and 0.5 ml. of 30% hydrogen peroxide was heated for 12 hr. at 56°, followed by 10 hr. at 100°. Isolated and recrystallized as in the case of the isomer (IIb), it yielded 0.27 g. (47%) of tan crystals, dec. about 340°. The analytical sample crystallized from methanol as light yellow irregular crystals, m.p. 340° dec., and was identical to the perchlorate prepared from an authentic[4] sample of the bromide.

Anal. Calcd. for $C_{15}H_{14}ClNO_4$: C, 58.53; H, 4.59; N, 4.55. Found: C, 58.44; H, 4.64; N, 4.60.

7-Methyl-10-methoxyphenanthridizinium Perchlorate (IId).—The procedure was the same as in the preparation of the 7,10-dimethylphenanthridizinum perchlorate (IIc), except that the reaction time at 56 and 100° was 3 hr. each. From 0.36 g. of 3-methoxy-12-methylpyrido[2,1-*b*]benzo[*f*]-[1,3]thiazepinium perchlorate[2] (Id), 3 ml. of acetic acid, and 0.5 ml. of hydrogen peroxide, 0.13 g. (40%) of a yellow crystalline material was obtained, m.p. 319–320°. The analytical sample crystallized as needles, m.p. 322–323°. This material was identical with the perchlorate salt obtained from an authentic sample of bromide.[4]

Anal. Calcd. for $C_{15}H_{14}ClNO_5$: C, 55.65; H, 4.36; N, 4.33. Found: C, 55.78; H, 4.42; N, 4.37.

Nitration of 12-Methylpyrido[2,1-*b*]benzo[*f*][1,3]thiazepinium Perchlorate (Ia).—A solution of 1 g. of 12-methylpyrido[2,1-*b*]benzo[*f*][1,3]thiazepinium perchlorate in 20 ml. of concentrated nitric acid was heated at 100° for 16 hr. The solution was concentrated under reduced pressure, then 20 ml. of ethanol was added and the solution was once more concentrated. The residue was crystallized from methanol–ethyl acetate, affording 0.43 g. (38%) of colorless crystals, m.p. 240–245° dec. The analytical sample consisted of fine colorless needles, m.p. 255–257° and had the composition expected for a mononitration product, λ_{max} mμ (log ε) 215 (4.30), 270 (4.24); λ_{min} 238 (4.03).

Anal. Calcd. for $C_{14}H_{11}ClN_2O_6$: C, 45.36; H, 2.99; N, 7.56. Found: C, 44.97; H, 2.94; N, 7.88.

Aromatic Nuclei by the Sulfur Extrusion Reaction. II.[1] Phenanthridizinium Salts with a Substituent in Ring A

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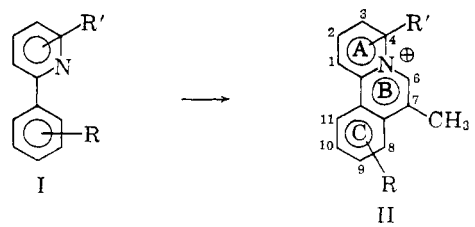
Through the use of the oxidative sulfur extrusion reaction, the first phenanthridizinium salts (VI) with alkyl substituents in ring A (pyrido ring) have been prepared. It was observed that the cyclization of 2-(4-*t*-butylphenylthio)pyridinium iodide (IVg) in polyphosphoric acid to yield the thiazepinium perchlorate (V) was accompanied by sulfur extrusion to afford some of the corresponding phenanthridizinium salt (VIg). When 2-(phenylthio)pyridine (VII) is heated in polyphosphoric acid in the presence of air, the corresponding sulfone (VIII) is formed.

