Pseudoazulenes. Part VI.[1] Indenopyrazoles and the Attempted Preparation of an Indenoisoxazole

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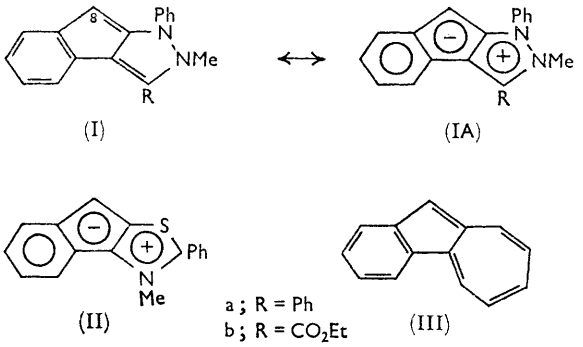
2-Methyl-1,3-diphenylindeno[2,1-*c*]pyrazole and its 3-ethoxycarbonyl analogue, derivatives of a novel pseudoazulenic system containing two fused five-membered rings, have been prepared. The direction of addition of nitrilimines to indanone-enamines has been established. The pseudoazulenes are protonated on the five-membered carbon ring. Azo-coupling, tropylation, formylation, and condensation with *p*-dimethylaminobenzaldehyde has been carried out on the diphenyl-compound; the structures of the products and of their conjugate acids are discussed. Attempts to synthesise the *ortho*-quinonoid 2-methyl-1,3-diphenylindeno[1,2-*c*]pyrazole and the benzenoid 2-ethyl-3-phenylindeno[1,2-*d*]isoxazole are described.

THE indenopyrazole (Ia) and the mesoionic indenothiazole (II), the first representatives of pseudoazulenes containing two fused five-membered rings, were recently reported.[2] The compounds are iso-π-electronic with derivatives of benz[*a*]azulene (III), each heteroatom contributing two π-electrons to the total of fourteen. We now give details of the preparation of the pyrazole (Ia) and its ethoxycarbonyl-analogue (Ib) and record their properties.

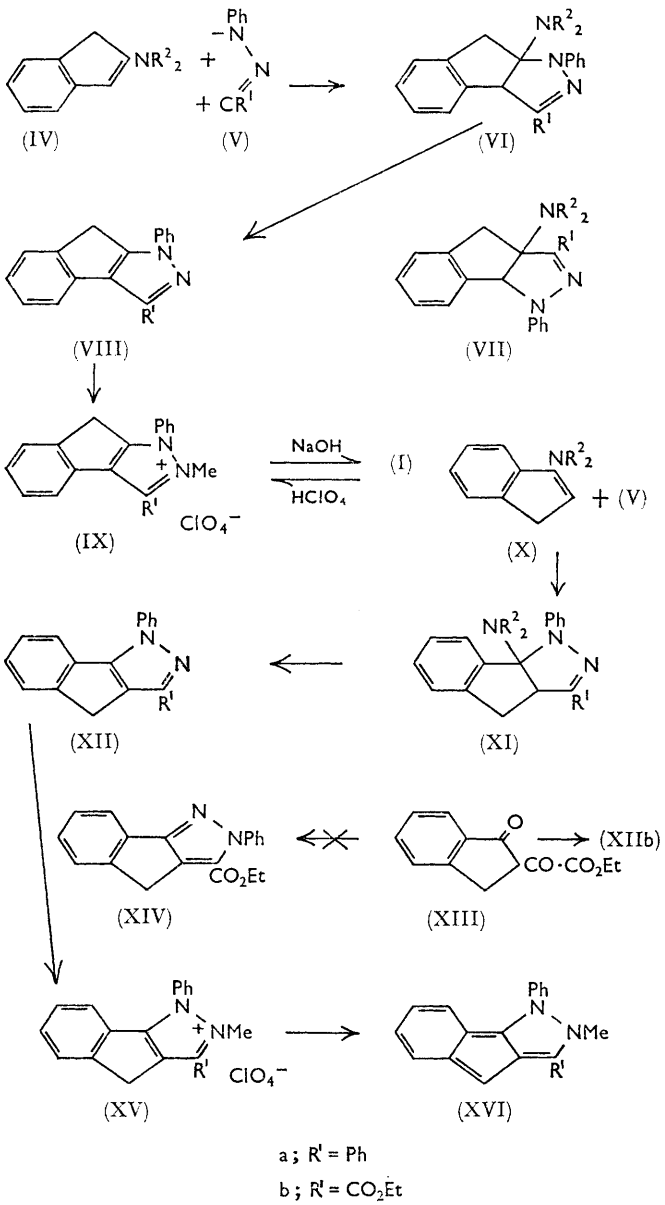
Synthesis.—Cycloaddition [3-5] of the piperidino- or

