12. pseudo*Azulenes. Part II.* A Tricyclic* cyclo*Penta*[b]-*thiapyran and Some Nitrogen Analogues.*

By G. V. Boyd.

The inherent instability of the indeno[1 : 2-*b*]pyran system has made possible the synthesis of the 2 : 4 : 5-triphenyl derivative of the new indeno-[1 : 2-*b*]thiapyran system, and of three substituted indeno[1 : 2-*b*]pyridines, from the corresponding pyrylium perchlorates. These *pseudo*azulenes * are green or blue bases; their solutions are susceptible to atmospheric oxidation. Their electronic absorption spectra are compared with that of the isosteric 1 : 2-benzazulene.

Derivatives of the *pseudo*azulenic * *N*-methyl*cyclo*penta[*b*]pyridine were first prepared by Armit and Robinson in 1922 and 1925. Condensing 6-aminopiperonaldehyde with 3-phenylindan-1-one, followed by quaternisation with methyl sulphate, yielded the salt (I; Y = $MeSO_4$), which on treatment with potassium hydroxide lost the elements of methyl hydrogen sulphate to form the green anhydro-base [1] (II). The structure of this compound is noteworthy because of the unfavourable *o*-quinonoid ring in its covalent canonical forms. Stabilisation is achieved by fusion to the aromatic *cyclo*pentapyridine system, together with the presence of the phenyl substituent, which seems important as attempts [2] to prepare the unsubstituted base (III) were inconclusive; a green amorphous solid was obtained, which decomposed in air and could not be purified.

It has now been found that the oxygen analogue, benzo[*b*]indeno[2 : 1-*e*]pyrylium tetrachloroferrate [3] (IV; Y = $FeCl_4$) does not yield the *pseudo*azulene (V) on treatment with base but affords 2-salicylideneindan-1-one (VI), a result not unexpected in view of a similar hydrolysis of 7 : 8-dimethoxybenzo[*b*]indeno[2 : 1-*e*]pyrylium chloride [3] (as IV).

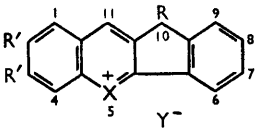
The 10-phenylbenzopyrylium salt (VII) was then examined in the hope that the phenyl substituent might stabilise the benzoindenopyran system. The perchlorate was prepared

* Part I, *J.*, 1958, 1978. The term *pseudo*azulene is there explained as denoting a bicyclic compound with the π-electron structure of azulene, achieved by a skeleton other than that of fused C_5 and C_7 rings.

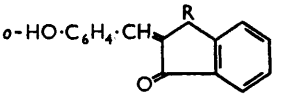
[1] Armit and Robinson, *J.*, 1925, **127**, 1604.
[2] *Idem*, *J.*, 1922, **121**, 827.
[3] Perkin, Robinson, and Turner, *J.*, 1908, **93**, 1085.

by acid-treatment of 3-phenyl-2-salicylideneindan-1-one (VIII), or, more efficiently, by condensing salicylaldehyde with 3-phenylindan-1-one in the presence of hydrogen chloride and perchloric acid.[4] The action of sodium hydroxide or sodium acetate on this salt again caused hydrolysis to the salicylidene compound rather than the formation of the anhydro-base (IX). This observation indicated that the oxygen analogues of azulene are less stabilised than the *N*-methyl analogues; and at the same time it opened a way into the field of the *N*-substituted *cyclo*penta[*b*]pyridines and of the hitherto unknown *cyclo*penta[*b*]thiapyrans.

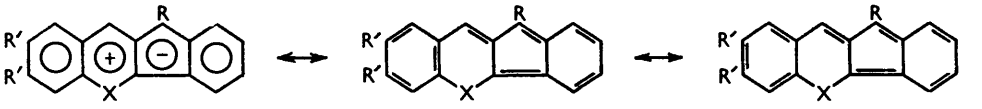
2 : 4 : 5-Triphenyl-5*H*-indeno[1 : 2-*b*]pyrylium tetrachloroferrate (X; Y = $FeCl_4$) was made by condensing 3-phenylindan-1-one with phenyl styryl ketone in the presence of ferric chloride and acetic anhydride, or, in much poorer yield, from 2-benzylidene-3-phenylindan-1-one and acetophenone. The corresponding perchlorate, like its 2 : 3-benzo-analogue, did not form an anhydro-base on treatment with alkali but suffered ring opening to the nearly colourless *pseudo*-base (XI). This is formulated as an αβ-unsaturated δ-diketone in accordance with Berson's recent spectroscopic work [5] on the *pesudo*-base of triphenylpyrylium. Structure (XI) represents a vinylogous β-diketone which accounts for the weakly acidic properties of the *pseudo*-base: it dissolves in alcoholic potassium hydroxide with a red colour, being reprecipitated on dilution with water. Treatment with acids regenerates the salts (X).



