142. *Heterocyclic Iso-π-electronic Analogues of Azulene.*

By D. Leaver, J. Smolicz, and (the late) W. H. Stafford.

Some heterocyclic analogues of benzazulenes, in which the seven-membered ring is replaced by a pyran, thiopyran, pyridine, pyrazine, or 1,4-thiazine ring, have been synthesised. Their visible absorption spectra, together with those of previously known, related compounds, are discussed. The positions of the visible absorption bands of the sulphur compounds, relative to those of the analogous nitrogen compounds, are related to the varying possibilities for sulphur *d*-orbital resonance in the different cyclic skeletons.

Compounds with the basic structures (I), (II), and (III) have been described previously.[1,2] Such compounds are iso-π-electronic analogues of 2-phenylbenz[*f*]azulene (Ie) and dibenz[*a*,*g*]azulene (IIId) and, along with related compounds, have been referred to as " pseudoazulenes." [3] In view of the availability of suitable starting materials, we chose to synthesise compounds possessing these tri- and tetra-cyclic skeletons for a more extensive investigation of the effect of structure on their physical properties, particularly light absorption.

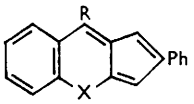
o-Mercaptobenzaldehyde was prepared from di-(*o*-carboxyphenyl) disulphide by conversion into the *N*-methylanilide, reduction of the disulphide linkage with zinc dust, and treatment with lithium aluminium hydride.[4] Unlike previous workers,[5] we found that the aldehyde undergoes extensive resinification on heating or attempted steam-distillation and we preferred to use the final ethereal solution (stored at 0°) directly for subsequent reactions. The mercapto-aldehyde, like its oxygen analogue, salicylaldehyde,[1a] reacted readily with indan-2-one in presence of piperidine acetate to give the indenothiopyran (IIIc) in good yield. Reaction with 3-phenylcyclopent-2-enone was less rapid and resulted in the formation of a blue substance as well as the required purple thiopyran (Id). The latter was purified by chromatography on alumina which caused the blue substance to disappear and, apparently, to be converted into the thiopyran. Ketones containing less reactive methylene groups (acetophenone, 3,4-diphenylcyclopent-2-enone) did not react with *o*-mercaptobenzaldehyde in alkali or acid to yield the expected *o*-mercaptobenzylidene-ketones or benzothiopyrylium salts; coloured solutions were sometimes produced but only the original ketones, resinified aldehyde, or products of unknown constitution could be isolated. Similarly, indan-1-one failed to react with *o*-mercaptobenzaldehyde in presence of piperidine acetate.

Indeno[2,1-*b*]quinoline [6] reacted readily with methyl iodide, and the methiodide, on treatment with sodium carbonate, yielded 5-methylindeno[2,1-*b*]quinoline (IIIa). Treibs and Schroth [7] reported the preparation of the same compound but without details. In contrast, indeno[1,2-*b*]quinoline [6] reacted very slowly with methyl iodide, and with dimethyl sulphate it afforded a quaternary salt which could not be converted into the base (IVa). The difficulty of methylation, in this instance, may be ascribed to the reduced nucleophilicity of the nitrogen atom resulting from the direct attachment of a benzene ring to the 2-position of the quinoline nucleus. The failure of the quaternary salt to lose a proton is in accord with the observations of Armit and Robinson [8] and of Boyd [9] who

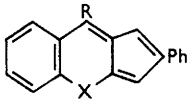
[1] Boyd, (*a*) *Chem. and Ind.*, 1957, 1244; (*b*) *J.*, 1958, 1978.
[2] Los and Stafford, *J.*, 1959, 1680.
[3] Mayer, *Angew. Chem.*, 1957, **69**, 481.
[4] Weygand, Eberhardt, Linden, Schäfer, and Eigen, *Angew. Chem.*, 1953, **65**, 525.
[5] Friedländer and Lenk, *Ber.*, 1912, **45**, 2083.
[6] Clemo and Felton, *J.*, 1952, 1667.
[7] Treibs and Schroth, *Angew. Chem.*, 1959, **71**, 578; 1960, **72**, 636.
[8] Armit and Robinson, *J.*, 1922, 827.
[9] Boyd, *J.*, 1959, 55.

experienced difficulty in preparing related bases which require to be formulated with one or more quinonoid benzene rings.

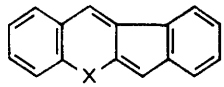
In view of this experience with the indenoquinolines, we expected indeno[1,2-*b*]-quinoxaline [10] to be methylated preferentially at $N_{(10)}$ although a report [11] that 2-methyl-3-phenylquinoxaline is methylated mainly at $N_{(4)}$ would lead to the alternative prediction (*viz.*, preferential methylation at $N_{(5)}$). The indenoquinoxaline formed a methiodide which, on basification, gave a mixture of two coloured compounds separable by virtue of their different basicities. The more basic (blue-purple) compound, isolated as its complex with 2,4,7-trinitrofluorenone, is formulated as the 10-methyl compound (Va) rather than the isomer (IVb) because the latter (formed from the $N_{(5)}$-methiodide) would