[1] Part V, G. V. Boyd and F. W. Clark, *J. Chem. Soc.* (*C*), 1966, 859.
[2] G. V. Boyd, *Tetrahedron Letters*, 1965, 1421.
[3] R. Fusco, G. Bianchetti, and D. Pocar, *Gazzetta*, 1961, **91**, 1233.
[4] M. E. Kuehne, S. J. Weaver, and P. Franz, *J. Org. Chem.*, 1964, **29**, 1582.
[5] (*a*) R. Huisgen, M. Seidel, G. Wallbillich, and H. Knupfer, *Tetrahedron*, 1962, **17**, 3; (*b*) R. Huisgen, R. Sustmann, and G. Wallbillich, *Ber.*, 1967, **100**, 1786.

morpholino-enamines (IV) of 2-indanone to the nitrilimines (Va, b) followed by acid-treatment of the inter-



mediate aminopyrazolines (VIa, b) * gave the pyrazoles (VIIIa, b) in good yield. Single pyrazoles were formed in these reactions; their orientations require discussion since Huisgen *et al.*[5a] have found that 1,3-dipoles may add to polarised double bonds in both directions. These authors later showed[5b] that in two cases diphenylnitrilimine (Va) reacts with enamines solely in the sense depicted in Scheme 1: (IV) + (V) ⟶ (VI), and (X) + (V) ⟶ (XI), and Kuehne *et al.*[4] have advanced arguments based on spectroscopic comparisons which favour this orientation; its generality, however, remains to be established. We assign structures (VIII) rather than the alternatives (XII) to our pyrazoles on the following grounds. (i) The other possible orientation (VII) of the intermediate pyrazolines is ruled out since this would lead to the pyrazoles (XII), which we synthesised from the alternative enamine, 3-pyrrolidinoindene (X), and also, in the case of (XIIb), from 2-ethoxalyl-1-indanone (XIII) and phenylhydrazine. It is fortunate that the latter reaction does not afford the isomeric pyrazole (XIV) which cannot be the product of a nitrilimine reaction.† (ii) The stabilities (see below) of the derived pseudoazulenes (I) and (XVIa) are in accord with the benzenoid character of the former and the *ortho*-quinonoid character of the latter. (iii) The chemical shifts of the methylene protons on the cyclopentadiene ring of the pyrazoles (VIIIa, b) obtained from 2-indanone-enamines are identical (τ 6·12), the methylene protons of both pyrazoles (XIIa, b) derived from 1-indanone-enamine resonate at τ 6·23. Hence, the two pairs belong to isomeric series, and in the latter the methylene group is further removed from the deshielding *N*-phenyl group and, moreover, is attached to a position



SCHEME 1

of higher electron-density of the pyrazole nucleus. Our conclusions are thus in agreement with Huisgen's work.[5b]

Since the indenopyrazoles (VIIIa, b) are colourless, lack NH absorption in their i.r. spectra, and exhibit methylene but not vinyl proton signals they do not

* A small quantity of the aminopyrazoline (VIb; NR_2^2 = morpholino) was isolated. Its n.m.r. spectrum contained signals at τ 6·12 (s, 2H), 4·52 (s, 1H) and two four-proton signals at 6·25 and 6·90 (morpholino-protons). The compound was unstable and yielded the pyrazole (VIIIb) on attempted recrystallisation. Smooth extrusion of the basic moiety is frequently observed [3,4,5b] in 1,3-dipolar cycloadditions to enamines.