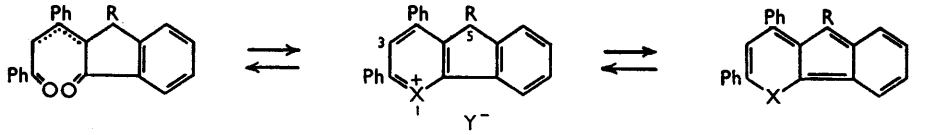
(I): X = NMe, R = Ph, R′R′ = OCH_2O
(IV): X = O, R = H, R′ = H
(VII): X = O, R = Ph, R′ = H



(VI): R = H
(VIII): R = Ph



(II): X = NMe, R = Ph, R′R′ = OCH_2O
(III): X = NMe, R = H, R′R′ = OCH_2O
(V): X = O, R = H, R′ = H
(IX): X = O, R = Ph, R′ = H



(XI): R = Ph

(XIX): R = H

(X): X = O, R = Ph
(XII): X = S, R = Ph
(XIV): X = NPh, R = Ph
(XVII): X = NMe, R = Ph
(XVIII): X = O, R = H
(XX): X = S, R = H

(XIII): X = S, R = Ph
(XV): X = NPh, R = Ph
(XVI): X = NMe, R = Ph

(XXI): X = NPh, R = H
(XXII): X = NMe, R = H

Formation of *pseudo*-bases is one example of the susceptibility of pyrylium salts to nucleophilic attack. The reaction with amines to yield pyridines has long been known; [6] recently Dimroth and his co-workers [7] obtained derivatives of nitrobenzene by reaction

[4] Cf. Le Fèvre, *J.*, 1933, 1532.
[5] Berson, *J. Amer. Chem. Soc.*, 1952, **74**, 358.
[6] Baeyer and Piccard, *Annalen*, 1911, **384**, 208.
[7] Dimroth *et al.*, *Angew. Chem.*, 1956, **68**, 519; *Chem. Ber.*, 1957, **90**, 1634, 1668.

with the potassium derivative of nitromethane, and Hafner [8] prepared azulenes by reaction with sodium *cyclo*pentadienylide. Pertinent to the present work is Wizinger's and Ulrich's synthesis [9] of thiapyrylium salts by the action of sodium sulphide on pyrylium salts, followed by acidification. Application of this elegant reaction to the pyrylium salt (X; Y = ClO_4) gave an excellent yield of the yellow 2 : 4 : 5-triphenyl-5*H*-indeno[1 : 2-*b*]-thiapyrylium perchlorate (XII; Y = ClO_4), which readily lost the elements of perchloric acid on treatment with sodium hydroxide, sodium acetate, or hot water, to yield the dark green *cyclo*penta[*b*]thiapyran (XIII).

This *pseudo*azulene, like the *cyclo*pentapyrans described in Part I, dissolves in acids to yellow solutions containing the cation (XII), and resists alkaline hydrolysis. It differs from them in its stability in boiling acetic acid, and in its sensitivity towards oxygen: the green colour of solutions in organic solvents, while stable for several hours in an atmosphere of nitrogen, fades within a few minutes on exposure to the air. The solid, however, has been kept unchanged in an open bottle for two weeks. Susceptibility to oxidation is also a property of the indenoquinoline (II) and is attributed to the presence of the quinonoid ring.

The action of aniline on 2 : 4 : 5-triphenyl-5*H*-indeno[1 : 2-*b*]pyrylium perchlorate led to the *N*-phenylpyridinium perchlorate (XIV; Y = ClO_4), which formed bluish-green 1 : 2 : 4 : 5-tetraphenylindeno[1 : 2-*b*]pyridine (XV) on decomposition with sodium hydroxide. Reaction of the pyrylium perchlorate with methylamine yielded the blue anhydro-base (XVI) directly, which was characterised as the pale yellow perchlorate (XVII; Y = ClO_4). Methylamine is thus a stronger base than the methylindenopyridine; the reverse relation holds with the *N*-phenyl compounds.

