# Syntheses of *N*-[$\beta$-(4-Pyridyl)-vinyl]-indoline and Related Compounds

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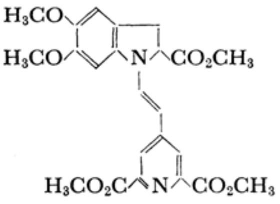
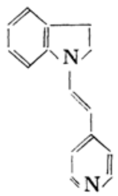
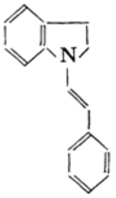
In 1961, Dreiding *et al.*[1] reported the structure of pentamethylneobetanidine (I). The skeleton conjugated system of I is *N*-[$\beta$-(4-pyridyl)-vinyl]-indoline (II). This paper is concerned with developing a method of synthesizing the novel conjugated system containing nitrogen (II) and a related compound (III). In order to find out such a new method, the authors prepared simpler analogous compounds, IV, V, VI and VII.

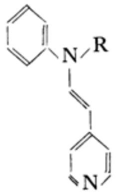
Heyningen's method[2] was modified to synthesize IV and V, which were obtained by the condensation of *N*-alkyl-*N*-formylanilines with $\gamma$-picoline, using sodium hydride and a trace of ethanol as the condensing agents. VI and VII were synthesized by modifying Herr's method,[3] in which *N*-alkylanilines and phenylacetaldehyde in benzene were heated under reflux. The condensation of *N*-formylindoline with $\gamma$-picoline by the modification of Heyningen's method gave II. III was obtained, by the modification of Herr's method, from indoline and phenylacetaldehyde.

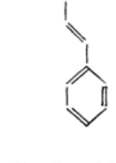
The ultraviolet absorption spectra of the compounds II—VII are very characteristic. II possesses an absorption maximum at 371 m$\mu$ in a neutral or a weak basic ethanol solution, while under acid conditions a bathochromic shift is observed, the absorption maximum being at 435 m$\mu$ (Table 1). The shift is assumed to correspond to change of the conjugated system of II into that of VIII in an acid solution. The spectra of IV and V are similarly characterized. III in an acid solution does not display the absorption

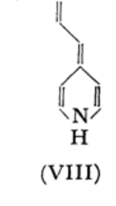

(I)

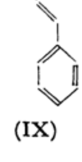

(II)


(III)


(IV) R=$CH_3$
(V) R=$C_2H_5$


(VI) R=$CH_3$
(VII) R=$C_2H_5$


(VIII)


(IX)

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[1] H. Wyler and A. S. Dreiding, *Helv. Chim. Acta*, **44**, 2491 (1961).

[2] E. V. Heyningen, *J. Am. Chem. Soc.*, **80**, 5470 (1958).

[3] M. E. Herr and F. W. Heyl, *ibid.*, **74**, 3627 (1952).

TABLE 1. ULTRAVIOLET ABSORPTION MAXIMA (m$\mu$, EtOH)

| Compd. | Basic | Neutral | Acid |
|---|---|---|---|
| II | 250 | 250 | 252 |
| | 371 | 371 | 435 |
| III | 255 | 255 | 257 |
| | 310 | 310 | 270 |
| | 352 | 351 | |
| IV | 243 | 243 | 248 |
| | 350 | 350 | 405 |
| V | 245 | 245 | 250 |
| | 351 | 351 | 405 |
| VI | 246 | 246 | 246 |
| | 332 | 332 | |
| VII | 234 | 234 | 234 |
| | 333 | 332 | |

maxima corresponding to 310 m$\mu$ and 351 m$\mu$ in a neutral or a weak basic solution. This shows the formation of the conjugated system of IX. The characteristic spectra of VI and VII are similar to those of III.

## Experimental[4]

**$N$-Methyl-$N$-[$\beta$-(4-pyridyl)-vinyl]-aniline (IV).** In 100 m*l* flask 2.4 g of sodium hydride was mixed with 14.0 g of $\gamma$-picoline and 6.8 g of *N*-methylformanilide. A few drops of ethanol were then added, and the reaction mixture was stirred for an hour. The mixture was cooled in ice, decomposed by the drop-by-drop addition of acetic acid and water to neutralize it, and then extracted with ether. After the ether had been removed, the residue was distilled under reduced pressure to give 0.8 g of a yellow oil, bp 161 °C/4 mmHg; the IR spectrum showed bands at 2940, 2850 (C–H), 1675, 1630 (C=C), 3035, 1595, 1500 (aromatic), 832 (4-substituted pyridine), 1350 and 1265 ($C_{arom.}$–N)cm$^{-1}$.

