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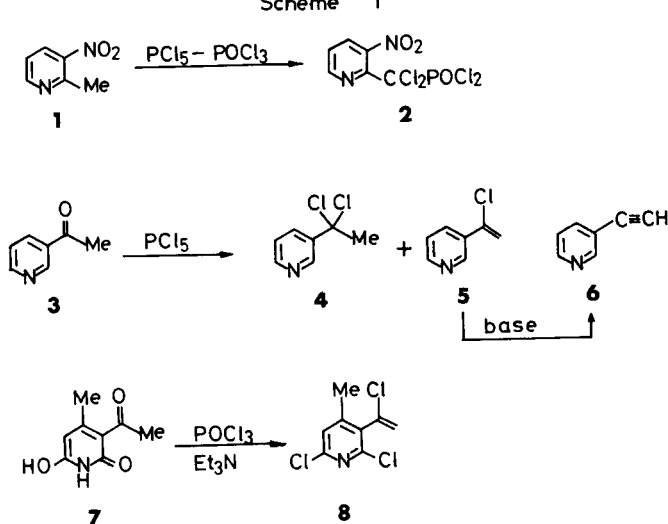
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Reaction of 3-acetyl-4,6-dimethyl-2-(1H)pyridone (**9a**) with phosphoryl chloride gives 2-chloro-3-ethynyl-4,6-dimethylpyridine (**10a**). 3-Acetyl-4-hydroxy-6-methyl-2-(1H)pyridone (**14a**) and 3-acetyl-2,6-dimethyl-4-(1H)pyridone (**21**) undergoes similar reaction to give the corresponding ethynyl (**16** and **23**) and chlorovinyl (**15** and **22**) pyridines, respectively. The chlorination of 3-acetylpyridine and pyrimidine derivatives is further described.

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Previously, we have reported that an active methyl group of pyridine or pyrimidine is readily chlorinated, on heating with phosphorus pentachloride in phosphoryl chloride, to give a trichloromethyl pyridine or pyrimidine derivative (2-5). The same reaction of 2-methyl-3-nitropyridine (**1**) gave rise to the phosphorylated compound, dichloro-(3-nitro-2-pyridyl)methylphosphonic dichloride (**2**) (4). On the other hand, reaction of the ketone with phosphorus pentachloride or phosphorus trichloride is reported to give the *gem*-dichloride or vinyl chloride, which, on treatment with a strong base, is transformed to the alkyne. For instance, 3-acetylpyridine (**3**) reacts with phosphorus pentachloride to give *gem*-dichloroethylpyridine (**4**) (7) and 3-(1-chlorovinyl)pyridine (**5**) (6,7), which, on treatment with alkalis, is transformed to 3-ethynylpyridine (**6**) (6,8). Recently, Dimroth, *et al.* (9), reported the reaction of 3-acetyl-6-hydroxy-4-methyl-2-(1H)pyridone (**7**) with phosphoryl chloride in the presence of triethylamine to give 2,6-dichloro-3-(1-chlorovinyl)-4-methylpyridine (**8**). The present paper reports a continuation of our study on chlorination of acetylpyridine derivatives in the absence of a base such as triethylamine to give ethynylpyridine derivatives.

Scheme 1

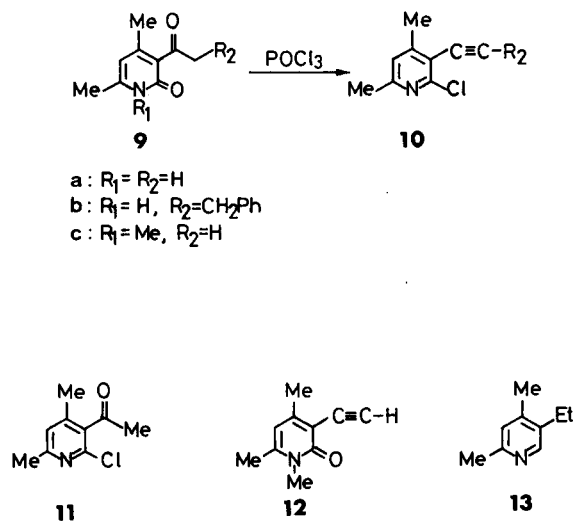


When 3-acetyl-4,6-dimethyl-2-(1H)pyridone (**9a**) was heated in phosphoryl chloride for 4 hours, 2-chloro-3-ethynyl-4,6-dimethylpyridine (**10a**) was obtained in 12% yield. When the reaction time was extended for 20 hours longer, the yield of the product **10a** improved to 33%.

