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CONDENSATION OF INDOLE AND FORMALDEHYDE IN THE PRESENCE OF AIR AND SENSITIZERS

A FACILE SYNTHESIS OF INDOLO [3.2-*b*] CARBAZOLE

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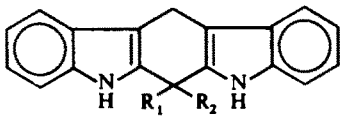
Abstract—The condensation of indole and formaldehyde, in the presence of strong acid, gives indolo [3.2-*b*]carbazole (**3**), provided that air, light and an aromatic ketone (sensitizer) are present. If the conditions for a sensitized photochemical reaction are not fulfilled, a cyclic tetramer, built up by four indole residues and four methylene bridges, is formed.

MAAS[1] in 1954 tried to prepare compounds of type **1** by condensing 3,3′-diindolylmethane (**2**) with aromatic ketones in strong acid solution. Indole and formaldehyde may be substituted for 3,3′-diindolylmethane as starting materials.



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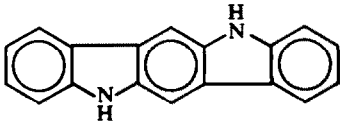
The elemental analyses were, however, in obvious disagreement with the anticipated structures, as shown by the following example (attempted condensation of 3,3′-diindolylmethane with benzophenone): Found: C, 83·48; H, 4·38; N, 11·13. Calc. for $C_{30}H_{22}N_2$: C, 87·75; H, 5·36; N, 6·83%.

It has now been found that all products gave identical mass spectra exhibiting a parent ion peak at *m/e* 256. This indicates that the structure of the starting ketone has no influence on that of the product. Comparison with an authentic sample[2,3] showed that the product was, in fact, indolo [3.2-*b*] carbazole (**3**). No traces of indolo [2.3-*b*] carbazole (**4**) could be detected.



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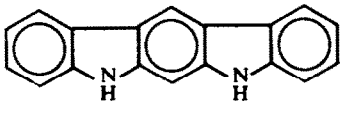

