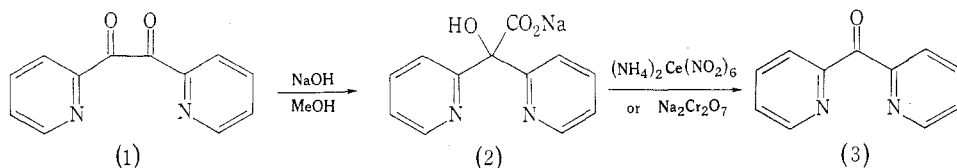


# AN IMPROVED SYNTHESIS OF DI-2-PYRIDYL KETONE

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Di-2-pyridyl ketone (3) is currently receiving attention<sup>1,2</sup> as an interesting chelating agent, with an ability<sup>2</sup> to undergo ligand reactions. It was first prepared by the reaction of 2-pyridylmagnesium iodide<sup>3</sup> or 2-pyridyllithium<sup>4</sup> with ethyl 2-picolinate, in 10% yield in each case. Subsequently it has been prepared by oxidation<sup>5</sup> of di-2-pyridylmethane (previously obtained by reaction of 2-picolyllithium with 2-bromopyridine) by lead dioxide oxidation<sup>6</sup> of 2,2'-pyridil (1) in 24% yield and by reaction<sup>7</sup> of 2-pyridyllithium with 2-cyanopyridine in 42% yield. Because of the ready availability of 2,2'-pyridil (1), the lead dioxide oxidation appears to be<sup>2</sup> the existing method of choice, despite the poor yield.



We describe here a two-step route from 2,2'-pyridil (1) to di-2-pyridyl ketone (3) in an overall yield of 70%, via sodium 2,2'-pyridilate (2). Sodium 2,2'-pyridilate (2) is prepared in 94% yield by heating 2,2'-pyridil (1) under reflux with sodium hydroxide in methanol, as described by Klosa.<sup>8,9</sup> The sodium salt (2) can be converted into di-2-pyridyl ketone (3) in 62% yield by sodium dichromate or in essentially quantitative yield in a milder process using ceric ammonium nitrate<sup>10</sup> in acetic acid. Under the latter conditions, the undistilled material (> 90% yield) has an infrared spectrum identical with that of the pure, distilled material, which was obtained in 75% yield. For further reaction, the undistilled material is of adequate purity.

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The conversion of (2) into (3) involves formation of the free carboxylic acid, its spontaneous decarboxylation, and easy oxidation of the resulting di-2-pyridyl-methanol in a single process. Both steps of the sequence are easy to perform and the yield is greatly improved over the other methods: in particular, this improvement over the lead dioxide oxidation<sup>6</sup> more than compensates for the additional step.

### Experimental

The infrared spectrum was measured with a Perkin-Elmer 257 grating infrared spectrophotometer and melting points are uncorrected.

#### *Sodium 2,2'-Pyridilate (2)*

This compound was prepared by heating 2,2'-pyridil (1) with sodium hydroxide in methanol, as described by Klosa.<sup>8,9</sup> Yield 94%;  $\nu_{\max}$  (Nujol mull) 3230w, 1642s, and 1585s  $\text{cm}^{-1}$ . The product can be used in the following reaction without further purification.

#### *2,2'-Dipyridyl Ketone (3)*

(i) Sodium 2,2'-pyridilate (12.0 g, 0.048 mol) was dissolved in acetic acid (30 ml) and treated with sodium dichromate (9.6 g, 0.032 mol) in acetic acid (25 ml). The reaction mixture was allowed to stand for 24 hr at 10° and was then neutralized with sodium carbonate. The neutralized solution was extracted with chloroform and the chloroform extract was dried (sodium sulphate) and concentrated by solvent removal under reduced pressure. The residue was distilled and the fraction distilling between 120–140°/0.2 mm was collected. The pale yellow liquid thus obtained solidified as a colourless solid and was recrystallized from ethanol. Yield 5.4 g (62%); m.p. 54°, picrate 178° (lit.<sup>6</sup> m.p. 54°, picrate 180–181°).  $\nu_{\max}$  (Nujol mull) 1680s, 1320s, 1285s, 1240m, 1162m, 1158m, 1095m, 1060m, 1000s, 958s, 950s, 835m, 795m, 765m, 752s, 714m, 705m, 670s  $\text{cm}^{-1}$ .

(ii) Sodium 2,2'-pyridilate (5.04 g, 0.02 mol) was dissolved in glacial acetic acid (30 ml) and after rapid evolution of carbon dioxide, water (30 ml) was added and this was followed by ceric ammonium nitrate (12.1 g, 0.022 mol). The reaction mixture was warmed on the water-bath for 5 min, by which time the reaction was complete. The reaction mixture was neutralized by addition of solid sodium carbonate and the resulting suspension was shaken with excess chloroform and the mixture filtered through Celite, before separation of the chloroform extract, which was then dried (sodium sulphate) and concentrated to a pale yellow oil (3.6 g, 98%). This was distilled at 146°/0.3 mm to yield the pure ketone (2.8 g, 75%).

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