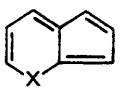
Attention was then turned to compounds lacking the 5-phenyl substituent. 2 : 4-Diphenyl-5*H*-indeno[1 : 2-*b*]pyrylium perchlorate (XVIII; Y = ClO_4) was prepared from indan-1-one and phenyl styryl ketone (31% yield) or from 2-benzylideneindan-1-one and acetophenone (9%). On hydrolysis with sodium acetate it gave the cream-coloured amphoteric *pseudo*-base (XIX) which was isolated in low yield after a troublesome purification. The derived thiapyrylium salt (XX; Y = ClO_4) decomposed on treatment with sodium hydroxide to an ill-defined yellow solid, which was not further examined. In the nitrogen series, however, the stable blue anhydro-base, 1 : 2 : 4-triphenylindeno-[1 : 2-*b*]pyridine (XXI), was readily obtained. The action of methylamine on the pyrylium perchlorate afforded a basic blue amorphous solid, probably impure 1-methyl-2 : 4-diphenylindeno[1 : 2-*b*]pyridine (XXII), which decomposed when kept and could not be purified.

The three indenopyridines closely resemble the sulphur compound: they are attacked by oxygen, resist the action of alkali and of acetic acid, and dissolve in acids to pale yellow solutions from which they are regenerated on basification.

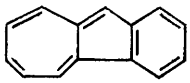
In the presence of the unfavourable *o*-quinonoid ring, the diphenylindeno[1 : 2-*b*]-thiapyran system, unlike the *N*-phenyl and *N*-methyl analogues, thus requires the stabilising influence of a phenyl substituent in the five-membered ring for its formation (and, presumably, existence), while even this is not sufficient for the oxygen compound. Stabilisation of energetically unfavoured structures by aromatic groups is well known; *e.g.*, tetraphenyl*cyclo*pentadienone is stable but *cyclo*pentadienone itself seems incapable of any but the briefest existence.[10] The varying requirements for the 5-phenyl group, together with the lability of the *N*-methyl compound (XXII), suggest the following order of decreasing stability in the *pseudo*azulenes (XXIII): X = NPh > NMe > S > O. It is interesting that the resonance energies of the five-membered heterocyclic analogues of benzene are in the same sequence: 1-phenylpyrrole (76 kcal./mole) [11] > thiophen

[8] Hafner, *Angew. Chem.*, 1957, **69**, 393.
[9] Wizinger and Ulrich, *Helv. Chim. Acta*, 1956, **39**, 207.
[10] Deschamps, *Compt. rend.*, 1958, **246**, 3065.
[11] Schomaker and Pauling, *J. Amer. Chem. Soc.*, 1939, **61**, 1778.

(27·7) [12] > furan (22·2).[12] The resonance energy of 1-methylpyrrole does not seem to have been recorded.

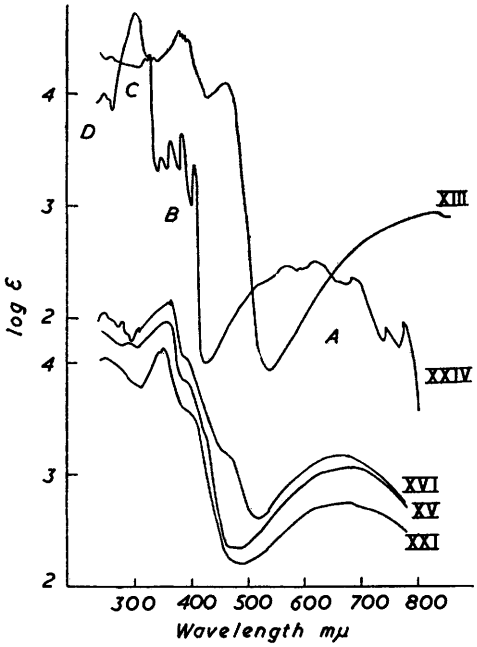


(XXIII)



(XXIV)

Spectra (*see Table*).—But for lack of fine structure, the spectra of the four *pseudo*-azulenes resemble that of the unsubstituted isosteric 1 : 2-benzazulene (XXIV) (see Figure). The spectrum of the indenothiapyran exhibits two intense absorption bands



