mole) of pyridine-3-aldehyde in 50 ml. of ethanol was added 10 ml. of 50% potassium hydroxide solution over a period of 20 min. The mixture was stirred for 4 hr. and was then acidified with ice-cold acetic acid. Crystallization of the precipitate from ethanol gave 1.1 g. (21%) of yellow needles, m.p. 137–138°.

Four other chalcones were prepared by this method: *1-(2-hydroxyphenyl) - 3 - (4 - pyridyl)propenone, 1 - (2 - hydroxy-4 - methoxyphenyl) - 3 - (2 - pyridyl)propenone, 1 - (2 - hydroxy-4 - methoxyphenyl) - 3 - (4 - pyridyl)propenone* and *1 - (2-hydroxy - 4 - methoxyphenyl) - 3 - (2 - thienyl)propenone;* the other chalcones were prepared by the following procedure.

(2) *1-(2-Hydroxyphenyl)-3-(2-pyridyl)propenone* was prepared by sodium methoxide condensation. To a mixture of 2.72 g. (0.02 mole) of 2'-hydroxyacetophenone and 3.20 g. (0.03 mole) of pyridine-2-aldehyde in 40 ml. of methanol was added a solution of 1.1 g. of sodium in 20 ml. of methanol. The reaction mixture was kept overnight at room temperature and was then poured onto crushed ice and acetic acid. The precipitate which formed was crystallized from benzene, giving 1.1 g. (24%) of the chalcone as yellow needles, m.p. 98–99°.

Melting points, percentage yields and analytical data of the chalcones are given in Table IV.

Acknowledgment. We wish to express our thanks to the National Institutes of Health, Bethesda, Md., for the provision of a research grant.

DUBLIN, IRELAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Aromatic Cyclodehydration. XLIX. Pyrido[2,1-b]benzo[f]-1,3-thiazepinium Salts[1]

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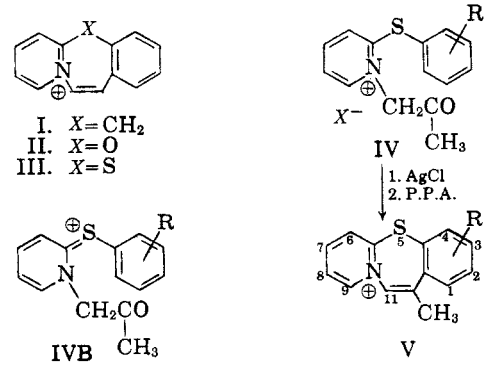
Received June 5, 1961

The first pyrido[2,1-b]benzo[f]-1,3-thiazepinium salts have been prepared by quaternization of suitable 2-phenylthiopyridines with iodoacetone, followed by cyclization of the quaternary salts in polyphosphoric acid at 160°. The new pyridobenzothiazepinium salts include the 12-methyl perchlorate and three of its derivatives.

The success met with[3] in the synthesis of the first morphanthridizinium salts (I) led to an extension of the general method to the preparation of the first pyridobenzoxazepinium salts (II),[4] in which the methylene bridge has been replaced by an oxygen atom. A logical sequel was an attempt to prepare the related but unknown pyrido[2,1-b]benzo[f]-1,3-thiazepinium salts (III). The nearest approach to such a system appears to be 11-phenyldibenzo-[b,f][1,4]thiazepine which was reported[5] to have been synthesized with the expectation that it might show quasi-aromatic properties. The unshared electrons on the sulfur bridge of the new pyridobenzothiazepinium salts (III) would be expected to delocalize (to a small extent) into the pyridine ring, conferring on the system a resonance stabilization which has no counterpart in the morphanthridizinium system (I). On the other hand it would not be expected that delocalization of the unshared electrons from sulfur would be so extensive as that from the oxygen bridge of the pyridobenzoxazepinium salts (II).[6]

The acetonyl quaternary iodides (VI, X = I) were readily formed by the reaction of iodoacetone with the easily prepared[7] 2-arylthiopyridines(V). The quaternary iodides were converted to the corresponding chlorides (VI, X = Cl) before all cyclization attempts. It had been found earlier[3] that 1-acetonyl-2-benzylpyridinium chloride, when refluxed for five days in 48% hydrobromic acid, was cyclized to the morphanthridizinium ion (I) in 75% yield. Under the same reaction conditions the 1-acetonyl-2-phenylthiopyridinium salt (VI) was recovered unchanged (as the perchlorate).



