The Fine Structure of Azulene. Part I. cyclo*Hepta*[bc]*acenaphthylene and* cyclo*Hepta*[def]*fluorene.*

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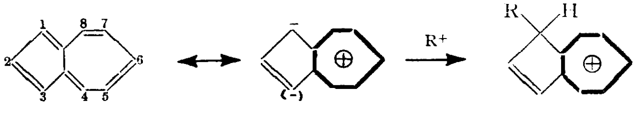
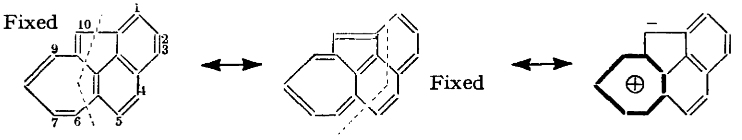
A synthesis of *cyclo*hepta[*bc*]acenaphthylene (II) from acenaphthene is described, together with an attempted synthesis of the isomeric *cyclo*hepta[*def*]fluorene (III) by ring expansion of *cyclo*penta[*def*]phenanthrene (IV) with diazoacetic ester. The properties of the hydrocarbon (II) are discussed, together with the unusual results of the latter synthesis.

It has been suggested by Anderson, Nelson, and Tazuma (*J. Amer. Chem. Soc.*, 1953, **75**, 4980) and by Stafford and Reid (*Chem. and Ind.*, 1954, 277) that azulene (I) is best represented as a resonance hybrid of two types of canonical forms, (*a*) the classical covalent forms and (*b*) betaine structures. In the latter the cationic character is associated with the seven-membered ring and the anionic character equally with the equivalent 1- and 3-positions in the five-membered ring. This formulation interprets the reactions of the azulenes and includes them within the class of anhydro-salts which Galloway, Reid, and Stafford (*Chem. and Ind.*, 1954, 724) have indicated often possess comparable colour and reactivity because of a highly dipolar character. On this basis azulene is an aromatic system with the unusual features that two positions possess a high electron density balanced by an attenuation of the π-electron density in the seven-membered ring. One typical property is the ready polarisability of the system; in appropriate circumstances an electron pair may be developed on either $C_{(1)}$ or $C_{(3)}$ and shared with an electrophilic group. The basicity of the azulenes manifests both this polarisability and the stability of the polarised state once the electrons have been shared, *i.e.*, it reflects the stability of the corresponding *cyclo*pentadienyl*cyclo*heptatrienylium ion (I*c*). These criteria, the polarisation of the ground state and the ready polarisability to an excited state, with their corollaries of colour and basicity, represent an efficient method of identifying typical azulenic character, for this is synonymous with considerable contribution of betaine forms



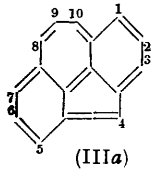
(I*a*) (I*b*) (I*c*)



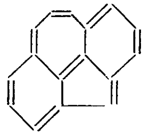
(II*a*) (II*b*) (II*c*)

1 : 2-Benzazulene is the only azulene so far synthesised and studied which possesses only one chemically recognisable position for the adoption of anionic character, so similar systems in which the five-membered ring is more closely enveloped deserve study. Two structures were selected for a preliminary examination, *cyclo*hepta[*bc*]acenaphthylene (II) and *cyclo*hepta[*def*]fluorene (III). These are both capable of representation as *cyclo*polyolefins but if all reasonable structures, both of covalent and of betaine type, are written then differences are obvious. Covalent structures for (II) are represented by (II*a* and *b*), in which, respectively, the classical naphthalene and azulene forms all contribute with the fixed bond structure indicated in the remaining portion of the molecule, thereby giving five reasonable covalent canonical forms. The betaine structures are, in part, represented by (II*c*), in which the seven-membered ring donates an electron to $C_{(10)}$ while the naphthalene portion may again be written as varying in the normal manner.

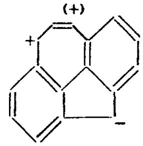
The source of the enhanced electron-density at $C_{(10)}$ should also include the naphthalene portion. For the compound (III) there are only two purely covalent forms, (III*a* and *b*), in neither of which the diphenyl or azulene structural type is preserved. Both involve complete double-bond character for the central bond. Betaine contributants are also limited to two structures (III*c*) in which only positions 8 and 10 may act as electron sources. It would therefore be expected that a hydrocarbon of structure (II) would be typically azulenic, whereas one of structure (III) would be a typical *cyclo*polyolefin.



