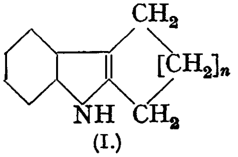
324. *The Action of Nitric Acid on Polycyclic Indole Derivatives. Part XIII. Indeno(2′ : 3′ : 2 : 3)indole.*

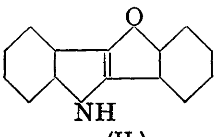
By N. M. Beyts and S. G. P. Plant.

1-*Acetylindeno*(2′ : 3′ : 2 : 3)*indole* on nitration in acetic acid gives an addition compound, formed by the attachment of NO_2 and OAc, as the main product together with a smaller quantity of a simple *nitro*-derivative, and thereby exhibits reactivity which is abnormal in an indole of this degree of complexity. The closely related, but more complex, 3-*acetylindeno*(2′ : 3′ : 2 : 1)-β-*naphthindole* gives only a nitro-substitution product under similar conditions.

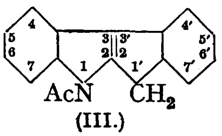
Although the *N*-acyl derivatives of indoles of the type (I; $n = 1$ or 2) readily form addition products by the attachment of either 2OH or OH and NO_2 at the 2 : 3-position on treatment with nitric acid in acetic acid solution, it has been clearly shown that analogous substances are formed far less readily when the indole skeleton is contained in polycyclic systems containing four rings fused together (Oakeshott and Plant, J., 1928, 1840; Bryant and Plant, J., 1931, 93). A notable exception to the latter observation is the case of coumarono(2′ : 3′ : 3 : 2)indole (II), in which the ring attached to the indole



(I.)



(II.)



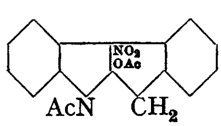
(III.)

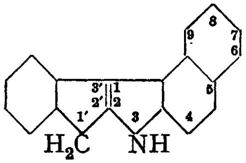
nucleus is heterocyclic in character, since it has been observed that the main products of the nitration of its *N*-acyl derivatives are substances formed by the addition of NO_2 and OAc (Cawley and Plant, J., 1938, 1214).

It has now been found that 1-*acetylindeno*(2′ : 3′ : 2 : 3)*indole* (III) has exceptional reactivity in this direction and on nitration it has given not only a simple *nitro*-derivative but a relatively large amount of 3-*nitro*-2-*acetoxy*-1-*acetyl*-2 : 3-*dihydroindeno*(2′ : 3′ : 2 : 3)-*indole* (IV). The acetylation of the hydroxyl group in this reaction, also observed in the case of the acylcoumarono(2′ : 3′ : 3 : 2)indoles, is a very unusual feature. The position of the substituent in the nitro-derivative has not been definitely established, but the substance was different from 5-*nitro*-1-*acetylindeno*(2′ : 3′ : 2 : 3)*indole*, which was synthesised by applying Fischer's reaction to β-hydrindone-*p*-nitrophenylhydrazone and acetylating the product. It is, however, extremely probable that the substituent occupies the 6-position, as has been shown to be the case in analogous reactions with the simpler *N*-acylated indoles of this type. 1-*Benzoylindeno*(2′ : 3′ : 2 : 3)*indole* has been prepared, but attempts to obtain a similar addition product from it were unsuccessful.

The 3-*acetyl* derivative of the more complex, but closely related, *indeno*(2′ : 3′ : 2 : 1)-β-*naphthindole* (V), obtained from β-*hydrindone*-β-*naphthylhydrazone*, was treated with nitric acid under similar conditions, and a simple *mononitro*-derivative was isolated in good yield, indicating that the ability to form addition compounds is diminished by the presence of the additional benzene nucleus, as was observed in the coumarono(2′ : 3′ : 3 : 2)-indole series.

(IV.)





(V.)

EXPERIMENTAL.

Nitration of 1-*Acetylindeno*(2′ : 3′ : 2 : 3)*indole*.—Acetyl chloride (3 c.c.) was added gradually with shaking to a solution of indeno(2′ : 3′ : 2 : 3)indole (3 g., prepared as described by Armit and Robinson, J., 1922, **121**, 827) in acetone containing aqueous potassium hydroxide (3 g. of 66%). The careful addition of water then precipitated 1-*acetylindeno*(2′ : 3′ : 2 : 3)*indole*, which was purified by grinding with alcohol and crystallisation from glacial acetic acid, from which it separated in colourless needles, m. p. 131° (Found : N, 6·0. $C_{17}H_{13}ON$ requires N, 5·7%). It was readily hydrolysed to the original indole by refluxing with aqueous alcoholic alkali. The corresponding *benzoyl* compound, which formed brown prisms, m. p. 169—170°, from glacial acetic acid, was similarly prepared with the aid of benzoyl chloride (Found : N, 4·7. $C_{22}H_{15}ON$ requires N, 4·5%).

