Non-benzenoid Aromatic Heterocycles. IV[*] [1]. *An Attempted Synthesis of Indolo[3, 2-b]indole: A Hetero-pentalene*

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Since the proposal of pentalene (I) by Robinson[2] as a possible aromatic substance, it has been the subject of many studies. Although dibenzopentalene and a few other condensed pentalene derivatives have recently been synthesized (showing non-aromatic polyene properties), the synthesis of pentalene or even benzopentalene is still awaited, and the results of theoretical treatments on the stability of these compounds by several groups of workers are not in accordance[3].

It has been found that substitution of –C=C– groups in a conjugated compound by hetero-atoms results in a system which shows properties of the original compound to a certain extent. These facts led the authors to attempt a synthesis of indolo[3, 2-b]indole (II) as a model of diazadibenzopentalene in order to add some experimental data concerning the stability of the proposed pentalene ring system[4]. As possible routes to indolo[3, 2-b]indole, intramolecular dehydration of 2-(*o*-aminophenyl)-indolone (III) or dehydrogenation of *N*, *N*′-dihydroindolo[3, 2-b]indole (dindole) (IV) may be considered. These two compounds, III and IV, have been prepared[5] by reduction of *o*, *o*′-dinitrobenzil by Raney nickel or by zinc and hydrochloric acid, respectively.

An attempted intramolecular condensation of 2-(*o*-aminophenyl)indolone has been briefly reported by Ruggli et al.[5], but as nothing has been described about the condensation reagent, the present authors tried to dehydrate it using a variety of condensation catalysts, none of which gave an identifiable product.

Next, the dehydrogenation of dindole was tried. When dindole was refluxed with chloranil in *n*-butanol, an intense violet coloration took place, but the color faded away gradually and tetrachlorohydroquinone was isolated from the reaction mixture. Neither, in this case, was the expected indolo[3, 2-b]indole, obtained, and an amorphous polymeric product was obtained. The elemental composition of this substance is not very far from $C_{14}H_{10}ON_2$. Attempts to isolate this colored substance were not successful, but the absorption curve of this substance in the visible region is quite similar to 2-(*o*-aminophenyl)indolone and the R_f value of this compound is the same as 2-(*o*-aminophenyl)-indolone. From these facts and the supplemental data described in the experimental

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[*] Presented at the meeting of the Chemical Society of Japan, Tokyo, October, 1959.

[1] Part III, H. Kato, T. Ogawa and M. Ohta, This Bulletin, 33, 1468 (1960).

[2] J. W. Armit and R. Robinson, *J. Chem. Soc.*, **1922**, 827.

[3] Cf. for example, W. Baker and J. F. W. McOmie, "Non-benzenoid Aromatic Compounds" in "Progress in Organic Chemistry", Vol. 3, Butterworths Scientific Publications, London (1955), p. 44.

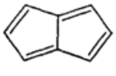
[4] During the course of this investigation, a series of condensed azapentalenes have been prepared by Treibs. W. Treibs, *Naturwissenschaften*, **46**, 170 (1959).

[5] P. Ruggli et al., *Helv. Chim. Acta*, **18**, 845 (1935).

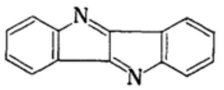
part, it may be concluded that the colored compound is 2-(*o*-aminophenyl)indolone.

These experimental data, although negative, indicate that at least some interaction exists between the two compounds (IV and chloranil) and dehydrogenation has occurred in dindole. On the basis of these data, it seemed reasonable to assume that dehydrogenation of dindole gave indolo[3, 2-b]indole as an intermediate product, but this compound is so unstable that it took up traces of water present in butanol and gave 2-(*o*-aminophenyl)indolone. When rigidly dehydrated *n*-butanol was used as solvent, the beginning of coloration required a longer period and on addition of a small amount of water, the coloration took place at once. This fact also lends some support to the above described assumption.

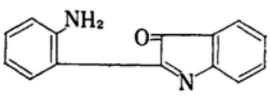
During the course of this investigation, the authors have known that Treibs[6] also attempted dehydrogenation of dindole using many catalysts, but indolo[3, 2-b]indole was not prepared.



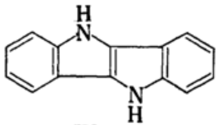
I



II



III



IV

Experimental

Attempted Cyclodehydration of 2-(*o*-Aminophenyl) indolone.—2-(*o*-Aminophenyl)indolone[5] was treated with the following reagents under warming or at room temperature: polyphosphoric acid, concentrated sulfuric acid, acetic acid, triethylamine, and piperazine. Polyphosphoric acid and sulfuric acid gave a yellow amorphous substance, accompanied by the starting material. Acetic acid yielded a yellow polymeric substance, and in the case of triethylamine the starting material was recovered unchanged.

Reaction of Dindole with Chloranil.—a) A butanolic solution (30 ml.) of dindole[5] (0.5 g.) and chloranil (0.6 g.) was gently refluxed for four hours. At first a deep violet coloration took place, but it faded away gradually, and after four hours the solution became pale brown. The solvent was removed under reduced pressure and the residue was washed with ether and purified by chromatography (alumina-benzene). The yellow powder from the eluate was repeatedly recrystallized first from benzene-benzine and then from benzene giving yellow amorphous powder. It does not show a distinct melting point (about 300°C).

Found: C, 74.02; H, 4.40. Calcd. for $C_{14}H_{10}\cdot ON_2$: C, 75.65; H, 4.54%.

The ether washings in the above experiment were extracted with 10% aqueous sodium hydroxide and the aqueous layer was acidified which hydrochloric acid. The white crystals (0.47 g.) which separated out were recrystallized from acetic acid giving white needles, m. p. 234°C (in a sealed tube), undepressed on admixture with tetrachlorohydroquinone.

b) When chloranil or dindole alone was refluxed in *n*-butanol, no coloration took place, and chloranil gave no tetrachlorohydroquinone.

c) Dindole and chloranil was heated cautiously until the coloration took place, and the colored solution in situ was used for spectroscopic measurement. (λ_{max} 550 mμ; with a small shoulder at about 490 mμ; intensity unspecified). The shape of the curve in the visible region is the same with 2-(*o*-aminophenyl)indolone. Attempts to isolate this colored substance (by chromatography) were unsuccessful. The colored substance and 2-(*o*-aminophenyl)indolone gave the same spot in paper chromatography (R_f=0.95, solvent: butanol-pyridine-water, 4 : 1 : 2). This colored substance seemed a little more unstable than 2-(*o*-aminophenyl)indolone, but when 2-(*o*-aminophenyl)indolone was heated with chloranil in *n*-butanol, it decomposed rapidly to give a yellow solution.

d) When rigidly dehydrated *n*-butanol (freshly twice distilled) was used as solvent, the beginning of coloration was delayed and the intensity of the color was feeble and on addition of a small amount of water, the color was intensified immediately.

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[6] W. Treibs, private communication.