The voluminous pale yellow precipitate was filtered, washed thoroughly with water, dried and recrystallized (Table 1).

Compound 2a: ^{1}H-NMR ($CDCl_3$): δ 845 (m, 1H, H-6); 7.9-7.2 (m, 6H, H-Ar+H-3, H-4); 7.1-6.95 (m, 1H, H-5); 1.65 (s, 1H, NH). $J_{3,4}$= 8.3; $J_{4,5}$= 6.2; $J_{5,6}$= 5.0 Hz.

Table 1. Characteristics of 1-(α-pyridyl)-3-aryltriazenes (2)

No	X	R		Analysis %			m.p.	%	re-cryst.
2a	H	H	$C_{11}H_{10}N_4$ (198.23)	calc. C 66.65	H 5.09	N 28.27	177-78	34	B
				found C 66.79	H 5.28	N 28.53			
2b	OCH_3	H	$C_{12}H_{12}N_4O$ (228.26)	calc. C 63.14	H 5.30	N 24.55	188-89	58	B
				found C 63.14	H 5.30	N 24.55			
2c	Br	H	$C_{11}H_9BrN_4$ (277.14	calc. C 47.67	H 3.27	N 20.22	206-07	39	B
				found C 47.24	H 3.42	N 20.31			
2d	Cl	H	$C_{11}H_9ClN_4$ (232.68)	calc. C 56.74	H 3.90	N 24.08	195-96	74	T
				found C 56.39	H 3.85	N 24.12			
2e	Cl	3-CH_3	$C_{12}H_{11}ClN_4$ (246.71)	calc. C 58.35	H 4.49	N 22.71	166-67	57	B
				found C 58.02	H 4.20	N 22.52			
2f	Cl	4-CH_3	$C_{12}H_{11}ClN_4$ (246.71)	calc. C 58.35	H 4.49	N 22.72	208-09	64	T
				found C 58.12	H 4.31	N 22.50			
2g	Cl	5-CH_3	$C_{12}H_{11}ClN_4$ (246.71	calc. C 58.35	H 4.49	N 22.71	211-12	80	ME
				found C 58.21	H 4.17	N 22.43			
2h	Cl	6-CH_3	$C_{12}H_{11}ClN_4$ (246.71)	calc. C 58.35	H 4.49	N 22.72	154-56	46	EA
				found C 58.05	H 4.36	N 22.48			

Abbreviations: B: Benzene; T: Toluene; ME: Methyl ethyl ketone; EA: Ethyl acetate

3-Aryltetrazolo(1,5-a)pyridinium salts (4)

To a solution of same as before (3) (13.3 g; 3.1 cmol) in dichloromethane (200 ml), crystalline 1-(α-pyridyl)-3-aryltriazene (2) (1.o cmol) was added and the mixture was refluxed. A deep coloured solution was formed which turned to

Table 2. Characteristics of tetrazolo(1,5-a)pyridinium bromides (4)

No	X	R		Analysis %			m.p.	%	m.p.of analogons BF_4 salt
4a	H	H	$C_{11}H_9BrN_4$ (277.14)	calc. C 47.67	H 3.27	N 20.22	300	84	246
				found C 47.24	H 3.42	N 10.05			
4b	OCH_3	H	$C_{12}H_{11}BrN_4O$ (307.27)	calc. C 46.90	H 3.61	N 18.28	358	77	179
				found C 46.72	H 3.45	N 18.42			
4c	Br	H	$C_{11}H_8Br_2N_4$ (356.05)	calc. C 37.11	H.2.26	N 15.74	310	82	207
				found C 37.24	H 2.02	N 15.90			
4d	Cl	H	$C_{11}H_8BrClN_4$ (311.59)	calc. C 42.40	H 2.59	N 18.08	307	87	198
				found C 42.11	H 2.38	N 18.31			
4e	Cl	9-CH_3	$C_{12}H_{11}BrClN_4$ (325.61)	calc. C 44.27	H 3.40	N 17.21	242	76	208
				found C 43.98	H 3.22	N 17.11			
4f	Cl	7-CH_3	$C_{12}H_{11}BrClN_4$ (352.61)	calc. C 44.27	H 3.40	N 17.21	294	81	252
				found C 43.92	H 3.09	N 17.45			
4g	Cl	6-CH_3	$C_{12}H_{11}BrClN_4$ (325.61)	calc. C 44.27	H 3.40	N 17.21	250	78	204
				found C 44.00	H 3.13	N 17.12			
4h	Cl	5-CH_3	$C_{12}H_{11}BrClN_4$ (325.61)	calc. C 44.27	H 3.40	N 17.21	303	61	204
				found C 43.88	H 3.26	N 17.37			

yellow within some minutes and an orange precipitate deposited. After 30 min the mixture was cooled, ether (100 ml) was added and the precipitate was filtered. The orange crystals (perbromide salts) were then mixed with nitromethane (20 ml) and cyclohexene (2 ml). The orange colour rapidly disappeared and a colourless crystalline mass of bromide salt precipitated which, after addition of 100 ml of ether, was filtered and recrystallized from methanol-ethyl ether. For data see Table 2).

