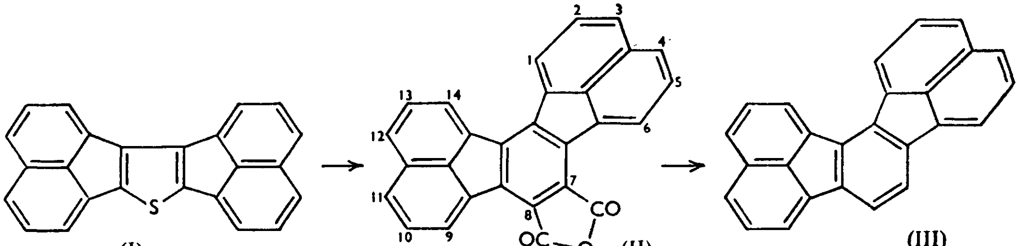
293. *Synthesis of Fluoranthenes. Part XIII.* Synthesis of Benzo*[1 : 2-a, 3 : 4-a′]- *and of Benzo*[1 : 2-a, 4 : 5-a′]-*diacenaphthylene.*

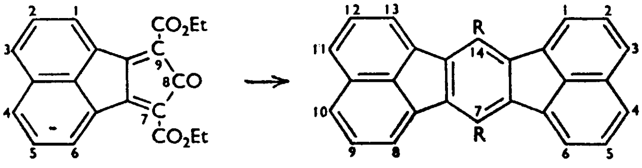
By S. Horwood Tucker.

Benzo[1 : 2-*a*, 3 : 4-*a*′]diacenaphthylene-7 : 8-dicarboxylic anhydride (II) has been converted into the parent hydrocarbon (III). Diethyl 8-oxo*cyclo*pent[*a*]acenaphthylene-7 : 9-dicarboxylate (IV) and acenaphthylene, by a Diels–Alder reaction, give an ester (V; R = CO_2Et) which by combined hydrolysis and decarboxylation gives the isomeric hydrocarbon (V; R = H).

THIENO[*aa*′]DIACENAPHTHYLENE [1] (I) reacts with maleic anhydride to give benzo[1 : 2-*a*, 3 : 4-*a*′]diacenaphthylene-7 : 8-dicarboxylic anhydride [2] (II). The barium salt of the dicarboxylic acid, derived from the anhydride (II), when heated with copper gives benzo[1 : 2-*a*, 3 : 4-*a*′]diacenaphthylene (III).



(I) (II) (III)



(IV) (V)

The isomeric benzo[1 : 2-*a*, 4 : 5-*a*′]diacenaphthylene (V; R = H) was synthesised as follows. Condensation of acenaphthenequinone with diethyl acetonedicarboxylate [3] gives diethyl 8-oxo*cyclo*pent[*a*]acenaphthylene-7 : 9-dicarboxylate [4] (IV). When this diester (IV) and acenaphthylene are heated together at *ca.* 250°, carbon monoxide and hydrogen are removed, and diethyl benzo[1 : 2-*a*, 4 : 5-*a*′]diacenaphthylene-7 : 14-dicarboxylate (V; R = CO_2Et) is formed. This diester is hydrolysed and decarboxylated in one step

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* Part XII, *J.*, 1954, 227.

[1] Dziewonski, *Ber.*, 1903, **36**, 962.

[2] Clapp, *J. Amer. Chem. Soc.*, 1939, **61**, 2733.

[3] Cf. Dilthey, ter Horst, and Schommer, *J. prakt. Chem.*, 1935, **143**, 208.

[4] Allen and VanAllan, *J. Org. Chem.*, 1952, **17**, 845.

by heating it with 100% phosphoric acid:[5] benzo[1 : 2-*a*, 4 : 5-*a′*]diacenaphthylene (V; R = H) is produced. The intermediate dihydro-derivative of (V; R = H) has also been isolated.