With the exception of the examples recorded in the first paper of this series,[1] the only synthesis of methylphenanthridizinium salts (II. R′ = H, R = CH_3) has been carried out by the use of the aromatic cyclodehydration method.[3,4] While this method provides for the introduction of a methyl group into rings B and C, its usefulness as a means for the synthesis of compounds with an alkyl group in ring A is severely limited by the difficulty in obtaining the proper 2-phenylpyridines (I, R′ = CH_3). Since the various 2-bromo(methylpyridines) are readily available,[5] it seemed probable that the aryl sulfides (III) derived from them might be converted to thiazepinium salts (IV). These could in turn be made to undergo sulfur extrusion yielding phenanthridizinium salts (V) having a methyl group in ring A. It was hoped that such a study would provide additional information concerning the effect of substituents on the sulfur extrusion reaction.



The major results of this study are summarized in Table I. It will be noted that the yields of the phenylthiopyridines (III) was quite high, only one being below 90%. The quaternization reactions using iodoacetone were successful with the exception of that involving the sulfide IIIf in which the nitrogen of the pyridine ring has two *ortho* substituents. This sterically hindered amine yielded no quaternary salt even after six months.

It was found that the direct cyclization of the quaternary iodides (IV) in polyphosphoric acid was usually quite successful. The earlier practice[6] had been to convert the iodides to the chlorides before cyclization to avoid complications which might rise out of the instability of the iodide ion in acid media. It had been anticipated that cyclization of the quaternary salt IVg, in which there is a *t*-butyl group in the phenyl group *para*

(1) For the preceding communication of this series, see *J. Org. Chem.*, **27**, 4475 (1962).

(2) This research was supported by a research grant (NSF-G 19901) of the National Science Foundation. Taken in part from a thesis submitted in partial fulfillment of the requirements for the Ph.D. degree, Duke University.

(3) C. K. Bradsher and L. E. Beavers, *J. Am. Chem. Soc.*, **77**, 453 (1955).

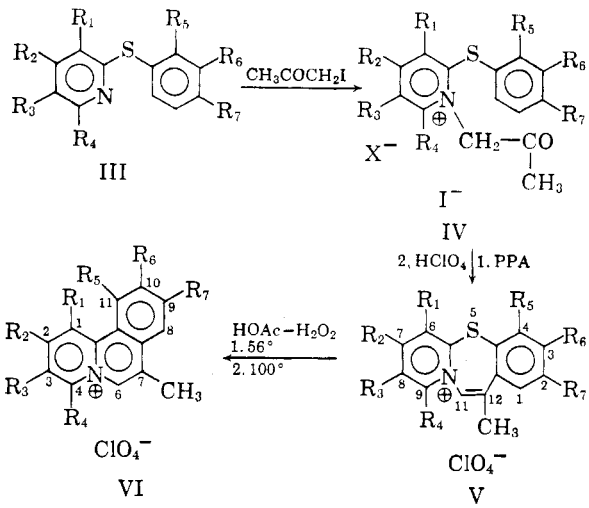
(4) C. K. Bradsher and K. B. Moser, *ibid.*, **81**, 1941 (1959).

(5) F. H. Case, *ibid.*, **68**, 2574 (1946).

(6) C. K. Bradsher, L. D. Quin, R. E. LeBleu, and J. W. McDonald, *J. Org. Chem.*, **26**, 4944 (1961).

TABLE I

PHENANTHRIDIZINIUM SYNTHESIS



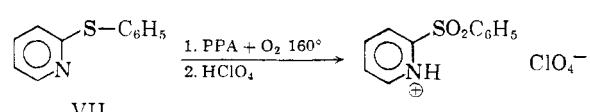
	R1	R2	R3	R4	R5	R6	R7	III[a] %	IV Days	IV %	V %	VI Time, hr. 56°	VI Time, hr. 100°	VI %
a	Me	H	H	H	H	H	H	96	5	60	81	12	12	0[b]
b	H	Me	H	H	H	H	H	93	1	82[c]	80[d]	12	12	29
c	H	Me	H	H	Me	H	H	98	1	80	85[e]	12	8	23
d	H	Me	H	H	H	Me	H	91	1	82	69[f]	12	8	37
e	H	H	Me	H	H	H	H	96	5	89	52	12	12	24[g]
f	H	H	H	Me	H	H	H	97	180	0[h]				
g	H	H	H	H	H	H	*t*-Bu	80	10	82	14[i]	[j]		

