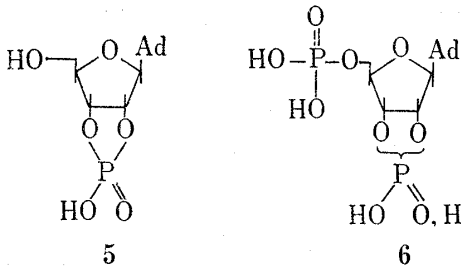
added to the reaction mixture. The mixture was further heated at 80° for 6 hr. After removal of protecting group, adenosine 5′-diphosphate (ADP) and adenosine 5′-triphosphate (ATP) were obtained in 25% and 28% yields, respectively, along with adenosine 5′-phosphate (31% yield). These polyphosphates travelled as single spots on paper chromatograms in 5% disodium hydrogen phosphate-isoamyl alcohol system (ADP, *Rf* 0.70; ATP, *Rf* 0.80).

Phosphorylation of unprotected free nucleoside by the present method was attempted. When phosphorous acid (0.8 mmole) was reacted with mercuric chloride (0.8 mmole) in N-methylimidazole (16 mmole) and then was further treated with adenosine (0.1 mmole), adenosine 2′,3′-cyclic phosphate (**5**) and adenosine 2′(3′),5′-diphosphate (**6**) were obtained in 39% and 33% yields, respectively. The cyclic phosphate (**5**) was converted with 0.1N hydrochloride acid into adenosine 2′(3′)-phosphate in quantitative yield. These compounds (**5** and **6**) were identified by the comparsion by paper chromatography with an authentic sample synthesized according to Khorana.[2]



5 6

Chart 2

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2) M. Smith, J.G. Moffatt, and H.G. Khorana, *J. Amer. Chem. Soc.*, **80**, 6204 (1958); J.G. Moffatt and H.G. Khorana, *ibid.*, **83**, 663 (1961).

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A Convenient Synthesis of Pyrazolines from β-Carbonylethylthiosulfates

Although the reaction of alkylthiosulfates with amines has been extensively studied, particularly by Milligan[1] and later by us,[2] little has hitherto been reported relating to the chemical behaviors toward hydrazines. Recently, we found that β-carbonylethylthiosulfates reacted with amines to give β-carbonylethylamines in a comparatively good yield.[3] This reaction is believed to proceed through the intermediate formation of vinylketones by the initial elimination of the hydrogen atom at the methylene group adjacent to the carbonyl group with amines. This result suggests that the use of hydrazines instead of amines would form pyrazolines directly and conveniently, because phenyl vinyl ketone reacts with phenylhydrazine to give 1,3-diphenylpyrazoline.[4]

1) B. Milligan and J.M. Swan, *J. Chem. Soc.*, **1959**, 2969; *idem*, *ibid.*, **1961**, 1194; *idem*, *Rev. Pure Appl. Chem.*, **12**, 72 (1962).
2) *a*) S. Hayashi, M. Furukawa, Y. Fujino and K. Shiraishi, *Chem. Pharm. Bull.* (Tokyo), **19**, 2247 (1971); *b*) M. Furukawa, K. Shiraishi and S. Hayashi, *ibid.*, **20**, 1921, 2315 (1972).
3) M. Furukawa, T. Yuki, R. Kiyofuji, K. Kojima and S. Hayashi, *Chem. Pharm. Bull.* (Tokyo), **21**, 811 (1973).
4) *a*) W.G. Young and J.D. Roberts, *J. Am. Chem Soc.*, **68**, 649 (1946); *b*) K.V. Auwers, *Chem. Ber.*, **65**, 831 (1932).

When β-arylcarbonylethylthiosulfates (I) was heated with two equivalent amounts of phenylhydrazine in water for 0.5—3 hr under reflux, 1-phenyl-3-aryl-2-pyrazoline (II) (R, mp: H, 151—152°; CH_3O, 138—140°; Br, 123—124°) was obtained in 23—52% yields. The structure of this compound was confirmed by the infrared (IR) and mass spectra and elemental analysis. Especially, the structure of 1,3-diphenyl-2-pyrazoline (II, R=H) was established by identification with an authentic sample[4a] by mixed melting point determination and comparison of the IR spectrum.

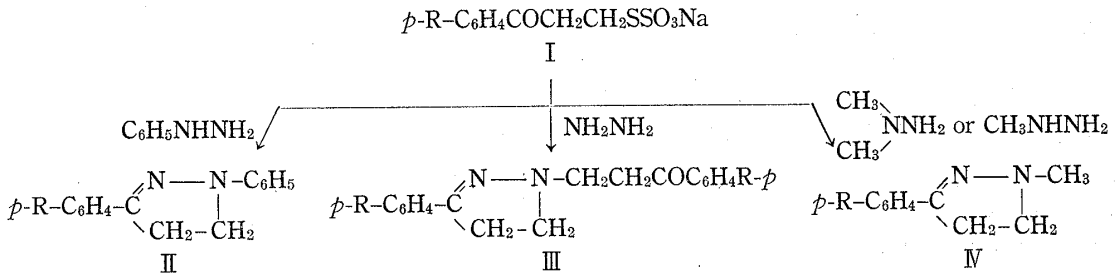

Chart 1

On the other hand, treatment of I with two equivalent amounts of hydrazine hydrate in water at room temperature gave 1-β-arylcarbonylethyl-3-aryl-2-pyrazoline (III) (R, mp: H, 105—105.5°; CH_3O, 142—143°; Br, 136—138°) in 35—77% yields, as the only product isolated. The structure of this compound was established by the IR and Mass spectra and elemental analysis.

In the reaction of I with N,N-dimethylhydrazine, demethylation was unexpectedly observed. When I was heated with two equivalent amounts of N,N-dimethylhydrazine in water for 7—10 hr under reflux, 1-methyl-3-aryl-2-pyrazoline (IV) (R, mp: CH_3O, 68—70°; Br, 68—69°), was obtained in a low yield. This compound gave a satisfactory elemental analysis and had IR, nuclear magnetic resonance and mass spectra consistent with the structure. Further evidence for the structure was provided by the fact that the same compound was formed by the reaction of I with methylhydrazine under the similar conditions.

As described above, the reaction between I and hydrazines provides a novel, convenient and efficient method for preparation of pyrazolines. In addition, I would afford a convenient rout for the synthesis of other heterocyclic ring systems and therefore the reactions with other basic nucleophiles are currently being investigated.

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