(III*a*)

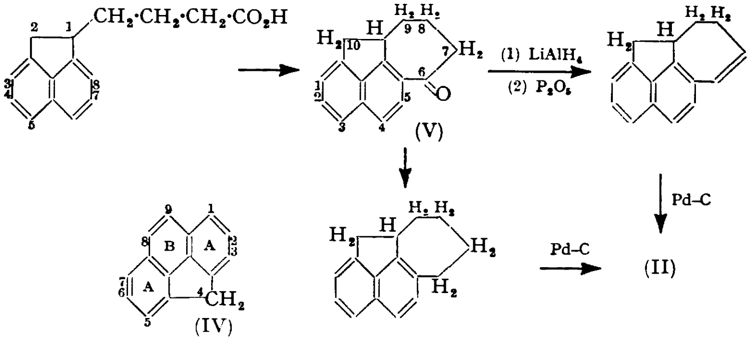


(III*b*)



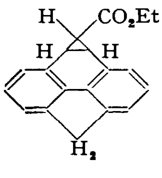
(III*c*)

The hydrocarbon (II) was synthesised from γ-1-acenaphthenylbutyric acid (cf. Bachmann and Sheehan, *J. Amer. Chem. Soc.*, 1941, **63**, 204) which was prepared from 1-acenaphthenylacetic or preferably from β-1-acenaphthenylpropionic acid by the Arndt–Eistert reaction. Ring-closure, by polyphosphoric acid, of the butyric acid gave 6 : 7 : 8 : 9-tetrahydro-6-oxo*cyclo*hepta[*bc*]acenaphthene (V) in excellent yield, which is best converted into the desired product (II) by successive reduction with lithium aluminium hydride, dehydration to 8 : 9-dihydro*cyclo*hepta[*bc*]acenaphthene, and dehydrogenation. The azulene was isolated by extraction into syrupy phosphoric acid followed by dilution, and was obtained as dark red leaflets which form a trinitrobenzene complex.

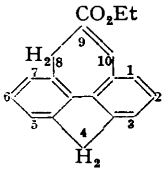


Synthesis of the isomer (III) was attempted by the method used by Treibs (*Ber.*, 1948, **81**, 38) to prepare 1 : 2-benzazulene. *cyclo*Penta[*def*]phenanthrene (IV) was made to react with diazoacetic ester, and from analogous work on phenanthrene (Drake and Sweeney, *J. Org. Chem.*, 1946, **11**, 67 ; Cook, Dickson, and Loudon, *J.*, 1947, 750) the product should be a *cyclo*propane compound (VI*a*) ; this should rearrange to (VI*b*) and on dehydrogenation then give an ester derived from (III). In fact two esters which were azulenic (extractable into phosphoric acid) were isolated and both on hydrolysis and decarboxylation yielded the isomer (II). Substantial attack must have occurred in ring A and presumably on the 1 : 2- and 2 : 3-bonds in that ring. The significance of this is discussed below. The material which was not extractable into phosphoric acid was separated by alkaline hydrolysis into a neutral fraction, mostly unchanged hydrocarbon (IV), and a homogeneous acid fraction. In the latter a structure of type (VI) must be involved for (*a*) dehydrogenation gave no evidence of formation of derivatives of (II) and (*b*) ultra-violet absorption spectra were in accord with a diphenyl formulation (Fig. 2). Structures (VI*a* and *b*) were differentiated by a combination of infra-red spectroscopy and oxidative degradation.

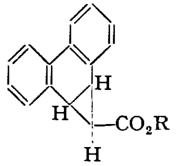
The structure (VI*a*) for the analogous product from phenanthrene was proved by Drake and Sweeney by oxidative degradation to a *cyclo*propane derivative. If the presence of a fluorene rather than a diphenyl structure had no effect on the stability of a *cyclo*propane ring it follows that oxidation of a structure such as (VI*a*) would lead to a product retaining the *cyclo*propane ring. Our product from the analogue (IV) was, however, readily oxidised to fluorenone-4 : 5-dicarboxylic acid, and so must have the *cyclo*heptatriene structure (VI*b*), and this was confirmed by infra-red spectroscopy.



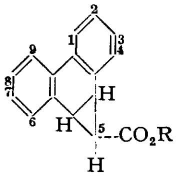
(VI*a*)



(VI*b*)



(VII*a*)



(VII*b*)

Repetition of the work of Drake and Sweeney and of Cook, Dickson, and Loudon with phenanthrene gave however results different from theirs. Cook, Dickson, and Loudon describe a methyl ester of m. p. 145° and both groups of workers found that the parent acid has m. p. 258°. In contrast, our methyl ester had m. p. 210° and our acid m. p. 248°.

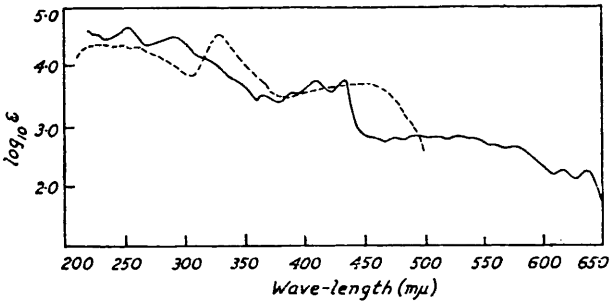


FIG. 1. *Absorption spectrum of* cyclo*hepta*[bc]*acenaphthylene,* —— *in hexane,* – – – – *in* 8N-HCl.

Both m. p.s were depressed on admixture with samples supplied by Dr. Loudon, so isomorphism is eliminated. The ultra-violet spectra (Fig. 2 and Table 1) showed that none the less the compounds were closely related.