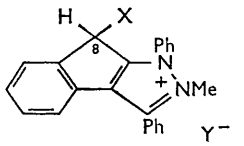
† We take this opportunity to clear up some confusion in the literature concerning 3-ethoxycarbonyl-1-phenyl-4*H*-indeno[1,2-*c*]pyrazole (XIIb). This compound was synthesised from 2-ethoxalyl-1-indanone by both Ruhemann,[6] who assigned the correct structure to it, and Leuchs and Kowalski,[7] who regarded it as the isomer (XIV). Fusco *et al.*[3] prepared 3-ethoxycarbonyl-1-phenyl-8*H*-indeno[2,1-*c*]pyrazole (VIIIb) by the nitrilimine route, formulated it correctly but misnamed it as a derivative of indeno[1,2-*c*]pyrazole. The wrong name also appears in the abstract of the Italian paper (*Chem. Abs.*, 1962, **57**, 2209).

[6] S. Ruhemann, *J. Chem. Soc.*, 1912, **101**, 1729.
[7] H. Leuchs and G. Kowalski, *Ber.*, 1925, **58**, 2288.

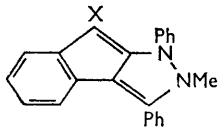
exist as the pseudoazulene tautomers (Ia, b; H in place of Me), in contrast to certain cyclopenta[*b*]pyridines which exist partly,[8] or wholly,[9] in the pseudoazulenic form. The pyrazoles (VIIIa, b) on methylation afforded the colourless salts (IXa, b) which on deprotonation with sodium hydroxide gave the stable, intensely coloured indeno[2,1-*c*]pyrazoles (Ia, b). In the indeno[1,2-*c*]-pyrazole series treatment of the pyrazolium salt (XVa) with alkali resulted in a red compound which rapidly decomposed in solution. We believe this to be the pseudoazulene (XVIa), the instability of which was not surprising in the light of our experience with similar *ortho*-quinonoid anhydro-bases.[10]

Properties.—The pyrazoles (Ia, b), like other heterocyclic analogues of azulene, are highly coloured and the long-wave absorption band (see Table) is shifted bathochromically by 15 mμ when the solvent is changed from ethanol to the less polar hexane; indicative of a greater charge separation in the ground state [cf. (IA)] than in the first excited state. This phenomenon is much enhanced in the mesoionic compound (II).[2] In acid solution the absorption band in the visible region disappears, due to protonation, to form the pyrazolium ions (IXa, b). That protonation does, in fact, occur in the expected position on the cyclopentadiene ring is demonstrated by the disappearance of the vinyl proton (H-8) signals in the spectra of the bases (Ia, b) when they are dissolved in trifluoroacetic acid and the appearance of a two-proton methylene singlet near τ 6; the spectrum of the pyrazole (Ia) in deuteriosulphuric acid likewise exhibits a one-proton methylene singlet at τ 6·37. When a solution of compound (Ia) in deuteriochloroform is shaken with deuterium oxide containing a trace of deuteriosulphuric acid for 1 hr. the n.m.r. spectrum of the organic phase shows almost complete incorporation of deuterium at C-8 (XVIIIa); this indicates that the equilibrium (Ia) ⇌ (XVIIa) ⇌ (XVIIIa) ⇌ (XVII; H = X = D) is forced towards (XVIIIa) by the presence of an excess of deuterium oxide.

A number of electrophiles, other than the proton, attack the indenopyrazole (Ia). Acetyl chloride and also t-butyl chloride–aluminium chloride reacted visibly with it but no pure products could be isolated. However, treatment with benzenediazonium chloride, tropylium fluoroborate, and the Vilsmeier–Haack reagent afforded the salts (XVIIb, c, and e), respectively, and thence the substituted bases (XVIIIb, c, and e). The n.m.r. spectra of the conjugate acids of these derivatives confirm that substitution has occurred at C-8 since the two-proton methylene singlet found in the spectrum of the parent cation (IXa) is now absent. Unlike other pseudoazulenes,[1,11] the pyrazole (Ia) condenses neither with benzaldehyde nor salicylaldehyde in the presence of acid. However, the more reactive *p*-dimethylaminobenzaldehyde afforded the bright orange salt (XIXe). The pyrazole (Ia) failed to react either with triethyloxonium fluoroborate [12a] or with

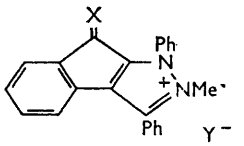


(XVII)

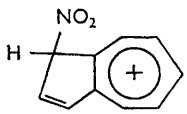


(XVIII)

a: X = D
b: X = N_2Ph
c: X = ·CH·CH:CH·CH:CH·CH:CH
d: X = ·C:CH·CH_2·CH:CH·CH:CH
e: X = CHO



(XIX)



(XX)

a: X = :CHO⁻
b: X = :N·NHPh
c: X = :C·CH_2·CH_2·CH:CH·CH:CH
d: X = :CHOH
e: X = :CH·C_6H_4·NMe_2-*p*

triphenylmethyl perchlorate,[12a,b] possibly due to the bulk of these reagents.