The great difference in ease of cyclization evidenced when the methylene bridge is replaced by sulfur can best be explained by invoking resonance. If B makes any significant contribution to the res-

(1) For the preceding communication of this series see *J. Org. Chem.*, **26**, 3278 (1961).

(2) This research was supported by a research grant (NSF-G6215) of the National Science Foundation.

(3) K. B. Moser and C. K. Bradsher, *J. Am. Chem. Soc.*, **81**, 2547 (1959).

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(6) For a discussion of the effect of delocalization on the bond angles of diphenyl ether and diphenyl sulfide see R. J. Gillespie, *J. Am. Chem. Soc.*, **82**, 5978 (1960).

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TABLE I

2-PHENYLTHIOPYRIDINES

Aryl Subst.	Yield,[a] %	B.P. (Mm.)	Formula	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found
H	99	154–158 (6)[b]	$C_{11}H_9NS$						
2-CH_3	84	165–175 (6)	$C_{12}H_{11}NS$	71.60	71.20	5.51	5.66	6.96	6.75
3-CH_3	77	174–180 (3)	$C_{12}H_{11}NS$	71.60	71.42	5.51	5.59	6.96	6.82
4-CH_3	94	175–180 (6)	$C_{12}H_{11}NS$	71.60	71.29	5.51	5.41	6.96	7.06
4-Cl	87	185–190 (10)	$C_{11}H_8NSCl$	59.59	59.81	3.64	3.85	6.32	6.57

[a] Based on 2-bromopyridine. [b] Lit.[7] b.p. 160–162° (8 mm.).

TABLE II

1-ACETONYL-2-PHENYLTHIOPYRIDINIUM SALTS

R	VI X	Yield, %	M.P.	Formula	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found
H	I	91	177–178[a]	$C_{14}H_{14}INOS$	45.29	45.24	3.80	3.75	3.77	3.78
H	ClO_4	—	153–154[b]	$C_{14}H_{14}ClNO_5S$	48.91	49.05	4.10	4.26	4.10	4.07
2-CH_3	I	86	159–160[c]	$C_{15}H_{16}INOS$	46.76	46.62	4.19	4.17	3.63	3.71
2-CH_3	ClO_4	—	169–171[b]	$C_{15}H_{16}ClNO_5S$	50.35	50.27	4.51	4.42	3.83	4.01
3-CH_3	ClO_4	—	126–127[d]	$C_{15}H_{16}ClNO_5S$	50.35	50.40	4.51	4.33	3.83	3.96
4-CH_3	I	89.5	163–164[b]	$C_{15}H_{16}INOS$	46.76	46.89	4.19	4.22	3.63	3.72
4-CH_3	ClO_4	—	159–161[e]	$C_{15}H_{16}ClNO_5S$	50.35	50.35	4.51	4.31	3.83	4.25
4-Cl	I	68.5	167–168[f]	$C_{14}H_{13}ClINOS$	41.45	41.57	3.23	3.22	3.45	3.57
4-Cl	ClO_4	—	226–229[f]	$C_{14}H_{13}Cl_2NO_5S$	44.45	44.40	3.46	3.49	3.70	3.77

[a] Colorless diamond-shaped crystals. [b] Colorless needles. [c] Yellow needles. [d] Yellow microcrystalline powder. [e] Colorless irregular needles. [f] Light yellow irregular crystals.

onance hybrid, the phenylthio ring would not be expected to undergo electrophilic attack as readily as does that of the benzyl group.