Absorption spectra of 1 : 2-*benzazulene and the* pseudo*azulenes.*

The upper log ε scale refers to 1 : 2-benzazulene [13] (XXIV) and 2 : 4 : 5-triphenylindeno[1 : 2-*b*]-thiapyran (XIII). The lower scale refers to 1-methyl-2 : 4 : 5-triphenylindeno[1 : 2-*b*]pyridine (XVI). The curves for 1 : 2 : 4 : 5-tetraphenylindeno[1 : 2-*b*]pyridine (XV) and 1 : 2 : 4-triphenylindeno[1 : 2-*b*]pyridine (XXI) are displaced downwards by 0·2 and 0·4 unit in log ε, respectively.

Ultraviolet and visible spectra.

Compound †	Absorption max. (mμ) and log ε (in parentheses) D-Band	C-Band	B-Band	A-Band
1 : 2-Benzazulene [13] (XXIV) (in *cyclo*hexane)	222 (4·07) 248 (4·00)	298 (4·73) 307 (4·70) 321 (4·34)	346 (3·43) 363 (3·50) 383 (3·66) 404 (3·36)	565 (2·46) 615 (2·50) 682 (2·35) 742 (1·91) 776 (1·96)
2 : 4 : 5-Triphenylindeno[1 : 2-*b*]thiapyran (XIII)	260 (4·33) 320 (4·30) 324 (4·30) 327 (4·30)	380 (4·56) 385 (4·54) 389 (4·50) 392 (4·48)	460 (4·08)	825 (2·93)
1-Methyl-2 : 4 : 5-triphenylindeno[1 : 2-*b*]pyridine (XVI)	240 (4·45) 278 (4·37) 308 (4·30)	356 (4·55) 360 (4·55)	386* (4·05) 450* (3·21)	670 (3·16)
1 : 2 : 4 : 5-Tetraphenylindeno[1 : 2-*b*]-pyridine (XV)	294 (4·38)	356 (4·57)	390* (4·05)	685 (3·26)
1 : 2 : 4-Triphenylindeno[1 : 2-*b*]pyridine (XXI)	250 (4·45)	350 (4·53)	394* (3·96)	675 (3·15)

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

[12] Wheland, " Resonance in Organic Chemistry," Chapman and Hall Ltd., London, 1955, p. 99.
[13] Kloster-Jensen, Kováts, Eschenmoser, and Heilbronner, *Helv. Chim. Acta*, 1956, **39**, 1057.

centred at 385 and 460 mμ and a broad long-wave band, which correspond to the " C," " B," and " A " bands, respectively, of benzazulene.[13] The spectra of the nitrogen compounds are very similar; in every case the " B " band appears as a shoulder near 390 mμ; the spectrum of compound (XVI) has a second inflexion at 450 mμ.

The position of the absorption maxima in the visible spectra of substituted azulenes has been much discussed,[14] as charasteristic displacements are observed which depend on the position of the substituents. Introduction of a phenyl group into position 1 of azulene produces a bathochromic shift of 40 mμ [15] in the peak at the longest wavelength, compared with a bathochromic shift of only 10 mμ in passing from compound (XXI) to the analogously substituted phenyl derivative (XV). The weakness of the effect of the phenyl substituent in this case is ascribed to crowding: a molecular model shows that the 4- and the 5-phenyl group in the tetraphenylindenopyridine cannot both be co-planar with the ring system.[16]

Experimental

Operations with *pseudo*azulenes were carried out in an atmosphere of nitrogen. Absorption spectra were measured under nitrogen in dioxan containing a little quinol. Under these conditions the log ε values did not decrease by more than 0·01 unit during the determinations.

Hydrolysis of 10H-*Benzo*[b]*indeno*[2 : 1-e]*pyrylium Tetrachloroferrate.*—A suspension of the tetrachloroferrate [3] (IV; Y = $FeCl_4$) (1·4 g.) in ethanol (20 ml.) was shaken with 10% aqueous sodium hydroxide (30 ml.) and filtered. Addition of dilute hydrochloric acid to the filtrate precipitated 2-salicylideneindan-1-one (VI) (0·7 g.), which, after recrystallisation from ethanol, had m. p. 206° (decomp.), undepressed on admixture with an authentic specimen.[17]

3-*Phenyl*-2-*salicylideneindan*-1-*one* (VIII).—A solution of 3-phenylindan-1-one (4 g.) and salicylaldehyde (4 g.) in warm ethanol (30 ml.) was treated with potassium hydroxide (5·4 g.) in water (5·5 ml.) and set aside for 4 days. Addition of dilute acetic acid precipitated the *salicylidene derivative* (5·36 g., 75%), yellow needles (from aqueous acetone), m. p. 196·5—197° (decomp.) (Found: C, 84·6; H, 5·0. $C_{22}H_{16}O_2$ requires C, 84·5; H, 5·2%).