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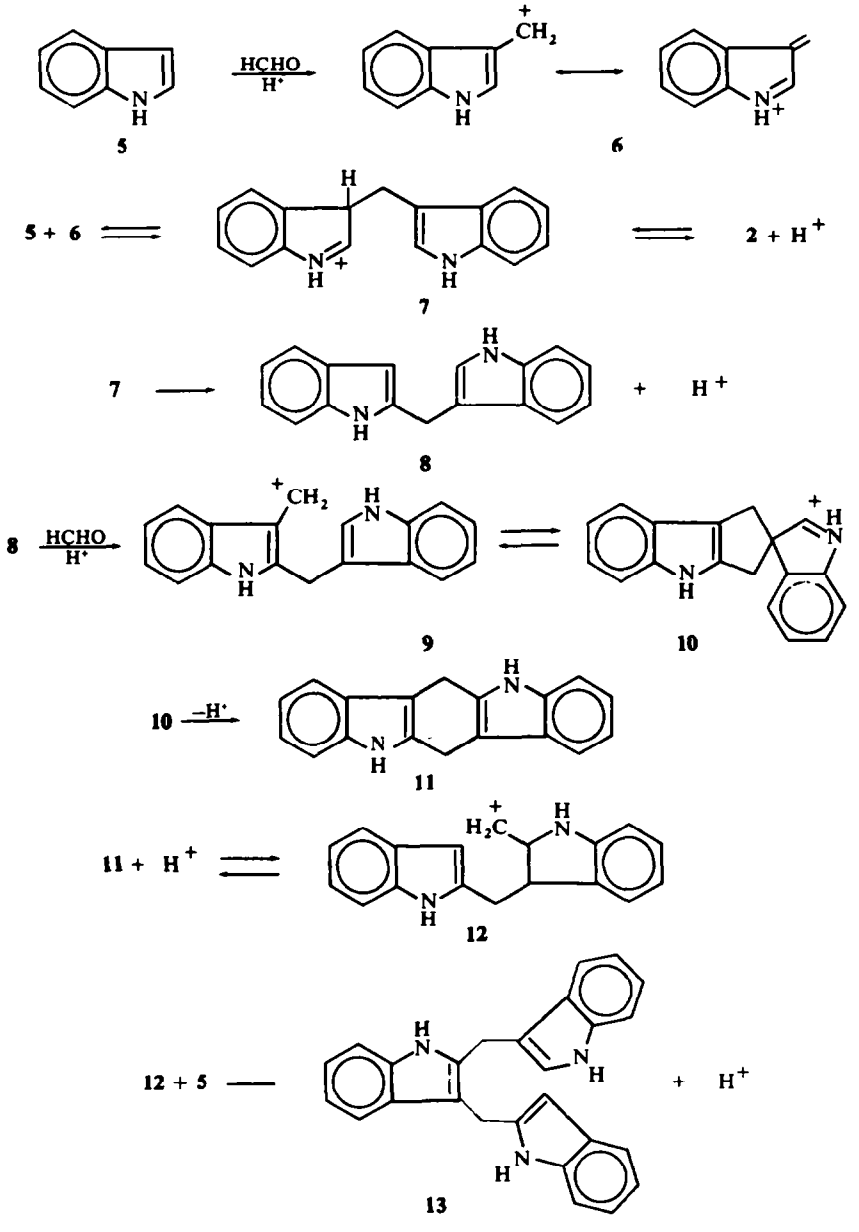
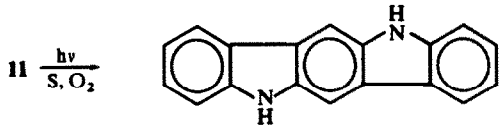
The presence of an aromatic ketone is, however, vital. Omission of the ketone gives a tetrameric condensation product (see preceding paper), built up by four methylene bridges and four indole residues. These observations suggested that the aromatic ketone functions as a sensitizer for a light-induced dehydrogenation. In accordance with this hypothesis, indolo [3.2-*b*] carbazole is not formed if the reaction occurs in the absence of light or air. To summarize: The formation of indolo [3.2-*b*] carbazole from 3,3′-diindolylmethane requires the presence of protons, air, light and a sensitizer. A possible mechanism is shown in the scheme below.





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If the last reaction, where S = sensitizer, is prevented, trimers and, finally, tetramers may be formed *via* **13**.

EXPERIMENTAL

Indolo [3.2-b] *carbazole.*

Method A. Sulfuric acid (1·0 ml) was added to a soln of 3,3'-diindolylmethane (2·46 g) and benzophenone (or acetophenone) (1·0 g) in MeOH (250 ml). The soln was refluxed (0·5 hr) without light and air protection. After (24 hr) at 25° the mixture was filtered and recrystallized from quinoline, yield 0·35 g (26%); m.p. 460°. The mass spectrum showed the following strong peaks (more than 10% of the base peak) at *m/e* 256 (100%), 257 (21%), 255 (30%) and *m/2e* 128 (29%). The IR spectrum was identical with that from an authentic sample.[2,3]

Method B. Sulfuric acid (1·0 ml) was added to a soln of indole (2.34 g), 38% formaldehyde (1·8 ml) and benzophenone (1·0 g) in MeOH (250 ml). The soln was treated as described above, yield 0·43 g (17%). O_2-bubbling through the reaction mixture increased the yield to 22%.

Acknowledgement—I thank Dr. B. Robinson and Dr. H. M. Grotta for providing samples for comparison.

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[2] H. M. Grotta, C. J. Riggle and A. E. Bearse, *J. Org. Chem.* **26** 1509 (1961)
[3] B. Robinson, *J. Chem. Soc.* 3097 (1963)