

require from 6 to 8 weeks of growth before the reserve supply of manganese contained in the seed is apparently used up in the plant's growth and before a chlorotic condition develops.

The first effect to be noted in the growth of plants from which manganese has been withheld is a lack in the development of chlorophyll in the newly formed tissues or the growing parts of the plant. This condition increases with time and finally results in the tips of the branches dying back and a cessation of further growth of any consequence in the plant.

It appears that leguminous plants are more sensitive to the lack of manganese than are the non-legumes because of the plants produced from pea and radish seeds planted at the same time, the pea plants were first to develop a chlorotic condition, thus suggesting that manganese is apparently concerned in nitrogen assimilation and the synthesis of proteins.

Apparently manganese plays the role of a necessary catalyst in plant metabolism and together with iron functions in the synthesis of chlorophyll.

Summary

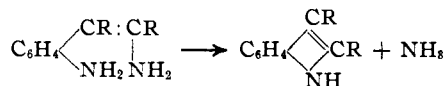
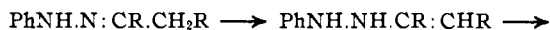
The results thus far obtained in this investigation afford direct evidence that manganese has a function to perform in the formation of chlorophyll and consequently in carbon assimilation and possibly in the synthesis of protein. The results evidence a new and useful function of manganese in nature which has not heretofore been definitely established.

LEXINGTON, KENTUCKY

NOTE

The Mechanism of the Fischer Indole Synthesis.—For the mechanism of the Fischer indole synthesis (with which must be included Brunner's preparation of oxindoles from acid hydrazides¹ and the Drechsel-Baeyer method for tetrahydrocarbazoles²) four suggestions have been made.

Robinson and Robinson³ supposed that an unsaturated azine was first formed, which underwent an *orthobenzidine* rearrangement followed by elimination of ammonia.



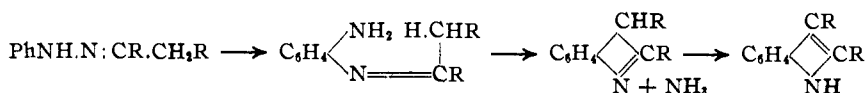
Cohn⁴ suggested an *orthosemidine* change with subsequent loss of ammonia

¹ Brunner, *Monatsh.*, **17**, 479 (1896); **18**, 95, 527 (1897); Ger. pats. 218, 477, 218, 727.

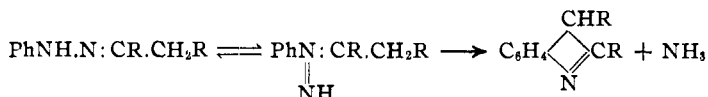
² Drechsel and Baeyer, *Ann.*, **278**, 105 (1894).

³ Robinson and Robinson, *J. Chem. Soc.*, **113**, 639 (1918).

⁴ Cohn, "Die Carbazolgruppe," 1919, p. 12.

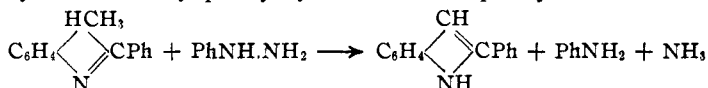


The explanation of Bamberger and Landau,⁵ founded upon the formation of dimethylaniline oxide by methylation of phenylhydroxylamine with dimethyl sulfate, assumes a tautomeric form of the hydrazones



The method of elimination of the ammonia is not explained and the hypothesis entirely fails to account for the formation of N-methylindoles from phenylmethylhydrazones.⁶ The tautomerism of phenylhydroxylamine, upon which the theory is based is, moreover, not necessary for the explanation of the production of dimethylaniline oxide, as Bamberger himself admits.

Reddelien⁷ discovered that the anil of acetophenone is oxidized by phenylhydrazone or by phenylhydrazones to 2-phenylindole.

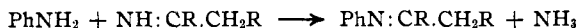


He, therefore, suggested the following stages for the Fischer synthesis.

