1,3-Dipolar Character of Six-membered Aromatic Rings. Part XI.[1] 1-Oxido-3-phenylphthalazinium

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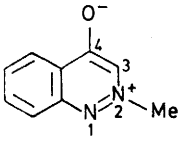
1-Oxido-3-phenylphthalazinium with styrene and with diphenylacetylene gives the expected cycloadducts. However, reactions with dimethyl acetylenedicarboxylate and with phenylacetylene gave in each case three isomeric products, the structures of which have been elucidated. Mechanisms are suggested for their formation and interconversion.

DIAZA-HETEROAROMATIC betaines such as 2-methyl-4-oxidocinnolinium (1)[1-3] and 3-methyl-1-oxidophthalazinium (2)[1] show 1,3-dipolar character but give cycloadducts preferentially with acetylenic dipolarophiles. 3-Aryl-1-oxidophthalazinium betaines (arylphthalazin-4-ones[4]) were known before 1940: we now report the first 1,3-dipolar cycloadditions of 1-oxido-3-phenylphthalazinium (3), which disclose complex behaviour different from that previously encountered with heteroaromatic betaines.



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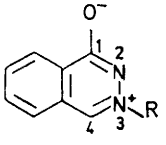


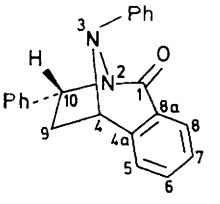
(2) R = Me
(3) R = Ph

3-Aryl-1-oxidophthalazinium betaines were first prepared in low yields by Rowe[4] and his co-workers by coupling 2-hydroxynaphthalene-1-sulphonic acid with diazotised anilines followed by treatment with acid. We made 1-oxido-3-phenylphthalazinium (70% overall) by a modification of the method of Lund.[5,6] Reduction of *N*-anilinophthalimide[5] with sodium borohydride in tetrahydrofuran yielded *N*-anilino-3-hydroxyphthalimidine, which was thermally rearranged to the betaine (3).

Cycloadditions with Olefins.—3-Methyl-1-oxidophthalazinium and 2-methyl-4-oxidocinnolinium are unreactive towards olefins.[1] However, like 1-aryl-3-oxidopyridiniums,[7] the betaine (3) reacted with styrene at 120 °C to yield the cycloadduct (4) in 65% yield. The i.r. spectrum showed a conjugated carbonyl group [ν(C=O) 1 700 cm^{-1}] and the mass spectrum had a parent peak at *m/e* 326. The n.m.r. spectrum (220 MHz) showed a low-field doublet of doublets ($J_{4,9\text{-}exo}$ 6, $J_{4,9\text{-}endo}$ 1 Hz) at δ 5.10 assignable to the bridgehead proton, H-4. A second doublet of doublets ($J_{9\text{-}endo,10\text{-}exo}$ 5, $J_{9\text{-}exo,10\text{-}exo}$ 8.5 Hz) was assigned to H-10-*exo* and the two-proton multiplet ($J_{9\text{-}exo,9\text{-}endo}$ 12.5 Hz) at δ 2.84 to H-9-*endo* and H-9-*exo*. All assignments were confirmed by double irradiation experiments: *e.g.* on irradiation at the frequency of H-4, the H-9-multiplet was simplified while the H-10-*exo* signal was unaffected. The betaine (3) was unreactive towards *N*-phenylmaleimide, dimethyl fumarate, tetracyanoethylene, and phenyl isocyanate. Acrylonitrile did react, but formed unstable cycloadducts, which we did not characterise.

Cycloadditions with Acetylenes.—The betaine (3) reacted with diphenylacetylene in *o*-dichlorobenzene to give the yellow cycloadduct (5), ν(C=O) 1 715 cm^{-1}, *m/e* 400, one-proton n.m.r. singlet at δ 5.72 for H-4.

1-Oxido-3-phenylphthalazinium (3) reacted with dimethyl acetylenedicarboxylate in refluxing xylene to produce the expected cycloadduct (8), m.p. 176—177 °C, ν(C=O) 1 715 cm^{-1}, *m/e* 364. The n.m.r. spectrum showed a one-proton singlet at δ 6.26 for H-4, and two three-proton singlets at δ 3.80 and 3.84 for the two ester methyl groups. However, use of chloroform as solvent for the cycloaddition gave a crystalline isomer (85%), m.p. 150 °C, *m/e* 364. Structure (9) for this isomer is supported by the i.r. absorptions for αβ-unsaturated



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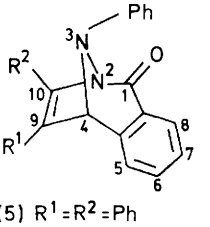


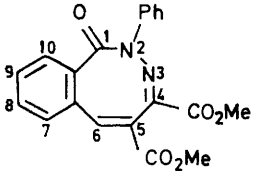
(5) R^1 = R^2 = Ph
(6) R^1 = H, R^2 = Ph
(7) R^1 = Ph, R^2 = H
(8) R^1 = R^2 = CO_2Me

ester groups [ν(C=O) 1 730 cm^{-1}] and amide [ν(C=O) 1 650 cm^{-1}]. The n.m.r. spectrum showed a low field one-proton singlet at δ 8.24 assigned to the single vinyl proton, H-6, and two three-proton singlets at δ 3.73 and 3.82 assigned to the two ester methyl groups.