[a] Yields calculated from 2-bromopyridine. [b] A large part (63%) of the starting material was recovered. [c] With chloroacetone in boiling ethanol, an 84% yield of the quaternary chloride was obtained. [d] Yield from cyclization of the chloride. [e] Yield obtained by cyclization of the crude chloride. The over-all yield from the sulfide (IIIc) was 73%. [f] Yield from the crude chloride. The over-all yield from the sulfide (IIId) was 48%. [g] Part (40%) of the starting material was recovered. [h] Likewise, in boiling ethanol with chloroacetone no quaternary salt was obtained. [i] As a by-product an 11% yield of the desulfurized product (phenanthridizinium salt, VIf) was obtained. [j] Since the phenanthridizinium salt (VIf) was available from the previous step, no attempt was made to carry out the oxidative sulfur extrusion reaction.

to the sulfur atom, might be difficult. Efforts to cyclize a lower homolog (R_7 = CH_3) were reported[6] to have failed. The surprising observation was that some of the sulfur extrusion product, 7-methyl-9-*t*-butylphenanthridizinium perchlorate (VIg) was isolated. This appears to be the first instance in which sulfur extrusion has been encountered during a polyphosphoric acid-catalyzed cyclization.

The yields in the sulfur extrusion step (V→VI) were poor, but no effort was made to find the optimum conditions for each reaction. Only one reaction failed completely. 6,12-Dimethylpyrido-[2,1-*b*][1,3]thiazepinium perchlorate (Va) did not yield any sulfur extrusion product (VIa) and the majority of the starting material was recovered. The explanation that the methyl group (R_1) in the pyridine ring acts in a purely steric way to prevent oxidation of the adjacent sulfur atom does not seem adequate. It has been reported[1] that the presence of a methyl group adjacent to the sulfur atom, but situated in the benzene ring (V. R_5 = CH_3) does not prevent ring contraction (31% yield). Since Ve, the isomer of Va in which the methyl is *para* rather than *ortho* to the sulfur atom, also reacted sluggishly (40% of the starting material (Ve) was recovered) it seems likely that electronic as well as steric factors may be operative in the failure of Va to undergo sulfur extrusion. The ultraviolet absorption spectra of the new thiazepinium (V) and phenanthridizinium salts are recorded in Table II.

When it was learned that the polyphosphoric acid cyclization of 1-acetonyl-2-(4-*t*-butylphenylthio)pyridinium iodide (IVg) was accompanied by sulfur extrusion in hot polyphosphoric acid, the question arose whether the reaction was purely thermal or whether air oxidation was involved. While this question is still unanswered, it has been demonstrated that when a simple analog of IVg,



VII VIII

2-phenylthiopyridine (VII), was heated in polyphosphoric acid at 150–160° while a stream of oxygen was passed through, the corresponding