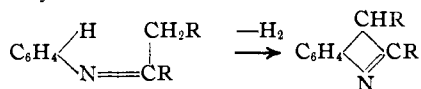
I. Reduction of the phenylhydrazone (during the oxidation in III) to aniline and ketone imide.⁸



II. Condensation of these two products with elimination of NH₃.



III. Ring-closure by oxidation of this anil.



IV. Rearrangement of the indolenine to an indole.

Against Robinson's theory may be urged the total absence of any *para* isomerization products in the product of reaction, and the fact that no increase in yield is observed when *p*-tolylhydrazones are used. The same objection holds against Cohn's explanation. Bamberger's theory has already been dealt with and there remains only the suggestion of Reddelien. This seems to fail in the case of phenylmethylhydrazones,

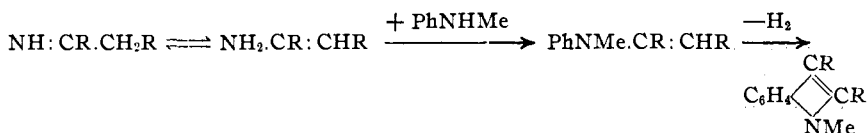
⁵ Bamberger and Landau, *Ber.*, **52**, 1097 (footnote) (1919).

⁶ Degen, *Ann.*, **236**, 153 (1886).

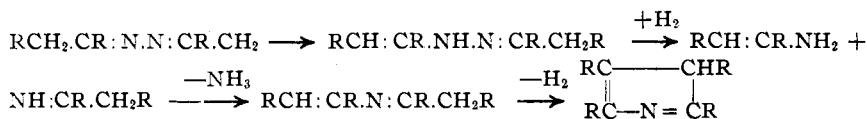
⁷ Reddelien, *ibid.*, **388**, 179 (1912).

⁸ The reaction is thus not self-starting. Autoxidation and reduction would, however, account for the trace of aniline and ketone imide necessary for the reaction to commence and it would then proceed to completion.

but a slight modification avoids the difficulty. It is only necessary to suppose that the ketone imide reacts in its tautomeric form.



Thus modified, Reddelien's theory fulfils all the conditions required: (a) an indolenine is the primary product where this is possible;⁹ (b) *isobutyraldehyde* and ketones of the type $\text{CHMe}_2\text{.CO.R}$ are converted into indolenines with extraordinary ease¹⁰ (due to the ready oxidizability of the $-\text{CHMe}_2$ group); (c) the reaction succeeds with phenylmethylhydrazones;⁶ (d) the *tertiary* nitrogen atom, *i. e.*, that remote from the benzene nucleus, is the one removed; (e) acid hydrazides undergo a similar condensation to oxindoles. Moreover, it explains very simply the Piloty-Robinson synthesis of pyrroles from azines of enolizable ketones.¹¹



The difference between the α - and β -phenylhydrazino-naphthalenes¹² also finds an explanation in Reddelien's theory. The β -compound probably exists largely in the *orthoquinonoid* form, in which there is a readily oxidizable $\alpha\text{-CH}_2$ group. The quinonoid form of the α -compound has a *para* CH_2 group and presents no easily oxidizable $\beta\text{-CH}_2$. The yield of carbazole from the β -compound is accordingly excellent, while that from the α -compound is very small. The dinaphthylhydrazines¹³ exhibit similar differences.

MANCHESTER, ENGLAND

CECIL HOLLINS

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⁹ Plancher and Testoni, *Gazz. chim. ital.*, **30**, ii, 558 (1900).

¹⁰ Plancher, *Ber.*, **31**, 1496 (1898). Grgin, *Monatsh.*, **27**, 731 (1906). Jennisch, *ibid.*, **27**, 1223 (1906).

¹¹ Piloty, *Ber.*, **43**, 497 (1910); Ref. 3. Piloty's work seems to have been overlooked by Robinson.

¹² Schopf, *ibid.*, **29**, 265 (1896). Japp and Maitland, *J. Chem. Soc.*, **83**, 267 (1903). Bucherer and Seyde, *J. prakt. Chem.*, **77**, 403 (1908); Ger. pat. 208,960.

¹³ Bucherer and Schmidt, *J. prakt. Chem.*, **79**, 369 (1909).