The first absorption band (see Table) of the benzeneazo-derivative (XVIIIb) is shifted bathochromically by only 4 mμ from that of the parent compound; thus there is little conjugation of the azo-chromophore with the pseudoazulene nucleus which, as in related cases,[1] can be attributed to steric hindrance to coplanarity. The tropyl compound absorbs at the same visible wavelength as the parent base; this, together with its n.m.r. spectrum which shows six vinyl protons in three pairs (τ 3·59, 4·07, and 4·60, respectively) and a one-proton methine triplet (τ 7·34) is consistent with structure (XVIIIc) and rules out products of possible prototropic rearrangement such as (XVIIId). Unlike the red azo- and tropyl compounds the formyl derivative is yellow and does not absorb above 1606 $cm.^{-1}$ in the carbonyl region. Thus, like 1-formylazulenes [13] and formylated pseudoazulenes [1,9,11] this compound is best represented as the oxide (XIXa). The formyl derivative crystallises with one mol. of ethanol but the hemiacetal structure (XVIII; X = CH(OH)·OEt), although consistent with the i.r. spectrum, can be excluded because such a molecule would be expected to absorb at the same visible wavelength as the parent base.

[8] C. B. Reese, *J. Amer. Chem. Soc.*, 1962, **84**, 3979.
[9] W. Treibs, W. Schroth, H. Lichtmann, and G. Fischer, *Annalen*, 1961, **642**, 97.
[10] G. V. Boyd, *J. Chem. Soc.*, 1959, 55.
[11] W. Treibs and W. Schroth, *Annalen*, 1961, **642**, 82.
[12] (*a*) K. Hafner, A. Stephan, and C. Bernhard, *Annalen*, 1961, **650**, 42; (*b*) E. C. Kirby and D. H. Reid, *Tetrahedron Letters*, 1960, No. **27**, 1.
[13] (*a*) D. H. Reid, W. H. Stafford, and W. L. Stafford, *J. Chem. Soc.*, 1958, 1118; (*b*) D. H. Reid and E. C. Kirby, *ibid.*, 1961, 163.

The substituted pyrazoles (XVIIIb, c, e) form crystalline perchlorates in which the proton is attached to C-8 (XVII). Thus the i.r. spectrum of the yellow benzeneazo-salt (XVIIb) shows no NH band, and the long-wave absorption of the tropyl salt (XVIIc) is the

Electronic spectra of indenopyrazoles and their conjugate acids

$\lambda_{max.}$ (mμ) (log ε in parentheses)

Compound	In EtOH	In hexane	In acetic acid containing 1% of 70% perchloric acid
(Ia)	246 (4·31), 304 (3·93), 475 (3·38)	490 (3·60)	256 (4·22), 303 (3·92)
(Ib)	233 * (4·27), 317 (4·11), 554 (3·88)	570 (3·56)	254 (3·83), 319 (3·65)
(XVIIIb)	253, 409, 479 †		265 (4·07), 405 (4·58)
(XVIIIc)	247 (4·32), 303 (3·95), 474 (3·39)		256 (4·24), 301 (3·94)
(XVIIIe)	253—262 (4·41), 329 (4·42), 360 * (3·68)		254 (4·60) 288 (4·25)
(XIXe)			271 (4·45), 472 (4·47) ‡

* Inflexion. † Accurate log ε values could not be determined because of the sparing solubility of this compound. ‡ In acetonitrile.