10-*Phenyl*-10H-*benzo*[b]*indeno*[2 : 1-e]*pyrylium Perchlorate* (VII; Y = ClO_4).—(*a*) Concentrated hydrochloric acid (6 ml.) was slowly added to a refluxing solution of the above salicylidene compound (1·5 g.) in acetic acid (25 ml.) and heating was continued for 15 min. Adding 20% perchloric acid to the cooled solution precipitated the *pyrylium perchlorate* (1 g., 53%), orange plates, m. p. 239—240° (decomp.) (from acetic anhydride–acetic acid) (Found: C, 67·0; H, 3·4. $C_{22}H_{15}O_5Cl$ requires C, 66·9; H, 3·8%).

(*b*) A solution of 3-phenylindan-1-one (3·12 g.) and salicylaldehyde (1·83 g., 1 mol.) in ether (50 ml.) containing 72% perchloric acid (5 ml.) was saturated with dry hydrogen chloride at 0°. During 24 hr. at 0° the solution deposited the foregoing perchlorate (4 g., 67·5%), m. p. and mixed m. p. 237—239°.

Hydrolysis of the perchlorate with cold aqueous-alcoholic sodium hydroxide or with sodium acetate in hot dilute acetic acid regenerated 3-phenyl-2-salicylideneindan-1-one.

2 : 4 : 5-*Triphenyl*-5H-*indeno*[1 : 2-b]*pyrylium Salts* (X).—Anhydrous ferric chloride (45 g.) was slowly added to an ice-cold solution of 3-phenylindan-1-one (17·1 g.) and phenyl styryl ketone (17·1 g., 1 mol.) in ether (150 ml.) and acetic anhydride (30 ml.). The mixture was refluxed for 1·5 hr., left overnight, then diluted with acetic acid, and the red *tetrachloroferrate* (23·7 g., 48·6%) was filtered off and washed successively with acetic acid and ether. It separates from acetone–ether in deep yellow platelets, m. p. 246—247° (decomp.) (Found: C, 61·0; H, 3·9. $C_{30}H_{21}OCl_4Fe$ requires C, 60·5; H, 3·6%). This chloroferrate was obtained in 20% yield by a similar condensation of equimolecular (0·05M) amounts of 2-benzylidene-3-phenylindan-1-one [18] and acetophenone. A solution of the chloroferrate (18·6 g.) in warm acetone (550 ml.) on treatment with 72% perchloric acid (5 ml.) deposited the *perchlorate*, yellow needles, m. p. 269·5—270° (decomp.) (Found: C, 72·4; H, 4·3. $C_{30}H_{21}O_5Cl$ requires C, 72·5; H, 4·3%).

[14] Gordon, *Chem. Rev.*, 1952, **50**, 185.
[15] Plattner, Fürst, Gordon, and Zimmermann, *Helv. Chim. Acta*, 1950, **33**, 1910.
[16] For a related case see Los, Saxena, and Stafford, *Proc. Chem. Soc.*, 1957, 352.
[17] Perkin and Robinson, *J.*, 1907, **91**, 1087.
[18] Pfeiffer and de Waal, *Annalen*, 1935, **520**, 185.

2-(3-*Oxo*-1 : 3-*diphenylprop*-1-*enyl*)- *or* 2-(3-*Oxo*-1 : 3-*diphenylpropylidene*)-3-*phenylindan*-1-*one* (XI).—A mixture of the foregoing perchlorate (1·5 g.) and sodium acetate (0·5 g.) was boiled for 3 min. with acetic acid (20 ml.) containing water (3 ml.). The resulting clear yellow solution was poured into water, whereupon the pseudo-*base* separated (1·22 g., 97·5%). It crystallises from ethanol–acetone in cream-coloured needles, m. p. 153—154° (decomp.) (Found: C, 87·1; H, 5·1. $C_{30}H_{22}O_2$ requires C, 86·9; H, 5·4%). It dissolves in 10% ethanolic potassium hydroxide to a red solution from which it is reprecipitated on dilution with water. The *pseudo*-base (20 mg.) in acetone (3 ml.) was treated with 72% perchloric acid (3 drops). The solution became orange with a green fluorescence; ether precipitated the pyrylium perchlorate (X; Y = ClO_4) (20 mg.), m. p. and mixed m. p. 269° (decomp.).

