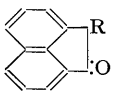
349. *Acenaphthyleno-compounds. Part II.**

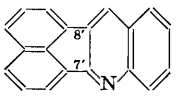
By J. B. Duthie and S. G. P. Plant.

The ease with which acenaphthenone undergoes self-condensation to 8-acenaphthylideneacenaphthen-7-one has prevented its use in some well-known reactions of the $-CH_2 \cdot CO-$ group. Nevertheless, ethyl 8-ketoacenaphthene-7-glyoxylate has been prepared and used for the synthesis of derivatives of acenaphthyleno(7′ : 8′-4 : 5)pyrazole. Acenaphthyleno-compounds in general have been found not readily to undergo polymerisation at 300°, but methyl acenaphthyleno(7′ : 8′-2 : 3)indole-1-carboxylate gave 1-methylacenaphthyleno(7′ : 8′-2 : 3)indole and carbon dioxide.

The results described in a previous communication * indicate that interest attaches to compounds which contain the acenaphthylene system fused to other cyclic structures. Acenaphthenone (I; R = H) appears to be a convenient starting point for the preparation of some of these substances, and Sircar and Gopalan (*J. Indian Chem. Soc.*, 1932, **9**, 297) have obtained acenaphthyleno(7′ : 8′-2 : 3)quinoline (II) from it by condensation with *o*-aminobenzaldehyde (see also Buu-Hoï and Cagniant, *Compt. rend.*, 1943, **216**, 447). Attempts have now been made to prepare the quinolone (III) by heating the ketone (I; R = H) with anthranilic acid, an application of Niementowski's reaction (*Ber.*, 1894, **27**, 1394; see also Tiedtke, *Ber.*, 1909, **42**, 621), but the ketone was readily converted under these conditions into 8-acenaphthylideneacenaphthen-7-one (IV) by a self-



(I)



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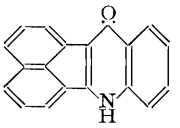

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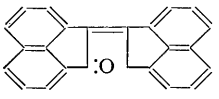


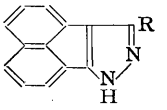
(IV)

condensation process. This is reminiscent of observations by Blount and Plant (*J.*, 1937, 376) who found that *cyclo*pentanone was converted first into *cyclo*pentylidene*cyclo*pentanone in a similar experiment. An alternative route to (III) would be from aniline and ethyl 8-ketoacenaphthene-7-carboxylate (I; R = CO_2Et), but efforts to obtain the latter have been unsuccessful. Ethyl 8-ketoacenaphthene-7-glyoxylate (I; R = $CO \cdot CO_2Et$) has been prepared from (I; R = H) and ethyl oxalate in ethanolic sodium ethoxide, but it did not give (I; R = CO_2Et) on pyrolysis under a variety of conditions. Only 8-acenaphthylideneacenaphthen-7-one was obtained in attempts to condense acenaphthenone with ethyl carbonate in the presence of sodium ethoxide, and similar results attended efforts to prepare (I; R = CHO) with ethyl formate under analogous conditions.

The ester (I; R = $CO \cdot CO_2Et$) might form the starting point for the preparation of various heterocyclic substances, and ethyl acenaphthyleno(7′ : 8′-4 : 5)pyrazole-3-carboxylate (V; R = CO_2Et), obtained from it by the action of hydrazine, has been converted through the acid (V; R = CO_2H) into acenaphthyleno(7′ : 8′-4 : 5)pyrazole (V; R = H). A similar reaction with phenylhydrazine has given an analogous product for which two structures (VI and VII; R = CO_2Et) are possible (the corresponding forms of the product from hydrazine would be readily interconvertible as tautomerides). The same structural problem arose with the substance obtained by Beyer and Claisen (*Ber.*, 1887, **20**, 2178) from phenylhydrazine and ethyl benzoylpyruvate, $Ph \cdot CO \cdot CH_2 \cdot CO \cdot CO_2Et$, but this was shown to be ethyl 1 : 5-diphenylpyrazole-3-carboxylate by the fact that it was also prepared by the action of benzenediazonium chloride on ethyl α-phenacylaceto-acetate, $CH_3 \cdot CO \cdot CH(CH_2 \cdot CO \cdot Ph) \cdot CO_2Et$ (Bischler, *Ber.*, 1892, **25**, 3143), and by analogy the above product is regarded as (VI; R = CO_2Et). An attempt to establish this structure in a way analogous to that of Bischler has failed, since it has been found by Mr. M. F. A. Jones in this laboratory that the action of 8-bromoacenaphthen-7-one

* The paper by Bannister and Plant, *J.*, 1948, 1247, is considered as Part I.