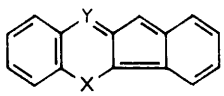
(Ia: R = CO_2Me; X = NMe)
(Ib: R = H; X = NMe)
(Ic: R = H; X = O)
(Id: R = H; X = S)
(Ie: R = H; X = CH:CH)



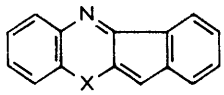
(IIa: R = CO_2Me; X = NMe)
(IIb: R = H; X = NMe)
(IIc: R = H; X = O)



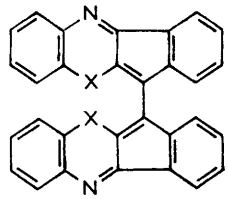
(IIIa: X = NMe)
(IIIb: X = O)
(IIIc: X = S)
(IIId: X = CH:CH)



(IVa: X = NMe; Y = CH)
(IVb: X = NMe; Y = N)
(IVc: X = S; Y = N)



(Va: X = NMe)
(Vb: X = S)



(VIa: X = NMe)
(VIb: X = S)

possess a quinonoid ring and, by analogy with the *N*-methylindenoquinoline (IVa), would probably not be formed under the conditions of the experiment. The less basic (blue) compound was also produced when a solution of the base (Va) was kept exposed to air. Its molecular weight (by mass spectrometry) indicated that it was formed from two molecules of the precursor with loss of two atoms of hydrogen (oxidative dimerisation). By analogy with a similar oxidative dimer, isolated [12] as a by-product in the preparation of indeno[2,1-*a*]phenalene, the blue compound is formulated as (VIa). Further evidence for this structure was furnished by Mr. J. M. Wilson who reported that the mass spectrum showed peaks which could correspond to fragments formed by fission at the single bond connecting the two five-membered rings.

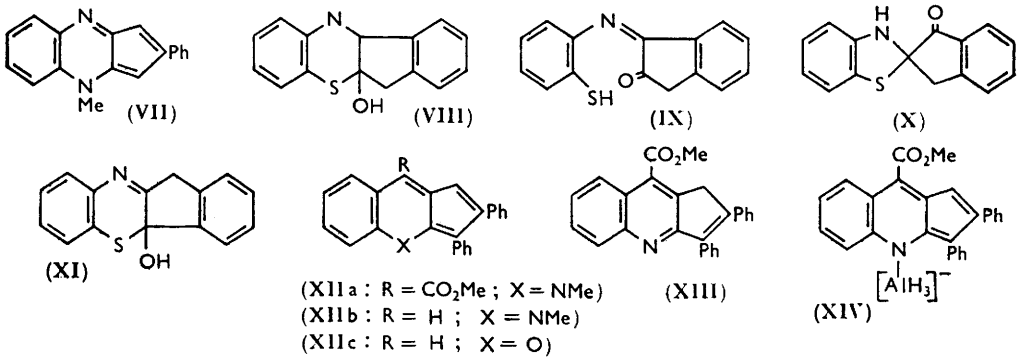
4-Phenylcyclopent-3-ene-1,2-dione, formed by nitrosation of 3-phenylcyclopent-2-enone and removal of the hydroxyimino-group, condensed with *o*-phenylenediamine to give 2-phenylcyclopenta[*b*]quinoxaline. Methylation and treatment with ammonia then afforded the *N*-methyl compound (VII) which, although decomposed by air and light, did not yield a dimer.

Indane-1,2-dione and *o*-aminobenzenethiol, in presence of piperidine acetate, yielded a colourless compound which we formulate as the thiazine (VIII). The compound yielded analytical results consistent with this structure and had a very weak infrared absorption at 3620 $cm.^{-1}$ attributed to the hydroxyl group; the absence of a carbonyl absorption excludes such isomeric structures as (IX) and (X). The same compound was formed when a yellow hydrochloride, produced by conducting the condensation in presence of hydrochloric acid, was treated with base. The hydrochloride, although lacking a

[10] Perkin, Roberts, and Robinson, *J.*, 1912, **101**, 232.
[11] Cook, Garner, and Perry, *J.*, 1942, 710.
[12] Aitken and Reid, *J.*, 1956, 3487.

hydroxyl band in the infrared region, had absorption at 1890 and 2495 cm.$^{-1}$ considered to be due to a C:NH$^+$ group [13] and providing further evidence for structure (VIII). [Although compound (VIII) is formally a pseudo-base derived from a thiazinium cation, the very low basicity of the related anhydro-base (Vb) indicates that the cation would only be formed in much more concentrated acid.] The isomeric structure (XI) is considered unlikely because, when heated above its melting point, the colourless compound lost water and a reddish-purple compound was formed. The ease of formation and stability of the latter indicate that it possesses structure (Vb) rather than the quinonoid (IVc) which would be formed from compound (XI). Solutions of the benzoindenothiazine (Vb) were relatively stable in light and air but, when the compound was made by the alternative procedure of boiling the thiazine (VIII) with hydrochloric acid, an oxidative dimer (VIb), separable by chromatography, was also formed. Higher concentrations of acid and longer reaction times gave more dimer. The mass spectrum of the dimer was similar to that of its nitrogen analogue (VIa).

