

**A new synthesis of 4(or 5)-L-aminoethylglyoxaline, one of the active principles of ergot / by Frank Lee Pyman. The synthesis of r-histidine (preliminary note) / by Frank Lee Pyman.**

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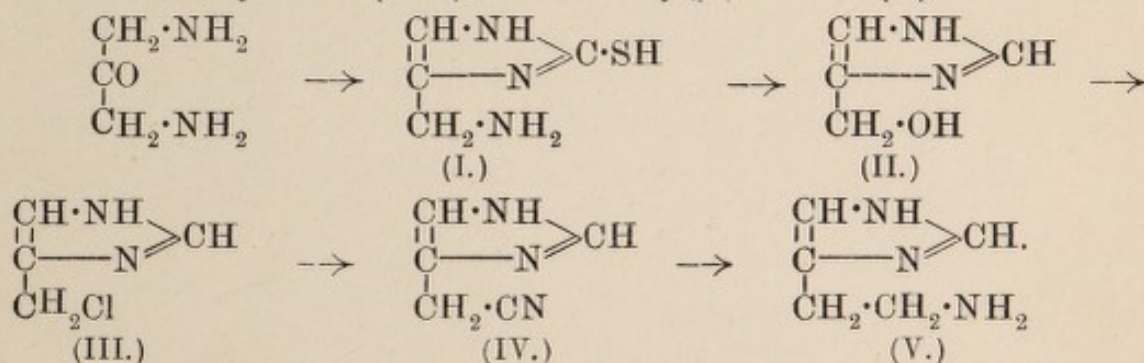
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\*90. "A new synthesis of 4(or 5)- $\beta$ -aminoethylglyoxaline, one of the active principles of ergot." By Frank Lee Pyman.

The following synthesis of 4(or 5)- $\beta$ -aminoethylglyoxaline affords a convenient method for its preparation.

Diaminoacetone dihydrochloride when heated with potassium thiocyanate yields 2-thiol-4(or 5)-aminomethylglyoxaline (I) [m. p. 188° (corr.)], which on oxidation with nitric acid gives 4(or 5)-hydroxymethylglyoxaline (II) [m. p. 93—94° (corr.)]. The hydrochloride of the latter is converted by phosphorus pentachloride into 4(or 5)-chloromethylglyoxaline hydrochloride (III) [m. p. 144—145° (corr.)], and this, when suitably treated with potassium cyanide, gives rise to 4(or 5)-cyanomethylglyoxaline (IV) [m. p. 138—140° (corr.)]. The latter base, on reduction with sodium and alcohol, yields 4(or 5)- $\beta$ -aminoethylglyoxaline (V).



A number of salts of these compounds, and several derivatives obtained as by-products in the various stages of the synthesis, were also described.

\*91. "The synthesis of *r*-histidine." (Preliminary note.)

By Frank Lee Pyman.

4(or 5)-Chloromethylglyoxaline hydrochloride, of which the synthetical preparation is described in the preceding communication, is a valuable compound for the synthesis of substances containing the glyoxaline complex, for it reacts readily with ethyl sodioacetoacetate, ethyl sodiomalonate, and similarly constituted compounds, forming the corresponding 4(or 5)-glyoxalinemethyl ( $\text{C}_3\text{H}_3\text{N}_2 \cdot \text{CH}_2^-$ ) derivatives. By the use of this salt, the synthesis of *r*-histidine has been effected as follows. 4(or 5)-Chloromethylglyoxaline hydrochloride and ethyl sodiochloromalonate readily condense, yielding *ethyl* 4(or 5)-glyoxalinemethylchloromalonate



(I), of which the *sesquioxalate*,  $(C_{11}H_{15}O_4N_2Cl)_4(C_2H_2O_4)_3$ , melts and decomposes at  $176^\circ$  (corr.). This base, on hydrolysis with 20 per cent. hydrochloric acid, gives *r*- $\alpha$ -chloro- $\beta$ -glyoxaline-4(or 5)-propionic acid (II) [m. p.  $201^\circ$  (corr.)], which, when heated with strong ammonia at  $110^\circ$ , yields *r*-histidine (*r*- $\alpha$ -amino- $\beta$ -glyoxaline-4(or 5)-propionic acid, (III) [melting and decomposing at  $283^\circ$  (corr.)], identical in all respects with that obtained by racemising the naturally-occurring amino-acid *l*-histidine.