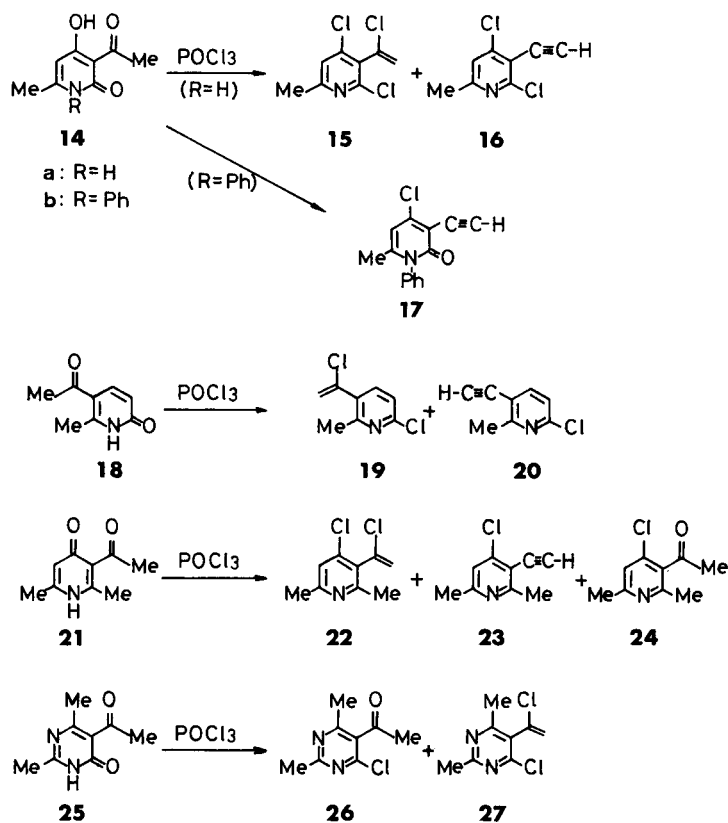
Similarly, 4,6-dimethyl-3-(3-phenylpropionyl)-2-(1H)pyridone (**9b**), prepared from **9a** and benzaldehyde, was heated in phosphoryl chloride for 4 hours to give 2-chloro-4,6-dimethyl-3-(3-phenyl-1-propynyl)pyridine (**10b**) in 11% yield. Refluxing for 20 hours gave a 34% yield of the product **10b**.

3-Acetyl-1,4,6-trimethyl-2-(1H)pyridone (**9c**) was heated in phosphoryl chloride for 4 hours to give 3-acetyl-2-chloro-4,6-dimethylpyridine (**11**) (9%) and **10a** (5%). Refluxing for 20 hours gave rise to 3-ethynyl-1,4,6-trimethyl-2-(1H)pyridone (**12**) (17%) together with **10a** (24%). Upon catalytic reduction, compound **10a** was reduced to 5-ethyl-2,4-dimethylpyridine (**13**).

Scheme 2



Scheme 3



Heating of 3-acetyl-4-hydroxy-6-methyl-2(1*H*)pyridone (**14a**) and 5-acetyl-6-methyl-2-(1*H*)pyridone (**18**) in phosphoryl chloride gave the corresponding chlorovinyl (**15** and **19**) and ethynyl (**16** and **20**) derivatives, respectively. The same reaction of 3-acetyl-2,6-dimethyl-4-(1*H*)pyridone (**21**) gave 3-acetyl-4-chloro-2,6-dimethylpyridine (**24**) besides the formation of the chlorovinyl (**22**) and ethynyl (**23**) derivatives.

Reaction of 3-acetyl-4-hydroxy-6-methyl-1-phenyl-2-(1*H*)pyridone (**14b**) affords a low yield of the ethynyl derivative (**17**).

Heating of 5-acetyl-2,6-dimethyl-4-(3*H*)pyrimidone (**25**) in phosphoryl chloride afforded the 4-chloro (**26**) and the 4-chloro-5-(1-chlorovinyl) derivative (**27**), but the 5-ethynyl derivative was not obtained.

