889. *4-Pyrones. Part IV.*[1] *Preparation and Reactions of Some 4-Pyridones and Thiopyridones.*

By MOHAMED A.-F. ELKASCHEF, MICHAEL H. NOSSEIR, and
(MRS.) AWATEF ABDEL-KADER.

1-Alkyl-4-pyridones and their 2,5-dibromo-derivatives are converted by phosphorus pentasulphide into dibromothiopyridones which revert to the pyridones on oxidation.

IN this paper we confirm results and a mechanism previously established by us.[2,3] Butylamine reacts with thiopyrones to give 1-butyl-4-thiopyridones, and also with the corresponding pyrones to give 1-butyl-4-pyridones. The weaker base, benzylamine, reacts only with the thiopyrones (which have a stronger $-T$ effect), to give 1-benzyl-4-thiopyridones.

The new pyridones afford 3,5-dibromo-derivatives and are converted into their sulphur analogues by phosphorus pentasulphide. The thiopyridones, with hydrogen peroxide in acetic acid, give the 1-alkyl-anhydro-1-hydroxypyridine-4-sulphonic acids. Bromination of the thiopyridones gave only resins, but their dibromo-compounds were obtained by the action of phosphorus pentasulphide on 1-alkyl-3,5-dibromo-4-pyridones. 1-Alkyl-3,5-dibromopyridine-4-sulphonic acids could not be obtained as the anhydropyridine-4-sulphonic acids resisted bromination and oxidation of the 1-alkyl-3,5-dibromo-4-thiopyridones by hydrogen peroxide afforded 3,5-dibromopyridones.

EXPERIMENTAL

Action of Butylamine on 2,6-*Dimethyl*-4-*pyrone*.—The pyrone (1 g.) and butylamine (5 c.c.) were refluxed in ethanol (30 c.c.) for 8 hr. 1-*Butyl*-2,6-*dimethyl*-4-*pyridone* (0·9 g.), left on evaporation of the solvent, crystallised from light petroleum (b. p. 70—80°) and had m. p. 65° (Found: C, 73·5; H, 9·3; N, 8·2. $C_{11}H_{17}NO$ requires C, 73·7; H, 9·5; N, 7·9%).

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[1] Part III, preceding paper.
[2] Elkaschef and Nosseir, *J. Amer. Chem. Soc.*, 1960, **82**, 4344.
[3] Elkaschef, Nosseir, and Abdel-Kader, *J.*, 1963, 440.

In a similar experiment with benzylamine the pyrone was recovered (m. p. and mixed m. p.[2] 132°).

Bromination of 1-*Butyl*-2,6-*dimethyl*-4-*pyridone*.—The pyridone (1 g.) in acetic acid (20 c.c.) was treated with bromine (2 g.) in acetic acid (5 c.c.), a solid (1·5 g.) separating. This was boiled with sodium hydrogen carbonate in alcohol and then collected. The 3,5-*dibromo-derivative* (1·4 g.), recrystallised from dilute ethanol, had m. p. 180° (Found: C, 39·4; H, 4·6; N, 4·3; Br, 47·1. $C_{11}H_{15}Br_2NO$ requires C, 39·2; H, 4·4; N, 4·2; Br, 47·4%).

Action of Amines on 2,6-*Dimethyl*-4-*thiopyrone*.—The thiopyrone (0·5 g.) and butylamine (4·0 c.c.) were refluxed in ethanol (40 c.c.) for 8 hr. 1-*Butyl*-2,6-*dimethyl*-4-*thiopyridone* (0·3 g.) that separated on concentration crystallised from ethanol and had m. p. 206° (Found: C, 67·5; H, 9·0; N, 6·9; S, 16·2. $C_{11}H_{17}NS$ requires 3, 67·7; H, 8·8; N, 7·2; S, 16·4%).

A similar experiment with benzylamine gave 1-*benzyl*-2,6-*dimethyl*-4-*thiopyridone* (0·4 g.), m. p. 208° (from ethanol) (Found: C, 73·2; H, 6·6; N, 5·6; S, 13·8. $C_{14}H_{15}NS$ requires C, 73·3; H, 6·6; N, 6·1; S, 14·0%).

Action of Amines on 2,6-*Diphenyl*-4-*thiopyrone*.—This thiopyrone (0·5 g.) and butylamine (4 c.c.) were refluxed in ethanol (40 c.c.) for 8 hr.; the 1-*butyl*-2,6-*diphenyl*-4-*thiopyridone* that remained on evaporation solidified under chloroform–ethanol (yield 0·4 g.) and, crystallised therefrom (canary-yellow), had m. p. 221° (Found: N, 3·9; S, 10·3. $C_{21}H_{21}NS$ requires N, 4·4; S, 10·0%).

A similar experiment with benzylamine gave yellow 1-*benzyl*-2,6-*diphenyl*-4-*thiopyridone* (0·5 g.), m. p. 161° (from ethanol) (Found: N, 4·1; S, 9·0. $C_{24}H_{19}NS$ requires N, 4·0; S, 9·1%).

Oxidation of 1-*Butyl- and* 1-*Benzyl*-2,6-*dimethyl*-4-*thiopyridone*.—To a hot solution of the pyridone (0·5 g.) in acetic acid (20 c.c.), 30% hydrogen peroxide (5 c.c.) was added and the whole was heated for $\frac{1}{2}$ hr. Evaporation gave nearly quantitative yields of *anhydro*-1-*butyl*-, m. p. 260° (Found: C, 54·4; H, 7·5; N, 5·4; S, 1·3. $C_{11}H_{17}NO_3S$ requires C, 54·3; H, 7·0; N, 5·8; S, 13·2%), and *anhydro*-1-*benzyl*-1-*hydroxypyridine*-4-*sulphonic acid*, m. p. 257° (Found: C, 60·7; H, 5·6; N, 5·4; N, 11·6. $C_{14}H_{15}NO_3S$ requires C, 60·6; H, 5·5; N, 5·1; S, 11·5%).

Action of Phosphorus Pentasulphide on 1-*Alkyl*-3,5-*dibromo*-4-*pyridones*.—The 1-alkyldibromopyridones (1 g.) in dry benzene (40 c.c.) and pure phosphorus pentasulphide (2 g.) were refluxed for 2 hr. The yellow *products* that remained on the evaporation were washed with aqueous ammonium sulphide solution and recrystallised (see Table).

3,5-Dibromo-4-thiopyridones.

1-Subst.	2,6-Subst.	M. p.	Cryst. from	Found (%) S	Formula	Required (%) S
Me	Me	300°	AcOH	9·5	$C_8H_9NSBr_2$	10·3
Et	Me	262	$CHCl_3$–EtOH	9·9	$C_9H_{11}NSBr_2$	9·9
Me	Ph	244	AcOH	7·0	$C_{18}H_{13}NSBr$	7·4
Et	Ph	276	$CHCl_3$–EtOH	6·7	$C_{19}H_{15}NSBr_2$	7·1

Oxidation of 1-*Alkyl*-3,5-*dibromo*-4-*thiopyridones*.—Oxidation was carried as for the unbrominated thiopyridines mentioned above.[2] The products, crystallised from ethanol, were the 3,5-dibromo-4-pyridones (m. p. and mixed m. p.).

NATIONAL RESEARCH CENTRE, DOKKI, CAIRO, U.A.R.

[*Received, September 3rd,* 1962.]