

246. *The Action of Nitric Acid on Polycyclic Indole Derivatives.*
 Part XIV. *Acenaphthylene(7' : 8' : 2 : 3)indole.*

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The double bond in the 2 : 3-position in the 1-acylacenaphthylene(7' : 8' : 2 : 3)indoles has been shown to be relatively reactive so that nitration in acetic acid has given not only the 6(or 4)-nitro-derivatives, but also, in some cases, compounds formed by the addition of NO₂ and OAc.

PRODUCTS formed by the addition of 2OH, NO₂ and OH, or NO₂ and OAc, at the 2 : 3-position frequently accompany the nitro-derivatives prepared by the nitration of certain *N*-acylindoles in acetic acid, but the feature is generally less well developed in the more complex polycyclic indoles than in the simpler substances such as 2 : 3-dimethylindole and tetrahydrocarbazole (*J.*, 1928, 1840; 1931, 93; 1932, 2192; 1933, 955). Fennell and Plant (*J.*, 1932, 2872) found that nitration of 1-acyl-2 : 3-diphenylindoles resulted in formation of additive compounds containing the phenanthracarbazole skeleton, and the observations suggest that the addition reactions are more likely to proceed with substances in which the indole structure is fused at the 2 : 3-position to an active double bond in another polynuclear system. In this connection, interest attaches to acenaphthylene(7' : 8' : 2 : 3)indole (I), which has been prepared by Sircar and Gopalan (*J. Indian Chem. Soc.*, 1932, 9, 297; see also Korczynski, Brydowna, and Kierzek, *Gazzetta*, 1926, 56, 903) by applying the Fischer reaction to acenaphthenone phenylhydrazone.



The action of one molecular proportion of nitric acid on its 1-*acetyl*, 1-*benzoyl*, 1-*carbomethoxy*-, 1-*carbethoxy*-, and 1-*cinnamoyl* derivatives in hot acetic acid has given in each case a simple nitro-compound. There is little doubt that the substituent in these substances occupies the 6-position, which is the one almost invariably taken in analogous cases. This has been partly proved by the synthesis of one of them by converting *acenaphthenone m-nitrophenylhydrazone* into the corresponding indole and cinnamoylating the product, and by converting three of the others into the same cinnamoyl derivative by hydrolysis and subsequent acylation, results which leave only the 4-position as a possible alternative.

Furthermore, the 1-carbomethoxy- and the 1-carbethoxy-derivative have given substantial quantities of the addition compounds, *methyl* and *ethyl 3-nitro-2-acetoxy-2 : 3-dihydroacenaphthylene(7' : 8' : 2 : 3)indole-1-carboxylate* (II; R = Me or Et), which are obviously analogous to the nitroacetoxy-compounds already described (*J.*, 1931, 1990; 1938, 1214; 1939, 1534) and indicative of the reactive character of the double bond. The 1-cinnamoyl derivative has also given a colourless *substance*, evidently additive in type, the structure of which is less obvious. Its molecular formula appears to be C₂₉H₂₀O₆N₂, which suggests the addition of OH and OAc at the double bond together with a nitro-group as a substituent.

In studying other applications of the Fischer reaction to hydrazones of acenaphthenone, it was noted that the process went normally with the 2-*chloro-5-nitrophenylhydrazone* and the *p-bromophenylhydrazone*, but the corresponding indole was not obtained from the *o-nitrophenylhydrazone*.

EXPERIMENTAL.

1-*Acyl- and 1-Alkyl-acenaphthylene(7' : 8' : 2 : 3)indoles*.—Acetyl chloride (1.8 c.c.) was gradually added, with shaking, to a solution of acenaphthylene(7' : 8' : 2 : 3)indole (1 g., m. p. 235°, prepared by

the method of Sircar and Gopalan, *loc. cit.*) in acetone (20 c.c.) containing aqueous potassium hydroxide (3.4 g. of 66%). The addition of water precipitated 1-acetylacenaphthylene(7' : 8' : 2 : 3)indole, which was obtained from cyclohexanone in orange-red prisms (0.9 g.), m. p. 207° (Found : N, 4.8. C₂₀H₁₃ON requires N, 4.9%).