2 : 4 : 5-*Triphenyl*-5H-*indeno*[1 : 2-b]*thiapyrylium Perchlorate* (XII; Y = ClO_4).—A suspension of the foregoing pyrylium perchlorate (2·0 g.) in acetone (60 ml.) was shaken for 5 min. with 10% aqueous sodium sulphide (12 ml.). The clear bluish-red solution was treated with 20% perchloric acid (18 ml.). The *thiapyrylium perchlorate* crystallised in yellow needles (1·92 g., 93%), m. p. 246—247° (decomp.) (Found: C, 70·3; H, 4·2; S, 7·1. $C_{30}H_{21}O_4SCl$ requires C, 70·2; H, 4·1; S, 6·3%).

When a suspension of the thiapyrylium perchlorate (1·7 g.) in boiling ethanol (60 ml.) was treated with a solution of sodium hydroxide (0·8 g.), or of sodium acetate (0·8 g.), in water (2 ml.), 2 : 4 : 5-*triphenylindeno*[1 : 2-b]*thiapyran* (XIII) separated in dark-green prismatic needles (1·1 g., 80·5%), m. p. 177—178° (not raised by crystallisation from ethyl acetate) (Found: C, 87·0; H, 4·7; S, 7·7. $C_{30}H_{20}S$ requires C, 87·3; H, 4·9; S, 7·8%). Hot water alone also decomposed the perchlorate, but more slowly. Adding perchloric acid to the dark green solution of the thiapyran in chloroform changed the colour to yellow; ether then precipitated the thiapyrylium perchlorate, m. p. and mixed m. p. 246—247° (decomp.). Dilute solutions of the thiapyran in organic solvents lost their green colour in 1—20 min., depending on the concentration, on exposure to air; but they were stable for at least 24 hr. in an atmosphere of nitrogen. The thiapyran (100 mg.) was refluxed with 10% ethanolic potassium hydroxide (10 ml.) for 20 min. On cooling, it (90 mg.) was recovered. It (20 mg.) dissolved in acetic acid (5 ml.) to a yellow solution with a green fluorescence. The solution was refluxed for 10 min. and then poured into water; the thiapyran (19 mg.) was recovered.

1 : 2 : 4 : 5-*Tetraphenylindeno*[1 : 2-b]*pyridine* (XV).—A suspension of the pyrylium perchlorate (X; Y = ClO_4) (2·5 g.) in ethanol (50 ml.) was treated with aniline (2 ml.) and refluxed for 10 min. On cooling, the resulting solution deposited 1 : 2 : 4 : 5-*tetraphenyl*-5H-*indeno*-[1 : 2-b]*pyridinium perchlorate* (XIV; Y = ClO_4) (1·7 g., 59%), which separated from acetic acid in pale yellow prisms, m. p. 280—282° (decomp.) (Found: N, 2·4. $C_{36}H_{26}O_4NCl$ requires N, 2·45%). This salt, on decomposition with aqueous-alcoholic sodium hydroxide, afforded the bluish-green *anhydro-base* (86%), needles (from aqueous acetone), m. p. 257° (Found: C, 91·8; H, 5·4; N, 3·1. $C_{36}H_{25}N$ requires C, 91·7; H, 5·4; N, 3·0%).

1-*Methyl*-2 : 4 : 5-*triphenylindeno*[1 : 2-b]*pyridine* (XVI) was prepared in 55% yield by shaking the pyrylium perchlorate (X; Y = ClO_4) (1·5 g.) with ethanol (50 ml.) and 30% aqueous methylamine (6 ml.) for 30 min. The anhydro-base was filtered off, washed successively with water and ethanol, and recrystallised from aqueous acetone, dark-blue needles, m. p. 170—171° (Found: C, 91·0; H, 5·55; N, 3·1. $C_{31}H_{23}N$ requires C, 90·9; H, 5·5; N, 3·4%). The *perchlorate* separates from acetone–ether in pale yellow needles, m. p. 180—181·5° (decomp.) (Found: N, 2·45. $C_{31}H_{24}O_4NCl$ requires N, 2·75%). Sodium hydroxide regenerates the *pseudo*azulene from this salt.