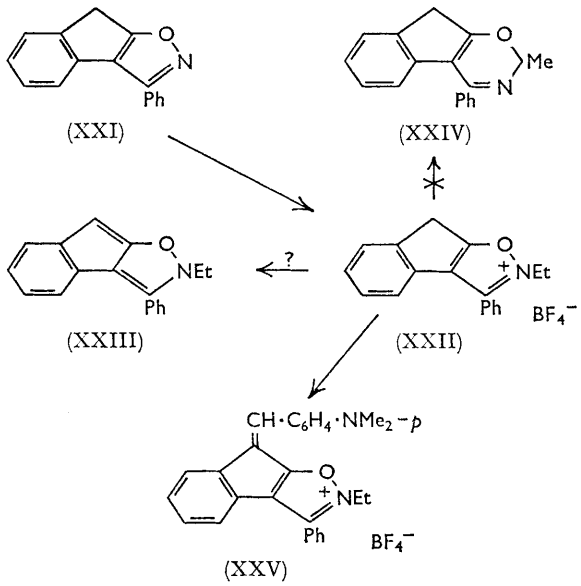
same as that of the parent cation (IXa). The protonated formyl compound (XVIIe) exhibits a carbonyl-stretching frequency at 1690 cm.$^{-1}$. These observations rule out the conjugated structures (XIXb, c, d) in which the proton is attached to the substituent group as with 1-benzeneazo-, 1-formyl-, and 1-nitroazulenium cations.[14] The situation here is analogous to that of 4,6,8-trimethyl-1-nitroazulene which is protonated on C-1 (XX);[14] there, as in our compounds, protonation on the nucleus relieves overcrowding by raising the substituent out of the molecular plane.

A Pseudoazulenic Isoxazole.—We attempted to prepare an isoxazole analogue of the indenopyrazoles (I). Alkylation of 3-phenyl-8*H*-indeno[1,2-*d*]isoxazole (XXI) * with methyl iodide or sulphate was not successful but triethyloxonium fluoroborate gave the isoxazolium salt (XXII) in good yield. Deprotonation with sodium hydroxide gave a red solution ($\lambda_{max.}$ (EtOH) 442 mμ) from which no pure compound could be isolated; an ethanolic solution of it was stable for several minutes at −70° but this rapidly darkened on reaching room temperature and deposited brown amorphous material. It was not possible to regenerate the isoxazolium cation by the addition of fluoroboric or perchloric acid to the red solution. The n.m.r. spectrum of a deuteriochloroform solution of the red material was inconclusive but it ruled out (no methyl doublet and no methine quartet)

* The synthesis of this compound was reported [15] after our work had been completed. Since we used an identical route, details are not repeated.

[14] J. Schulze and F. A. Long, *J. Amer. Chem. Soc.*, 1964, **86**, 322.

the 1,3-oxazine (XXIV) formed by ring expansion of the cation (XXII), a reaction which is stated [16] to occur when certain tetra-substituted isoxazolium salts are treated with dilute alkali. Our failure to obtain a stable isoxazole anhydro-base was unexpected, although its transient existence could be demonstrated by the formation of the purple styryl derivative (XXV) on treatment of



SCHEME 2

the isoxazolium salt (XXII) with *p*-dimethylaminobenzaldehyde.

EXPERIMENTAL

Infrared spectra were recorded as Nujol mulls with a Perkin-Elmer 257 spectrometer and electronic spectra with a Perkin-Elmer UV 137 instrument. ^{1}H N.m.r. spectra were measured at 60 Mc./sec. on a Perkin-Elmer R 10 spectrometer.

Enamines of 1- and 2-indanone were prepared by the methods of Bergmann [17] and Blomquist,[18] respectively.

1,3-*Diphenyl*-8H-*indeno*[2,1-c]*pyrazole* (VIIIa).—A solution of 2-pyrrolidinoindene (10·05 g.) and triethylamine (6·05 g., 1·1 mol.) in dichloromethane (200 ml.) was stirred under an atmosphere of nitrogen and a suspension of α-chlorobenzaldehyde phenylhydrazone [19] (12·62 g., 1 mol.) in dichloromethane (50 ml.) was added. The mixture was stirred at room temperature for 12 hr., after which the solvent was removed and the residue was heated under reflux for 30 min. with a mixture of conc. hydrochloric acid (50 ml.), water (120 ml.), and ethanol (170 ml.). When

[15] G. Bianchi, R. Gandolfi, P. Grünanger, and A. Perotti, *J. Chem. Soc. (C)*, 1967, 1598.

[16] J. F. King and T. Durst, *Canad. J. Chem.*, 1962, **40**, 882.

