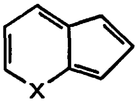
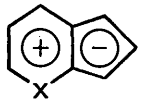
402. pseudo*Azulenes. Part I. Some Derivatives of* cyclo*Penta*[b]*pyran.**

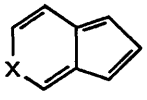
By G. V. Boyd.

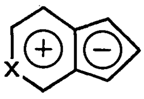
The preparation of three derivatives of the new heterocyclic system *cyclo*penta[*b*]pyran, isoelectronic with azulene, is described. These are stable, deeply coloured, basic compounds which show some resemblance to the azulenes.

It is well known that replacement of the group CH:CH of an aromatic ring by an atom X, capable of providing two mobile electrons, results in a molecule that more or less retains the aromatic character of the parent.[1] Azulene should thus give rise to the heterocyclic systems (I) and (II), which may be represented as resonance hybrids between the Kekulé-type forms (a) and the dipolar forms (b), in which each ring has a share of an aromatic sextet.

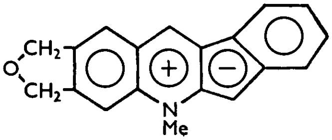

(Ia)


(Ib)

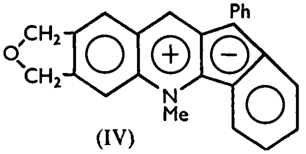

(IIa)


(IIb)

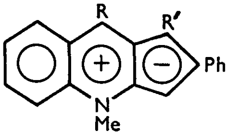
Derivatives of the system (I; X = NMe) have been known for over thirty years, since Armit and Robinson prepared the indenoquinolines (III) [2] and (IV) [3] in order to show that aromatic character may be associated with a five-membered carbon ring in a suitable combination. In a recent Communication [4] Los, Saxena, and Stafford report the synthesis of the simpler quinindenes (V; R = H or CO_2Me, R′ = H or Ph), and Mayer [5] and Anderson [6] have discussed the potential aromatic character of the *cyclo*pentathiopyrans (I and II; X = S). This paper describes the preparation of three derivatives of *cyclo*penta[*b*]pyran; the synthesis of 1 : 2-diphenylbenzo[*b*]*cyclo*penta[*e*]pyran (as VIII) has just been reported.[4]



(III)



(IV)



(V)

Attempts to make benzo[*b*]*cyclo*penta[*e*]pyran (VIII) and its 2-methyl derivative by condensing salicylaldehyde with *cyclo*pent-2-enone and 3-methyl*cyclo*pent-2-enone, respectively, were discouraging. Attention was then turned to 3-phenyl*cyclo*pent-2-enone which, as a vinylogue of acetophenone, was expected to undergo the standard reactions leading to benzopyrylium salts. The salicylidene derivative [7] (VI) of this ketone on being heated in acetic acid–hydrochloric acid gave a brown solution of the benzopyrylium chloride (VII; Y = Cl), from which perchloric acid precipitated the yellow perchlorate. When the brown pyrylium chloride solution was poured into water, purple 2-phenylbenzo[*b*]*cyclo*penta[*e*]pyran (IX), m. p. 207°, separated in 91% yield. It

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* For preliminary account of part of this work see *Chem. and Ind.*, 1957, 1244.

[1] For a recent discussion see Baker in Todd (Ed.), " Perspectives in Organic Chemistry," Interscience Publ. Inc., London, 1956, p. 36.

[2] Armit and Robinson, *J.*, 1922, **121**, 827.

[3] *Idem, ibid.*, 1925, **127**, 1604.

[4] Los, Saxena, and Stafford, *Proc. Chem. Soc.*, 1957, 352.