Reaction of 3-acetylpyridine (**3**) with phosphoryl chloride under the same condition gave 3-(1-chlorovinyl)pyridine (**5**) in 24% yield. However, refluxing of acetophenone in phosphoryl chloride resulted in the formation of a resinous product, from which both chlorovinyl and ethynyl derivatives could not be detected. Similar reaction of propiophenone resulted in the recovery of the starting material.

## EXPERIMENTAL

All melting and boiling points were uncorrected. Ir spectra were measured with JASCO IR-S spectrometer. Nmr spectra were measured on a Hitachi-Perkin Elmer R-20 spectrometer and reported as  $\delta$  value (ppm) relative to tetramethylsilane as an internal standard. Mass spectra were obtained on a Hitachi M-52G mass spectrometer. Preparative gas chromatography was carried out on a Wilkens Aerograph "Autoprep" Model A-700 using helium as a carrier gas.

### 2-Chloro-3-ethynyl-4,6-dimethylpyridine (**10a**).

#### A.

A mixture of 3-acetyl-2,4-dimethyl-2(1*H*)pyridone (**9a**) (10) (4.95 g.) and phosphoryl chloride (24 ml.) was refluxed for 20 hours. Excess phosphoryl chloride was distilled off under reduced pressure. The residue was poured onto crushed ice, and the pH was adjusted to 5-7 with 10% sodium carbonate under ice-water cooling. The mixture was extracted with chloroform. The organic layer was dried over anhydrous sodium sulfate, evaporated *in vacuo* to give a residue, to which hexane was added. Insoluble crystals were collected by filtration; they were washed with hexane. The hexane soluble fraction gave 1.65 g. (33%) of the product **10a** as needles (from petroleum ether), m.p. 65-66°; ir (chloroform): 3300 ( $\equiv$  C-H), 2120 (C $\equiv$  C)  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  2.40 (3H, s), 2.45 (3H, s), 3.63 (1H, s,  $\equiv$  C-H), 6.97 (1H, s, ring-H).

Anal. Calcd. for  $\text{C}_8\text{H}_8\text{ClN}$  (**10a**): C, 65.27; H, 4.87; N, 8.46. Found: C, 65.49; H, 4.80; N, 8.47.

#### B.

Similarly, compound **9a** (1.65 g.) and phosphoryl chloride (7 ml.) were refluxed for 4 hours to give 0.2 g. (12%) of the product **10a**.

4,6-Dimethyl-3-(3-phenylpropionyl)-2-(1H)pyridone (**9b**).

A mixture of compound **9a** (6.6 g.), benzaldehyde (8.48 g.), sodium hydroxide (4 g.), and 95% ethanol (150 ml.) was stirred at room temperature for 30 minutes. The reaction mixture was acidified with 10% hydrochloric acid. Crystals separated were collected by suction, washed with 80% ethanol and recrystallized from methanol to give 8.0 g. (80%) of 4,6-dimethyl-3-(3-phenyl-2-propenyl)-2-(1H)pyridone as yellowish needles, m.p. 204-205°; ir (chloroform): 3200-2600, 1640  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{15}\text{NO}_2$ : C, 75.87; H, 5.97; N, 5.53. Found: C, 75.78; H, 5.94; N, 5.46.

This compound (3.04 g.) was hydrogenated in methanol (200 ml.) using 5% palladium on charcoal (0.3 g.) as a catalyst at room temperature. After hydrogen uptake had been completed, the catalyst was removed by filtration, and the filtrate was condensed to dryness giving a crystalline substance. Recrystallization from chloroform-hexane gave 2.8 g. (91%) of the product **9b** as needles, m.p. 106-108°; ir (chloroform): 3160-2680, 1680, 1640  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  2.10 (3H, s), 2.22 (3H, s), 3.0-3.5 (4H, m), 5.95 (1H, s), 7.23 (5H, s), 13.4 (1H, broad).

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{17}\text{NO}_2$  (**9b**): C, 75.27; H, 6.71; N, 5.49. Found: C, 75.09; H, 6.93; N, 5.21.

2-Chloro-4,6-dimethyl-3-(3-phenyl-1-propynyl)pyridine (**10b**).