In similar experiments using benzoyl chloride, methyl chloroformate, ethyl chloroformate, cinnamoyl chloride, methyl sulphate, or ethyl sulphate, instead of acetyl chloride, the following were respectively obtained in good yields : 1-benzoylacenaphthylene(7' : 8' : 2 : 3)indole, dark red prisms, m. p. 148—149°, from acetic acid (Found : N, 4.0. C₂₅H₁₅ON requires N, 4.1%); methyl acenaphthylene(7' : 8' : 2 : 3)-indole-1-carboxylate, golden brown plates, m. p. 154°, from acetic acid (Found : N, 4.5. C₂₀H₁₃O₂N requires N, 4.7%); ethyl acenaphthylene(7' : 8' : 2 : 3)indole-1-carboxylate, orange-red needles, m. p. 106°, from acetic acid (Found : N, 4.5. C₂₁H₁₅O₂N requires N, 4.5%); 1-cinnamoylacenaphthylene(7' : 8' : 2 : 3)indole, orange-red plates, m. p. 166°, from acetic acid (Found : N, 3.5. C₂₇H₁₇ON requires N, 3.8%); 1-methylacenaphthylene(7' : 8' : 2 : 3)indole, scarlet plates, m. p. 204°, from acetic acid, identical (mixed m. p.) with the product obtained by applying the Fischer reaction to acenaphthenone phenylmethylhydrazone as described by Sircar and Gopalan (*loc. cit.*); and 1-ethylacenaphthylene(7' : 8' : 2 : 3)indole, red plates, m. p. 182°, from acetic acid (Found : N, 5.3. C₂₀H₁₅N requires N, 5.2%).

All the above acyl compounds were hydrolysed to acenaphthylene(7' : 8' : 2 : 3)indole by refluxing their solutions in aqueous-alcoholic potassium hydroxide for $\frac{1}{2}$ hour, the indole crystallising on cooling. Attempts to repeat the preparation of the benzoyl and the carbethoxy-derivative were not always successful for no apparent reason, the unchanged indole being recovered on several occasions. In this connection it is of interest that an attempt to prepare the 1-phenylacetyl derivative under similar conditions with phenylacetyl chloride failed.

Nitration of 1-Acetyl- and 1-Benzoyl-acenaphthylene(7' : 8' : 2 : 3)indole.—When a suspension of the acetyl compound (1 g.) in glacial acetic acid (50 c.c.) at 110° was treated with nitric acid (0.15 c.c., *d* 1.5), dissolved in acetic acid (1 c.c.), with stirring, the solid soon went into solution, and, on cooling, 6(or 4)-nitro-1-acetylacenaphthylene(7' : 8' : 2 : 3)indole (0.4 g.) began to separate. It was collected after 3 hours and recrystallised from acetic acid, from which it was obtained in orange-red needles, m. p. 275° (Found : N, 8.5. C₂₀H₁₂O₃N₂ requires N, 8.5%).

After a solution of the 1-benzoyl compound (1.5 g.) in glacial acetic acid (20 c.c.) at its boiling point had been similarly treated 6(or 4)-nitro-1-benzoylacenaphthylene(7' : 8' : 2 : 3)indole (1 g.), orange-red needles, m. p. 225° (decomp.), from acetic acid, was obtained (Found : N, 6.9. C₂₅H₁₄O₃N₂ requires N, 7.2%).

Nitration of Methyl and Ethyl Acenaphthylene(7' : 8' : 2 : 3)indole-1-carboxylate.—After nitric acid (0.28 c.c., *d* 1.5) had been added to a solution of the methyl ester (2 g.) in glacial acetic acid (25 c.c.) at 115°, a red solid (0.5 g.) rapidly appeared. When cold, this was recrystallised from acetic acid, and methyl 6(or 4)-nitroacenaphthylene(7' : 8' : 2 : 3)indole-1-carboxylate obtained in red needles, m. p. 243° (decomp.) (Found : N, 8.2. C₂₀H₁₂O₄N₂ requires N, 8.1%). After the mother-liquor from the reaction mixture had been left overnight at room temperature, a colourless solid (0.2 g.) had separated, and, on recrystallisation from benzene, methyl 3-nitro-2-acetoxy-2 : 3-dihydroacenaphthylene(7' : 8' : 2 : 3)indole-1-carboxylate was isolated in colourless prisms, m. p. 208° (decomp.) (Found : C, 65.0; H, 4.1; N, 6.6. C₂₂H₁₆O₆N₂ requires C, 65.3; H, 4.0; N, 6.9%). When the above reaction was carried out at 100°, the yield of the nitro-compound was greater, but no addition product crystallised from the mother-liquor.

Similar treatment of the ethyl ester (1 g.) in acetic acid (6 c.c.) at 80° led to the rapid separation of ethyl 6(or 4)-nitroacenaphthylene(7' : 8' : 2 : 3)indole-1-carboxylate (0.6 g.), golden yellow needles, m. p. 218—219°, from acetic acid (Found : N, 8.0. C₂₁H₁₄O₄N₂ requires N, 7.8%), while ethyl 3-nitro-2-acetoxy-2 : 3-dihydroacenaphthylene(7' : 8' : 2 : 3)indole-1-carboxylate (0.3 g.), colourless prisms, m. p. 210—211° (decomp.), from alcohol (Found : C, 65.8; H, 4.4. C₂₃H₁₈O₆N₂ requires C, 66.0; H, 4.3%), crystallised from the mother-liquor when left for several hours at room temperature.