Los and Stafford's syntheses [2] of the azulene analogues (IIa), (IIb), and (IIc) were extended to the related compounds (XII) by using 2,3-diphenylcyclopent-2-enone instead of the 3,4-diphenyl compound. An attempt to reduce the methoxycarbonyl group of compound (XIII) with lithium aluminium hydride failed, but a deep-purple solution, unstable in air, was produced on mixing the reactants. This solution had an ultraviolet and visible absorption spectrum very similar to that of the compound (XIIa) and, on treatment of the solution with water, part of the original ester was regenerated. It seems probable that the purple entity is a complex anion (XIV) formed by co-ordination



of the nitrogen atom with aluminium hydride and abstraction of a proton from the five-membered ring by a hydride ion.

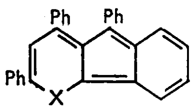
Our sulphur and oxygen analogues of azulene were relatively stable, crystalline solids which did not form stable complexes with 1,3,5-trinitrobenzene; their solutions, when stored in darkness, retained the original colour for several months but exposure to light caused fading. The nitrogen compounds, on the other hand, did not crystallise well and were, in most instances, purified and analysed as their complexes with 1,3,5-trinitrobenzene or 2,4,7-trinitrofluorenone; solutions faded rapidly, even in darkness, but the complexes were fairly stable in the solid state. Absorption spectra of the nitrogen compounds were measured by using solutions of the pure complexes and also with solutions of the free bases in the purest state available. In each instance the two spectra were almost the same at wavelengths above 250 mμ, and that of the complex is considered to be the most reliable since the cyclopentaquinoxaline (VII), which was obtained pure and crystalline, had a spectrum identical with that of its trinitrobenzene complex above 250 mμ. The complexes are presumably, therefore, completely dissociated in dilute solution.

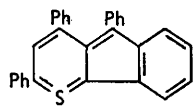
[13] Bellamy, " The Infrared Spectra of Complex Molecules," Methuen, London, 2nd edn., p. 260.

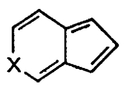
The electronic spectra of all the azulene analogues had three main absorption bands, but discussion of spectral shifts due to constitutional changes is restricted to those occurring in the longest-wavelength (visible) bands. That positional measurements of the maxima of these structureless, broad bands can be made with some accuracy is shown by the consistency of results for the series (I), (II), and (XII), presented in the Table.

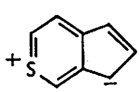
Los and Stafford [2] noted that, owing to molecular overcrowding, the 1-phenyl group in compound (IIa) makes no apparent contribution to the visible absorption [compare (Ia)]. A similar effect is apparent in compounds (XIIa) and (XIIb) [compare (Ia) and (Ib)] where a 3-phenyl group is subject to the steric effect of the *N*-methyl group. When the 9-methoxycarbonyl group is absent, a 1-phenyl group causes a shift, of +22 mμ, which is in good agreement with the value of +26 mμ observed in 1-phenylazulene.[14] 9-Methoxycarbonyl groups cause shifts of +42 and +41 mμ, respectively, in compounds (Ia) and (XIIa) [compare (Ib) and (XIIb)], figures which again correspond closely to the predicted [15] value of +45 mμ for a methoxycarbonyl group in the analogous 4-position of azulene. In the cyclopentapyrans (IIc) and (XIIc), where there is no group attached to the heteroatom, 1- and 3-phenyl groups have approximately the same spectral effect (+40 and +42 mμ) which is, however, greater than in azulene.

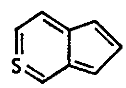
Previous workers [2,9,16] have noted that the nature of the heteroatom has a marked effect on the visible absorption of iso-π-electronic analogues of azulene and we find that the order of $\lambda_{max.}$ for analogous compounds of series (I), (III), and (V) is NMe > S > O. This is probably related to the availability of the unshared electrons of the hetero-atom for conjugative release towards the five-membered ring and is the same as that found in many other compounds containing nitrogen, sulphur, and oxygen auxochromic groups, *e.g.*, in the series *p*-nitroaniline (374 mμ),[17] *p*-nitrobenzenethiol (315 mμ),[18] and *p*-nitrophenol (312 mμ).[18] It has been reported, however, that for compounds of series (XV) [9] and (XVI),[16] those containing sulphur absorb at longer wavelengths than their nitrogen

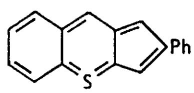

(XVa)

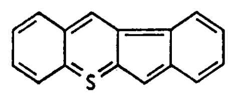

(XVb)


(XVIa)


(XVIb)


(XVIc)

(XVII)