(I; R = Br) on the sodium derivative of ethyl acetoacetate under some conditions leads to the formation of the compound (VIII).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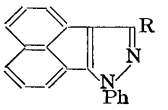
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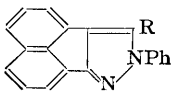
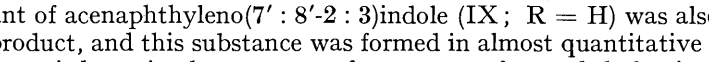
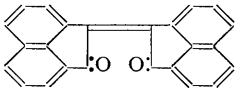

(VII)

Pyrolysis of the acid (VI; R = CO_2H) gave results which appeared to be fortuitous. The product was difficult to purify, but in some experiments a red compound, $C_{19}H_{12}N_2$, presumably (VI; R = H) although it was different in appearance from (V; R = H), was obtained. On one occasion a compound, m. p. 316° (decomp.), which appeared to have the composition $C_{39}H_{24}O_2N_4$, formed from equimolecular amounts of (VI; R = H) and (VI; R = CO_2H), was isolated. Acenaphthylene is rapidly polymerised by heat (Dziewoński and Leyko, *Ber.*, 1914, **47**, 1679), and it seemed possible that polymerisation might be effected in this series. A number of acenaphthyleno-compounds were accordingly heated at temperatures of about 300° for approximately 10 minutes. The substances (V; R = CO_2Et), (V; R = H), (VI; R = CO_2Et), (IX; R = H), (IX; R = Me), and (IX; R = Ac) were essentially unchanged in this way. Methyl acenaphthyleno(7′ : 8′-2 : 3) indole-1-carboxylate (IX; R = CO_2Me) also gave no polymer, but it decomposed to give carbon dioxide and a substantial quantity of 1-methylacenaphthyleno(7′ : 8′-2 : 3)-indole (IX; R = Me). This reaction may be represented by the scheme :



A small amount of acenaphthyleno(7′ : 8′-2 : 3)indole (IX; R = H) was also isolated from the reaction product, and this substance was formed in almost quantitative yield when the pyrolysis was carried out in the presence of an excess of β-naphthylamine. Presumably one or more of the methylated 2-naphthylamines were also then formed, but they could not be purified or identified. It is of interest in this connexion that Nölting (*Ber.*, 1888, **21**, 3154) obtained aniline, methylaniline, and dimethylaniline from the product of heating methyl phenylcarbamate, Ph·NH·CO_2Me, with lime at 260°.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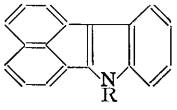
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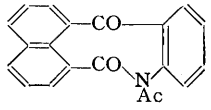
(X)

Koelsch (*J. Amer. Chem. Soc.*, 1944, **66**, 1983) found that 1-acetyl-6-bromo-2 : 3-diphenylindole could be oxidised by chromic acid in acetic acid solution to *N*-acetyl-2-benzoyl-5-bromobenzanilide, and the process has been extended by other workers to several indole derivatives. It has now been found that the same reaction can be applied to 1-acetylacenaphthyleno(7′ : 8′-2 : 3)indole (IX; R = Ac) with the formation of *o*-(8-carboxy-1-naphthoyl)acetanilide lactam (X).

Experimental

Action of Anthranilic Acid on Acenaphthenone.—After a mixture of anthranilic acid (2 g.) and acenaphthenone (2 g.) had been heated at 100° for 2 hours, the product was cooled, pulverised, and digested with ethanol (100 c.c.). When the residue (1·5 g.) was crystallised from acetone, yellow needles (1·1 g.; nitrogen free; m. p. 247°) were isolated, and these were further purified by adsorption from benzene on alumina. The 8-acenaphthylideneacenaphthen-7-one obtained (1 g.) then crystallised from chloroform in yellow needles, m. p. 262° (Found : C, 90·5; H, 4·5. Calc. for $C_{24}H_{14}O$: C, 90·6; H, 4·4%) (Graebe and Jequier, *Annalen*, 1896, **290**, 202, give m. p. 262°).

