Rudy, Schloesser and Watzel.[5] Similar precipitates are also formed with Al^{+++} and sodium triphosphate, but only in a certain range of concentrations. In some ranges the precipitate dissolves on standing, while in others an excess of one of the reactants is necessary. The effect with Al^{+++} salts was demonstrated for the range where precipitation does not occur as follows: 0.2 ml. of a 0.139 *M* solution of sodium triphosphate was mixed with 1.5 ml. of 0.033 *M* aluminum chloride and diluted to a volume of 4 ml. The resulting solution had a *p*H lower than 3.1 when measured with brom thymol blue indicator, whereas aluminum chloride solution alone at the same concentration had a *p*H of 3.6.

Mixtures of triphosphate with potassium fluoride were tested as representative of the monovalent cation salts. Its addition had no effect on the *p*H of sodium triphosphate solution.

A possible explanation for this effect is that polyvalent cations can form complex compounds with sodium triphosphate, even though the ordinary formulation of such a reaction would not account for the extent of the acid shift. Since a depression in *p*H has also been observed in a solution of sodium glycerophosphate on addition of magnesium chloride, it is not unlikely that similar complexes also occur with phosphoric esters other than the sodium triphosphate. This possibility should be taken into consideration when the effect of salts upon phosphatase activity is investigated.

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(5) H. Rudy, H. Schloesser and R. Watzel, *Chem. Abs.*, **35**, 1337 (1941).

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The Condensation of α-Picoline Methiodide with Aromatic Aldehydes

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Many aromatic aldehydes have been condensed with α-picoline to form stilbazole derivatives. The conditions used for bringing about this reaction are drastic, usually a mixture of the reagents with zinc chloride is heated at 180–230°. The procedure of Shaw and Wagstaff[1] involves somewhat milder conditions, boiling with acetic anhydride for ten hours, but even this procedure might not be applicable to aldehydes containing acid-sensitive groups.

It has been shown[2] that whereas α-picoline will not react with *p*-nitrosodimethylaniline, α-picoline methiodide will do so readily. But only a few condensations of α-picoline methiodide with aromatic aldehydes have been recorded: with *p*-dimethylaminobenzaldehyde,[3] and with *m*-dimethyl-, diethyl- and dipropylbenzaldehyde.[4] It has now been found that such condensations generally can be brought about under very mild conditions. When a solution of equivalent amounts of an aromatic aldehyde and α-picoline methiodide in a small amount of alcohol is treated with a few drops of piperidine and then allowed to stand at room temperature for some time, it deposits the condensation product in a crystalline form.

3′-Nitro-α-stilbazole methiodide forms coarse yellow needles from water that sinter at 235° and melt with decomposition at 256°[5]; yield 88% after eight hours.

Anal. Calcd. for $C_{14}H_{13}IN_2O_2$: C, 45.7; H, 3.5. Found: C, 45.8; H, 3.7.

4′-Hydroxy-α-stilbazole methiodide forms bright yellow prisms from water, that fall to a yellow powder on drying at 100° and then melt at 268–270°; yield 33% after three weeks.

Anal. Calcd. for $C_{14}H_{14}INO$: C, 49.6; H, 4.1. Found: C, 49.4; H, 4.3.

4′-Methoxy-α-stilbazole methiodide forms yellow needles from water that fall to a powder on drying and then melt with decomposition at 235–240°; yield 50% after eight hours.

Anal. Calcd. for $C_{15}H_{16}INO$: C, 50.9; H, 4.5. Found: C, 50.9; H, 4.5.

Furfurylidene-α-picoline methiodide, yellow prisms from water, that fall to an orange-yellow powder on drying, darkens at 200° and melts to a red liquid at 204–206°; yield 67% after eight hours.

Anal. Calcd. for $C_{12}H_{12}INO$: C, 46.0; H, 3.8. Found: C, 46.3; H, 4.2.

When the methiodides so obtained are heated at about 250° under reduced pressure, they dissociate, and the resulting stilbazole distils. For example 4′-methoxy-α-stilbazole methodide yields 4′-methoxy-α-stilbazole, colorless plates from dilute alcohol, m. p. 76° (reported[6] 75°). And furfurylidene-α-picoline methiodide yields furfurylidene-α-picoline, tan needles from dilute alcohol, m. p. 65–66° (reported[7] 51–53°).

Anal. Calcd. for $C_{11}H_9NO$: C, 77.2; H, 5.3. Found: C, 77.2; H, 5.2.

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(1) Shaw and Wagstaff, *J. Chem. Soc.*, 77 (1933).

(2) Kaufmann and Vallette, *Ber.*, **45**, 1739 (1912); *cf.* Mills and Smith, *J. Chem. Soc.*, **121**, 2726 (1922).

(3) Mills and Pope, *ibid.*, **121**, 946 (1922); *cf.* Doja and Prasad, *J. Indian Chem. Soc.*, **19**, 125 (1942).

(4) Cocker and Turner, *J. Chem. Soc.*, 59 (1940).

(5) Temperatures are corrected.

(6) Bialon, *Ber.*, **35**, 2788 (1902).

(7) Merck, *ibid.*, **21**, 2709 (1888).

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Catalytic Hydrogenation of Cyanoacetic Ethyl Ester

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While the Hofmann degradation of succinimide is the best method for obtaining β-alanine used in the synthesis of pantothenic acid, it is rather tedious. Weygand[1] applied hydrogenation to an aliphatic nitrile, *viz.*, cyanoacetic ethyl ester, for this synthesis. He utilized platinum oxide (10%

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(1) F. Weygand, *Ber.*, **74B**, 256 (1941).