TABLE 1. *Ultra-violet spectra* (*max. in* mμ).

Compound	M. p.	$\lambda_{max.}$	log ε	$\lambda_{max.}$	log ε	$\lambda_{max.}$	log ε	$\lambda_{max.}$	$\lambda_{max.}$
Me ester *	145°	308	3·72	296	3·68	270	4·14	—	—
Me ester †	210	306	3·66	296	3·66	270	4·14	—	—
Acid *	258	314	—	304	—	276	(infl.)	272	266
Acid †	248	308	—	295	(infl.)	276	(infl.)	272	267

* Previous work. † Present work.

Dr. Whiteley has examined, in the infra-red region, the acids, methyl esters, and reduction product of the acids with lithium aluminium hydride, which we obtained from the products (VI) and (VII) of interaction of *cyclo*penta[*def*]phenanthrene (IV) and phenanthrene with diazoacetic ester. A fundamental difference exists in the carbonyl absorption region for the acids and esters. These values (Table 2) should be compared with 1715 and 1740 cm.$^{-1}$ which would be regarded as of the right order for aliphatic acids and esters. A marked conjugation effect is shown by the *cyclo*pentano-compounds (VI) but not by the phenanthrene derivatives (VII), thus indicating structure (VI*b*) for the former. Further, in the three products related to (VII) a band was found at 1004 cm.$^{-1}$ where it is known that many *cyclo*propane derivatives absorb. The three compounds derived from the *cyclo*pentaphenanthrene had no band in this region but the acid and ester had a band at 843 and 847 cm.$^{-1}$ respectively, which is the appropriate region for the C–H bonding vibration of a system $R_2C{:}CHR$; this band was missing in the reduction

TABLE 2. *Infra-red spectra in* KBr *discs* (cm.$^{-1}$).

Acid (VI*b*)	1671	Ester (VI*b*)	1699
Acid (VII)	1722	Ester (VII)	1718

product. Structure (VI*b*) is therefore extremely likely and in agreement with the ultra-violet evidence there is a close structural relation between the product of Drake and Sweeney, and of Cook, Dickson, and Loudon, and that described by us. Further work (to be reported later) will indicate that the difference is steric (cf. VII*a* and *b*).

The stability of the dihydro-ester derivative of (III) to dehydrogenation indicates the energetic disfavour of a structure such as (III). The absorption spectrum of the hydrocarbon (II) (Fig. 1) conforms to a pattern common to the azulenes and many anhydro-salts (unpublished work). The absorption of acid solutions of the compound (II) resembles that in neutral solvents in general form, with a bathochromic shift. The only markedly new feature is that the parent has extensive absorption in the visible region; this is found in most compounds requiring a "betaine"-type formulation and it is this band which is often abnormally affected by substitution and most dependent on the polar character of the environment.

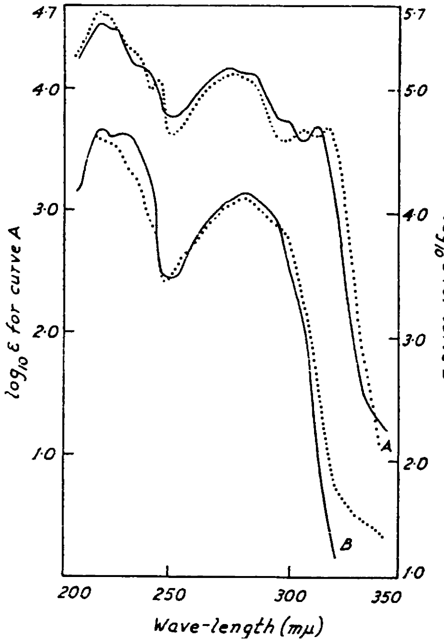


FIG. 2. *Absorption spectra (A) of (——) the acid, m. p.* 248°, *from phenanthrene and (. . . . . .) the product of its reduction with* $LiAlH_4$, *and (B) (——) the acid corresponding to the ester* (VI*b*) *and (. . . . . .) its reduction product with* $LiAlH_4$.

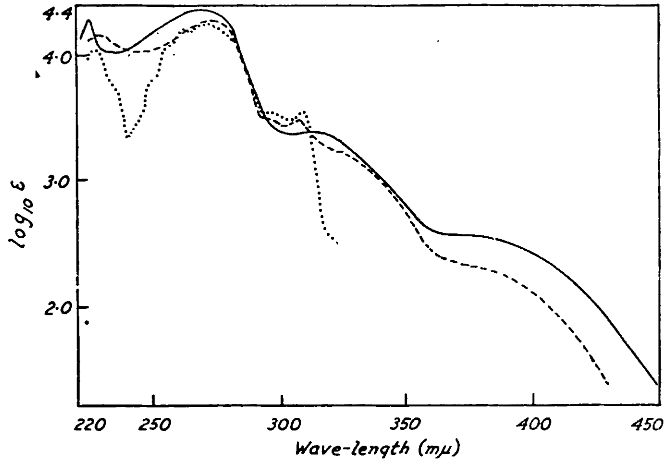


FIG. 3. *Absorption spectra of (——) fluorenone-*4 : 5*-dicarboxylic acid* (IX), (– – – –) *its dimethyl ester, and the diol* (VIII) *in* EtOH.