An attempt was made to synthesise the hydrocarbon (V; R = H) by the general method of Forrest and Tucker.[6] 1-Iodonaphthalene was heated with 1 : 5-dibromo-2 : 4-dinitrobenzene[7] in presence of copper, to give 1 : 5-di-(1-naphthyl)-2 : 4-dinitrobenzene, but the yield varied uncontrollably. Reduction by several methods gave no crystallisable diamine. Accordingly, the red oil obtained on reduction was diazotised at once. A very small amount of impure hydrocarbon (V; R = H) resulted.

Separation of *cis*- and *trans*-1 : 2-dimethylacenaphthene-1 : 2-diol has been improved,[8] but both the *cis*- and the *trans*-isomer, treated with acenaphthylene under a variety of conditions,[9] failed to give an isolable addition product.

EXPERIMENTAL

Synthesis of Benzo[1 : 2-a, 3 : 4-a′]*diacenaphthylene* (III).—Thieno[*aa′*]diacenaphthylene (II) (crystallised from dioxan), when treated with maleic anhydride,[2] gave benzo[1 : 2-*a*, 3 : 4-*a′*]diacenaphthylene-7 : 8-dicarboxylic anhydride (II). The barium salt prepared from this, when heated with copper,[10] gave a yellow sublimate, which, with excess of picric acid in acetone, formed rectangular magenta-coloured laths of a *picrate*, m. p. 239—240°, with slight shrinkage at 120° (Found: C, 69·0; H, 3·3; N, 7·8. $C_{26}H_{14},C_6H_3O_7N_3$ requires C, 69·2; H, 3·1; N, 7·6%). Chromatography of this picrate on alumina in benzene, and crystallisation from benzene–ethanol, then from ethyl acetate, yielded canary-yellow needles of *benzo*[1 : 2-a, 3 : 4-a′]*diacenaphthylene* (III), m. p. 232—233°, softening at 227° (Found: C, 95·6; H, 4·3. $C_{26}H_{14}$ requires C, 95·7; H, 4·3%). Its solutions fluoresce green. Its ultraviolet absorption spectrum in ethanol shows $\lambda_{\text{max.}}$ (log ε in parentheses) 352 (4·74), 336 (4·60), 281 (4·15), 270 (4·18), 242 mμ (4·68).

Synthesis of Benzo[1 : 2-a, 4 : 5-a′]*diacenaphthylene* (V; R = H).—*Diethyl* 8-*oxo*cyclo*pent*[a]*acenaphthylene*-7 : 9-*dicarboxylate* (IV). Acenaphthenequinone (crystallised from dioxan; m. p. 252°; lit., 261°; 0·91 g.), diethyl acetonedicarboxylate (1·01 g.), methanol (10 ml.), and redistilled triethylamine (1·0 ml.) in methanol (5 ml.) were mixed at room temperature. The quinone gradually dissolved to give a brown solution, with evolution of heat. In 30 min. the solution was purple. The purple needles which separated crystallised from acetic anhydride to give the ester (IV) which, heated rapidly, had m. p. 189—191° (lit.,[4] m. p. 196°) (0·86 g., 50%). When, instead of triethylamine, the recommended[3, 4] potassium hydroxide in aqueous methanol was used results were unreliable.

Diethyl benzo[1 : 2-a, 4 : 5-a′]*diacenaphthylene*-7 : 14-*dicarboxylate* (V; R = CO_2Et). The ester (IV) (0·35 g., 1 mol.) and acenaphthylene (0·32 g., >2 mol.) were heated at 125° until carbon monoxide evolution ceased (1 min.). The product was heated at the same temperature with chloranil (0·25 g., 1 mol.) for 5 min. The black melt dissolved completely in xylene, and the solution on storage gave green-yellow crystals. These were boiled with benzene. The insoluble residue (0·39 g.), with material recovered by adding the benzene extracts to the xylene liquors, was recrystallised from dioxan or nitromethane to give orange-yellow thick square plates (0·44 g., 93%), m. p. 310—312°, softening at 307°, of *ester* (V; R = CO_2Et) (Found: C, 81·6; H, 4·9. $C_{32}H_{22}O_4$ requires C, 81·7; H, 4·7%). Its solutions are orange-yellow with a deep green fluorescence.

When the above mixture, but with chloranil omitted, was heated at 230—250° for 4 hr., the product was almost entirely the above compound.