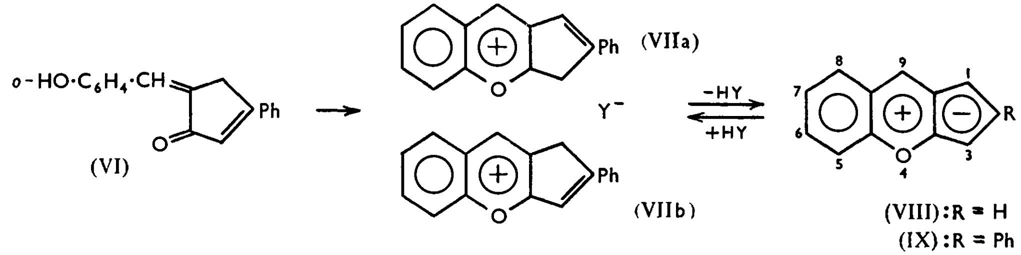
[5] Mayer, *Angew. Chem.*, 1957, **69**, 481.

[6] Anderson, *Diss. Abs.*, 1957, **17**, 1210.

[7] Borsche and Menz, *Ber.*, 1908, **41**, 202.

was also obtained in 41% yield by heating a benzene solution of equimolecular amounts of salicylaldehyde and 3-phenyl*cyclo*pent-2-enone for 2 hours in the presence of piperidine acetate; but in only 15% yield when 3-phenyl-5-salicylidene*cyclo*pent-2-enone was heated in benzene with the same catalyst for 21 hr. This low yield may be due to the unfavourable geometry of the salicylidene derivative.

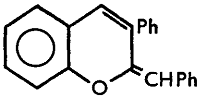
The formulation of the purple compound as (IX) follows from its analysis, from its lack of phenolic and ketonic properties, and from its behaviour as the anhydro-base of the benzopyrylium perchlorate (VII; Y = ClO_4), from which it is obtained by the action of alkali or water, and into which it can be converted by treatment with perchloric acid. The constitution of the perchlorate is extablished by analysis and by the method of its preparation. A definite choice between the tautomeric structures (VIIa) and (VIIb) for the cation is not yet possible; but the yellow colour of the perchlorate favours the form (VIIa), since (VIIb) represents a 2-styrylbenzopyrylium perchlorate which would be expected to be red, *e.g.*, 2-3′-methoxystyrylbenzopyrylium perchlorate.[8]



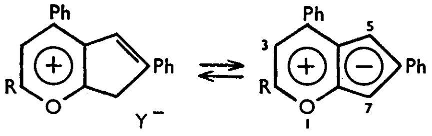
(VI) (VIIa) (VIIb) (VIII): R = H (IX): R = Ph

2-Phenylbenzo[*b*]*cyclo*penta[*e*]pyran dissolves in organic solvents with a deep red colour, and the solutions in concentrated hydrochloric and phosphoric acids are yellow with a faint bluish fluorescence, dilution with water regenerating the pyran. It is insoluble in, and not attacked by, boiling ethanolic potassium hydroxide; hot acetic acid decomposes it to a black tar. In its colour, basicity, and stability towards alkali, the *cyclo*pentapyran resembles the azulenes, and in the last respect differs markedly from the known quinonoid anhydro-bases of benzopyrylium salts, which are degraded by alkali. It is noteworthy that the yellow 2-benzylidene-3-phenylbenzopyran (X) also resists alkaline hydrolysis.[9]

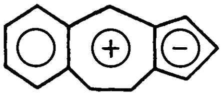
3-Phenyl*cyclo*pent-2-enone was then used in Dilthey's pyrylium synthesis.[10] Condensation with phenyl styryl ketone in the presence of ferric chloride and acetic anhydride gave 2 : 4 : 6-triphenyl*cyclo*penta[*b*]pyrylium chloroferrate (XI; Y = $FeCl_4$) in 45% yield. This salt was converted into the yellow perchlorate, treatment of which with alkali or water yielded nearly black 2 : 4 : 6-triphenyl*cyclo*penta[*b*]pyran (XII), m. p. 148°. Similarly, from *tert.*-butyl styryl ketone the yellow perchlorate (XIII; R = ClO_4) and the deep purple 2-*tert.*-butyl-4 : 6-diphenyl*cyclo*penta[*b*]pyran (XIV), m. p. 136·5 — 137·5°, were obtained.