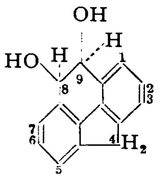
The basicity of the azulene (II), measured in the normal manner (Plattner, Heilbronner, and Weber, *Helv. Chim. Acta*, 1949, **32**, 574), is contrasted in Table 3 with those of azulene, 1 : 2-benzazulene and 5 : 6-benzazulene (W. Keller, Thesis, Eidg. Techn. Hochschule, Zurich, 1952). The values are expressed as the concentration of sulphuric acid which reduces by one-half the concentration of azulene present in an equal volume of toluene or *cyclo*hexane. The basicity of a hydrocarbon reflects the equilibrium, $\mathrm{Az} + \mathrm{H}^+ \rightleftharpoons \mathrm{AzH}^+$ (where Az = azulene). The forward reaction is favoured by a high polarisation of the ground state, and the reverse reaction is disfavoured by the stability of the resulting cation. In azulene and 5 : 6-benzazulene there are two positions which can act as proton acceptors : they are therefore comparable compounds. The large differences in basicity must arise from the influence of the condensed benzene ring on the initial degree of polarisation and/or the stability of the resulting cation. Both factors probably operate in the same direction, for in terms of resonance theory the more stable the cation type the higher the contribution of betaine forms, *i.e.*, the higher the degree of initial polarisation. Similarly, the compound (II) and 1 : 2-benzazulene have each one site for the addition of a proton; the high basicity of the compound (II) indicates that there is a large degree of initial polarisation and that the derived cation is much more stable. The close envelopment of the five-membered ring has thus enhanced, in this case, the azulenic character because it has increased the polarisation existing within the molecule. For the compound (III), where such polarisation is limited and where *cyclo*polyolefinic structures are the principal contributing structures, difficulty has been experienced in a synthesis which is typical of those normally employed for azulenes. It is therefore not the *cyclo*polyolefin contribution that is fundamental to azulene structure.

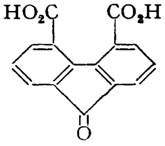
TABLE 3. *Basicity of polycyclic azulenes.*

	H_2SO_4 (%)		H_2SO_4 (%)
Compound (II)	44·2	5 : 6-Benzazulene	61·7
1 : 2-Benzazulene	53·6	Azulene	51·0

The results on the addition of diazoacetic ester to the *cyclo*pentaphenanthrene (IV) are of interest because it constitutes one of the few cases, apart from pyrene (Badger, Cook, and Gibb, *J.*, 1951, **3456**), where multiple attack occurs in a polycyclic compound containing one bond of outstandingly high double-bond character. The question therefore arises as to the effect of the five-membered ring on phenanthrene. With the more selective osmium tetroxide oxidation (Cook and Schoental, *J.*, 1948, **170**) no evidence of attack other than on the 8 : 9-bond was found. The resulting glycol (VIII) was oxidised readily to fluorenone-4 : 5-dicarboxylic acid (IX). As the latter was a key compound in all of this work it was obtained by Kruber's method (*Ber.*, 1934, **67**, 1000) and the absorption spectrum of both the acid and its dimethyl ester were determined [Fig. 3, where the spectrum of the glycol (VIII) is also recorded]. The indication is, therefore, that little reliance should be placed on the use of diazoacetic ester for the determination of bond order unless a more specific reagent is used comparatively and proof of homogeneity of product and of its structure are obtained. Indeed the mixture obtained in this reaction with *cyclo*penta[*def*]phenanthrene (IV) is more closely allied to the mixtures obtained by electrophilic attack on phenanthrene.

(VIII)





(IX)

The spectra recorded for diphenyl derivatives, apart from that of (VIII), are in accord with those for 9 : 10-dihydrophenanthrene, fluorene, and 8 : 9-dihydro*cyclo*penta[*def*]phenanthrene (Jones, *J. Amer. Chem. Soc.*, 1945, **67**, 2130). The last compound differs from the first two in one respect. The fine side maxima (*ca.* 310 mμ) on the principal diphenyl absorption (*ca.* 270 mμ) are absent when two bridges join the 2 : 2′-positions of the diphenyl nucleus. Only in the glycol (VIII) are two such bridges found and also these side maxima. The presence of the cinnamic acid type side chain in (VI*b*) has apparently little influence on the ultra-violet absorption, apart from a broadening of the absorption in the 220—230 mμ region. It is noticeable that after lithium aluminium hydride reduction this broadening disappears and the curve agrees closely with the others.