Diethyl 6*b* : 14*a*-*Dihydrobenzo*[1 : 2-a, 4 : 5-a′]*diacenaphthylene*-7 : 14-*dicarboxylate*.—This

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[5] Cf. Orchin and Regel, *J. Amer. Chem. Soc.*, 1951, **73**, 436; Berger and Olivier, *Rec. Trav. chim.*, 1927, **46**, 600; Moureu, Chovin, and Rivoal, *Bull. Soc. chim. France*, 1946, **13**, 106; 1948, **15**, 99.

[6] Forrest and Tucker, *J.*, 1948, 1137.

[7] Hodgson, *J. Soc. Dyers and Colourists*, 1926, **42**, 367.

[8] Criegee, Kraft, and Rank, *Annalen*, 1933, **507**, 177; Maxim, *Bull. Soc. chim. France*, 1928, **43**, 769; 1929, **45**, 1137.

[9] Cf. Campbell, Gow, and Wang, *Nature*, 1948, **162**, 857; Campbell and Gow, *J.*, 1949, 1555.

[10] Cf. Szmuszkovicz and Modest, *J. Amer. Chem. Soc.*, 1950, **72**, 577.

compound was isolated after a benzene solution (3 ml.) of diethyl 8-oxo*cyclo*pent[*a*]acenaphthylene-7 : 9-dicarboxylate (0·17 g.) and acenaphthylene (0·08 g.) had been boiled for 2 hr. On cooling, crystals separated and gave, from acetone, pale green hexagonal-sided thick plates of the *dihydro-compound*, m. p. 210—212° (0·16 g., 68%) (Found: C, 81·6; H, 4·9. $C_{32}H_{24}O_4$ requires C, 81·3; H, 5·1%).

Hydrolysis of the ester (V; R = CO_2Et). The ester (0·14 g.) was boiled in 2-ethoxyethanol (5 ml.) solution with 50% potassium hydroxide solution (2 ml.) for 4 hr. The solution was acidified, then filtered through charcoal to remove the precipitated dicarboxylic acid and silica (filtration was slow). The washed residue was extracted with aqueous ammonia, excess of ammonia removed by boiling, and glacial acetic acid added. The green-yellow precipitate was satisfactorily filtered off under slightly reduced pressure. It crystallised in pale yellow blades from acetic anhydride, was washed with acetic acid, and dried in air overnight. It sintered at 300° but was unmelted at 350°. The solvated *acid* (V; R = CO_2H) so isolated may not be pure (Found: C, 75·6; H, 3·85. $C_{28}H_{14}O_4,C_2H_4O_2$ requires C, 75·9; H, 3·8%). Crystallisation from propionic anhydride gave crystals of uncertain composition.

It was therefore considered preferable to hydrolyse and decarboxylate the ester in one operation by means of 100% phosphoric acid.[5]

Hydrolysis in 2-methoxyethanol gave similar results, but the product in this experiment was crystallised from pyridine, with production of short orange blade-prisms, unmelted at 350°, which consisted of *dipyridinium benzo*[1 : 2-a, 4 : 5-a′]*diacenaphthylene*-7 : 14-*dicarboxylate* (Found: C, 79·9; H, 4·3; N, 4·8. $C_{28}H_{14}O_4,2C_5H_5N$ requires C, 79·7; H, 4·2; N, 4·9%.)

Benzo[1 : 2-a, 4 : 5-a′]*diacenaphthylene* (V; R = H). The ester (V; R = CO_2Et) (0·56 g.) was heated with 100% phosphoric acid (10 ml.) in the vapour of boiling dimethyl phthalate (b. p. 282°; thermometer in vapour registered 275°) for 1 hr. whilst stirred with a copper-wire stirrer. The black-green solid was extracted thoroughly with benzene, and the extract chromatographed on alumina. The clear golden-yellow eluate was concentrated and gave golden-yellow needles, changing to yellow at 290°, but melting sharply at 315°, of *benzo*[1 : 2-a, 4 : 5-a′]-*diacenaphthylene* (Found: C, 95·5; H, 4·3. $C_{26}H_{14}$ requires C, 95·7; H, 4·3%). The filtrate deposited also short rod-prisms which were pale yellow and showed a bright green fluorescence when crushed. There was insufficient for further examination.