(X)



(XI) : R = Ph (XIII) : R = Bu^t (XII) : R = Ph (XIV) : R = Bu^t



(XV)

Tautomeric structures can again be written for the cations (XI) and (XIII), but the yellow colour of the perchlorates again seems to indicate the 7- rather than the 5-pyrylium

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[8] Buck and Heilbron, *J.*, 1922, **121**, 1206.
[9] Dickinson, Heilbron, and O'Brien, *J.*, 1928, 2077.
[10] Dilthey, *J. prakt. Chem.*, 1916, **94**, 53.

structure (as VIIb), which would correspond to the red styrylpyrylium perchlorates, such as 2 : 4-diphenyl-6-styrylpyrylium perchlorate.[11]

The *cyclo*pentapyrans (XII) and (XIV) closely resemble the benzo-compound (IX). They are indifferent to alkali and decompose in boiling acetic acid. Solutions of their salts exhibit an intense green and blue-green fluorescence, respectively, typical of pyrylium salts. It is significant that ammonia converts the perchlorates into the corresponding *cyclo*pentapyrans and not into derivatives of pyridine, a reaction characteristic of the usual pyrylium salts.

Spectra.—The ultraviolet spectra of polycyclic benzenoid hydrocarbons and those of the corresponding furans, thiophens, and pyrroles have been studied by Badger and

FIG. 1. *Absorption spectra of* (*A*) 5 : 6-*benzazulene* [13] (XV) *and* (*B*) 2-*phenylbenzo*[b]cyclo*penta*[e]-*pyran* (IX).

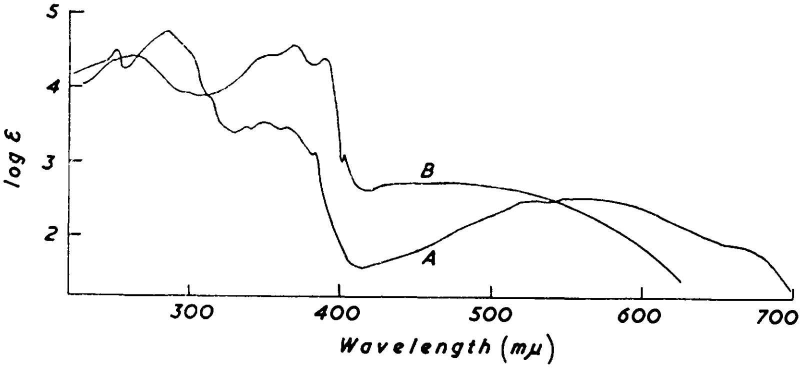
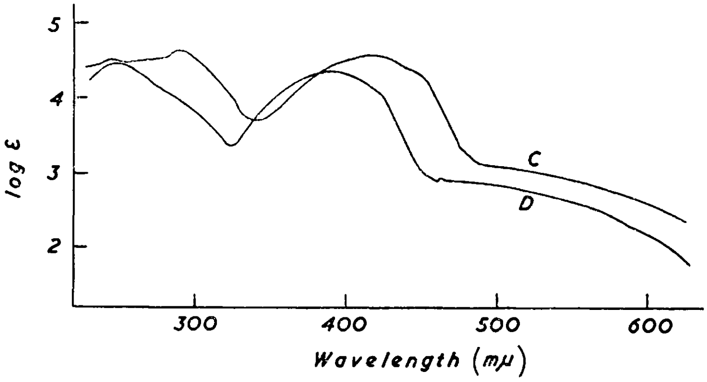


FIG. 2. *Absorption spectra of* (*C*) 2 : 4 : 6-*triphenyl*cyclo*penta*[b]*pyran* (XII) *and* (*D*) 2-tert.-*butyl*-4 : 6-*diphenyl*cyclo*penta*[b]*pyran* (XIV).