2 : 4-*Diphenyl*-5H-*indeno*[1 : 2-b]*pyrylium Tetrachloroferrate* (XVIII; Y = $FeCl_4$), orange rhombs (from acetone), m. p. 254—256° (decomp.) (Found: C, 56·5; H, 3·5. $C_{24}H_{17}OCl_4Fe$ requires C, 55·7; H, 3·3%), was obtained in the usual way, but without heating, from indan-1-one and phenyl styryl ketone (31·4%) or from 2-benzylideneindan-1-one and acetophenone (9%). It was converted into the yellow *perchlorate*, m. p. 269—270 (decomp.) (Found: C, 68·3; H, 4·05. $C_{24}H_{17}O_5Cl$ requires C, 68·5; H, 4·1%). The perchlorate (2 g.) was suspended in acetone (40 ml.), and a solution of sodium acetate (1 g.) in water (3 ml.) added. After 10 min. the mixture was filtered and poured into water. The dark gummy precipitate was dissolved in cold acetone and reprecipitated by water. After many repetitions of this procedure the *pseudo*-base, 2-(3-*oxo*-1 : 2-*diphenylprop*-1-*enyl*)- or 2-(3-*oxo*-1 : 2-*diphenylpropylidene*)-*indan*-1-*one*, was obtained as cream-coloured prisms (25 mg.), m. p. 128—129° (decomp.) (Found: C, 84·7: H, 5·5. $C_{24}H_{18}O_2$ requires C, 85·1; H, 5·4%). It forms the perchlorate on treatment

with perchloric acid, and dissolves in ethanolic potassium hydroxide with a red colour, being reprecipitated on addition of water.

2 : 4-*Diphenyl*-5H-*indeno*[1 : 2-b]*thiapyrylium perchlorate* (XX; Y = ClO_4), yellow, m. p. 228—229° (decomp.) (Found: C, 66·0; H, 3·85. $C_{24}H_{17}O_4SCl$ requires C, 66·0; H, 3·9%), was prepared from the foregoing pyrylium perchlorate in 80% yield as described for the 5-phenyl compound. This thiapyrylium salt (0·5 g.) was boiled for 10 min. with sodium hydroxide (0·3 g.) in water (1 ml.) and ethanol (25 ml.). The mixture was filtered from unchanged perchlorate (0·13 g.) and diluted with water. A dark-yellow ill-defined solid was precipitated, which was not further examined.

1 : 2 : 4-*Triphenyl*-5H-*indeno*[1 : 2-b]*pyridinium perchlorate*, pale yellow needles (from ethanol), m. p. 151—153° (decomp.) (Found: N, 2·5. $C_{30}H_{22}O_4NCl$ requires N, 2·8%), and 1 : 2 : 4-*triphenylindeno*[1 : 2-b]*pyridine* (XXI), blue needles, m. p. 239—240° (Found: C, 90·7; H, 5·3; N, 3·6. $C_{30}H_{21}N$ requires C, 91·1; H, 5·4; N, 3·5%), were prepared in 89% and 83% yields, respectively, by the methods described for the 5-phenyl compounds.

The three nitrogen anhydro-bases behaved like the sulphur compound when heated with ethanolic potassium hydroxide or with acetic acid, except that sodium hydroxide solution had to be used to decompose the acetates.

Attempt to prepare 1-*Methyl*-2 : 4-*diphenylindeno*[1 : 2-b]*pyridine* (XXII).—Shaking a suspension of 2 : 4-diphenyl-5*H*-indeno[1 : 2-*b*]pyrylium perchlorate (3·3 g.) in ethanol (100 ml.) for 1 hr. with 30% aqueous methylamine (12 ml.) gave a solid which was washed with ethanol, dissolved in dilute hydrochloric acid, and reprecipitated on basification as a blue powder (0·75 g.), m. p. *ca.* 133° (decomp.) (Found: C, 83·3; H, 5·35; N, 3·35%). This substance did not recrystallise; it decomposed to a pale green solid in a vacuum-desiccator overnight. Adding perchloric acid to an acetone solution yielded a red gum.

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WEST HAM COLLEGE OF TECHNOLOGY, LONDON, E.15. [*Received, July 28th,* 1958.]