Attempted Synthesis of Benzo[1 : 2-a, 4 : 5-a′]*diacenaphthylene* (V; R = H).—1 : 5-*Di*-(1-*naphthyl*)-2 : 4-*dinitrobenzene*. 1-Iodonaphthalene (3·81 g., 0·015 mol.), 1 : 5-dibromo-2 : 4-dinitrobenzene [7] (1·63 g., 0·005 mol.), and copper bronze (3 g.) were heated together at 244° (diethylene glycol vapour) for 2·5 hr., and the product extracted with benzene. The concentrated solution was chromatographed on alumina. The first small amount of eluate, fluorescing blue in ultraviolet light, was discarded. The following yellow eluate (150 ml.) on evaporation gave a red oil: this was dissolved in acetic acid and treated with an equal volume of ethanol. The liquid became turbid, and when boiled suddenly gave orange crystals: these recrystallised from carbon tetrachloride to give 1 : 5-*di*-(1-*naphthyl*)-2 : 4-*dinitrobenzene*, m. p. 212—213°, (0·84 g., 40%) (Found: C, 74·4; H, 3·9; N, 6·9. $C_{26}H_{16}O_4N_2$ requires C, 74·3; H, 3·8; N, 6·7%).

This procedure was unreliable, especially on a larger scale. Heating the above mixture at 282° (dimethyl phthalate) or at its b. p. (305°) for 30 min. gave the same capricious results. Clean yellow products were obtained but they did not always crystallise.

Reduction of the above dinitro-compound with hydrogen and Raney nickel in suspension in ethanol alone, or in solution in benzene and ethanol, gave no crystallisable product. Reduction by stannous chloride in glacial acetic acid saturated with dry hydrogen chloride gave in the usual way an oil: this was diazotised and then heated on the boiling-water bath. A brick-red solid was obtained. Its chromatographed (alumina) benzene solution gave a canary-yellow eluate with a deep green fluorescence, and a yellow solid was isolated: it crystallised in needles, from dioxan, softening at 290°, m. p. 300—310°. It appears to be crude benzo-[1 : 2-*a*, 4 : 5-*a*′]diacenaphthylene (V; R = H).

The crude diamine gave a green-yellow *picrate* in, and crystallised from, benzene; the crude product contained benzene of crystallisation which was lost at 80° (Found: C, 60·4; H, 3·5; N, 11·9. $C_{26}H_{20}N_2,2C_6H_3O_7N_3,2C_6H_6$ requires C, 61·6; H, 3·9; N, 11·5%).

cis- *and* trans-1 : 2-*Dimethylacenaphthene*-1 : 2-*diol*.[8]—Acenaphthenequinone was treated with methylmagnesium iodide in ether, and the solution with aqueous ammonium chloride (not mineral acid), in the usual way. The crude mixture of *cis*- and *trans*-diols (13·0 g.) was separated by crystallisation from acetone, giving thick square plates of *cis*-diol, m. p. 187—189° (3·13 g., 24%). When, during the crystallisation, needles began to separate with the plates, the filtrate was evaporated to dryness, and the residue crystallised from chloroform, to give *trans*-isomer, m. p. 182—183° (4·60 g., 35%). The *cis*-isomer is only slightly soluble in chloroform. Each isomer was heated with acenaphthylene in acetic anhydride, phthalic anhydride, and a trace of toluene-*p*-sulphonic acid,[11] and in phosphoric acid. No addition product could be isolated. The diol, acenaphthylene, chloranil, and a crystal of iodine were heated at 190°. Water was evolved. Chromatography in benzene on alumina gave an orange-fluorescent column (ultraviolet light) and eventually a red oil, which after treatment became solid, and melted at 180—220°.

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[11] Cf. Waldmann and Petrů, *Chem. Ber.*, 1950, **83**, 287; Waldmann and Schubert, *ibid.*, 1951, **84**, 139.