(XVIII)

analogues, a circumstance which we attribute to the participation of *d*-orbitals in the bonding of the sulphur atoms. Henbest [19] has suggested that *d*-orbital resonance in sulphur compounds is developed to a maximum when the sulphur atom bears a positive charge (sulphonium) and the electron-donor grouping is a carbanion (*e.g.*, $>S^{+}—^{-}C<$ ⟷ $>S{=}C<$). It is to be expected therefore, that in the sulphur analogues of azulene, canonical structures such as (XVIc), in which the sulphur atom is surrounded by ten electrons (decet structures), as well as the octet structures (XVIa), will contribute to the resonance hybrids together with the polar structures (XVIb). In our compounds, however, the conditions are not favourable for *d*-orbital resonance since the decet canonical structures (XVII) and (XVIII) contain destabilising quinonoid rings; hence the light absorptions reflect mainly the electron-donor properties of the hetero-atoms. That *d*-orbital resonance may not be entirely suppressed is indicated by the fact that, although

[14] Plattner, Furst, Gordon, and Zimmermann, *Helv. Chim. Acta*, 1950, **33**, 1910.
[15] Reid, Stafford, and Ward, *J.*, 1958, 1102.
[16] Anderson, Harrison, Anderson, and Osborne, *J. Amer. Chem. Soc.*, 1959, **81**, 1255.
[17] Morton and McGookin, *J.*, 1934, 903.
[18] Gillam and Stern, " An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold Ltd., London, 1st edn., p. 114.
[19] Henbest, *Ann. Reports*, 1956, **53**, 137.

the nitrogen and oxygen compounds of series (I) have very similar absorptions to those of series (III), the sulphur compound (Id), whose decet canonical structure contains only one quinonoid ring, absorbs at 20 mμ higher wavelength than compound (IIIc) whose decet structure has two such rings. The structure of the azulene analogues (XV) is a particularly favourable one in which to observe the effect of *d*-orbital resonance since the decet structure (XVb) is the only uncharged formula which does not contain a quinonoid ring; accordingly, the sulphur compound shows very large bathochromic shifts (140 and 155 mμ) compared with the nitrogen analogues (XVa; X = NPh and NMe).

The wavelength shift in the visible absorption band of azulene caused by replacement of a CH group by a (more electronegative) nitrogen atom would be expected to lie in the same direction as the shift caused by attachment of an electron-withdrawing (−*T*) group at the same position. The hypsochromic shifts caused by aza-replacement, in 1-aza-azulene,[20] 1,3-diaza-azulene,[21] and 1-azabenz[*b*]azulene,[22] are in accord with this view, but no other pair of corresponding azulene and aza-azulene is, at present, available for comparison. Further support for the prediction is, however, provided by a comparison of the compounds (Va), (Vb), and (VII), which are analogues of aza-azulenes, with the corresponding analogues of azulenes (IIIa), (IIIc), and (Ib), respectively; in each instance

Ultraviolet and visible absorption spectra and H_0 ($K = 1$) constants.

Compound †	$\lambda_{max.}$ (mμ) (log ε in parentheses)			Ref.	H_0 ($K = 1$)
Ia [a]	574 (3·06)			2	+1·28
Ib [a]	532 (3·01)			2	+2·80
Ic	470 (2·92)			2	−2·00
Id	520 (2·77)	406 (4·08)	278 (4·41)		−2·66
		385 (4·26)	265 (4·40)		
		368 (4·18)			
IIa [a]	574 (3·06)			2	−1·01
IIb [a]	554 (3·21)			2	−0·57
IIc	512 (2·92)			2	
XIIa [a]	574 (3·02)	378 (4·20)	305 (4·49)		−1·21
XIIb [a]	533 (3·10)	370 (4·09)	298 (4·44)		
XIIc	510 (2·89)	362 (4·43)	256 (4·59)		
IIIa [a]	531 (3·44)	355 (3·91)	298 (4·82)		+2·77
		320 * (4·4)			
IIIb	465 (3·36)			1*a*	−4·20
IIIc	500 (3·36)	366 (3·94)	299 (4·71)		−4·25
		350 (4·04)	292 (4·71)		
		334 (3·99)			
Va	579 (3·32)	352 (3·88)	297 (4·69)		+0·28
Vb	519 (3·35)	374 (3·97)	292 (4·66)		−2·65
		357 (4·07)	257 (4·37)		
			250 (4·35)		
VIa	610 (3·67)	362 * (4·2)	307 (4·89)		2·55
	411 (3·39)				
VIb [b]	572 (3·75)	381 (4·45)	299 (4·69)		3·31
	514 (3·73)	365 (4·43)	276 (4·69)		
VII	599 (3·00)	412 (4·43)	283 (4·62)		+1·07
		392 (4·51)			
XIV [b, e]	542	355	303, 266, 256, 250		
XVa; X = NPh [c]	685 (3·26)			9	
XVa; X = NMe [c]	670 (3·16)			9	
XVa; X = S [c]	825 (2·93)			9	
XVIa; X = NPh [d]	432 (3·30)			16	
XVIa; X = S [d]	465 (3·08)			16	

Only the visible bands are given if the compounds were previously known. * Inflexion. † Solvent = ethanol except where otherwise stated.

[a] Spectrum of 1,3,5-trinitrobenzene complex. [b] In tetrahydrofuran. [c] In dioxan. [d] In hexane. [e] Relative intensities of bands similar to those in other compounds of the series. [f] Most intense maximum in band.