A.

Following the same procedure given for the ethynylpyridine **10a**, compound **9b** (1.28 g.) was heated at reflux in phosphoryl chloride (3.5 ml.) for 20 hours. The chloroform extract gave a syrupy residue, which was submitted to silica gel column chromatography. Elution with hexane-benzene (1:1) gave 0.44 g. (34%) of the product **10b** as a colorless oil; ir (chloroform): 2260 ( $\text{C}\equiv\text{C}$ ), 1590  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  2.38 (3H, s), 2.45 (3H, s), 3.93 (2H, s), 6.93 (1H, s), 7.35-7.60 (5H, m); ms:  $m/e$  255 ( $\text{M}^+$ ).

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{14}\text{ClN}$  (**10b**): C, 75.14; H, 5.52; N, 5.47. Found: C, 75.01; H, 5.71; N, 5.27.

B.

Similarly, a mixture of compound **9b** (1.28 g.) and phosphoryl chloride (3.5 ml.) was refluxed for 4 hours to give 0.17 g. (11%) of the product **10b**.

3-Acetyl-1,4,6-trimethyl-2-(1H)pyridone (**9c**).

A suspension of compound **9a** (4.95 g.), dimethyl sulfate (3.78 g.), and anhydrous potassium carbonate (8.3 g.) in acetone (100 ml.) was stirred at room temperature for 15 hours. The reaction mixture was filtered and the filtrate was condensed to dryness. The residue was recrystallized from chloroform-hexane to give 3.5 g. (65%) of the product **9c** as needles, m.p. 98-99°; ir (chloroform): 1685, 1650  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  2.18 (3H, s), 2.33 (3H, s), 2.52 (3H, s), 3.50 (3H, s), 6.00 (1H, s).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{13}\text{NO}_2$  (**9c**): C, 67.02; H, 7.31; N, 7.82. Found: C, 67.09; H, 7.52; N, 7.76.

Reaction of **9c** with Phosphoryl Chloride.

A.

Employing the same procedure given for compound **10a**, the pyridone **9c** (3.58 g.) was heated at reflux in phosphoryl chloride (15 ml.) for 4 hours. The chloroform extract was submitted to silica gel column chromatography. Elution with hexane gave 180 mg. (5%) of the product **10a**. Subsequent elution with hexane-ether (10:1) yielded an oily substance, which was distilled to give 340 mg. (9%) of 3-acetyl-2-chloro-4,6-dimethylpyridine (**11**) as a colorless oil, b.p. 180°/14 mm; ir (chloroform): 1708  $\text{cm}^{-1}$ ; nmr (carbon tetrachloride):  $\delta$  2.18 (3H, s), 2.42 (3H, s), 2.47 (3H, s), 6.90 (1H, s).

*Anal.* Calcd. for  $\text{C}_8\text{H}_{10}\text{ClNO}$  (**11**): C, 58.86; H, 5.49; N, 7.63. Found: C, 59.32; H, 5.51; N, 7.54.

B.

Employing the same procedure given for compound **10a**, compound **9c** (1.79 g.) was heated at reflux in phosphoryl chloride (8 ml.) for 20 hours. The reaction mixture was condensed, and the residue was neutralized and then the mixture was extracted with chloroform. The chloroform solution was condensed, and the residue was purified by recrystallization from petroleum ether to give 400 mg. (24%) of the product **10a**. The aqueous layer was made alkaline with sodium bicarbonate. The solution was condensed to dryness under reduced pressure. The resulting residue was extracted with hot chloroform. The chloroform extract was submitted to silica gel column chromatography. Elution with chloroform gave 270 mg. (17%) of 3-ethynyl-1,4,6-trimethyl-2-(1H)pyridone (**12**) as needles (from chloroform-hexane), m.p. 161-162°; ir (chloroform): 3300 ( $\text{C}\equiv\text{H}$ ), 2120 ( $\text{C}\equiv\text{C}$ ), 1640  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  2.28 (3H, s), 2.34 (3H, s), 3.49 (1H, s,  $\text{C}\equiv\text{C}\text{-H}$ ), 3.50 (3H, s), 6.00 (1H, s, ring-H).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{11}\text{NO}$  (**12**): C, 74.51; H, 6.88; N, 8.69. Found: C, 74.24; H, 6.83; N, 8.59.