Compound 4a: ^{1}H-NMR (CD_3CN): δ 9.05 (d, 1H, H-6); 8.72 (t, 1H, H-4); 8.48 (d, 1H, H-3); 8.15 (t, 1H, H-5); 7.9 (s, 4H, H-Ar).

1-(2-Quinolyl)-3-aryltriazenes (9) and 1-(1-isoquinolyl)-3-aryltriazenes (6)

A solution of 2-aminoquinoline (8) (70 mmol) or 1-aminoisoquinoline (5) in acetonitrile (300 ml) was mixed with a solution of sodium hydrogen carbonate (20.0 g) in water (300 ml) and a solution of p-chlorophenyldiazonium fluoroborate (80 mmol) in acetonitrile (50 ml) was then added at 0°C with stirring. The mixture was stirred at 5°C for 5 h and was stored for additional 10 h in a refrigerator. The dark brown precipitate was filtered, washed with water and methanol and recrystallized from dioxane. Data of products are shown in Table 3.

Table 3. Characteristics of isoquinolyl-, quinolyl-, and phenanthridyltriazenes (6, 9 and 12)

No	Heterocycle		Analyses				m.p.	%
6a	IQ	C_6H_5-	$C_{15}H_{12}N_4$ (248.29)	calc. C 72.52	H 4.87	N 19.82	135-36	52
				found C 72.64	H 5.09	N 19.63		
6b	IQ	p-Br-C_6H_4-	$C_{15}H_{11}N_4Br$ (327.20)	calc. C 55.06	H 3.39	N 17.12	173-75	46
				found C 54.93	H 3.51	N 17.31		
9a	Q	C_6H_5-	$C_{15}H_{12}N_4$ (248.29)	calc. C 72.52	H 4.87	N 19.82	165-67	65
				found C 72.57	H 5.21	N 19.51		
9b	Q	p-Cl-C_6H_4-	$C_{15}H_{11}N_4Cl$ (282.75)	calc. C 63.78	H 3.92	N 21.36	186-88	87
				found C 63.81	H 4.21	N 21.55		
9c	Q	p-CH_3-C_6H_4-	$C_{16}H_{14}N_4$ (262.32)	calc. C 73.26	H 5.38	N 22.57	155-58	76
				found C 73.57	H 5.67	N 22.81		
9d	Q	p-Br-C_6H_4-	$C_{15}H_{11}N_4Br$ (327.20)	calc. C 55.05	H 3.39	N 17.13	196-97	81
				found C 55.41	H 3.62	N 17.43		
9e	Q	3,4-Cl-C_6H_3-	$C_{15}H_{10}Cl_2N_4$ (317.19)	calc. C 56.80	H 3.18	N 17.67	190-92	78
				found C 56.78	H 3.45	N 17.34		
12a	PA	p-Br-C_6H_4-	$C_{19}H_{13}BrN_4$ (377.26)	calc. -	-	N 14.95	155-57	67
				found -	-	N 15.20		
12b	PA	p-F-C_6H_4-	$C_{19}H_{13}FN_4$ (316.35)	calc. -	-	N 17.78	129-30	57
				found -	-	N 17.92		

Abbreviations: IQ: 1-Isoquinolyl; Q: 2-Quinolyl; PA: 6-Phenanthridyl

Aryltetrazolo(1,5-a)quinolinium (10) and tetrazolo(5,1-a)isoquinolinium salts (7)

To a mixture of tribromophenol bromine (72 g; 186 mmol) and dichloromethane (700 mol) solid triazene 6 or 9 was added with stirring at 40°C. After a period of 30

min the precipitated crystals were filtered off, suspended in nitromethane (40 ml) and treated with cyclohexene similarly as described for 4. The bromide salt were finally converted to fluoroborates in methanol solution by addition of hydrogen fluoroboric acid. Data for products are shown in Table 4.

Compound 10b: ^{1}H-NMR: δ 7.65, 8.25 (AA'BB', 4H; J_{AB}= 8.25 Hz); 8.81 (1H, d, J: 7.8, H-5); 7.8-8.4 (m, 5H).