TABLE II

ULTRAVIOLET ABSORPTION SPECTRA

Substituents	Formula	Maxima λ, mμ	Maxima log ε	Minima λ, mμ	Minima log ε
12-Methylpyrido[2,1-*b*]benzo[*f*][1,3]thiazepinium perchlorates (V)					
6-CH_3	Va	200	4.46	275	3.63
		314	3.80		
7-CH_3	Vb	203	4.53	273	3.76
		226*[a]	4.30		
		308	3.83		
4,7-di-CH_3	Vc	205	4.54		
		290*	3.72		
4,6-di-CH_3	Vd	206	4.49	283	3.71
		230*	4.32		
		313	3.75		
8-CH_3	Ve	203	4.46	281	3.65
		311	3.76		
7-Methylphenanthridizinium Perchlorates (VI)					
2-CH_3	VIb	223	4.42	227	4.40
		237	4.50	262	4.26
		255*	4.28	272	4.33
		268	4.34	316	3.62
		277	4.40	328	3.71
		324	3.76	347	3.82
		339	4.08		
		356	4.17		
2,11-di-CH_3	VIc	227*	4.44	258	4.07
		240	4.55	322	3.70
		283	4.49	334	3.73
		330	3.75	353	3.86
		345	3.98		
		362	4.06		
2,10-di-CH_3	VId	226	4.46	230	4.43
		243	4.57	269	4.23
		282	4.36	320	3.52
		330	3.70	334	3.69
		346	4.04	353	3.88
		362	4.16		
3-CH_3	VIe	230*	4.45	255	4.28
		238	4.50	262	4.30
		259	4.30	275	4.31
		269	4.36	298*	3.88
		278	4.32	317	3.70
		324	3.79	330	3.70
		339	4.06	347	3.79
		356	4.19		
9-*t*-Bu	VIf	225	4.44	205	4.05
		237	4.42	229	4.36
		271	4.39	253	4.24
		300*	3.84	315	3.76
		322	3.84	327	3.76
		337	4.08	344	3.82
		353	4.20		

[a] The asterisk (*) is used to denote a shoulder.

sulfone was formed and could be isolated in 25% yield as the perchlorate.

Experimental

All analyses were carried out by Dr. Ing. A. Schoeller, Kronach, Germany. All melting points were determined in capillaries in the Mel-Temp apparatus and, like the boiling points, are uncorrected. The ultraviolet absorption spectra were measured in 95% ethanol using 1-cm. matched quartz cells with a Cary Model 14 spectrophotometer.

2-Arylthiopyridines (III).—The procedure was essentially that described earlier[6,7] except that only a one-third molar excess of the mercaptan and triethylamine were employed, and the 2-day heating was carried out at steam bath temperature instead of 105–110°. The properties of the sulfides are recorded in Table III.

Picrates of the 2-Arylthiopyridines (III).—The picrates were prepared in ethanol solution and crystallized from methanol–ether (Table IV).

1-Acetonyl-2-arylthiopyridinium Salts (IV).—The quaternization reactions with iodoacetone were carried out at refrigerator temperature as described previously,[8] for the number of days indicated in Table I. The physical constants are reported in Table V.

1-Acetonyl-2-phenylthio-4-methylpyridinium Chloride (IVb. X = Cl).—A mixture of 0.05 mole of 2-phenylthio-4-methylpyridine and 0.15 mole of chloroacetone in 25 ml. of ethanol was refluxed for 30 hr. Most of the ethanol was evaporated, and ether added. After the mixture had stood for 24 hr. in the refrigerator, 12.4 g. (84%) of light yellow product was collected, m.p. 187–195°. An analytical sample was prepared from methanol–ether as colorless irregular needles, m.p. 205–207°.

Anal. Calcd. for $C_{15}H_{16}ClNOS$: C, 61.32; H, 5.49; N, 4.77. Found: C, 61.20; H, 5.43; N, 4.98.

12-Methylpyrido[2,1-*b*]benzo[*f*][1,3]thiazepinium Perchlorates (V).—For each gram of halide (either chloride or iodide) about 10 ml. of polyphosphoric acid was added, and the mixture was stirred for 12 hr. in a flask heated by a Wood's metal bath at 150–160°. At the end of the heating period the solution was diluted by the cautious addition of about 30 g. of ice. A 35% solution of perchloric acid was added until no further cloudiness was observed. The mixture was allowed to stand in the refrigerator for 24 hr., and the resulting precipitate collected and recrystallized from methanol (Norite). Thiazepinium salts were crystallized from methanol–ether (Table VI).