2,4-Dimethyl-5-ethylpyridine (**13**).

Compound **10a** (1.65 g.) was hydrogenated over 10% palladium on charcoal (150 mg.) in methanol (50 ml.) at room temperature. The catalyst was filtered, and the filtrate was condensed to dryness. The residue was dissolved in 10% sodium carbonate and the solution was extracted with ether. The organic layer was dried over anhydrous potassium carbonate, condensed and distilled to give 1.20 g. (89%) of the product **13** as an oil, b.p. 195-196°; nmr (carbon tetrachloride):  $\delta$  1.18 (3H, t,  $J = 7$  Hz), 2.18 (3H, s), 2.36 (3H, s), 2.56 (2H, q,  $J = 7$  Hz), 6.77 (1H, s), 8.08 (1H, s); picrate m.p. 155-156° (yellow needles from ethanol).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}$  (**13**-picrate): C, 49.45; H, 4.43; N, 15.38. Found: C, 49.72; H, 4.29; N, 15.29.

Reaction of 3-Acetyl-4-hydroxy-6-methyl-2-(1H)pyridone (**14a**) with Phosphoryl Chloride.

Employing the similar procedure given for compound **10a**, a mixture of compound **14a** (11) (3.34 g.) and phosphoryl chloride (15 ml.) was refluxed for 20 hours. After removal of excess phosphoryl chloride, the resulting residue was neutralized, and the mixture was extracted with chloroform. Evaporation of chloroform gave an oil, which was submitted to alumina column chromatography. Elution with hexane gave 640 mg. (17%) of 2,4-dichloro-3-ethynyl-6-methylpyridine (**16**) as needles (from petroleum ether), m.p. 45°; ir (chloroform): 3280 ( $\text{C}\equiv\text{H}$ ), 2140 ( $\text{C}\equiv\text{C}$ )  $\text{cm}^{-1}$ ; nmr (carbon tetrachloride):  $\delta$  2.48 (3H, s), 3.62 (1H, s,  $\text{C}\equiv\text{C}\text{-H}$ ), 7.12 (1H, s, ring-H).

*Anal.* Calcd. for  $\text{C}_8\text{H}_6\text{Cl}_2\text{N}$  (**16**): C, 51.65; H, 2.71; N, 7.53. Found: C, 51.36; H, 2.50; N, 7.73.

Subsequent elution with hexane gave 0.4 g. (9%) of 2,4-dichloro-3-(1-chlorovinyl)-6-methylpyridine (**15**) as an oil, b.p. 132-133°/15 mm; nmr (carbon tetrachloride):  $\delta$  2.48 (3H, s), 5.48 (1H, d,  $J = 2$  Hz), 5.82 (1H, d,  $J = 2$  Hz), 7.25 (1H, s).

*Anal.* Calcd. for  $\text{C}_8\text{H}_6\text{Cl}_3\text{N}$  (**15**): C, 43.19; H, 2.72; N, 6.30. Found: C, 43.41; H, 2.66; N, 6.20.

4-Chloro-3-ethynyl-6-methyl-1-phenyl-2-(1H)pyridone (**17**).

A mixture of 3-acetyl-4-hydroxy-6-methyl-1-phenyl-2-(1H)pyridone (**14b**) (**12**) (1.7 g.) and phosphoryl chloride (6 ml.) was refluxed for 20 hours. The reaction mixture was worked up similarly as above, and the chloroform extract was submitted to silica gel column chromatography. Elution with chloroform gave a crystalline substance, which was recrystallized from chloroform-hexane to give 100 mg. (6%) of compound **17** as prisms, m.p. 180-183°; ir (chloroform): 3300 ( $\text{C}\equiv\text{H}$ ), 2240 ( $\text{C}\equiv\text{C}$ ), 1655  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  1.96 (3H, s), 3.57 (1H, s,  $\text{C}\equiv\text{C}\text{-H}$ ), 6.27 (1H, s, ring-H), 7.1-7.6 (5H, m).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{10}\text{ClNO}$  (**17**): C, 69.00; H, 4.14; N, 5.75. Found: C, 68.89; H, 4.41; N, 5.43.

5-Acetyl-6-methyl-2-(1H)pyridone (**18**).