[17] E. D. Bergmann and E. Hoffmann, *J. Org. Chem.*, 1961, **26**, 3555.

[18] A. T. Blomquist and E. J. Moriconi, *J. Org. Chem.*, 1961, **26**, 3761.

[19] H. von Pechmann, *Ber.*, 1894, **27**, 320.

the mixture was cooled the *pyrazole* (14·63 g., 87%) separated, m.p. 174° (from benzene) (Found: C, 85·9; H, 5·3; N, 9·1. $C_{22}H_{16}N_2$ requires C, 85·7; H, 5·2; N, 9·1%). In one experiment the reaction mixture, after removal of the dichloromethane, was treated with ether; the precipitated triethylamine hydrochloride (85%) was filtered off and the filtrate was concentrated to give a little of the pyrazoline (VIa), m.p. 136—145°. Attempted crystallisation of the compound from ethanol resulted in the formation of the pyrazole (VIIIa).

The following pyrazoles were similarly prepared. 2-Morpholinoindene and ethyl chloro(phenylhydrazono)acetate gave 3-ethoxycarbonyl-1-phenyl-8*H*-[2,1-*c*]pyrazole (VIIIb) (76%), m.p. 165—166° (from ethyl acetate) (lit.,[3] 162—163°); 3-pyrrolidinoindene and α-chlorobenzaldehyde phenylhydrazone gave 1,3-*diphenyl*-4H-*indeno*[1,2-c]*pyrazole* (XIIa) (57%), m.p. 173—174° (from ethyl acetate) (Found: C, 85·5; H, 5·3; N, 9·0. $C_{22}H_{16}N_2$ requires C, 85·7; H, 5·2; N, 9·1%); and 3-pyrrolidinoindene and ethyl chloro(phenylhydrazono)acetate gave 3-ethoxycarbonyl-1-phenyl-4H-indeno[1,2-c]pyrazole (XIIb) (26%), m.p. 113—115° (lit.,[6] 117—118°) (Found: C, 74·9; H, 5·25; N, 9·2. Calc. for $C_{19}H_{16}N_2O_2$: C, 75·0; H, 5·3; N, 9·2%). The same pyrazole (mixed m.p. and identical i.r. spectrum) was obtained by condensing [6] 2-ethoxalyl-1-indanone with phenylhydrazine hydrochloride.

2-*Methyl*-1,3-*diphenylindeno*[2,1-c]*pyrazole* (Ia).—The diphenylindenopyrazole (VIIIa) (14·6 g.) was heated under reflux for 5 hr. with a solution of dimethyl sulphate (15 ml.) in toluene (220 ml.). After the oil which resulted when the mixture was cooled was separated, washed successively with benzene and ether, and dissolved in hot ethanol (60 ml.). Addition of 2N-sodium hydroxide to the filtered solution gave the *pyrazole* (7·5 g., 50%), dark red needles (from acetone), m.p. 171—172° (Found: C, 85·7; H, 5·4; N, 9·1. $C_{23}H_{18}N_2$ requires C, 85·7; H, 5·6; N, 8·7%), n.m.r. ($CDCl_3$): τ 6·91 (s, 3H, *N*-Me), 4·26 (s, 1H, H-8), 2—3 (m, 14H, aromatic protons). The pyrazole (1 g.) in acetic acid (10 ml.) was treated with 70% perchloric acid (1 ml.); addition of ether precipitated 2-*methyl*-1,3-*diphenyl*-8H-*indeno*[2,1-c]*pyrazolium perchlorate* (IXa) (1 g.), prisms (from acetic acid), m.p. 194° (Found: C, 65·1; H, 4·6; N, 6·5. $C_{23}H_{19}ClN_2O_4$ requires C, 65·3; H, 4·5; N, 6·6%), n.m.r. (CF_3CO_2H): τ 6·09 (s, 3H, *N*-Me), 5·99 (s, 2H, 8-CH_2), 2—3 (m, 14H, ArH). The perchlorate was also obtained by addition of perchloric acid to the oily methosulphate.