EXPERIMENTAL

M. p.s were determined on a Kofler block. Absorption spectra were determined with a Unicam S.P. 500 instrument.

γ-1-Acenaphthenylbutyric Acid.—*Method* I. Lithium aluminium hydride (5·475 g.) in ether (150 ml.) was added to a suspension of α-1-acenaphthenylacetic acid (21·2 g.) (Bachmann and Sheehan, *J. Amer. Chem. Soc.*, 1941, **63**, 204) at such a rate that the solution remained at the b. p. The mixture was set aside for 0·5 hr., then poured on ice in 4N-sulphuric acid (150 ml.). After 1 hr. the ether layer was separated and the aqueous phase was further extracted with ether and with benzene. The combined extracts were washed with water, dilute sodium hydroxide (2 × 100 ml.), and again water and dried (Na_2SO_4). Removal of the solvent and distillation (b. p. 149—151°/0·2 mm.) gave *2-1′-acenaphthenylethanol* as a pale yellow, viscous oil (14·02 g., 70·7%) (Found: C, 84·6; H, 8·0. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%).

Phosphorus tribromide (5·4 g.) in ether (20 ml.) was added to 2-1′-acenaphthenylethanol (30·4 g.) in ice-cold ether (200 ml.). The mixture was allowed to come to room temperature (1 hr.). The excess of tribromide was decomposed with water (500 ml.), and the separated ether layer was washed with water, sodium hydrogen carbonate solution, and water. The dried (Na_2SO_4) extract was concentrated under reduced pressure. Drying was completed by azeotropic distillation with benzene, and the residual oily bromide (28·5 g.) was used without further purification.

The crude bromide (28·5 g.) in benzene (100 ml.) was added to diethyl malonate (35 ml.) in absolute ethanol (300 ml.) in which sodium (5·9 g.) had previously been dissolved. The mixture was kept for 3 days in a refrigerator, then boiled under reflux for 3 hr. The solvent was removed under reduced pressure and the resulting ester hydrolysed by boiling 40% potassium hydroxide solution (125 ml.) for 1 hr. The solution was cooled and extracted with ether to remove alkali-insoluble material. The malonic acid was then precipitated with concentrated hydrochloric acid. Inorganic material was removed by washing with ice-cold water, and the crude acid was then dried over P_2O_5 under reduced pressure. The yield (19·9 g., 45·7%) was poor owing to formation of a water-soluble phosphorus-containing side-product. The crude acid had m. p. 160—165°, raised by recrystallisation from water to 163—164° (gas evolution). Difficulty was experienced in obtaining satisfactory analyses for this compound as it appears to retain water (Found: C, 70·7; H, 5·3. Calc. for $C_{17}H_{16}O_4$: C, 71·8; H, 5·7%).

2-1′-Acenaphthenylethylmalonic acid (9·36 g.) was heated for 25 min. at 175—180°, liberation of carbon dioxide then being complete. The product was dissolved in excess of dilute sodium hydroxide solution, and insoluble material was removed by extraction with ether followed by benzene. γ-1-Acenaphthenylbutyric acid was extracted into ether after acidification. The dried (Na_2SO_4) extract was distilled, leaving the acid as an oil which crystallised as pale-buff needles after several hours (yield, 6·23 g., 79%). The product was identical with that from Method II.

Method II. Pure, freshly distilled thionyl chloride (6·7 ml.) was added to a suspension of β-1-acenaphthenylpropionic acid (16·15 g.) in dry ether (75 ml.). A little pyridine (4 drops) was then added and the mixture was kept at room temperature for 2 hr.; dissolution was then complete. The solvent was removed under reduced pressure and excess of thionyl chloride was distilled off with successive portions (15 ml.) of benzene under reduced pressure. The residue, dissolved in ether (75 ml.), was added dropwise to a rapidly stirred solution of diazomethane (from 40 g. of *N*-methyl-*N*-nitrosourea) in ether (400 ml.). The ether and excess of diazomethane were removed after 1 hr. at room temperature. The residual diazo-ketone was dissolved in methanol (75 ml.) and added to silver oxide (0·75 g.) in methanol (30 ml.) which had been boiled together under reflux until a silver mirror had been formed. Liberation of nitrogen began immediately but the mixture was boiled for 30 min. Further silver oxide (1·5 g. after 30 min., 0·75 g. after 4 hr.) was added and boiling continued for a total of 8—9 hr. (until a test with concentrated hydrochloric acid for diazo-ketone was negative). The silver oxide was removed and the resulting pale yellow solution boiled with charcoal for 10 min. and filtered through Filter-cel. Sodium hydroxide solution (15 ml.; 40%) was added and the solution was boiled for 1 hr. Most of the methanol was removed under reduced pressure and the residue was taken up in water (200 ml.). Insoluble and tarry material was extracted with ether and benzene.

Acidification of the aqueous phase yielded the acid as an oil which was extracted into ether (300 ml.). This was washed with water to remove mineral acid and after drying (Na_2SO_4) and removal of the solvent the *acid* was obtained as an oil (13·4 g., 78%) which crystallised overnight. It was obtained analytically pure by distillation in a tube [b. p. (tube) 170°/0·05 mm.]. Crystallisation of the distillate from light petroleum (b. p. 40—60°)–ether (5 : 1) gave colourless needles, m. p. 71—73° (Found : C, 79·8; H, 6·9. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%).