Compound 7b: ^{1}H-NMR: δ 9.2-9.0 (m, 1H, H-10); 9.10 (s, 1H, H-5); 8.7-8.2 (m, 3H, H-7,8,9); 8.2-7.8 (AA'BB', 4H, J_{AB} = 9.5 Hz).

Table 4. Characteristics of tetrazolo(5,1-a)isoquinolinium, tetrazolo(1,5-a)-quinolinium and tetrazolo(1,5-f)phenanthridinium salts (7, 10, 13)

No	Hetero-cycle	Ar	Analyses		m.p.	%
7a	IQ	C_6H_5-	$C_{15}H_{10}BBrF_4N_4$ (413.01)	cald. C 43.60 H 2.44 N 13.57 found C 43.69 H 2.89 N 13.82	290-92	53
7b	IQ	4-Br-C_6H_4-	$C_{15}H_9BBr_2F_4N_4$ (491.92)	calc. C 36.62 H 1.84 N 11.39 found C 36.80 H.207 N 11.16	198-200	72
10a	Q	C_6H_5-	$C_{15}H_{11}BF_4N_4$ (334.11)	calc. C 63.76 H 3.31 N 16.72 found C 53.58 H 3.63 N 16.54	206-09	82
10b	Q	4-Cl-C_6H_4-	$C_{15}H_{10}BClF_4N_4$ (368.55)	calc. C 48.88 H 2.74 N 15.20 found C 49.06 H 3.06 N 14.90	247-48	87
10c	Q	4-Br-C_6H_4-	$C_{15}H_{10}BBrF_4N_4$ (413.01)	calc. C 43.60 H 2.44 N 13.57 found	208-09	79
10e	Q	3.4-Cl-C_6H_3-	$C_{15}H_9BCl_2N_4$ (403.00)	calc. C 44.59 H 2.25 N 13.87 found C 44.72 H 2.64 N 13.67	256-58	74
13a	PA	4-Br-C_6H_4-	$C_{19}H_{12}Br_2N_4$ (456.17)	calc. - - N 12.82 found - - N 11.93	238-40	66
13b	PA	4-F-C_6H_4-	$C_{19}H_{12}BrN_4F$ (395.26)	calc. - - N 14.25 found - - N 14.40	239-41	45

Abbreviations: IQ: Isoquinolyl; Q: 2-Quinolyl; PA: 6-Phenanthridyl

1-(6-Phenanthridyl)-3-aryltriazenes (12)

5-Aminophenanthridine (11) (0.5 g; 2.6 mmol) was dissolved in methanol (80 ml), the solution was mixed with a solution of sodium acetate hydrate (3.0 g) in water (30 ml), and the resulting mixture was treated with a saturated solution of diazonium fluoroborate (2.7 mmol) in acetonitrile at -2 — 0°C. The mixture was stirred for additional 6 h at this temperature and was stored overnight in a refrigerator. The precipitated crude product was filtered and recrystallized from benzene-cyclohexane (For data, see Table 3).

3-Aryltetrazolo(1,5-f)phenanthridinium bromides (13)

Phenanthridyltriazene (12) (1.2 mmol) was added to a solution of tribromophenol bromine (3) (2,0 g; 4.9 mmol) in dichloromethane (20 ml) at room temperature, whereupon a red solution was first formed and, in some minutes, a yellow solid precipitated. The product was filtered off after 15 min and was treated with cyclohexene as described above for the analogous cases. Data of the bromide salts are collected in Table 4.

N-Arylamino-quinolones, - isoquinolones and -phenanthridones (14, 15, 16)

A mixture of tetrazolium salt (7, 10, 13) (1.0 mmol) and acetonitrile (10 ml) was treated with a 10 per cent solution of tetraethylammonium hydroxide in water (5 ml) and the reaction mixture was stirred at room temperature. Gas evolution was observed and a solid was separated. The mixture was stored overnight, the product was filtered and recrystallized from toluene. For data, see Table 5.