A mixture of 5-acetyl-3,4-dihydro-6-methyl-2-(1H)pyridone (**13**) (3.06 g.) and palladium black (0.5 g.) was heated at 250° for 20 minutes. After cooling, the mixture was added to methanol, and the catalyst was removed by filtration. The filtrate was condensed to give a crystalline substance, which was recrystallized from ethyl acetate giving 1.47 g. (49%) of the product **18** as needles, m.p. 196-198°; ir (chloroform): 1685, 1650 cm<sup>-1</sup>; nmr (deuteriochloroform):  $\delta$  2.47 (3H, s), 2.71 (3H, s), 6.45 (1H, d, J = 9.6 Hz), 7.92 (1H, d, J = 9.6 Hz).

*Anal.* Calcd. for C<sub>8</sub>H<sub>9</sub>NO<sub>2</sub> (**18**): C, 63.56; H, 6.00; N, 9.27. Found: C, 63.29; H, 5.92; N, 9.37.

Reaction of **18** with Phosphoryl Chloride.

Following the similar fashion given for compound **10a**, compound **18** (0.453 g.) was heated at reflux in phosphoryl chloride (2.5 ml.) for 20 hours. After evaporation of excess phosphoryl chloride, the resulting residue was neutralized with sodium carbonate. The mixture was extracted with dichloromethane. The dichloromethane extract was submitted to silica gel column chromatography using dichloromethane as an eluant to give 0.288 g. of a colorless oil. Nmr spectroscopic study showed that the oil was the mixture of 6-chloro-3-ethynyl-2-methylpyridine (**20**) and 6-chloro-3-(1-chlorovinyl)-2-methylpyridine (**19**) (**20:19** = 13:7). This was submitted to automatic preparative gas chromatography (2 m column packed with 10% SE-30, helium at a flow rate of 400 ml./minute, oven temperature 125°) to give compound **20** (retention time 2.3 minutes) and compound **19** (retention time 5.7 minutes).

Compound **19**.

This compound had b.p. 95°/19 mm; nmr (deuteriochloroform):  $\delta$  2.59 (3H, s), 5.41 (1H, d, J = 1.8 Hz), 5.72 (1H, d, J = 1.8 Hz), 7.15 (1H, d, J = 7.8 Hz), 7.56 (1H, d, J = 7.8 Hz).

*Anal.* Calcd. for C<sub>8</sub>H<sub>8</sub>Cl<sub>2</sub>N: C, 51.10; H, 3.75; N, 7.45. Found: C, 50.80; H, 3.99; N, 7.38.

Compound **20**.

This compound was obtained as needles, m.p. 67° (from petroleum ether); ir (chloroform): 3330, 2120 cm<sup>-1</sup>; nmr (deuteriochloroform): 2.65 (3H, s), 3.43 (1H, s,  $\equiv$  C-H), 7.14 (1H, d, J = 8.1 Hz), 7.68 (1H, d, J = 8.1 Hz); ms: m/e 151 (M<sup>+</sup>).

*Anal.* Calcd. for C<sub>8</sub>H<sub>8</sub>ClN·1/5H<sub>2</sub>O: C, 61.91; H, 4.16; N, 9.02. Found: C, 62.24; H, 4.12; N, 9.34.

Reaction of 3-Acetyl-2,6-dimethyl-4-(1H)pyridone (**21**) with Phosphoryl Chloride.

## A.

Following the similar fashion given for compound **10a**, compound **21** (**14**) (1.65 g.) was heated at reflux in phosphoryl chloride (7 ml.) for 4 hours. After distillation of excess phosphoryl chloride, the resulting residue was neutralized with sodium carbonate. The mixture was extracted with chloroform. The extract was submitted to silica gel column chromatography. Elution with benzene afforded 0.22 g. (11%) of 4-chloro-3-(1-chlorovinyl)-2,6-dimethylpyridine (**22**), b.p. 109-110°/17 mm; nmr (deuteriochloroform):  $\delta$  2.51 (3H, s), 2.60 (3H, s), 5.54 (1H, d, J = 2.1 Hz), 5.85 (1H, d, J = 2.1 Hz), 7.12 (1H, s).