Under more drastic conditions, in polyphosphoric acid at 150–160°, 1-acetonyl-2-phenylthiopyridinium chloride (IV) could be cyclized in 35% yield. It is not too surprising that the oxygen analog, 1-acetonyl-2-phenoxypyridinium chloride is not cyclized by polyphosphoric acid at 165°, since oxygen can acquire a positive charge through delocalization of electrons more readily than can sulfur. The results of the cyclization experiments are summarized in Table III.

It is less surprising to learn that introduction of a methyl group into the *ortho* and *meta* positions of the phenylthio ring has a beneficial effect on the yield of cyclization product than to find that a methyl group in the *para* position evidently *inhibits* cyclization. Since chlorine is known to be electron withdrawing it might have been predicted that cyclization into the chlorinated ring would be difficult at best. From *m*-methoxybenzenethiol,[8] following the same route except that the cyclization step was carried out at 100° in concentrated hydrochloric acid, 3-methoxy-12-methylpyrido[2,1-b-]benzo[f]-1,3-thiazepinium (V, R = OCH_3) perchlorate was obtained in 12% yield. This thiazepinium compound had an infrared absorption spectrum very similar to the oxygen analog, 3-methoxy-12-methylpyrido[2,1-b]benzo-[f]-1,3-oxazepinium perchlorate[4] (*Cf.* II), but the ultraviolet absorption spectrum (Table III) showed that the sulfur compound exhibited greater absorption at longer wave lengths [second maximum at 327 mμ (log ε 3.82) as compared with 288 mμ (log ε 4.08) reported[4] for the oxygen analog].

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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 determined in 95% ethanol solution using the *Warren Spectracord* spectrophotometer with 1-cm. silica cells.

2-Arylthiopyridines. The procedure was essentially that reported earlier[7] for the preparation of phenylthiopyridine. A mixture containing 1 mole equivalent of 2-bromopyridine with 2 equivalents each of arylthiol and triethylamine was heated for 2 days at 105–110°. The reaction mixture was made alkaline with sodium hydroxide and extracted with benzene. The washed benzene extract was concentrated and the residue distilled under reduced pressure. The results are summarized in Table I.

1-Acetonyl-2-phenylthiopyridinium salts (IV). 2-Arylthiopyridine (0.1 mole) and iodoacetone (0.11 mole) with 1 ml. of dimethylformamide were placed in a stoppered flask and allowed to stand in the refrigerator for 2 days. Trituration of the product with ethyl acetate gave material suitable for cyclization. The analytical samples were prepared by crystallization from methanol. Perchlorates were obtained by addition of 35% perchloric acid to an aqueous solution of the iodide and recrystallized from methanol. The results are summarized in Table II.

12-Methylpyrido[2,1-b]benzo[f]-1,3-thiazepinium perchlorates (V). A 25-g. portion of the 1-acetonyl-2-phenylthiopyridinium iodide in 300 ml. of water was stirred for 4 hr. with an aqueous suspension of thoroughly washed silver chloride which had been prepared from 32 g. of silver nitrate. The silver halides were filtered and the filtrate concentrated at 100° under vacuum until only a small amount of oily solid remained. To this was added approximately 200 ml. of

TABLE III

12-METHYLPYRIDO[2,1-b]BENZO[f]1,3-THIAZEPINIUM PERCHLORATES (V)

V, R =	Yield, %	M.P.[c]	Formula	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found
H	35[a]	163–164[d]	$C_{14}H_{12}ClNO_4S$	51.61	51.48	3.71	3.70	4.30	4.51
4-CH_3	61	252–255[e]	$C_{15}H_{14}ClNO_4S$	53.02	53.34	4.15	4.50	4.12	4.39
3-CH_3	54	133–135[f]	$C_{15}H_{14}ClNO_4S$	53.02	53.04	4.15	4.11	4.12	4.40
3-OCH_3	12[b]	241.5–242.5[g]	$C_{15}H_{14}ClNO_5S$	50.63	50.56	3.97	4.08	3.94	4.20