6 : 7 : 8 : 9-*Tetrahydro*-6-*oxo*cyclo*hepta*[bc]*acenaphthene*.—Phosphoric oxide was dissolved in 90% phosphoric acid to give a mixture of definite pentoxide content, by heating the mixture in a boiling-water bath with frequent swirling. The acid was added in one portion and, on continuation of the heating, dissolved to a deep orange solution. Swirling is necessary to ensure initimate contact. The reaction is best terminated by pouring the mixture into cold water after a preliminary cooling and should be done as soon as a dark scum begins to form on the surface of the phosphoric acid. The product was exhaustively extracted into ether, and washed with water and alkali to remove unchanged acid (which was recovered), and the ether layer was dried (Na_2SO_4) and distilled, to give the substiantially pure *ketone*, m. p. 109—111°; purification by crystallisation from acetone–ether (1 : 2) followed by two sublimations at 125°/0·05 mm. yielded colourless prisms, m. p. 110—111° (with sublimation) (Found : C, 86·0; H, 6·2. $C_{16}H_{14}O$ requires C, 86·4; H, 6·4%). The *dinitrophenylhydrazone* formed red prisms, m. p. 243° (Found : N, 13·8. $C_{22}H_{18}O_4N_4$ requires N, 13·9%). Some comparative experiments are tabulated.

Acid (g.)	Wt. of P_2O_5 / Wt. of acid	P_2O_5 (%) in acid	Time (min.)	Temp.	Yield (%)	Unchanged (%)
4·84	20 : 1	83	75	75°	38·2	46·3
10·26	25 : 1	78	140	100	57·1	—
9·63	30 : 1	78	45	100	82·6	Trace
9·27	30 : 1	78	40	100	86·3	Trace

6 : 7 : 8 : 9-*Tetrahydro*-6-*hydroxy*cyclo*hepta*[bc]*acenaphthene*.—A solution of the ketone (6·66 g.) in ether (90 ml.) and benzene (60 ml.) was added to lithium aluminium anhydride (0·75 g.) in ether (25 ml.) at such a rate as to maintain vigorous boiling. Boiling was continued for 1 hr. and the mixture poured into a cold saturated solution of ammonium chloride. After 1 hr. dilute sulphuric acid was added to complete the decomposition. The organic phase was separated and further extraction with ether (2 × 300 ml.) ensured complete separation of the alcohol. The extract was dried (Na_2SO_4) and the solvent was removed under reduced pressure, yielding the *alcohol* (6·70 g.) as colourless crystals, m. p. 140—143°. A sample crystallised successively from acetone, alcohol, and again from acetone melted at 144—145° (Found : C, 85·6; H, 7·1. $C_{16}H_{16}O$ requires C, 85·7; H, 7·2%).

8 : 9-*Dihydro*cyclo*hepta*[bc]*acenaphthene*.—The alcohol (4·50 g.) was dehydrated by phosphoric oxide (4·50 g.) in benzene (60 ml.). The solution became warm and was set aside for 30 min. without external heating. A further quantity of phosphoric oxide (3 g.) was added and the mixture was shaken for 2 hr., then poured into water and extracted with ether. The ether extracts were washed with water, sodium hydrogen carbonate solution, and water before being dried (Na_2SO_4). On removal of the solvent an oil (3·96 g.) was obtained which crystallised. Sublimation at 90°/0·05 mm. gave white crystals contaminated with a little red material. Recrystallisation from light petroleum (b. p. 40—60°) after passage through a short column of alumina gave the *hydrocarbon* as colourless platelets, m. p. 77—79° (Found : C, 93·1; H, 7·1. $C_{16}H_{14}$ requires C, 93·2; H, 6·8%). The *trinitrobenzene* complex had m. p. 135—137° (Found : C, 62·9; H, 4·1; N, 9·8. $C_{16}H_{14},C_6H_3O_6N_3$ requires C, 63·0; H, 4·1; N, 10·0%).

6 : 7 : 8 : 9-*Tetrahydro*cyclo*hepta*[bc]*acenaphthene*.—This was prepared by Clemmensen reduction of the ketone in toluene with hydrochloric acid and amalgamated zinc. The toluene solution, after the reaction was complete, was separated and dried (Na_2SO_4) and evaporated, and the residue was sublimed at 80—85°/0·05 mm. and recrystallised from methanol containing a little light petroleum. The hydrocarbon crystallised as white needles melting over the range 45—67°. Analysis indicated that the material was substantially the desired hydrocarbon.