*Anal.* Calcd. for C<sub>8</sub>H<sub>8</sub>Cl<sub>2</sub>N (**22**): C, 53.49; H, 4.49; N, 6.93. Found: C, 53.63; H, 4.71; N, 6.94.

Subsequent elution with chloroform afforded 1.09 g. (59%) of 3-acetyl-4-chloro-2,6-dimethylpyridine (**24**), b.p. 118-120°/15 mm; ir (chloroform): 1704 cm<sup>-1</sup>; nmr (deuteriochloroform):  $\delta$  2.46 (3H, s), 2.51 (3H, s), 2.54 (3H, s), 7.08 (1H, s).

*Anal.* Calcd. for C<sub>8</sub>H<sub>10</sub>ClNO (**24**): C, 58.87; H, 5.49; N, 7.63. Found: C, 58.42; H, 5.58; N, 7.61.

## B.

A mixture of **21** (1.65 g.) and phosphoryl chloride (7 ml.) was refluxed for 20 hours. The reaction mixture was worked up similarly as above. The chloroform extract was submitted to silica gel column chromatography.

Elution with dichloromethane gave 1.0 g. of an oil. The oil was found to be a mixture of **22** and 4-chloro-3-ethynyl-2,6-dimethylpyridine (**23**) by nmr spectroscopic and gas chromatographic analysis (**22:23** = 7:3). The oil was dissolved in petroleum ether and cooled in a refrigerator to give a crystalline substance. Recrystallization from petroleum ether afforded 4-chloro-3-ethynyl-2,6-dimethylpyridine (**23**) as needles of m.p. 63°; ir (chloroform): 3360 ( $\equiv$  C-H), 2120 (C $\equiv$ C, weak) cm<sup>-1</sup>; nmr (deuteriochloroform):  $\delta$  2.50 (3H, s), 2.68 (3H, s), 3.65 (1H, s,  $\equiv$  C-H), 7.08 (1H, s).

*Anal.* Calcd. for C<sub>8</sub>H<sub>8</sub>ClN (**23**): C, 65.27; H, 4.87; N, 8.46. Found: C, 65.12; H, 4.91; N, 8.62.

Subsequent elution with chloroform gave 0.42 g. (23%) of **24** as an oil.

Reaction of 5-Acetyl-2,6-dimethyl-4-(3H)pyrimidone (**25**) with Phosphoryl Chloride.

## A.

Employing the similar procedure given for compound **10a**, a mixture of the pyrimidone (**25**) (**15**) (1.66 g.) and phosphoryl chloride (8 ml.) was refluxed for 45 minutes. The neutralized solution was extracted with chloroform. The chloroform solution was distilled to give 1.38 g. (74%) of 5-acetyl-4-chloro-2,6-dimethylpyrimidine (**26**) as an oil, b.p. 121°/16 mm [lit. (**16**) b.p. 104°/8 mm].

## B.

A mixture of compound **25** (1.66 g.) and phosphoryl chloride (8 ml.) was refluxed for 20 hours. Similar treatment as above gave 0.8 g. (39%) of 4-chloro-5-(1-chlorovinyl)-2,6-dimethylpyrimidine (**27**), b.p. 112-114°/15 mm; nmr (carbon tetrachloride):  $\delta$  2.50 (3H, s), 2.60 (3H, s), 5.48 (1H, d, J = 2 Hz), 5.84 (1H, d, J = 2 Hz).

*Anal.* Calcd. for C<sub>8</sub>H<sub>8</sub>Cl<sub>2</sub>N<sub>2</sub> (**27**): C, 47.32; H, 3.97; N, 13.79. Found: C, 47.39; H, 3.94; N, 13.75.

Reaction of 3-Acetylpyridine (**3**) with Phosphoryl Chloride.

Employing the similar procedure given for compound **10a**, a mixture of compound **3** (1.21 g.) and phosphoryl chloride (7 ml.) was refluxed for 20 hours. The neutralized mixture was extracted with chloroform. The organic layer was condensed and the resulting residue was chromatographed on a silica gel column. Elution with benzene gave 0.34 g. (24%) of 3-(1-chlorovinyl)pyridine (**5**) as an oil, b.p. 92-93°/18 mm [lit. (**7**) b.p. 92°/12 mm]; picrate: m.p. 143-144° [lit. (**7**) m.p. 140-141°].

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