Found: C, 76.99; H, 6.78; N, 12.56%. Calcd for $C_{14}H_{14}N_2$: C, 79.96; H, 6.71; N, 13.32%.[5]

**$N$-Ethyl-$N$-[$\beta$-(4-pyridyl)-vinyl]-aniline (V).** The procedure was identical with that described above. The product had a bp of 168°C/5 mmHg (yield, 8.1%); the IR spectrum had bands at 2980, 2930, 1880 (C–H), 1675, 1630 (C=C), 3050, 1595, 1495 (aromatic), 835 (4-substituted pyridine), 1350 and 1240 ($C_{arom.}$–N) cm$^{-1}$.

Found: N, 11.17%. Calcd for $C_{15}H_{16}N_2$: N, 12.49%.[5]

**$N$-[$\beta$-(4-Pyridyl)-vinyl]-indoline (II).** A mixture of 0.24 g of sodium hydride, 1.4 g of $\gamma$-picoline, 0.74 g of *N*-formylindoline, and two drops of ethanol was treated as above. By molecular distillation the crude product gave 0.1 g of a yellow oil, bp 130°C/10$^{-3}$ mmHg; $\nu$ 2930, 2860, 1470 (C–H), 1670, 1640 (C=C), 3030, 1600, 1495 (aromatic), 832 (4-substituted pyridine), 1365, 1265 ($C_{arom.}$–N) cm$^{-1}$; $\lambda_{max}^{EtOH}$ 250 and 371 m$\mu$ (13000 and 10700).

Found: N, 10.38%. Calcd for $C_{15}H_{14}N_2$: N, 12.60%.[5]

**$N$-Methyl-$N$-styrylaniline (VI).** To a solution of 2.4 g of phenylacetaldehyde in 100 m*l* of benzene, 2.5 g of *N*-methylaniline were added; the mixture was then heated under reflux using a moisture trap. After two hours the calculated amount of water had collected in the trap. The solvent was removed and distilled under nitrogen to give 3.2 g of a faint yellow liquid, bp 170°C/2 mmHg; $\nu$ 2950, 2850 (C–H), 1680, 1635 (C=C), 3045, 1595, 1500 (aromatic), 755, 700 (monosubstituted phenyl), 1340 and 1260 ($C_{arom.}$–N) cm$^{-1}$; the NMR spectrum showed a *N*-methyl singlet at $\tau$ 6.98 and two vinylproton doublets ($J=14$ cps), at $\tau$ 4.50 and 2.79.

Found: C, 85.78; H, 7.19; N, 6.59%. Calcd. for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69%.

**$N$-Ethyl-$N$-styrylaniline (VII).** A similar procedure with *N*-ethylaniline gave a faint yellow liquid, bp 194°C/3 mmHg (yield, 82%); the IR spectrum had bands at 2980, 2940, 2880 (C–H), 1675, 1635 (C=C), 3050, 1590, 1495 (aromatic), 755, 700 (monosubstituted phenyl), 1350 and 1240 ($C_{arom.}$–N) cm$^{-1}$; the NMR spectrum showed two vinylproton doublets ($J=14$ cps), at $\tau$ 4.40 and 2.82.

Found: C, 85.41; H, 7.56; N, 6.33%. Calcd for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27%.

**$N$-Styrylindoline (III).** When treated as above, 1.2 g of indoline gave a faint yellow solid, which was recrystallized from methanol and which melted at 81°C; yield, 1.76 g; the IR spectrum had bands at 2925, 2850, 1465 (C–H), 1675, 1640 (C=C), 3030, 1595, 1500 (aromatic), 745, 690 (monosubstituted phenyl), 1340 and 1265 ($C_{arom.}$–N) cm$^{-1}$. The UV spectrum showed $\lambda_{max}^{EtOH}$ 255, 310 and 351 m$\mu$ (5200, 20300 and 30400); the NMR spectrum revealed two methylene triplets, centered at $\tau$ 6.35 and 7.02, and two vinylproton doublets ($J=14$ cps), at $\tau$ 4.68 and 2.75, which supported the trans-configuration of the double bond.

Found: C, 86.76; H, 6.87; N, 6.17%. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33%.

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[4] Melting points and boiling points are not corrected.

[5] The compounds IV, V and VI are very unstable in the air, and in microanalysis, the found value does not show the good agreement with calculated one, even after repeated purification. This seems to result from the fact that the compounds are easily oxidized by air. However, the structure of each compound is supported by the IR and UV spectra.