Non-benzenoid Aromatic Heterocycles. II[1]. *Reaction of Pyrylium Salt with Potassium Hydrosulfide*

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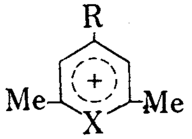
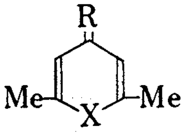
In the preceding paper[1], the conversion of 2, 6-dimethyl-4-methoxypyrylium salt (Ia) into 4-pyrone derivatives on treatment with sodium salts of active methylene compounds has been described. In the present communication, the reaction of this type with potassium hydrosulfide on 2, 6-dimethyl-4-methoxypyrylium perchlorate (Ia) is reported. When pyrylium salt Ia was treated with potassium hydrosulfide at room temperature, attack at the 4 position and removal of methoxyl group took place, and 2, 6-dimethyl-4-thiopyrone (IIa) was obtained. When this reaction was carried out under reflux and under a current of hydrogen sulfide, substitution of sulfur atom to both the 1 and 4 positions occurred, and 2, 6-dimethyl-1-thia-4-thiopyrone (IIb) was obtained. These compounds (IIa and IIb) have so far been prepared respectively by treating 2, 6-dimethyl-4-pyrone (IIc) with phosphorus pentasulfide[2], and by treating 2, 6-dimethyl-4-thiopyrone (IIa) with potassium hydrosulfide[3]. In the absence of hydrogen sulfide, the product was a mixture of the above two compounds. Starting from 2, 6-dimethyl-4-methylmercaptopyrylium perchlorate (Ib), 2, 6-dimethyl-1-thia-4-thiopyrone (IIb) was also obtained by the same method. An attempt to prepare 2, 6-dimethyl-4-pyrone (IIc) and -1-thia-4-pyrone (IId) by the action of potassium hydroxide on 2, 6-dimethyl-4-methylmercaptopyrylium (Ib) and -1-thiapyrylium perchlorate (Ic), respectively, was unsuccessful. This result is in agreement with the report of King[4] on



Ia : R=OMe, X=O
Ib : R=SMe, X=O
Ic : R=SMe, X=S



IIa : R=S, X=O
IIb : R=S, X=S
IIc : R=O, X=O
IId : R=O, X=S

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[1] Part I : M. Ohta and H. Kato, This Bulletin, 32, 707 (1959).

[2] L. C. King et al., *J. Am. Chem. Soc.*, 73, 300 (1957).

[3] F. Arndt et al., *Rev. faculté sci. univ. Istanbul*, A13, 57 (1948). *Chem. Abstr.*, 42, 4176 (1948).

[4] L. C. King et al., *J. Org. Chem.*, 20, 448 (1955).

the order of ease of replacement of methoxyl and methylmercapto group, and with the observation of the present author in the preceding paper¹⁾, where the methylmercapto group is reported to be not mobile.

Experimental

2, 6-Dimethyl-4-thiopyrone (IIa).—Into a suspension of Ia (5 g.) in methanol was added a methanol solution of potassium hydrosulfide (prepared from 5 g. of potassium hydroxide) at room temperature and with stirring. After an hour, the mixture was acidified with conc. hydrochloric acid and was poured into an aqueous solution of sodium bicarbonate. The precipitate (4.3 g., m. p. 144°C) was recrystallized from ethanol affording yellow needles (2 g.), m. p. 145°C. No m. p. depression occurred on admixture with an authentic specimen²⁾.

2, 6-Dimethyl-1-thia-4-thiopyrone (IIb).—Into a suspension of Ia (10 g.) in methanol was added a methanol solution of potassium hydrosulfide (prepared from 10 g. of potassium hydroxide) under a current of hydrogen sulfide and under reflux and stirring. After an hour, the mixture was treated by the above method and the precipitate (6.1 g., m. p. 106~119°C) was recrystallized from ligroin affording red needles, m. p. 116~117°C* (Found: C, 54.33; H, 5.56%).

The same compound was obtained starting from Ib by the same method (yield, poor).

When Ia was refluxed with potassium hydrosulfide in the absence of hydrogen sulfide, the product (1.7 g., m. p. 102~103°C) was a mixture of IIa and IIb (Examined by micro m. p. determination apparatus: The mixture consists of yellow needles (IIa) and red needles (IIb), and these compunds melted at their respective melting points.), the separation of which by recrystallization or by chromatography (alumina-benzene) was very troublesome.

Action of Potassium Hydroxide on Ib and Ic.—When Ib or Ic was treated with potassium hydroxide in methanol, a small amount of hydrogen sulfide was evolved, but the product was an unpurifiable resinous substance.

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* Reported m.p.³⁾ 116~117°C.