When a suspension of the acetyl compound (2 g.) in glacial acetic acid (13 c.c.) at 50° was treated with nitric acid (0·7 g., *d* 1·5, dissolved in 2·5 c.c. of acetic acid), the temperature rose to 58° and a clear solution resulted. 6(?)-*Nitro*-1-*acetylindeno*(2′ : 3′ : 2 : 3)*indole* (0·5 g.), crystallising in orange plates, m. p. 275° (decomp.), from *cyclo*hexanone, soon separated on cooling (Found : C, 69·6; H, 4·1. $C_{17}H_{12}O_3N_2$ requires C, 69·9; H, 4·1%), and after a few hours the solution was filtered and the filtrate left for some days. The 3-*nitro*-2-*acetoxy*-1-*acetyl*-2 : 3-*dihydroindeno*(2′ : 3′ : 2 : 3)*indole* (1·2 g.) which then slowly separated was obtained in colourless prisms, m. p. 177—180° (decomp.) on recrystallisation from glacial acetic acid (Found, before recrystallisation : C, 64·9; H, 4·4; N, 7·8; after recrystallisation : C, 64·8; H, 4·6; N, 7·9. $C_{19}H_{16}O_5N_2$ requires C, 64·8; H, 4·5; N, 8·0%). It is clear from the analytical figures that acetylation of the hydroxyl group took place during the reaction and not on subsequent recrystallisation.

5-*Nitro*-1-*acetylindeno*(2′ : 3′ : 2 : 3)*indole*.—When solutions of equal weights of β-hydrindone and *p*-nitrophenylhydrazine in hot alcohol were mixed, the hydrazone rapidly separated in yellow needles, m. p. 232° (decomp.). After this had been refluxed for an hour with equal volumes of glacial acetic acid and concentrated hydrochloric acid, the addition of water precipitated 5-*nitroindeno*(2′ : 3′ : 2 : 3)*indole*, which formed crimson plates, m. p. 255°, from acetic acid (Found : C, 71·6; H, 4·1. $C_{15}H_{10}O_2N_2$ requires C, 72·0; H, 4·0%). The indole was refluxed with acetic anhydride for 3½ hours and 5-*nitro*-1-*acetylindeno*(2′ : 3′ : 2 : 3)*indole* separated on cooling in yellow needles; it crystallised from acetic acid in yellow needles, m. p. 247° (Found : N, 9·5. $C_{17}H_{12}O_3N_2$ requires N, 9·6%). The same product was obtained when the indole was acetylated with acetyl chloride and alkali in acetone as described for indeno(2′ : 3′ : 2 : 3)indole.

Nitration of 3-*Acetylindeno*(2′ : 3′ : 2 : 1)-β-*naphthindole*.—The β-*naphthylhydrazone* of β-hydrindone, which formed yellow plates, m. p. 176° (decomp.), from alcohol, separated when hot alcoholic solutions of the hydrazine (5 g.) and ketone (4 g.) were mixed (Found : N, 10·1. $C_{19}H_{16}N_2$ requires N, 10·3%). When it was boiled for not more than 5 minutes with glacial acetic acid, *indeno*(2′ : 3′ : 2 : 1)-β-*naphthindole*, crystallising in yellow prisms, m. p. 208—209°, from alcohol, separated on cooling (Found : N, 5·5. $C_{19}H_{13}N$ requires N, 5·5%). This was converted into its 3-*acetyl* derivative, which formed colourless prisms, m. p. 185°, from *cyclo*hexanone, by a process similar to that used in the case of indeno(2′ : 3′ : 2 : 3) indole (Found : C, 84·4; H, 5·1. $C_{21}H_{15}ON$ requires C, 84·8; H, 5·1%). When the acetyl derivative (1·9 g.), suspended in glacial acetic acid (20 c.c.) at 50°, was treated with nitric acid (0·45 g., *d* 1·5, dissolved in 2 c.c. of acetic acid), ?-*nitro*-3-*acetylindeno*(2′ : 3′ : 2 : 1)-β-*naphthindole* (1·5 g.) separated as a yellow solid. On recrystallisation from *cyclo*hexanone and then from anisole it was obtained in feathery yellow needles, m. p. 265° (decomp.) (Found : C, 74·0; H, 4·3. $C_{21}H_{14}O_3N_2$ requires C, 73·7; H, 4·1%).

THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, September* 16*th*, 1939.]