Christie,[12] who find that the spectra are fundamentally similar. A similar comparison of azulenes with corresponding derivatives of the heterocyclic systems (I) and (II) must be deferred until analogously constituted compounds are available. However, the spectrum of 2-phenylbenzo[*b*]*cyclo*penta[*e*]pyran resembles that of the unsubstituted 5 : 6-benzazulene [13] (XV) (Fig. 1), and this in turn is reported [4] to be similar to that of the corresponding nitrogen-compound (V; R = H, R′ = H). The two trisubstituted *cyclo*-pentapyrans have similar spectra (Fig. 2); substitution of the phenyl for the *tert.*-butyl group produces the expected bathochromic shift

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[11] Dilthey and Fischer, *Ber.*, 1924, **57**, 1653.

[12] Badger and Christie, *J.*, 1956, 3438.

[13] Kloster-Jensen, Kováts, Eschenmoser, and Heilbronner, *Helv. Chim. Acta*, 1956, **39**, 1057.

Ultraviolet and visible spectra.

Compound	Absorption max. (mμ) and log ε (in parentheses)			
5 : 6-Benzazulene [13] (XV) (in ethanol)	252 (4·46)	285 (4·72)	352 (3·53)	552 (2·51)
			339 (3·46)	531 (2·49)
			364 (3·46)	668 (1·88)
			382 (3·11)	
2-Phenylbenzo[*b*]*cyclo*penta[*e*]pyran (IX) ...	—	260 (4·40)	370 (4·55)	470 (2·70)
			346 * (4·37)	
			364 * (4·47)	
			389 (4·36)	
			403 (3·09)	
2 : 4 : 6-Triphenyl*cyclo*penta[*b*]pyran (XII) ...	247 (4·49)	290 (4·61)	418 (4·56)	*ca.* 508 * (3·07)
2-*tert*.-Butyl-4 : 6-diphenyl*cyclo*penta[*b*]pyran (XIV)		248 (4·46)	393 (4·34)	462 (2·92)

* Inflexion. Solvent, dioxan, except where otherwise stated.

EXPERIMENTAL

All the pyrylium perchlorates suffered some decomposition on attempted recrystallisation. The analytical specimens were therefore prepared by adding perchloric acid (70%) to a chloroform solution of the pyran.

2-Phenylbenzo[b]cyclo*penta*[e]*pyran* (IX).—(*a*) A suspension of 3-phenyl-5-salicylidene-*cyclo*pent-2-enone [7] (3 g.) in acetic acid (50 ml.) and concentrated hydrochloric acid (25 ml.) was boiled for 10 min. The colour changed from red to brown and the solid dissolved. The cold solution was poured into a large volume of water, and the precipitated cyclo*pentapyran* (2·55 g., 91%), m. p. 206°, recrystallised from benzene, from which it separated in flat purple prisms, m. p. 207—207·5° (Found: C, 88·2; H, 4·5. $C_{18}H_{12}O$ requires C, 88·5; H, 4·9%).

(*b*) A solution of 3-phenyl*cyclo*pent-2-enone (158 mg.), salicylaldehyde (122 mg., 1 mol.), piperidine (2 drops), and acetic acid (1 drop) in benzene (5 ml.) was refluxed for 2 hr. On cooling, the pyran (100 mg., 41%) crystallised, having m. p. 206—207°, undepressed on admixture with the above specimen

(*c*) A suspension of 3-phenyl-5-salicylidene*cyclo*pent-2-enone (500 mg.) in benzene (25 ml.) was refluxed for 21 hr. in the presence of a small amount of piperidine and acetic acid; the clear red solution was evaporated to dryness and unchanged salicylidene compound removed by washing with aqueous sodium hydroxide; the residue (70 mg., 15%) had m. p. and mixed m. p. 207—207·5°.

The pyran was recovered after being boiled for 2 hr. with ethanolic 10% potassium hydroxide. The pyran (100 mg.) in acetic acid (5 ml.) was refluxed for 20 min.: dilution with water yielded a black tar.