[20] Nozoe, Seto, Matsumura, and Terasawa, *Chem. and Ind.*, 1954, 1357.
[21] Nozoe, Mukai, and Murata, *J. Amer. Chem. Soc.*, 1954, **76**, 3352.
[22] Anderson and Tazuma, *J. Amer. Chem. Soc.*, 1952, **74**, 3455.

substitution of N for CH causes a shift (+67, +48, and +19 mμ) in the same direction as that produced by, *e.g.*, a methoxycarbonyl group at the same position or at the analogous 4-position (predicted [15]) of azulene.

The value of the Hammett acidity function [23] (H_0) for which the distribution coefficient between benzene and aqueous sulphuric acid is unity, was measured for each compound by the spectrophotometric method described for azulenes.[24] Heilbronner [25] has pointed out that such measurements do not provide an accurate comparison of basicities unless the distribution coefficient of the free base between the two phases is the same, or nearly so, for all the compounds examined. Since this condition is clearly not satisfied, the data (Table) serve only to show that the nitrogen analogues of azulene are considerably more basic than the corresponding oxygen and sulphur compounds. The two oxidative dimers were apparently less basic than the corresponding monomers, a characteristic which is also shown by the bi(indenophenalenyl) of Aitken and Reid [12] and provides further evidence for our proposed structures.

Experimental

Extracts were dried over anhydrous sodium sulphate and evaporated under reduced pressure. Ultraviolet and visible spectra were measured for ethanol solutions, unless otherwise stated, on a Unicam SP 500 quartz spectrophotometer. Tetrahydrofuran was dried with lithium aluminium hydride. The light petroleum used had b. p. 40—60° unless otherwise stated.

o-*Mercaptobenzaldehyde.*—*N*-Methylaniline (24 g.) in pyridine (equal volume) was added, dropwise with shaking, to an ice-cooled solution of di-(*o*-chlorocarbonylphenyl) disulphide [26] (32 g.) in benzene (1200 ml.) which was afterwards boiled for 1 hr., washed with 2N-hydrochloric acid, followed by water, and dried. Evaporation yielded the bis-*N*-methylanilide (45 g.) as a pale yellow viscous oil. A solution of the oil (40 g.) in acetic acid (400 ml.) was boiled in a stream of carbon dioxide, and zinc dust (12 g.) was added in small portions during 3 hr. The solution was then filtered, diluted with water (1 l.), and extracted with ether (3 × 500 ml.). The extract was washed with sodium carbonate solution followed by water, dried, and evaporated in a stream of carbon dioxide to yield *o*-mercapto-*N*-methylbenzanilide (33 g.), prisms, m. p. 92—93° [from light petroleum (b. p. 80—100°)] (lit.,[4] m. p. 85°) (Found: C, 69·1; H, 5·5; N, 5·8; S, 13·0. Calc. for $C_{14}H_{13}NOS$: C, 69·1; H, 5·4; N, 5·8; S, 13·2%).

Lithium aluminium hydride (3 g.) in dry ether (300 ml.) was added dropwise during 45 min. to a stirred solution of the *N*-methylanilide (26 g.) in tetrahydrofuran (150 ml.) at <0°. Stirring was continued for 18 hr. at 0°, excess of hydride was destroyed by ice, and 0·05N-hydrochloric acid (300 ml.) was added dropwise to dissolve the precipitate. More ether was added and the ether layer was separated, washed with water, and dried. The resulting pale yellow solution of *o*-mercaptobenzaldehyde was stored at 0°. The yield of aldehyde was estimated as 60% (for final stage) by formation, from an aliquot part, of the orange 2,4-dinitrophenylhydrazone, m. p. 269—270° (from acetic acid) (lit.,[4] m. p. 269°).

Benzo[b]*indeno*[1,2-e]*thiopyran* (IIIc).—Indan-2-one (0·9 g.) and *o*-mercaptobenzaldehyde (ether solution containing 0·9 g.) were boiled in ethanol (20 ml.) containing piperidine acetate (~0·1 g.) for 30 min. The *thiopyran*, reddish-brown plates, m. p. 209—209·5° (from ethanol) (Found: C, 82·4; H, 4·3; S, 13·1. $C_{16}H_{10}S$ requires C, 82·0; H, 4·3; S, 13·6%), crystallised on cooling. Evaporation of the mother-liquor and chromatography of the residue in benzene on alumina yielded a further small quantity (total, 1·2 g.).

2-*Phenylbenzo*[b]*cyclopenta*[e]*thiopyran* (Id).—3-Phenylcyclopent-2-en-1-one (1·3 g.) and *o*-mercaptobenzaldehyde (ether solution containing 1·1 g.) were boiled in benzene (50 ml.) containing piperidine acetate (~0·1 g.) for 1·5 hr. during which the solution became deep green. Concentration and chromatography on alumina in light petroleum–benzene gave a blue zone which gradually became fainter whilst a more slowly moving reddish-purple zone became stronger. A second chromatographic purification of the eluted reddish-purple material afforded

[23] Paul and Long, *Chem. Rev.*, 1957, **57**, 11.
[24] Plattner, Heilbronner, and Weber, *Helv. Chim. Acta*, 1949, **32**, 574.
[25] Heilbronner, "Non-Benzenoid Aromatic Compounds," ed. Ginsburg, Interscience Publ. Inc. New York, 1959, p. 262.
[26] Reissert and Manns, *Ber.*, 1928, **61**, 1312.

the *thiopyran* (0·05 g.), reddish-brown plates, m. p. 234—235° (from ethanol) (Found: C, 82·6; H, 4·8; S, 11·7. $C_{18}H_{12}S$ requires C, 83·0; H, 4·7; S, 12·3%).