cyclo*Hepta*[bc]*acenaphthylene*.—The foregoing hydrocarbon (3·0 g.) and 20% palladium–charcoal (0·6 g.) were heated under nitrogen rapidly to 260° (oil-bath). The temperature was kept steady for 4 min. and then raised during 1·5 min. to 300° where it was maintained for 3 min. Liberation of hydrogen began at >220° and had just ceased at the end of the heating. The dark product was taken up in benzene and filtered through a short alumina column; elution was completed with 100 ml. of benzene–light petroleum (1 : 1). The combined red eluates were extracted with syrupy phosphoric acid (3 × 100 ml.). The acid extract was washed with benzene before dilution with water (2 l.). The azulene was extracted with ether and the deep red extract was freed from acid by washing with water and sodium hydrogen carbonate solution before drying (Na_2SO_4) and concentration. The residue tended to pass from an oil to a solid but purification was completed by controlled elution with benzene–light petroleum (1 : 10) after adsorption from petroleum solution on alumina. The red material was thus separated from a brown strongly adsorbed impurity. The *hydrocarbon* crystallised readily as dark red leaflets, m. p. 142·5—143·5° (120 mg.), from light petroleum–benzene (Found: C, 94·9; H, 4·9. $C_{16}H_{10}$ requires C, 95·0; H, 5·0%). The *trinitrobenzene complex* formed orange-brown needles, m. p. 228—230° (Found: C, 64·0; H, 3·4; N, 10·0. $C_{16}H_{10},C_6H_3O_6N_3$ requires C, 63·6; H, 3·2; N, 10·1%).

cyclo*Hepta*[bc]*acenaphthylene and* 4 : 8-*Dihydro*cyclo*hepta*[def]*fluorene*-9-*carboxylic Acid from* cyclo*Penta*[def]*phenanthrene*.—The reaction between *cyclo*penta[*def*]phenanthrene (supplied by O. Kruber) and diazoacetic ester (Grundmann and Ottmann, *Annalen*, **1953**, **582**, **163**) was carried out in a 50-ml. pear-shaped flask, heated in an oil-bath and supplied with a small capillary dropping funnel, a nitrogen inlet tube, and an air-condenser drawn to a wide capillary at the exit end. The hydrocarbon (10 g.) was fused by raising the bath to 140° and this temperature was maintained while the diazoacetic ester (6·5 g.) was added dropwise during 2 hr. The mixture was stirred at this stage by a stream of nitrogen, and became reddish-brown. The temperature of the bath was finally raised during 5 hr. to 200° with only occasional stirring with the nitrogen stream. The reaction mixture was dissolved in benzene–light petroleum (3 : 1), and azulenic material was extracted into syrupy phosphoric acid (4 × 50 ml.). The acid layer was washed with further quantities of the same hydrocarbon mixture and was poured into water (2 l.). Extraction with ether gave the azulenic fraction. The solvent was removed from the dried extract (Na_2SO_4) to give a residue (4—5 g. in different experiments). When chromatographed on alumina (neutral) this gave two main bands. Elution with benzene gave the starting hydrocarbon (1·2 g.) which passes to some extent through the acid separation. Elution with benzene–ether (1 : 3) gave a band yielding a red azulenic oil (2 g.). A strongly adsorbed material, a brown oil (0·5 g.) eluted with acetone, accounted for the total amount chromatographed.

Chromatography of the red oil with slow elution by light petroleum–benzene gave two bands appearing green on the column but giving red eluates. The first yielded a red oil (1·4 g.) which tended to crystallise as needles but could not be obtained pure. The second gave an oil (0·6 g.) which showed no tendency to solidify. The two fractions were separately boiled for 2·5 hr. with 3% ethanolic potassium hydroxide (50 and 30 ml. respectively). The acids were obtained by pouring the mixtures into water, extraction of neutral material with benzene, acidification, and extraction with ether, and were amorphous solids (1 g. and 0·5 g. respectively). Decarboxylation in quinoline (20 ml. per g.) containing copper bronze (0·5 g. per g.) for 1 hr. at the b. p., cooling, extraction with ether, removal of quinoline by repeated extraction with dilute hydrochloric acid, washing with water, sodium hydrogen carbonate solution, and water, drying, and evaporation gave residues which on alumina each yielded one band which was eluted with light petroleum. The eluates yielded 150 and 30 mg., respectively, of the same crystalline hydrocarbon which formed from light petroleum deep red plates, m. p. 143·5—144·5°, identical (mixed m. p.) with *cyclo*hepta[*bc*]acenaphthylene. The trinitrobenzene complex, m. p. 228—230°, did not depress the m. p. of the derivative prepared from authentic material.

The brown oil eluted from the original column was subjected to the same procedure and gave a few mg. of the trinitrobenzene complex as above.

The material which was not extracted into phosphoric acid was examined. The original phase from the acid extract was washed with water and sodium hydrogen carbonate solution and dried (Na_2SO_4) and the solvent was removed by distillation. The residue was boiled for 3 hr. in ethanolic 3% potassium hydroxide (100 ml.). Most of the ethanol was removed by distillation under reduced pressure and the residue was taken up in water. Insoluble material was extracted into benzene and was worked up for starting hydrocarbon. The aqueous phase was acidified and the precipitated solid was found to be contaminated with a considerable amount of red material. The solid was taken up in benzene and again extracted with phosphoric acid. The phosphoric extract was diluted and the azulenic material re-extracted was decarboxylated, giving further quantites of the red azulene described above. The benzene solution containing material insoluble in phosphoric acid was washed and dried as before, and the residue after removal of the solvent was recrystallised repeatedly from ethanol. The product, 4 : 8-*dihydro*cyclo*hepta*[def]*fluorene*-9-*carboxylic acid*, was isolated as colourless needles (720 mg. of pure material), m. p. 258° (Found: C, 82·0; H, 4·7. $C_{17}H_{12}O_2$ requires C, 82·2; H, 4·9%).

