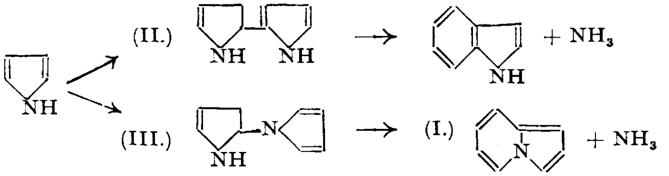
19. *Reactions of Furan Compounds. Part VI. Formation of Indole, Pyrrocoline, and Carbazole during the Catalytic Conversion of Furan into Pyrrole.*

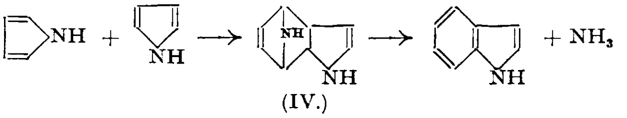
By Christopher L. Wilson.

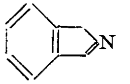
Reaction of furan and ammonia over an alumina catalyst at 400° gave pyrrole together with smaller amounts of indole, pyrrocoline, and carbazole. The formation of these by-products is discussed.

Yur'ev and Rakitin (*Ber.*, 1936, **69**, 44, 2492; D.R.P. 706,095; *Chem. Abs.*, 1942, **36**, 1957) have described the catalytic conversion of furan into pyrrole in 30% yield by passing a mixture with ammonia over an alumina catalyst at about 450°. A reinvestigation of this reaction confirmed their results and, in addition, led to the identification of three by-products, the formation of which presents an interesting problem. The compounds were indole, pyrrocoline (I) (also called indolizine), and carbazole. Pyrrocoline formed white crystals, m. p. 68—69°, with an odour like that of naphthalene, and its solution in dilute hydrochloric acid rapidly became opalescent. No comparison with authentic pyrrocoline has been possible, but its properties identify it with considerable certainty (cf. Beilstein, Erg.-Band, XX, p. 120).

It is not immediately obvious whether the benzopyrroles arose by interaction of pyrrole with itself or with furan. The constancy of the yield of pyrrole even when conversion of furan was very low supports the first view, since, if furan had reacted with pyrrole to give a benzopyrrole, decrease in conversion should have led to a fall in the yield of pyrrole. Furthermore, pyrrole under suitable conditions, *e.g.*, under the influence of acid, is known to be transformed into indole, and this is supposed (Allen, Gilbert, and Young, *J. Org. Chem.*, **1937**, **2**, 227, 235) to proceed through a dipyrrole (II). In like manner, the formation of pyrrocoline would involve an intermediate (III) but such a compound would be expected to be rearranged on heating to an α-substituted pyrrole rather than to pyrrocoline. Alternatively, initial reaction could be supposed to lead to the formation of a normal diene adduct (IV) were it not that this type of addition in the nitrogen heterocyclic series is the exception rather than the rule.







(V.)

It is noteworthy that no by-product possessing the ψ-*iso*indole (V) structure was isolated. ψ-*iso*Indole itself is unknown and attempts to make it have frequently given the dihydro-derivative instead, but this, too, was absent. The instability of ψ-*iso*indole has been connected (Ingold, J., **1933**, 1127) with the absence of alternative positions for the unshared electrons of the nitrogen atom. In pyrrole several such possibilities exist and increased stability results from resonance between them. Reference to pyrrocoline, which has not been mentioned before in this respect, confirms this view, since many dipolar forms can be constructed. It is to be noticed that resonance between the Kekulé type of structures, which is the main contribution to the stability of the benzene ring, is absent in pyrrocoline.

It is intended to search further for ψ-*iso*indole in the reaction product, since failure to detect it may have been due to a lack of appreciation of its properties.

EXPERIMENTAL.

Method.—Ammonia (11 l./hr.) was bubbled through furan at 15—25°, and the mixed vapours conducted over a granular activated alumina catalyst (200 c.c., 4—6 mesh; Messrs. Peter Spence Ltd.) at 400° ± 10°. The issuing material was passed through a trap at 0° to condense water, pyrrole, and a little furan, and then through one at — 78° to catch ammonia and the rest of the furan. The catalyst deteriorated fairly rapidly and was reactivated after the passage of each g.-mol. of furan by oxidation in a stream of air at 550°.

Products.—The total amount of furan passed through the tube was 7·5 g.-mols. (510 g., 540 c.c.) of which 222 c.c. (210 g.) were recovered. Fractionation of the rest of the product gave (1) water; (2) pyrrole (95 g.), b. p. 33·5—34·5°/16 mm., 130·5—132·5°/756 mm.; (3) b. p. 84—88°/12 mm. (6·0 g., which solidified); (4) b. p. 100—130°/20 mm. (2·0 g., which partly solidified); (5) b. p. 130—135°/22 mm., 124—128°/12 mm. (10 g.); (6) residue.

Fractions (3) and (4) were treated with petrol (b. p. 60—80°), and the insoluble solid recrystallised from petrol, giving white leaflets, m. p. 68—69°, which turned black on keeping (Found : C, 81·6; H, 6·25; N, 12·5. Calc. for C_8H_7N : C, 82·0; H, 6·0; N, 11·95%). These properties and those described earlier identified the substance as pyrrocoline. Like pyrrole, it gave a red pine-splint test. Fraction (5) also gave this test (Found : C, 82·1; H, 6·55; N, 11·65%); it could not be solidified, but extraction with boiling water and cooling gave pale yellow laminæ of indole (mixed m. p.), m. p. 44—46°.

The petrol extract from fractions (3) and (4), and also fraction (5), were shaken with dilute hydrochloric acid. Basification failed to yield dihydro*iso*indole (b. p. 213°). It was considered that *iso*indole would have a b. p. about the same as, or perhaps a little higher than, indole. Fraction (5) seemed, however, to contain at least 85% of indole. The residue (6) consisted essentially of carbazole (identified by mixed m. p.), which sublimed on heating in a vacuum.

The following amounts of the three by-products were isolated : pyrrocoline, 6 g.; indole, 8 g.; carbazole, 5 g.

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