Ethyl 8-Ketoacenaphthene-7-glyoxylate.—A suspension of acenaphthenone (16·8 g.) in ethyl oxalate (150 c.c.) was added during 10 minutes with mechanical stirring to a solution of sodium

(2·5 g.) in dry ethanol (35 c.c.) kept below 10°. Stirring was continued for 2 hours at 0—5°, and an orange solid separated. While the mixture was still cold, concentrated sulphuric acid (3 c.c.)–ice (25 g.) was carefully added, and the whole poured into water (500 c.c.). When the solid was crystallised from ethanol, *ethyl 8-ketoacenaphthene-7-glyoxylate* (23 g.) was obtained in yellow plates, m. p. 104° (Found: C, 71·8; H, 4·4. $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%). It was readily dissolved by dilute aqueous sodium hydroxide, and its solution in ethanol gave an intense blue colour with ferric chloride.

Acenaphthyleno(7′ : 8′-4 : 5)*pyrazole*.—A solution of ethyl 8-ketoacenaphthene-7-glyoxylate (5·36 g.) and hydrazine hydrate (1·12 g. of 90%) in glacial acetic acid (40 c.c.) was boiled under reflux for 15 minutes in darkness, and, when cold, stirred into ice-water (1 l.). After 6 hours, the yellow solid was collected and crystallised from ethanol, from which *ethyl acenaphthyleno*-(7′ : 8′-4 : 5)*pyrazole-3-carboxylate* separated in yellow needles (5·1 g.), m. p. 163° (Found: C, 72·4; H, 4·6. $C_{16}H_{12}O_2N_2$ requires C, 72·7; H, 4·5%). Further purification by adsorption from benzene on alumina did not change the colour or the m. p. When the reaction was carried out in daylight, the crude product was red and difficult to purify.

A solution of the ester (9 g.) in ethanol (400 c.c.) was boiled under reflux while concentrated aqueous sodium hydroxide was added dropwise until a test portion of the mixture no longer gave a turbidity with water. After a further ½ hour, most of the ethanol was distilled off, and the cold residue acidified with hydrochloric acid. The precipitate which slowly separated was dissolved in hot ethanol (125 c.c.), and the addition of water (12 c.c.) then caused the separation of *acenaphthyleno*(7′ : 8′-4 : 5)*pyrazole-3-carboxylic acid* in colourless plates (8 g.), m. p. 289° (decomp.) (Found: C, 70·8; H, 3·5. $C_{14}H_8O_2N_2$ requires C, 71·2; H, 3·4%). After the acid (1 g.) had been heated at 310° for 5 minutes, the product was cooled, pulverised, and extracted with ethanol (150 c.c.) in a Soxhlet apparatus. The extract was boiled with charcoal, filtered, and concentrated, and, on cooling, *acenaphthyleno*(7′ : 8′-4 : 5)*pyrazole*, colourless needles (0·5 g.; from ethanol), m. p. 239°, slowly separated (Found: C, 81·2; H, 4·3%; *M* (Rast), 210. $C_{13}H_8N_2$ requires C, 81·3; H, 4·2%; *M*, 192).

When this product (0·5 g.) was heated under reflux with acetic anhydride (10 c.c.) for ½ hour and the solution poured into water, *1-acetylacenaphthyleno*(7′ : 8′-4 : 5)*pyrazole*, pale straw-coloured plates (0·45 g.; from ethanol), m. p. 170—171°, was precipitated (Found: C, 76·8; H, 4·3. $C_{15}H_{10}ON_2$ requires C, 76·9; H, 4·3%). Its solutions in benzene and ethanol were colourless.