The *methyl ester* (105 mg.), obtained from the acid (100 mg.) with methanolic 3% hydrochloric acid, crystallised from benzene–light petroleum as colourless needles, m. p. 139—140°. Esterification with diazomethane gave the same product (Found: C, 82·9; H, 5·5. $C_{18}H_{14}O_2$ requires C, 82·4; H, 5·4%). The *ethyl ester*, prepared similarly, formed colourless needles, m. p. 141·5° (Found: C, 82·3; H, 5·9. $C_{19}H_{16}O_2$ requires C, 82·6; H, 5·8%).

4 : *8-Dihydro-9-hydroxymethylene*cyclo*hepta*[def]*fluorene*.—The foregoing acid (190 mg.) was reduced with lithium aluminium hydride (50 mg.) in ether (25 ml.). The ether layer after decomposition of the complex with dilute sulphuric acid was washed with sodium hydrogen carbonate to remove acid. Removal of the ether, after drying (Na_2SO_4), gave the *alcohol* (180 mg.) which crystallised from benzene–light petroleum as colourless needles, m. p. 143° (Found: C, 87·0, 87·1; H, 5·6, 6·1. $C_{17}H_{14}O$ requires C, 87·1; H, 6·0%). In concentrated sulphuric acid it gave a blue-black colour.

Fluorenone-4 : 5-*dicarboxylic Acid*.—The acid (700 mg.) prepared as above was boiled for 12 hr. in "AnalaR" acetic acid (60 ml.) containing "AnalaR" chromic oxide (4·5 g.). The mixture was then poured into water and was extracted exhaustively with ether. The yellow ether extract was washed with water, and the acidic material was extracted from it with sodium hydrogen carbonate solution, giving a yellow salt in solution. The aqueous extract was acidified with hydrochloric acid and the precipitated acid was recrystallised three times from acetone–benzene. It yielded yellow prisms (125 mg.), m. p. 285—287° (Kruber, *loc. cit.*, gave m. p. 285°). The methyl ester, prepared by diazomethane (large excess), crystallised from light petroleum–benzene, as yellow needles, m. p. 191° (Found: C, 69·0; H, 4·2. Calc. for $C_{17}H_{12}O_5$: C, 68·9; H, 4·1%). The m. p.s of the acid and ester were not depressed on admixture with samples prepared by Kruber's method.

4b : 5a-*Dihydro*-5H-cyclo*propa*[def]*phenanthrene-5-carboxylic Acid*.—Phenanthrene (25 g.) was treated with diazoacetic ester (6 g.) under Drake and Sweeney's conditions (*J. Org. Chem.*, 1946, **11**, 67) and the ester resulting was separated from hydrocarbons by hydrolysis with ethanolic potassium hydroxide as described above. The alkali-soluble material was isolated by acidification and converted into the methyl ester by reaction with diazomethane followed by chromatography on alumina. The pure *ester* crystallised from light petroleum–benzene as colourless needles, m. p. 210° (Found: C, 81·4; H, 5·7. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%).

This was reduced with lithium aluminium hydride to an *alcohol*, forming colourless needles, m. p. 148° (Found: C, 86·1; H, 6·1. $C_{16}H_{14}O$ requires C, 86·4; H, 6·4%).

The ester (120 mg.) was hydrolysed with potassium hydroxide to give a quantitative yield of acid, m. p. 247—248° (from methanol), not raised by further crystallisation from methanol or benzene.

cis-8 : 9-*Dihydroxy*-8 : 9-*dihydroxy*cyclo*penta*[def]*phenanthrene*.—*cyclo*Penta[*def*]phenanthrene (410 mg.) was treated with osmium tetroxide (550 mg., 1 mol.) in dry thiophen-free benzene (15 ml.) containing pure pyridine (345 mg., 2 mols.). The mixture was left for 4 days during which crystals separated. After filtration the residue was washed with a little benzene, then taken up in methylene chloride, and after filtration the solvent was removed and the residue was weighed (1·20 g., 91%). The complex was redissolved in methylene dichloride and was shaken with an aqueous solution (100 ml.) of mannitol (10 g.) and potassium hydroxide (1 g.). The methylene chloride layer was separated and dried (Na_2SO_4). Removal of the solvent left a pale crystalline residue which was treated in boiling ethanol with charcoal for 10 min. Removal of the ethanol after filtration gave the yellow cis-*glycol* which after several recrystallisations from benzene formed colourless needles fusing to a yellow liquid at 180° (300 mg., 67% based on complex) (Found: C, 80·3; H, 5·5. $C_{15}H_{22}O_2$ requires C, 80·4; H, 5·4%).

This glycol (90 mg.) was boiled in glacial acetic acid containing chromic oxide (0·5 g.) for 2 hr. The acidic fraction of the product, crystallised three times from benzene–acetone, yielded yellow needles (15 mg.), m. p. 286° which did not depress the m. p. of fluorenone-4 : 5-dicarboxylic acid and had an identical absorption spectrum.

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