Preparation of Meso-ionic ψ-Pyrido[2,1-b]-3,4-dihydro-4-keto-(and imino)-thiazole[1] *by a New Mode of Formation**

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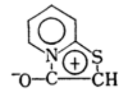
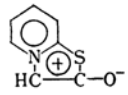
Duffin and Kendall[2] have prepared a meso-ionic compound I[3] by the reaction of (2-pyridylthio)-acetic acid and acetic anhydride. In an attempt to prepare meso-ionic compounds of the type II, in which the positions of CH and CO groups in the meso-ionic ring are reversed, the authors have carried out the reaction between *S*-acetyl-2-mercaptopyridine (yellow liquid, b. q. 96~99°C/3.5 mmHg; absence of band between 1600 and 1700 cm^{-1} due to non-benzenoid double bond system[4], ν_{cos} 1050, 952, 770 cm^{-1}[5]; Found: C, 54.56; H, 4.86; N, 9.30. Calcd. for C_7H_7NOS: C, 54.90; H, 4.61; N, 9.15%.) and chloroacetic acid. The reaction product was, quite unexpectedly, identical with I instead of the expected quaternary salt.





The same compound I was formed by the following reactions: i) *S*-benzoyl-2-mercaptopyridine (white needles, m. p. 44~45°C, b. p. 172°C/3 mmHg; Found: C, 66.76; H, 4.39; N, 6.48. Calcd. for $C_{12}H_9NOS$: C, 66.97; H, 4.22; N, 6.51%.) and chloroacetic acid (accompanied by benzoic acid); ii) *S*-acetyl- or *S*-benzoyl-2-mercaptopyridine and chloroacetamide; iii) (2-pyridylthio)-acetamide (white leaflets, m. p. 80°C; Found: C, 49.88; H, 4.88; N, 16.68. Calcd. for $C_7H_8N_2OS$: C, 50.00; H, 4.80; N, 16.66%.) and acetyl chloride (accompanied by acetamide)[6]; iv) sodium 2-pyridylmercaptide and chloroacetyl chloride, followed by acetic anhydride and sodium acetate.

This type of ring formation was further extended to the preparation of the unknown corresponding meso-ionic acyl-imino derivatives III by the reaction with chloroacetonitrile: the reaction of *S*-acetyl-2-mercaptopyridine with chloroacetonitrile in benzene gave III (R=Me yellow needles, m. p. 73~74°C; absence of ν_{CN} in 2200~2300 cm^{-1}; Found: C, 51.52; H, 5.06; N, 13.58. Calcd. for $C_9H_8N_2 \cdot OS+H_2O$: C, 51.42; H, 4.80; N, 13.33%;

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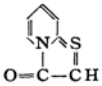
[1] The authors have adopted the nomenclature and symbol proposed by Baker. (W. Baker, W. D. Ollis and V. D. Poole, *J. Chem. Soc.*, **1949**, 311; W. Baker and W. D. Ollis, *Chem. & Ind.*, **1955**, 910.)

[2] G. F. Duffin and J. D. Kendall, *J. Chem. Soc.*, **1951**, **734**.

[3] Duffin and Kendall (*J. Chem. Soc.*, **1956**, **361**) are now of the opinion that compounds of this type can be satisfactorily represented by the structural formula V, and that they should no longer be regarded as meso-ionic. The present authors belive that structure V certainly would contribute to some extent to resonance, but it is more probable that several dipolar canonical forms play important role in the resonance. Discussion on the structure of these types of compounds will be given in a detailed report.

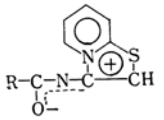


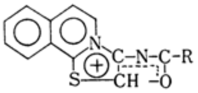
[4] E. Spinner, *J. Chem. Soc.*, **1960**, 1237.

[5] R. Sairs et al., *J. Am. Oil Chemists' Soc.*, **35**, 192 (1958).

[6] Duffin et al.[2] reported that when (2-quinolythio)-acetamide was treated with acetic anhydride, the starting material was recovered unchanged.

hydrochloride: yellow prisms; m. p. 250°C; Found: N, 12.04. Calcd. for $C_9H_9N_2OSCl$: N, 12.25%), and the reaction of *S*-benzoyl-2-mercaptopyridine gave III (R=Ph; yellow needles, m. p. 206°C. Found: C, 66.14; H, 3.75; N, 10.76. Calcd. for $C_{14}H_{10}N_2OS$: C, 66.13; H, 3.96; N, 11.02%.). Compound III was also prepared by the reaction of (2-pyridylthio)-acetonitrile (unstable yellow liquid, b. p. 118~120°C/3 mmHg; Found: C, 55.03; H, 3.90; N, 18.26. Calcd. for $C_7H_6N_2S$: C, 56.00; H, 4.03; N, 18.66%.) and acetyl or benzoyl chloride. The corresponding acyl-imino derivative (IV, R=Me; yellow needles, m. p. 215°C, absence of ν_{CN}, Found: C, 64.25; H, 4.40; N, 11.59. Calcd. for $C_{13}H_{10}N_2OS$: C, 64.46; H, 4.16; N, 11.59%. R=PhCO; yellow leaflets, m. p. 273°C, no ν_{CN}, Found: C, 71.30; H, 3.81; N, 9.49. Calcd. for $C_{18}N_{12}N_2OS$: C, 71.04; H, 3.98; N, 9.21%.) was prepared by treatment of (1-isoquinolylthio)-acetonitrile (white plates, m. p. 95.5°C, ν_{CN} 2240 cm^{-1}, Found: C, 65.91; H, 3.84; N,14.27: Calcd. for $C_{11}H_8N_2S$: C, 65.99; H, 4.03; N, 13.99%.) with acetyl or benzoyl chloride, but when (4-lepidyl-2-thio)-acetonitrile (colorless needles, m. p. 65°C, Found: C, 67.28; H, 4.71; N, 13.09. Calcd. for $C_{12}\cdot H_{10}N_2S$: C, 67.28; H, 4.71; N, 13.08%.) was treated with acyl chloride by the same method, the starting material was recovered unchanged. The failure of ring formation in this case might be ascribed to the steric hindrance by the hydrogen at 8 position of quinoline nucleus.





The starting material, 1-mercaptoisoquinoline and 2-mercapto-4-lepidine were prepared in almost quantitative yield and in high purity by treatment of the corresponding chloro derivatives with thioacetic acid.

The preparation of intermediate compounds, discussions on the mechanism of formation and the structure, properties and reactions of III and IV and the extension of this type of ring formation to the syntheses of other new meso-ionic ring systems will be reported shortly.

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