

## 2,2'-Vinylidenedipyridine and its Diquaternary Salts

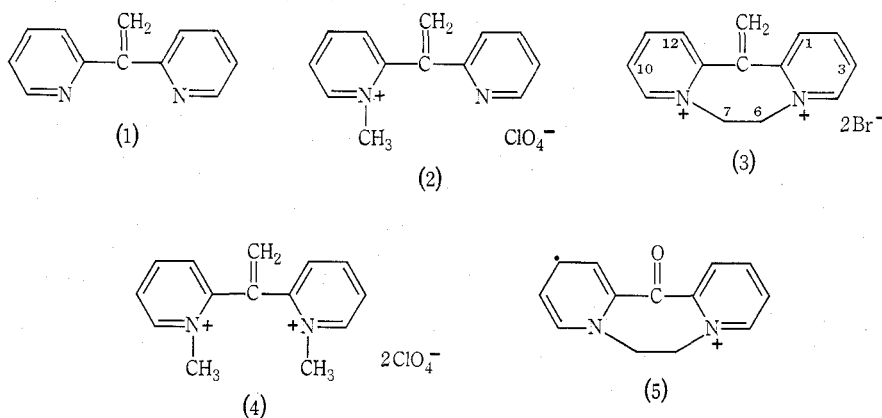
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### Abstract

2,2'-Vinylidenedipyridine, the first example of a vinylidenedipyridine, has been prepared from di-2-pyridyl ketone by way of a Wittig reaction. It forms diquaternary salts with dimethyl sulphate and ethylene dibromide.

Most of the isomeric vinylenedipyridines have been prepared.<sup>1</sup> There has, however, been no report of a vinylidenedipyridine. We now describe the preparation and some of the properties of 2,2'-vinylidenedipyridine (1) and its diquaternary salts.



Attempts to perform a Wittig reaction on di-2-pyridyl ketone using methyltriphenylphosphonium bromide and phenyllithium in ether gave only a small amount of the desired olefin. Using methyltriphenylphosphonium bromide and sodium methylsulphanyl carbanion<sup>2</sup> in dimethyl sulphoxide, however, 2,2'-vinylidenedipyridine (1) was obtained in over 40% yield. Compound (1) was characterized by conversion into

<sup>1</sup> E.g. Thayer, H. I., and Corson, B. B., *J. Amer. Chem. Soc.*, 1948, **70**, 2330; Dornow, A., Machens, H., and Bruncken, K., *Chem. Ber.*, 1951, **84**, 147; Campbell, P. G., and Teague, P. C., *J. Amer. Chem. Soc.*, 1954, **76**, 1371; Jerchel, D., and Melloh, W., *Justus Liebigs Ann. Chem.*, 1959, **622**, 53; Bodalski, R., Malkiewicz, A., and Michalski, J., *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1965, **13**, 139 (*Chem. Abstr.*, 1965, **63**, 8310); Beggiato, G., Favaro, G., and Mazzucato, U., *J. Heterocycl. Chem.*, 1970, **7**, 583.

<sup>2</sup> Corey, E. J., and Chaykovsky, M., *J. Amer. Chem. Soc.*, 1962, **84**, 866.

the quaternary *N*-methyl salt (2). When pure, the olefin (1) is an amber-coloured liquid. It darkens on standing and rapidly deteriorates on heating above about 120°.

Because of our interest in heterocyclic diquaternary salts as one-electron transfer agents and potential herbicides<sup>3,4</sup> 2,2'-vinylidenedipyridine was treated in turn with ethylene dibromide and excess dimethyl sulphate. With the former reagent the hygroscopic diquaternary salt 6,7-dihydro-13-methylene-13*H*-dipyrido[1,2-*d*:2',1'-*g*]-[1,4]diazepinium(2+) dibromide (3) was obtained, while with the latter the *N,N'*-dimethyl diquaternary salt was formed. It was conveniently isolated as the diperchlorate (4).