3-*Ethoxycarbonyl*-2-*methyl*-1-*phenyl*-8H-*indeno*[2,1-c]-*pyrazolium Perchlorate* (IXb).—This was obtained (81%) as needles (from acetic acid) [m.p. 230—231° (decomp.) (Found: C, 57·45; H, 4·8; N, 6·7. $C_{20}H_{19}ClN_2O_6$ requires C, 57·35; H, 4·6; N, 6·7%), n.m.r. (CF_3CO_2H): τ 6·06 (s, 2H, 8-CH_2), 5·79 (s, 3H, *N*-Me), 5·25 (q, 2H), and 8·48 (t, 3H, Et), 2—3 (m, 9H, ArH)] from 3-ethoxycarbonyl-1-phenyl-8*H*-indeno[2,1-*c*]pyrazole (VIIIb) and dimethyl sulphate and subsequent treatment with perchloric acid. The perchorate (1·25 g.) was treated with chloroform (100 ml.) and 2N-sodium carbonate (50 ml.); the aqueous phase was extracted with chloroform (2 × 20 ml.), the combined chloroform extracts were dried ($MgSO_4$), and the solvent was removed to leave a purple oil (0·82 g., 82%) which solidified on contact with light petroleum. 3-*Ethoxycarbonyl*-2-*methyl*-1-*phenyl*-*indeno*[2,1-c]*pyrazole* (Ib) crystallised from light petroleum (b.p. 60—80°) as purple needles, m.p. 113° (Found: C, 75·5; H, 5·8; N, 8·8. $C_{20}H_{18}N_2O_2$ requires C, 75·45; H, 5·7; N, 8·8%), n.m.r. ($CDCl_3$): τ 4·42 (s, 1H, H-8), 5·48 (q, 2H) and 8·46 (t, 3H, Et), 6·56 (s, 3H, *N*-Me), 2—3 (m, 9H, ArH).

2-*Methyl*-1,3-*diphenylindeno*[1,2-c]*pyrazolium Perchlorate* (XVa).—This was obtained [(95%), m.p. 191° (from acetic acid) (Found: C, 65·2; H, 4·35; N, 6·55. $C_{23}H_{19}ClN_2O_4$ requires C, 65·3; H, 4·5; N, 6·6%)] similarly from 1,3-diphenyl-4*H*-indeno[1,2-*c*]pyrazole. When the salt was shaken with a mixture of benzene and aqueous sodium carbonate the organic phase became red ($\lambda_{max.}$ 475 mμ) but no definable product could be isolated from it. When the benzene was removed under reduced pressure at room temperature and replaced by alcohol the absorption maximum was shifted to 447 mμ; this indicates that the anhydro-base, 2-methyl-1,3-diphenylindeno[1,2-*c*]pyrazole (XVIa), may have been present.

Reactions of the Indenopyrazole (Ia).—(*a*) A suspension of the pyrazole (2 g.) in dioxan (10 ml.) was added to an ice-cold solution of benzenediazonium chloride prepared from aniline (0·58 g.), 1·5N-hydrochloric acid (30 ml.), and sodium nitrite (0·44 g.) and containing sodium acetate (2 g.); the resulting yellow solid (2·68 g.) was washed with ether, suspended in ethanol (15 ml.), and treated with 2N-sodium hydroxide (10 ml.) to give 8-*benzeneazo*-2-*methyl*-1,3-*diphenylindeno*[2,1-c]*pyrazole* (XVIIIb) (1·49 g., 80%), dark red cubes (from toluene), m.p. 222° (Found: C, 81·2; H, 5·35; N, 13·65. $C_{29}H_{22}N_4$ requires C, 81·65; H, 5·2; N, 13·15%). The yellow *hydroperchlorate* [(XVIIb; Y = ClO_4), m.p. 281° (decomp.) (Found: C, 66·1; H, 4·6; N, 10·5. $C_{29}H_{23}ClN_4O_4$ requires C, 66·1; H, 4·4; N, 10·6%)] was obtained by treatment of a suspension of the base in acetic acid with perchloric acid followed by the addition of ether.