Table 5. Characteristics of N-arylamino-quinolones, -isoquinolones and -phenanthridones (14, 15, 16; Ar = 4-Br-C_6H_4)

No	Analyses		m.p.	%	Spectroscopic data
14	$C_{15}H_{11}BrN_2O$ (315.18)	calc. C 57.15 H 3.52 N 8.89 found C 57.02 H 3.70 N 9.06	196	78	IR(KBr): 2900-3300(NH); 1640 (C=O) cm^{-1} MS: 315 (M^+) 52% 171 ($BrC_6H_4NH^+$) 100%
15	$C_{15}H_{10}Br_2N_2O$ (394.09)	calc. C 45.71 H 2.56 N 7.11 found C 45.55 H 2.33 N 7.01	185	74	IR(KBr): 3100-3300(NH); 1640 (C=O) cm^{-1} MS: 394 (M^+M 26% 171 ($BrC_6H_4NH^+$) 100%
16	$C_{19}H_{13}BrN_2O$ (365.24)	calc. C 62.48 H 3.59 N 7.67 found C 62.22 H 3.70 N 7.49	255	82	IR(KBr): 3100-3300(NH); 1660 (C=O) cm^{-1} MS: 365 (M^+) 100% 171 ($BrC_6H_4NH^+$) 39%

3-(4-Chlorophenyl)-1-methylcrotonaldehyde (17)

A solution of 3-p-chlorophenyl-6-methyltetrazolo(1,5-a)pyridinium fluoroborate (4g) (0.6 g; 1.9 mmol) in acetonitrile (10 ml) was stirred and treated with a 10 per cent solution of tetraethylammonium hydroxide in water (6 ml). After a period of 2 g the reaction mixture was poured onto water (30 ml) and was extracted with dichloromethane. Crystallization from ether-petroleum ether gave 0.36 g (73%) of colourless crystals, m.p. 55-57°C. Calc. for $C_{12}H_{11}N_4ClO$: C, 54.86; H, 4.22; N, 21.33. Found: C, 54.55; H, 4.02; N, 21.10. ^{1}H-NMR ($CDCl_3$): δ 9.43 (s, 1H, CHO); 8.1-7.3 (AA'BB', 4H, H-Ar); 6.75 (t, 1H, H-olef.); 4.0 (d, 2H, CH_2) and 1.85 (s, 3H, CH_3).

Reaction of tetrazolo(1,5-a)pyridinium salts (4) with sodium methoxide

Method (a). A solution of tetrazolo(1,5-a)pyridinium salt (4) (10 mmol) in acetonitrile was treated with a solution of sodium methoxide in methanol (prepared from 1.55 g /67 mmol/ sodium in 150 ml of methanol), and the resulting red solution was stored at room temperature for 15 h. The precipitated diene ether (18) was filtered off, the mother liquor was evaporated and the residue was treated with water. A colourless precipitate was formed which was crystallized from toluene (Table 6).

Method (b). A solution of tetrazolo(1,5-a)pyridinium salt (4) (1o mmol) in acetonitrile was treated with sodium methoxide as above. The resulting reaction mixture, after a 15 h storage, was evaporated, the residue was triturated with toluene, the colourless precipitate filtered off and recrystallized from toluene (Table 6).

Table 6. Characteristics of N-arylaminopyridones (19)

No m.p.	%	Analyses C	H	N	Cl	Method	^{1}H-NMR shifts and couplings H-6	H-5	H-4	H-3
19a		$C_{19}H_9ClN_2O$ (220.67)					7.33	5.95	7.17	6.23
R = H Ar = 4-Cl-C_6H_4-		calc. 59.87	4.72	12.70	16.07	(a)	(Ar: 6.22; 6.86; AA'BB' J_{AB} = 8.14; $J_{3,4}$ = 7.10 $J_{4,5}$=7.02; $J_{5,6}$=6.40 Hz)			
198	26									
19b		$C_{12}H_{11}ClN_2O$ (234.69)				(a)	7.47	6.13	-	6.42
R = 4-CH_3		calc. 61.41	4.72	11.94	15.11		(Me: 2.28; Ar: 6.38; 6.88 AA'BB': J_{AB} = 8.12:			
Ar=4-Cl-C_6H_4-		found 61.52	5.10	12.13	14.96		$J_{5,6}$ = 6.85 Hz)			
195	22									
19c		$C_{12}H_{11}ClN_2O$ (234.69)				(b)	7.53	-	7.41	6.52
R = 5-CH_3		calc. 61.41	4.72	11.94	15.11		(Me: 2.02; Ar: 6.22;			
Ar = 4-Cl-C_6H_4-		found 61.84	4.92	11.76	14.87		6.86 AA'BB': J_{AB} = 8.18 Hz)			
167	72									

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[8]A mechanism similar to the case of related systems (see ref. 1 and 7) is supposed.

[9]To the best of our knowledge electrophilic aromatic bromination by tribromophenol bromine (TBB) was first carried out by us[10]. Our earlier observation (see ref. 2) showed that TBB is, in the respect, superior to the generally used N-bromo succinimide. In the cases presented here, TBB proved to be the only reagent to accomplish the desired ring closure.

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