5-*Methylindeno*[2,1-b]*quinoline* (IIIa).—Indeno[2,1-*b*]quinoline [6] (0·5 g.) and methyl iodide (5 ml.) were boiled in benzene (20 ml.) for 2 hr. to give, on cooling, 5-methylindeno[2,1-*b*]-quinolinium iodide (0·8 g.), m. p. 237—238° (from ethanol). The methiodide (0·7 g.) was shaken with 10% aqueous sodium carbonate and chloroform for 30 min. and the purple chloroform solution was dried and evaporated under nitrogen. Trituration of the residue with, and recrystallisation from, methanol afforded 5-methylindeno[2,1-*b*]quinoline (0·38 g.), m. p. 129—131° with previous softening (lit.,[7] m. p. 131°) [trinitrobenzene *complex*, dark purple rods, m. p. 161—161·5° from ethanol (Found: C, 62·0; H, 3·6; N, 12·4. $C_{23}H_{16}N_4O_6$ requires C, 62·2; H, 3·6; N, 12·6%)].

5-*Methylindeno*[1,2-b]*quinolinium Methyl Sulphate*.—Indeno[1,2-*b*]quinoline [6] and dimethyl sulphate in boiling benzene afforded an almost quantitative yield of the quaternary *salt*, needles (from ethanol), no melting below 330° (Found: S, 9·8. $C_{18}H_{17}NO_4S$ requires S, 9·35%), which gave no colour with basic reagents.

10-*Methylindeno*[1,2-b]*quinoxaline* (Va).—Indeno[1,2-*b*]quinoxaline [10] (1·5 g.) and methyl iodide (10 ml.) were heated at 110—120° in a sealed tube for 2·5 hr., to yield crude 10-methylindeno[1,2-*b*]quinoxalinium iodide (1·7 g.). The methiodide (1·5 g.) was shaken with chloroform and 2N-aqueous ammonia, and the blue-purple chloroform layer was washed with water and extracted with 2N-hydrochloric acid (3 × 100 ml.) which left the blue oxidative dimer in the organic layer. A second chloroform extract, obtained from the aqueous layer after basification with ammonia, was concentrated under nitrogen, cooled to 0°, and diluted with methanol, thereby affording 10-methylindeno[1,2-*b*]quinoxaline (1 g.), deep violet irregular crystals, m. p. 128—130° with previous softening [2,4,7-*trinitrofluorenone complex*, dark needles, m. p. 193° (from ethanol) (Found: C, 63·9; H, 3·2; N, 12·5. $C_{29}H_{17}N_5O_7$ requires C, 63·6; H, 3·1; N, 12·8%)]. A solution of the base (0·5 g.) in ethanol (200 ml.), during 1 month in darkness and air, changed from purple-violet to blue and deposited *bi*-(10-*methylindeno*[1,2-b]*quinoxalin*-11-*yl*) (0·4 g.), dark needles, m. p. 324° (from ethanol) (Found: C, 83·1; H, 5·1; N, 11·8%; *M*, 462. $C_{32}H_{22}N_4$ requires C, 83·1; H, 4·8; N, 12·1%; *M*, 462).

4-*Phenylcyclopent*-3-*ene*-1,2-*dione*.—Concentrated hydrochloric acid (1·2 ml.) was added slowly, with cooling and shaking, to 3-phenylcyclopent-2-en-1-one (4 g.) and isopentyl nitrite (4·3 g.) in ethanol (25 ml.). The solution was then maintained at 50—60° for 10 min. and 5-*hydroxyimino*-3-*phenylcyclopent*-2-*en*-1-*one* (3·6 g.), m. p. 197—198° (from ethanol), was collected by filtration (Found: C, 70·8; H, 5·0; N, 7·4. $C_{11}H_9NO_2$ requires C, 70·6; H, 4·9; N, 7·5%). Addition of concentrated hydrochloric acid (15 ml.) to the hydroxyimino-ketone (3 g.) in 40% aqueous formaldehyde (25 ml.), and heating at 50—60° for 5 min., afforded the *dione* (2·1 g.), yellow plates, m. p. 194—195° (from ethyl acetate) (Found: C, 76·3; H, 4·5. $C_{11}H_8O_2$ requires C, 76·7; H, 4·7%).