[a] A cyclization attempt carried out in refluxing 48% hydrobromic acid (5 days) yielded only starting material (recovered as the perchlorate). [b] Over-all yield from *m*-methoxybenzenethiol. The procedure was the same as in the other cases, except that cyclization was carried out by heating for 24 hr. in concentrated hydrochloric acid. [c] All analytical samples were recrystallized from methanol. [d] Long colorless needles, λ_{max} 316 mμ, log ε 4.86. [e] Light brown needles, λ_{max} mμ (log ε) 275 (3.71), 322 (3.73). [f] Nearly colorless microcrystalline powder, λ_{max} 323 mμ, log ε 3.92. [g] Bright yellow needles, λ_{max} mμ (log ε) 235 (4.36), 327 (3.82).

polyphosphoric acid[9] and the mixture heated and stirred for 12 hr. in a Wood's metal bath at 150–160°. The mixture was diluted by the cautious addition of about 200 g. of ice in small portions. After the mixture had cooled to room temperature, 35% perchloric acid was added until no further cloudiness was observed. The mixture was allowed to stand in the refrigerator for 4 days, after which the solid material was collected and recrystallized from methanol (Norit) and ethyl acetate. The results are summarized in Table III.

(9) We are indebted to the Victor Chemical Co. for a generous gift of polyphosphoric acid.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HOPE COLLEGE]

Synthesis of *N*-Substituted Aminothianaphthenes by Condensation of Amines with Hydroxythianaphthenes by Reduction of *N*-Substituted Aminothianaphthene 1,1-Dioxides

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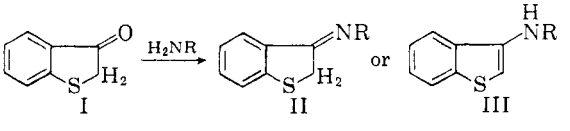
Received February 20, 1961

By condensing primary aliphatic amines and secondary aromatic amines with 3-hydroxythianaphthene, the corresponding 3-thianaphthenylamines have been synthesized. By the reaction of aliphatic secondary amines with 3-bromothianaphthene 1,1-dioxide and the reduction of the resulting aminothianaphthene 1,1-dioxides with lithium aluminum hydride, the corresponding thianaphthenylamines were formed. A method for the preparation of 2-hydroxythianaphthene in good yields has been found. Its condensation with amines has been explored.

The first attempt at synthesis, which involved the reduction of the substituted 3-amino-2-nitrothianaphthenes, proved unsuccessful. Also 3-hydroxythianaphthene was condensed with nitrosoamines to give anils.[1] Subsequent reduction with lithium aluminum hydroxide yielded only tarry materials.

Prior to this work, the only *N*-substituted aminothianaphthene which had been reported is 2-(1-piperidinyl)thianaphthene.[2] It was prepared by heating 2-bromothianaphthene in an autoclave with piperidine.

The condensation of aniline with 3-hydroxythianaphthene[3] has been reported by Fries and Bartholomaus,[4] who state that 3-keto-2,3-dihydrothianaphthene (II) is formed. No evidence for this structure was given. Although it is known that 3-hydroxythianaphthene exists almost entirely in the keto form,[5,6] it was considered possible that the effect of heat might cause a tautomeric shift to form III. The infrared spectrum of the



compound prepared in our laboratory shows a sharp N-H stretching band at 3400 cm.$^{-1}$ and no band at 1600–1700 cm.$^{-1}$, where the band for the Schiff's base should appear. The same N—H stretching band at 3400 cm.$^{-1}$, with no band at 1600–1700 cm.$^{-1}$, was observed in the spectrum of the compound made from benzylamine and 3-hydroxythianaphthene.

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