7-Methylphenanthridizinium Perchlorates (VI).—To a mixture containing 2 mmoles of the thiazepinium perchlorate and 12 ml. of acetic acid, 1 ml. of 30% hydrogen peroxide was added, and the resulting suspension heated in an acetone vapor bath (56°) with magnetic stirring. The thiazepinium salt dissolved rapidly, and heating was continued at 56° for about 12 hr., followed by a second heating period of about equal length (see Table I) at 100°. The solution was then allowed to stand in the refrigerator for 24 hr., and the crys-

TABLE III

2-ARYLTHIOPYRIDINES (III)

Comp.	B.p., (mm.)	$n^{25}D$	Formula	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found
a	130–132(0.5)	1.6330	$C_{12}H_{11}NS$	71.60	71.43	5.51	5.61	6.96	6.91
b	132–134(0.5)	1.6280	$C_{12}H_{11}NS$					6.96	6.70
c	120–122(0.5)	1.6182	$C_{13}H_{13}NS$	72.52	72.31	6.08	5.93	6.51	6.78
d	148–151(0.6)	1.6172	$C_{13}H_{13}NS$	72.52	72.00	6.08	6.20	6.51	6.39
e	130–132(0.4)	1.6298	$C_{12}H_{11}NS$					6.96	6.64
f	130–131(0.5)	1.6240	$C_{12}H_{11}NS$	71.60	71.11	5.51	5.46	6.96	7.03
g	205–210(8)	[a]	$C_{15}H_{17}NS$					5.76	5.73

[a] The material crystallized on storage, m.p. 46–49°.

TABLE IV

PICRATES OF 2-ARYLTHIOPYRIDINES (III)

Comp.	M.p.	Form	Formula	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found
a	150–152	Bright yel. need.	$C_{18}H_{14}N_4O_7S$	50.23	50.09	3.28	3.41	13.02	12.89
b	159–160	Irreg. yel. plates	$C_{18}H_{14}N_4O_7S$	50.23	50.11	3.28	3.24		
c	127–129	Yel. prisms	$C_{19}H_{16}N_4O_7S$	51.35	51.88	3.63	3.51	12.61	12.63
d	134–136	Sm. yel. need.	$C_{19}H_{16}N_4O_7S$	51.35	51.35	3.63	3.30	12.61	12.89
e	165–167	Yel. need.	$C_{18}H_{14}N_4O_7S$	50.23	50.04	3.28	3.46	13.02	13.08

TABLE V

1-ACETONYL-2-ARYLTHIOPYRIDINIUM SALTS (IV)

Comp.	X^-	M.p.[a]	Form[b]	Formula	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found
a	I	162–163	Yel. powd.	$C_{15}H_{16}INOS$	46.76	46.88	4.19	4.18	3.63	3.89
a	ClO_4	159–161	Col. need.	$C_{15}H_{16}ClNO_5S$	50.35	50.05	4.51	4.52	3.83	4.08
b	I	180–182	Col. irreg.	$C_{15}H_{16}INOS$	46.76	46.64	4.19	4.15	3.63	3.76
b	ClO_4	192–194	Col. diamonds	$C_{15}H_{16}ClNO_5S$	50.35	50.35	4.51	4.50	3.83	3.90
c	I	190–191	Col. irreg.	$C_{16}H_{18}INOS$	48.13	48.34	4.54	4.61	3.51	3.69
c	ClO_4	191–193	Col. diamonds	$C_{16}H_{18}ClNO_5S$	51.68	51.74	4.88	4.92	3.77	3.76
d	I	170–171	Col. irreg.	$C_{16}H_{18}INOS$	48.13	48.25	4.54	4.56	3.51	3.80
d	ClO_4	164–165	Col. irreg. pl.	$C_{16}H_{18}ClNO_5S$	51.68	51.76	4.88	5.06	3.77	3.91
e	I	171–173	Col. irreg. need.	$C_{15}H_{16}INOS$	46.76	46.89	4.19	4.23	3.63	3.78
e	ClO_4	150–152	Col. irreg. need.	$C_{15}H_{16}ClNO_5S$	50.35	50.44	4.51	4.66	3.83	3.92
g	I	168–169	Yel. irreg.[c]	$C_{18}H_{22}INOS$	50.59	50.92	5.19	5.12	3.28	3.37
g	ClO_4	167–168	Col. pl.[c]	$C_{18}H_{22}ClNO_5S$	54.06	54.16	5.55	5.56	3.50	3.55

[a] All melting points are for analytical samples. All preparations melted within 10° of the analytical sample. [b] All samples were crystallized from methanol–ether. [c] From methanol.