4-*Methyl*-2-*phenylcyclopenta*[b]*quinoxaline* (VII).—Reaction of the foregoing dione (2 g.) with *o*-phenylenediamine (1·3 g.) in hot ethanol yielded 2-*phenylcyclopenta*[b]*quinoxaline* (2·5 g.), needles, m. p. 236·5—237·5° (Found: C, 83·4; H, 4·9; N, 11·5. $C_{17}H_{12}N_2$ requires C, 83·6; H, 4·9; N, 11·5%). The quinoxaline (0·9 g.) and methyl iodide (20 ml.) were heated at 80—85° for 1 hr. in a sealed tube and the solid product was washed with hot benzene to yield 4-*methyl*-2-*phenylcyclopenta*[b]*quinoxalinium iodide* (0·75 g.), orange needles, m. p. 240—241° (decomp.) (Found: N, 7·2; I, 33·3. $C_{18}H_{15}IN_2$ requires N, 7·25; I, 32·9%). The methiodide (0·5 g.) was shaken with 2N-aqueous ammonia, and the resulting black solid (0·3 g.) was crystallised from methanol under nitrogen to give the free *base*, dark needles, m. p. 160° (decomp.) (Found: C, 83·6; H, 5·4; N, 10·75. $C_{18}H_{14}N_2$ requires C, 83·7; H, 5·5; N, 10·8%). The *trinitrobenzene complex* formed dark blue needles, m. p. 147° (decomp.) (Found: N, 14·8. $C_{24}H_{17}N_5O_6$ requires N, 14·9%).

10a,11-*Dihydro*-10a-*hydroxybenzo*[b]*indeno*[1,2-e][1,4]*thiazine* (VIII).—(*a*) Indane-1,2-dione (0·4 g.) and *o*-aminobenzenethiol (0·35 g.) were boiled in ethanol (30 ml.) containing piperidine acetate (~0·1 g.) for 15 min. On being cooled, the solution deposited the *thiazine* (0·34 g.), needles, m. p. 211—212° (decomp.) (from ethanol) (Found: C, 71·4; H, 4·45; N, 5·3; S, 12·5. $C_{15}H_{11}NOS$ requires C, 71·1; H, 4·4; N, 5·5; S, 12·7%).

(*b*) Indane-1,2-dione (0·8 g.) and *o*-aminobenzenethiol (0·7 g.) in 2N-aqueous hydrochloric acid, kept at 40—50° for 15 min., gave a precipitate of 10a,11-*dihydro*-10a-*hydroxybenzo*[b]-*indeno*[1,2-e]-[1,4]-*thiazinium chloride* (1·4 g.), yellow needles, m. p. 145—146° (decomp.) (from

acetone) (Found: C, 61·5; H, 3·8; Cl, 12·5; N, 5·0; S, 11·4. $C_{15}H_{12}ClNOS$ requires C, 62·2; H, 4·2; Cl, 12·3; N, 4·8; S, 11·1%). Treatment of the hydrochloride with aqueous ammonia yielded the thiazine.

Benzo[b]*indeno*[1,2-e][1,4]*thiazine* (Vb).—(*a*) When the foregoing thiazine (0·2 g.) was heated at 210° for 1—2 min. it formed a dark red mass which after chromatography in light petroleum–benzene on alumina, afforded the *benzoindenothiazine* (0·04 g.), dark needles, m. p. 169·5—170° (from ethanol) (Found: C, 76·3; H, 3·9; N, 6·2; S, 13·4. $C_{15}H_9NS$ requires C, 76·55; H, 3·9; N, 5·95; S, 13·6%).

(*b*) When the foregoing hydrochloride (1·1 g.) was heated for 3 min. in boiling 0·2N-aqueous hydrochloric acid it became reddish-brown; chromatography in light petroleum–benzene on alumina then gave two main coloured zones. The first zone gave a deep red eluate which afforded the benzoindenothiazine (0·09 g.) as in (*a*) above. The second zone gave a violet eluate which yielded *bi*(*benzo*[b]*indeno*[1,2-e][1,4]*thiazin*-11-*yl*) (0·02 g.), dark prisms, no melting below 350°, from benzene–chloroform (Found: C, 76·8; H, 3·4; N, 6·0; S, 13·6%; *M*, 468. $C_{30}H_{16}N_2S_2$ requires C, 76·9; H, 3·4; N, 6·0; S, 13·7%; *M*, 468). When the hydrochloride (0·54 g.) was heated in more concentrated (2N) hydrochloric acid, it darkened less rapidly (5 min. at 100° followed by 30 min. at 80—90°) and the product, treated as above, gave monomer (0·01 g.) and dimer (0·085 g.) in different proportions.

2,3-*Diphenylcyclopent*-2-*en*-1-*one*.—Methyl γ-phenylacetoacetate [27] (65 g.) in dry ether (100 ml.) was added, slowly with stirring, to finely divided sodium (7·8 g.) in dry ether (400 ml.), and the mixture was boiled for 6 hr. After the suspension had been cooled, phenacyl bromide (67·5 g.) was added and boiling was continued for 4 hr. The solution was then washed with 2N-hydrochloric acid, aqueous sodium carbonate, and water, dried, and evaporated, to give methyl α-phenacyl-γ-phenylacetoacetate (96 g.) as a viscous orange oil. The oil (55 g.), in ethanol (150 ml.), was added, dropwise with stirring, to 5% aqueous sodium hydroxide (1 l.) at 95° under nitrogen, and the whole was then heated on a boiling water-bath for 30 min., boiled for 5 min., cooled, and extracted with chloroform. The extract was washed with water, dried, and evaporated and the viscous residue was distilled to give a pale yellow oil, b. p. 162—164°/0·5 mm. Trituration with ether afforded the diphenylcyclopentenone (28·5 g.), prisms, m. p. 95—96° (from methanol) (lit.,[28] m. p. 95°).