(*b*) Addition of tropylium fluoroborate (0·28 g.) in acetonitrile (10 ml.) to a suspension of the pyrazole (Ia) (0·5 g.) in acetonitrile (10 ml.) caused immediate discharge of the colour; addition of ether precipitated the fluoroborate (XVIIc; Y = BF_4) (0·68 g., 88%), m.p. 190—194°, which on treatment with 2N-sodium hydroxide afforded the red 8-*cyclohepta*-2,4,6-*trienyl*-2-*methyl*-1,3-*diphenylindeno*[2,1-c]-*pyrazole* (XVIIIc) (0·55 g., 86%), m.p. 148—149° (from acetone) (Found: C, 87·1; H, 5·8; N, 6·9. $C_{30}H_{24}N_2$ requires C, 87·3; H, 5·9; N, 6·8%). The *hydroperchlorate* [(XVIIc; Y = ClO_4), m.p. 209° (decomp.) (Found: C, 68·2; H, 5·1; N, 5·5. $C_{30}H_{25}ClN_2O_4,H_2O$ requires C, 67·85; H, 5·1; N, 5·3%)] was prepared in the usual way.

(*c*) 8-*Formyl*-2-*methyl*-1,3-*diphenylindeno*[2,1-c]*pyrazole* (XVIIIe). An ice-cold mixture of dimethylformamide (10 ml.) and phosphoryl chloride (1·9 g., 2 mol.) was stirred for 30 min.; a suspension of the pyrazole (Ia) (2 g.) in dimethylformamide (20 ml.) was added and the mixture was stirred for a further 12 hr. The resulting solution was treated with sodium acetate (8 g.) in water (100 ml.) whereupon the *formyl-compound* (1·72 g., 77%) separated, yellow needles (from ethanol), m.p. 227°, $\nu_{max.}$ (Nujol) 1606 $cm.^{-1}$ (Found: C, 79·1; H, 5·85; N, 7·2. $C_{24}H_{18}N_2O,C_2H_5OH$ requires C, 78·8; H, 6·1; N, 7·1%). This with perchloric acid gave the *hydroperchlorate* (XVIIe; Y = ClO_4), m.p. 248—249° (Found: C, 62·9; H, 4·4; Cl, 8·1; N, 6·4. $C_{24}H_{19}ClN_2O_5,\frac{1}{2}H_2O$ requires C, 62·7; H, 4·4; Cl, 7·7; N, 6·1%).

(*d*) 3-*Methyl*-8-p-*dimethylaminobenzylidene*-1,3-*diphenyl*-8H-*indeno*[2,1-c]*pyrazolium perchlorate* (XIXe; Y = ClO_4). This was prepared by heating a solution of the pyrazolium perchlorate (IXa) (1 g.) and *p*-dimethylaminobenzaldehyde (0·36 g.) in acetic acid (5 ml.) under reflux for 24 hr.; the

product was obtained as bright orange prisms (from acetonitrile), m.p. 277—279° (Found: C, 69·2; H, 5·3; N, 7·3. $C_{32}H_{28}ClN_3O_4$ requires C, 69·4; H, 5·1; N, 7·6%).

Attempted Preparation of an Indeno[1,2-d]*isoxazole.*—*2-Ethyl-3-phenyl-*8H*-indeno*[1,2-d]*isoxazolium Tetrafluoroborate* (XXII). 3-Phenyl-8*H*-indeno[1,2-*d*]isoxazole (XXI) (1 g.) was added to a solution of triethyloxonium fluoroborate in dichloromethane (20%; 10 ml.); after 24 hr. ether (15 ml.) was added to precipitate the *isoxazolium salt* (1·12 g., 75%), pale yellow cubes (from acetic acid), m.p. 151° (decomp.), n.m.r. (CF_3CO_2H): τ 2·3 (m, 9H), 5·70 (s, 2H), 5·16 (q, 2H), and 8·22 (t, 3H) (Found: C, 62·0; H, 4·5; N, 4·05. $C_{18}H_{16}BF_4NO$ requires C, 61·9; H, 4·6; N, 4·0%). Treatment of this salt with aqueous sodium hydroxide gave a red product from which no pure compound could be isolated. The purple 8-p-*dimethylaminobenzyldiene-derivative* (XXV), m.p. 225° (decomp.) (from acetonitrile) (Found: C, 67·7; H, 4·8; N, 5·6. $C_{27}H_{25}BF_4N_2O$ requires C, 67·5; H, 5·2; N, 5·8%) was deposited when a solution of the above fluoroborate (1 g.) and *p*-dimethylaminobenzaldehyde (0·43 g.) in acetonitrile (5 ml.) was kept at room temperature for 2 hr.

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