TABLE VI

PYRIDO[2,1-*b*]BENZO[*f*][1,3]THIAZEPINIUM PERCHLORATES (V)

Comp.	M.p.	Form	Formula	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found
a	212–214	Lt. yel. pl.	$C_{15}H_{14}ClNO_4S$	53.02	52.93	4.15	4.18	4.12	4.31
b	193–196	Lt. yel. irreg. needles[a]	$C_{15}H_{14}ClNO_4S$	53.02	53.22	4.15	4.22	4.12	4.58
c	184–186	Col. irreg. pl.	$C_{16}H_{16}ClNO_4S$	54.31	54.46	4.56	4.58	3.96	4.15
d	176–178	Yel. irreg. pl.	$C_{16}H_{16}ClNO_4S$	54.31	54.31	4.56	4.62	3.96	4.13
e	178–180	Sm. col. need.	$C_{15}H_{14}ClNO_4S$	53.02	53.27	4.15	4.14	4.12	4.28
g	134–135	Col. irreg. pl.	$C_{18}H_{20}ClNO_4S$	56.61	56.29	5.28	5.28	3.61	4.01

[a] Sample crystallized from methanol.

TABLE VII

7-METHYLPHENANTHRIDIZINIUM PERCHLORATES (VI)

Comp.	M.p.	Form	Formula	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found
b	>235	Col. irreg.	$C_{15}H_{14}ClNO_4$	58.53	58.85	4.59	4.45	4.55	4.87
c	185–186	Col. irreg. need.	$C_{16}H_{16}ClNO_4$	59.72	59.93	5.01	4.99	4.35	4.37
d	>290	Sm. col. need.	$C_{16}H_{16}ClNO_4$	59.72	59.87	5.01	5.19	4.35	4.58
e	262–264	Thin col. need.	$C_{15}H_{14}ClNO_4$	58.83	58.85	4.59	4.45	4.55	4.87
g	215–217	Lt. yel. pl.	$C_{18}H_{20}ClNO_4$	61.80	61.41	5.76	5.81	4.05	4.20

tals collected. The product was recrystallized from methanol–ethyl acetate.

2-(Phenylsulfonyl)pyridinium Perchlorate (VIII). To 40 ml. of polyphosphoric acid 4.4 g. of 2-(phenylthio)pyridine (VII) was added, and the mixture was stirred in a metal bath at 150–160° for 12 hr. while a stream of air was passed through. The mixture was diluted by the cautious addition of about 200 g. of ice, and to the resulting solution 35% perchloric acid was added until no further cloudiness was observed. The solid which precipitated when the solution had stood for 24 hr. in the refrigerator was collected and recrystallized from methanol–ether (Norite), yield 1.85 g. (25%), m.p. 184–187°. The analytical sample was prepared from methanol–ether as colorless plates, m.p. 190–192°, and had the composition of a perchlorate salt of the sulfone (VIII).

Anal. Calcd. for $C_{11}H_{10}ClNO_6S$: C, 41.32; H, 3.15; N, 4.38; S, 10.03. Found: C, 41.20; H, 2.86, N, 4.41; S, 9.90.

(7) L. G. S. Brooker, G. H. Keyes, R. H. Sprague, R. H. Van Dyke, E. Van Lane, G. Van Zandt, and F. L. White, *J. Am. Chem. Soc.*, **73**, 5329 (1951).