4-*Methyl*-2,3-*diphenylcyclopenta*[b]*quinoline* (XIIb).—Solutions of isatin (3·2 g.) in 30% aqueous potassium hydroxide (20 ml.) and of 2,3-diphenylcyclopent-2-enone (5 g.) in ethanol (40 ml.) were mixed, boiled for 8 hr., and poured into water (200 ml.). Addition of acetic acid precipitated 2,3-*diphenylcyclopenta*[b]*quinoline*-9-*carboxylic acid* (6·2 g.), pale yellow needles, m. p. 324° (from benzene) (Found: C, 82·2; H, 4·9; N, 4·1. $C_{25}H_{17}NO_2$ requires C, 82·6; H, 4·7; N, 3·9%). An intimate mixture of the acid (1 g.) and soda-lime (4 g.) was covered with soda-lime (2 g.) and heated under 10 mm. in a test tube. The brown sublimate which collected on the cooler parts of the tube was chromatographed in light petroleum–benzene on alumina and gave two fluorescent zones. Evaporation of the eluate from the first zone yielded 2,3-diphenylcyclopenta[*b*]quinoline as a buff solid which darkened in air and could not be purified. It was boiled with dimethyl sulphate in benzene for 3 hr. and the resulting solution was extracted with very dilute hydrochloric acid. Basification of the aqueous layer with sodium carbonate, extraction with chloroform, and evaporation of the dried extract gave a reddish-purple residue of 4-methyl-2,3-diphenylcyclopenta[*b*]quinoline which reacted with 1,3,5-trinitrobenzene in ethanol to form a *complex*, purple-black prisms, m. p. 135—136° (from ethanol saturated with trinitrobenzene) (Found: C, 68·5; H, 3·9; N, 10·0. $C_{31}H_{22}N_4O_6$ requires C, 68·1; H, 4·0; N, 10·3%).

Methyl 4-*Methyl*-2,3-*diphenylcyclopenta*[b]*quinoline*-9-*carboxylate* (XIIa).—2,3-Diphenylcyclopenta[*b*]quinoline-9-carboxylic acid (4 g.) was boiled in methanol (140 ml.) containing sulphuric acid (15 ml.) to form *methyl* 2,3-*diphenylcyclopenta*[b]*quinoline*-9-*carboxylate* (3·2 g.), pale yellow needles, m. p. 207·5—208° (from methyl acetate) (Found: C, 82·9; H, 5·4; N, 3·9. $C_{26}H_{19}NO_2$ requires C, 82·7; H, 5·1; N, 3·7%). The ester (1·2 g.) and dimethyl sulphate (15 ml.) were boiled in benzene (35 ml.) for 4 hr. and diluted with benzene (200 ml.). Extraction with 10% aqueous acetic acid and basification of the extract with sodium carbonate yielded a dark blue solid which, on precipitation from chloroform with methanol, afforded the free *base* (XIIa) (0·45 g.) as blue-black needles, m. p. 178·5—179° (from methanol) (Found: C, 83·1;

[27] Viscontini and Merckling, *Helv. Chim. Acta*, 1952, **35**, 2280.
[28] Borsche and Klein, *Ber.*, 1939, **72**, 2082.

H, 5·7; N, 3·3. $C_{27}H_{21}NO_3$ requires C, 82·8; H, 5·4; N, 3·6%) [*1,3,5-trinitrobenzene complex*, blue-black prisms, m. p. 130—131°, from ethanol saturated with trinitrobenzene (Found: N, 8·9. $C_{33}H_{24}N_4O_8$ requires N, 9·3%)].

2,3-Diphenylbenzo[b]*cyclopenta*[e]*pyran* (XIIc).—2,3-Diphenylcyclopent-2-enone (2·4 g.), salicylaldehyde (1·2 ml.), and sodium hydroxide (2·5 g.) in 50% aqueous ethanol (50 ml.), during 12 hr. at room temperature, gave a precipitate of a sodium salt. Dilution with water and acidification then yielded *2,3-diphenyl-5-salicylidenecyclopent-2-en-1-one* (2·7 g.), yellow needles, m. p. 208—209° (from methanol) (Found: C, 85·1; H, 5·4. $C_{24}H_{18}O_2$ requires C, 85·2; H, 5·35%). A suspension of the salicylidene compound (1·5 g.) in acetic acid (20 ml.) and concentrated hydrochloric acid (8 ml.) was boiled for 1 hr., cooled, and poured into water. The reddish-brown solid precipitate was chromatographed twice, in light petroleum-benzene on alumina, to yield the *pyran* (0·24 g.), reddish-black prisms, m. p. 159—160° (from ethanol) (Found: C, 89·3; H, 5·0. $C_{24}H_{16}O$ requires C, 90·0; H, 5·0%).

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