Nitration of 1-Cinnamoylacenaphthylene(7' : 8' : 2 : 3)indole.—The cinnamoyl compound (2 g.) in acetic acid (50 c.c.) at 100°, on being similarly nitrated, yielded first 6(or 4)-nitro-1-cinnamoylacenaphthylene(7' : 8' : 2 : 3)indole (0.3 g.), orange-red needles, m. p. 261°, from nitrobenzene, identical (mixed m. p.) with the synthetical material described below (Found : N, 7.0. C₂₇H₁₆O₃N₂ requires N, 6.7%), and then a buff-coloured solid (0.7 g.), which, after several recrystallisations from benzene-light petroleum, gave an apparently pure substance in colourless prisms, m. p. 225° (decomp.) (Found : C, 70.4; H, 4.1; N, 5.9. C₂₆H₂₀O₃N₂ requires C, 70.7; H, 4.1; N, 5.7%).

Synthesis of 6(or 4)-Nitro-1-cinnamoylacenaphthylene(7' : 8' : 2 : 3)indole.—After an alcoholic solution of acenaphthenone (2 g.) and *m*-nitrophenylhydrazine (1.8 g.) had been boiled for 2 hours, the *m*-nitrophenylhydrazone (3.2 g.), red needles, m. p. 215° (decomp.) from isoamyl alcohol (Found : N, 13.7. C₁₈H₁₃O₂N₃ requires N, 13.9%), crystallised on cooling. A solution of the hydrazone (1.2 g.) in the minimum quantity of boiling alcohol was treated with concentrated hydrochloric acid (50 c.c.), the whole refluxed for 22 hours, and allowed to cool. The crude 6(or 4)-nitroacenaphthylene(7' : 8' : 2 : 3)indole (0.9 g.), which separated, was dissolved in acetone (30 c.c.) and cinnamoylated by the method described for the indole itself. On recrystallisation of the product from nitrobenzene, 6(or 4)-nitro-1-cinnamoylacenaphthylene(7' : 8' : 2 : 3)indole (0.8 g.) was obtained in orange-red needles, m. p. 261°, identical (mixed m. p.) with the substance mentioned above.

The 6(or 4)-nitro-derivatives of the acetyl, benzoyl, and carbomethoxy-compounds described above were hydrolysed by refluxing for an hour with aqueous-alcoholic potassium hydroxide, and the products, precipitated by water, cinnamoylated in the usual way. In each case the substance obtained was identical (mixed m. p.) with the above synthetical material.

Acenaphthenone o-nitrophenylhydrazone, red needles, m. p. 175°, from isoamyl alcohol (Found : N, 13.6%), was prepared like the *m*-isomer, but attempts to convert it into the corresponding indole were unsuccessful.

7-Chloro-4-nitroacenaphthylene(7' : 8' : 2 : 3)indole.—After a mixture of acenaphthenone (4 g.) and

2-chloro-5-nitrophenylhydrazine (4.5 g.) had been heated at 135—140° for $\frac{1}{2}$ hour, the product was crystallised from cyclohexanone, from which the 2-chloro-5-nitrophenylhydrazone separated in yellow prisms (3.5 g.), m. p. 226° (decomp.) (Found: N, 12.2. $C_{18}H_{12}O_2N_3Cl$ requires N, 12.4%). When a solution of the hydrazone (2.7 g.) in a mixture of alcohol (200 c.c.) and concentrated hydrochloric acid (100 c.c.) was refluxed for 14 hours, 7-chloro-4-nitroacenaphthylene(7' : 8' : 2 : 3)indole (1.7 g.), orange-red prisms, m. p. 279—282°, from cyclohexanone, gradually separated (Found: N, 9.3. $C_{18}H_9O_2N_2Cl$ requires N, 8.7%).

5-Bromoacenaphthylene(7' : 8' : 2 : 3)indole.—Acenaphthenone (1 g.) and *p*-bromophenylhydrazine (1.1 g.) in boiling alcohol gave the *p*-bromophenylhydrazone, yellow prisms (1.6 g.), m. p. 185° (decomp.), from alcohol (Found: N, 8.5. $C_{18}H_{13}N_2Br$ requires N, 8.3%). It was refluxed with aqueous-alcoholic hydrochloric acid for 17 hours, and when the solid obtained by adding water was crystallised from benzene, 5-bromoacenaphthylene(7' : 8' : 2 : 3)indole (in 55% yield) separated in orange-yellow needles, m. p. 200° (Found: N, 4.3. $C_{18}H_{10}NBr$ requires N, 4.4%).

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