2-Phenylbenzo[b]cyclo*penta*[e]*pyrylium perchlorate* (VII; Y = ClO_4), yellow, m. p. 231° (decomp. with previous darkening) (Found: C, 62·4; H, 3·7. $C_{18}H_{13}O_5Cl$ requires C, 62·7; H, 3·8%), was prepared by treating a chloroform solution of the anhydro-base with perchloric acid, or by adding perchloric acid to the brown pyrylium chloride solution prepared as in (*a*) above. Its spectrum could not be measured accurately as it decomposed too quickly in solution to the benzopyran, even in the presence of added perchloric acid. Treatment of the perchlorate with water or dilute aqueous sodium hydroxide regenerated the pyran.

2 : 4 : 6-*Triphenyl*cyclo*penta*[b]*pyrylium perchlorate* (XI; Y = ClO_4).—A solution of phenyl styryl ketone (6·3 g.) and 3-phenyl*cyclo*pent-2-enone (4·8 g., 1 mol.) in ether (45 ml.) and acetic anhydride (10 ml.) was slowly treated with anhydrous ferric chloride (14·7 g., 3 mol.) at 0°; the mixture was then refluxed for 1·5 hr., left overnight, and diluted with acetic acid (30 ml.); the red crude chloroferrate (XI; Y = $FeCl_4$) which separated (7·3 g., 44·7%) was washed successively with acetic acid and ether, and dissolved in warm acetone (120 ml.); addition of 70% perchloric acid (2 ml.) precipitated the yellow *pyrylium perchlorate* (5·2 g., 87%), m. p. 242° (decomp.) (Found: C, 69·4; H, 3·4. $C_{26}H_{19}O_5Cl$ requires C, 69·9; H, 4·3%), $\lambda_{max.}$ (in EtOH), 255 (log ε 4·32), 294 (4·15); 355 (4·14), 445 mμ (4·52).

The perchlorate (1·25 g.) was boiled for 10 min. with a solution of sodium hydroxide (0·8 g.) in ethanol (25 ml.) and water (2 ml.), 2 : 4 : 6-*triphenyl*cyclo*penta*[b]*pyran* (XII) (0·9 g., 93%; m. p. 147—148°) separating. The analytical sample crystallised from acetone in iodine-coloured prismatic needles, m. p. 148·5° (Found: C, 90·5; H, 5·4. $C_{26}H_{18}O$ requires C, 90·2; H, 5·2%).

The pyran was also formed when the perchlorate was treated with water or cold concentrated aqueous ammonia.

The *cyclo*pentapyran was recovered after 2 hr. in boiling ethanolic potassium hydroxide; it (100 mg.) was refluxed with acetic acid (10 ml.) for 20 min.; addition of 70% perchloric acid precipitated the perchlorate (XI; Y = ClO_4) (40 mg.); the filtrate gave a dark tar with water. Concentrated hydrochloric acid extracted the pyran from a chloroform solution as the sparingly soluble yellow chloride (XI; Y = Cl), which, with water, reverted to the pyran.

2-*tert*.-Butyl-4 : 6-diphenyl*cyclo*penta[*b*]pyrylium chloroferrate (28%) and *perchlorate* (XIII; Y = ClO_4), yellow needles, m. p. 224° (decomp.) (Found: C, 67·1; H, 5·3. $C_{24}H_{23}O_5Cl$ requires C, 67·5; H, 5·4%), $\lambda_{max.}$ (in EtOH) 274 (log ε, 3·80); 325 (4·08); 420 mμ (4·48), were similarly prepared from *tert*.-butyl styryl ketone and 3-phenyl*cyclo*pent-2-enone, but without heating of the reaction mixture. The perchlorate with water, sodium hydroxide, or aqueous ammonia gave 2-tert.-*butyl*-4 : 6-*diphenyl*cyclo*penta*[b]*pyran*, deep purple prismatic needles (from ethanol), m. p. 136·5—137·5° (Found: C, 88·5; H, 6·6. $C_{24}H_{22}O$ requires C, 88·3; H, 6·8%). This compound closely resembles the triphenyl analogue, except that it is completely decomposed after 20 min. in hot acetic acid, and its hydrochloride is quite soluble in concentrated hydrochloric acid.

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