The diquaternary salts (3) and (4), as expected, were soluble in water. Compound (3) was rather unstable in aqueous solution. Below pH 4.0 it gradually broke down while above pH 4.0 it deteriorated rapidly. Compound (4) was stable below about pH 8.0, its u.v. spectrum in water, for example at pH 5.3, being essentially unchanged after several days. Unlike related diquaternary salts from di-2-pyridyl ketone,<sup>5</sup> which on treatment with zinc powder in aqueous solution give highly coloured solutions of the corresponding radical cations [e.g. (5)], aqueous solutions of the salts (3) and (4) on treatment with zinc dust showed no visible change.

In keeping with this result polarographic examination of (3) in the pH range 2.5–4.0 and (4) in the pH range 2.5–8.0 showed little significant reduction above about –1.2 V against a standard calomel electrode. There was no evidence of a clear-cut one-electron reduction wave, as is observed with diquaternary salts of di-2-pyridyl ketone,<sup>5</sup> the current gradually increasing as the applied voltage decreased. It is therefore apparent that the salts (3) and (4) are not reduced to radical cations at least at potentials attainable in aqueous solution.

The salts (3) and (4) were tested as post-emergent herbicides at 8 lbs/acre against a number of flora but they were inactive (cf.<sup>4,5</sup>).

## Experimental

Microanalyses were performed by the Australian Microanalytical Service, Melbourne. U.v. absorption measurements were taken with approximately  $5 \times 10^{-5}$  M solutions. N.m.r. spectra (60 MHz) were determined for 10% w/v solutions with tetramethylsilane or sodium 3-trimethylsilylpropene-1-sulphonate as internal standard. Britton and Robinson and Sorenson buffers were used in the polarography experiments which were conducted at 20° with a standard calomel electrode and 0.001 M solutions.

### 2,2'-Vinylidenedipyridine (1)

Sodium hydride (0.15 mol) and freshly distilled (from  $\text{CaH}_2$ ) dimethyl sulphoxide (100 ml) were heated under nitrogen to 65–70° for about 1 h until the evolution of hydrogen ceased. The resultant yellow-green solution of sodium methylsulphinyl carbanion was cooled in an ice-bath until it started to crystallize. Methyltriphenylphosphonium bromide (0.15 mol) in dimethyl sulphoxide (200 ml) was then added and the resultant solution was stirred at 20° for 25 min by which time it had become dark red. On addition of di-2-pyridyl ketone (0.15 mol) in dimethyl sulphoxide (200 ml) the temperature rapidly rose to about 50° and the solution became greenish blue. It was stirred at 60° for 1 h and the dimethyl sulphoxide then removed by vacuum distillation. The residue was dissolved in 10% hydrochloric acid (500 ml) and repeatedly extracted with chloroform to remove the triphenylphosphine oxide. The aqueous layer was made alkaline and was then extracted with chloroform. The

<sup>3</sup> Dickeson, J. E., Eckhard, I. F., Fielden, R., and Summers, L. A., *J. Chem. Soc., Perkin Trans. 1*, 1973, 2885.

<sup>4</sup> Black, A. L., and Summers, L. A., *J. Chem. Soc. C*, 1971, 2271, and references cited therein.

<sup>5</sup> Black, A. L., and Summers, L. A., *J. Chem. Soc. C*, 1970, 2394.

red-brown chloroform extract was washed with water and dried ( $\text{MgSO}_4$ ). On removing the solvent under vacuum a brown oil was obtained. The oil was purified by eluting with benzene on a column of neutral alumina. The resultant liquid was distilled to give 2,2'-vinylidenedipyridine as a light amber-coloured liquid, b.p.  $98-100^\circ/0.1$  mm (yield 42%) (Found: C, 78.8; H, 5.7; N, 15.3.  $\text{C}_{12}\text{H}_{10}\text{N}_2$  requires C, 79.1; H, 5.5; N, 15.4%). The u.v. spectrum (ethanol) showed  $\lambda_{\text{max}}$  227, 242sh and 272 nm ( $\log \epsilon$  4.08, 4.00 and 3.91). The n.m.r. spectrum (carbon tetrachloride) consisted of a singlet at  $\delta$  6.05 ( $\text{CH}_2$ ), a multiplet at  $\delta$  6.97-7.70 (3,4,5,3',4',5' aromatic protons) and a doublet at  $\delta$  8.50-8.60 p.p.m. (6,6' aromatic protons).