1-Phenylacenaphthyleno(7′ : 8′-4 : 5)*pyrazole-3-carboxylic Acid*.—A mixture of purified phenylhydrazine (2·16 g.), ethyl 8-ketoacenaphthene-7-glyoxylate (5·36 g.), and glacial acetic acid (30 c.c.) was refluxed for 2½ hours in darkness, cooled, and poured into ice-water (500 c.c.); the precipitated *ethyl 1-phenylacenaphthyleno*(7′ : 8′-4 : 5)*pyrazole-3-carboxylate* crystallised from ethanol in yellow plates (4·8 g.), m. p. 161° (Found: C, 77·6; H, 4·8%; *M* (Rast), 308. $C_{22}H_{16}O_2N_2$ requires C, 77·6; H, 4·7%; *M*, 340). When this substance was saponified by the method described above for the related ester, the sodium salt gradually separated from the ethanol solution. Acidification of its solution in water precipitated *1-phenylacenaphthyleno*(7′ : 8′-4 : 5)-*pyrazole-3-carboxylic acid*, colourless needles (yield, 85%; from aqueous ethanol), m. p. 262° (decomp.) (Found: C, 76·7; H, 3·9. $C_{20}H_{12}O_2N_2$ requires C, 76·9; H, 3·8%).

When the acid (1 g.) was heated at 265° until effervescence ceased (about ½ minute), the nature of the product varied in different experiments. On four occasions nothing pure was isolated, and twice *1-phenylacenaphthyleno*(7′ : 8′-4 : 5)*pyrazole*, a microcrystalline scarlet solid (yield, 0·5 g. and 0·1 g. respectively; from glacial acetic acid), m. p. 197°, was obtained (Found: C, 84·8; H, 4·3; N, 10·6. $C_{19}H_{12}N_2$ requires C, 85·1; H, 4·5; N, 10·4%). On one occasion a *substance*, $C_{39}H_{24}O_2N_4$, golden-brown needles (0·5 g.; from glacial acetic acid), m. p. 316° (decomp.), was isolated (Found: C, 80·6, 80·6; H, 4·2, 4·3. $C_{39}H_{24}O_2N_4$ requires C, 80·7; H, 4·1%). These last two substances were not sufficiently soluble in camphor for molecular-weight determinations.

Pyrolysis of Methyl Acenaphthyleno(7′ : 8′-2 : 3)*indole-1-carboxylate*.—(*a*) When this urethane (1 g.; Bannister and Plant, *loc. cit.*) was heated at 300° for 10 minutes, carbon dioxide, identified with lime water, was evolved. The residue was refluxed with benzene (25 c.c.), and the hot solution filtered from insoluble material (0·1 g.), cooled, and diluted with more benzene (75 c.c.). The solute was adsorbed on alumina and separated into three fractions: (i) 1-methylacenaphthyleno(7′ : 8′-2 : 3)indole, scarlet plates (0·2 g.), m. p. 204° (Found: C, 88·7; H, 5·2; N, 6·0%; *M* (Rast), 277. Calc. for $C_{19}H_{13}N$: C, 89·4; H, 5·1; N, 5·5%; *M*, 255), identified by mixed m. p.; (ii) unchanged methyl acenaphthyleno(7′ : 8′-2 : 3)indole-1-carboxylate (0·5 g.), m. p. 154°; and (iii) acenaphthyleno(7′ : 8′-2 : 3)indole (0·05 g.), brown plates, m. p. 234°, identified

by mixed m. p. The same three substances were isolated in a number of similar experiments in varying yields which appeared to be unconnected with the time of pyrolysis (5—25 minutes).

(*b*) A mixture of the urethane (0·5 g.) and β-naphthylamine (2·5 g.) was heated under reflux at 300° for 10 minutes, cooled, and repeatedly ground with dilute hydrochloric acid until nothing more was extracted. When the residue was crystallised from ethanol, acenaphthyleno(7′ : 8′-2 : 3)indole was obtained in orange plates (0·4 g.), m. p. 234°, identified by mixed m. p.

Oxidation of 1-*Acetylacenaphthyleno*(7′ : 8′-2 : 3)*indole*.—A solution of the acetyl compound (5 g.) in boiling glacial acetic acid (250 c.c.) was rapidly cooled, with stirring, and treated with chromic anhydride (2·4 g.) in water (15 c.c.). The whole was shaken at 15—20° for 18 hours and then at 70° for 10 minutes, filtered from unchanged acetyl compound (1 g.), and gradually treated with water (3 l.), with stirring. After the orange-coloured precipitate (3 g.) had been recrystallised from methanol (twice) and then benzene, o-(8-*carboxy*-1-*naphthoyl*)*acetanilide lactam* was obtained in colourless prisms (0·6 g.), m. p. 184° (Found : C, 76·5; H, 4·1. $C_{20}H_{13}O_3N$ requires C, 76·2; H, 4·1%).

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