The N-methyl perchlorate salt (2) was prepared by treating 2,2'-vinylidenedipyridine (150 mg) with dimethyl sulphate (5 ml) at  $20^\circ$ . After standing for 5 min concentrated perchloric acid (5 ml) was added to the reaction mixture. The salt was precipitated by adding ethyl acetate. It crystallized from water as a white solid, m.p.  $215-217^\circ$  (Found: C, 52.5; H, 4.5; Cl, 11.9; N, 9.2.  $\text{C}_{13}\text{H}_{13}\text{ClN}_2\text{O}_4$  requires C, 52.6; H, 4.4; Cl, 12.0; N, 9.4%). The n.m.r. spectrum (deuterium oxide) consisted of a singlet at  $\delta$  4.21 ( $\text{CH}_3$ ), a doublet at  $\delta$  6.56-6.59 (one  $\text{CH}_2$  proton), a doublet at  $\delta$  7.05-7.08 (one  $\text{CH}_2$  proton) and a multiplet at  $\delta$  7.82-9.10 p.p.m. (aromatic protons).

The N,N'-dimethyl diperchlorate salt (4) was prepared by heating 2,2'-vinylidenedipyridine (3.0 g) and dimethyl sulphate (20 ml) at  $130^\circ$  for 1 h. The reaction mixture was cooled and concentrated perchloric acid (5 ml) was added. The salt was precipitated by adding ethyl acetate. It crystallized from water as a white solid, m.p.  $285-287^\circ$  (dec.) (Found: C, 40.95; H, 3.9; N, 6.5.  $\text{C}_{14}\text{H}_{16}\text{Cl}_2\text{N}_2\text{O}_8$  requires C, 40.9; H, 3.9; N, 6.8%). The u.v. spectrum (water, pH 5.3) showed  $\lambda_{\text{max}}$  278 ( $\log \epsilon$  4.16). The n.m.r. spectrum (deuterium oxide) consisted of a singlet at  $\delta$  4.27 ( $\text{CH}_3$ ), a singlet at  $\delta$  6.82 ( $\text{CH}_2$ ) and a multiplet at  $\delta$  8.10-9.05 p.p.m. (aromatic protons).

**6,7-Dihydro-13-methylene-13H-dipyrido[1,2-d:2',1'-g][1,4]diazepinium(2+) Dibromide (3)**

2,2'-Vinylidenedipyridine (1.5 g) was added to boiling ethylene dibromide (30 ml) and the solution refluxed for 1 h. The brick red solid which precipitated was collected and washed with acetone. It was very hygroscopic. It was purified by dissolving it in methanol and reprecipitating it with dry ether. The salt had m.p.  $180^\circ$  (dec.). The analysis corresponded to a monohydrate (Found: C, 43.5; H, 4.3; Br, 40.9; N, 7.5.  $\text{C}_{14}\text{H}_{14}\text{Br}_2\text{N}_2\cdot\text{H}_2\text{O}$  requires C, 43.3; H, 4.1; Br, 41.2; N, 7.2%). The u.v. spectrum (water pH 2.8) showed  $\lambda_{\text{max}}$  279 ( $\log \epsilon$  4.16). The n.m.r. spectrum (deuterium oxide) consisted of a singlet at  $\delta$  5.60 (6, 7- $\text{CH}_2$ ), a singlet at  $\delta$  6.90 (13- $\text{CH}_2$ ) and a multiplet at  $\delta$  8.12-9.10 p.p.m. (aromatic protons).

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