On heating in the absence of solvent, both the isomeric cycloadducts (8) and (9) rearranged to a third isomer (10), m.p. 190 °C, *m/e* 364. The i.r. spectrum showed three carbonyl groups: saturated ester (1 750 cm^{-1}), unsaturated ester (1 735 cm^{-1}), and ketone (1 705 cm^{-1}). A one-proton n.m.r. singlet at δ 6.28 was assigned to the bridgehead proton, H-8b, and two three-proton singlets at δ 3.84 and 3.90 were assigned to the two ester methyl

[1] Part X, N. Dennis, A. R. Katritzky, and M. Ramaiah, *J.C.S. Perkin I*, 1975, 1506.
[2] D. E. Ames and B. Novitt, *J. Chem. Soc.* (*C*), 1969, 2355.
[3] E. Lunt and T. L. Threlfall, *Chem. and Ind.*, 1964, 1805.
[4] F. M. Rowe, E. Levin, A. C. Burns, J. S. H. Davies, and W. Tepper, *J. Chem. Soc.*, 1926, 690; F. M. Rowe, D. A. W. Adams, A. T. Peters, and A. E. Gillam, *J. Chem. Soc.*, 1937, 90.
[5] H. Lund, *Tetrahedron Letters*, 1965, 3973.
[6] H. Lund, *Coll. Czech. Chem. Comm.*, 1965, **30**, 4237.
[7] N. Dennis, B. Ibrahim, and A. R. Katritzky, *J.C.S. Chem. Comm.*, 1974, 500.

groups. The upfield shift of the bridgehead proton (H-8b) signal is the result of absence of conjugation with the amide nitrogen atom.



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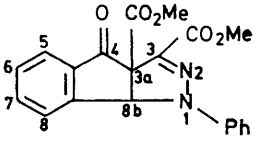

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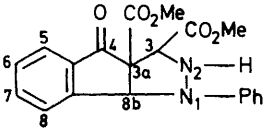

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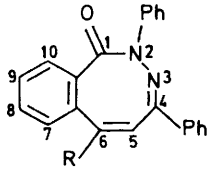
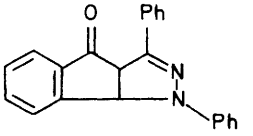
Catalytic hydrogenation of the isomer (10) over palladium–carbon (10%) yielded the dihydro-compound (11), which, in $(CD_3)_2SO$–D_2O, showed two one-proton



(12) R = H
(13) R = Br



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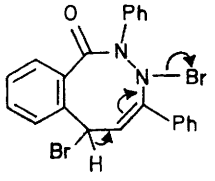

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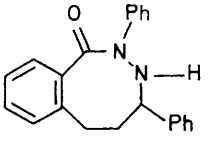


(16)

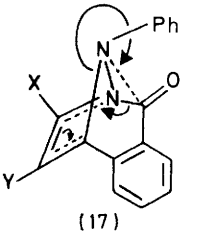
n.m.r. singlets at δ 5.86 and 6.32 for H-3 and -8b, and two three-proton singlets at δ 3.70 and 3.68 for the two ester methyl groups.

The betaine (3) reacted with phenylacetylene in refluxing xylene to give two isomeric products. One was the normal cycloadduct (6), m.p. 220 °C, ν(C=O) 1 710 cm^{-1}, showing a one-proton doublet at δ 6.02 (J 9 Hz) for the vinyl proton, H-9, and a second one-proton doublet at δ 4.74 (J 9 Hz) for the bridgehead proton, H-4. The second isomer (12), m.p. 145—146 °C, was an amide, ν(C=O), 1 650 cm^{-1}, m/e 324. The following evidence supported structure (12). A one-proton doublet at δ 6.60 [J 11 Hz (*cf.* J_{cis} 10 Hz; ref. 8), A of AB spectrum] was assigned to the vinyl proton, H-5. The signal due to the vinyl proton, H-6, originally buried under the aromatic envelope at δ 7.80—7.00, became visible as a doublet (J 11 Hz, B of AB spectrum) on addition of the lanthanide shift reagent $Pr(fod)_3$. Since the shift reagent complexes with the oxygen atom, the *peri*-proton, H-10, and the *ortho*-phenyl protons also suffer lanthanide-induced shifts. Structure (12) was confirmed by X-ray analysis.[9] Sublimation of (12) yielded crystalline (14), m.p. 228 °C, the structure of which was elucidated by X-ray crystallography.[10]

The betaine (3) reacted with phenylacetylene in *o*-dichlorobenzene to give the cycloadduct (6) as the major component along with two minor products but without formation of the adduct (12). One of the minor products was identified as the regioisomer (7), m.p. 195—196 °C, on the evidence of the n.m.r. spectrum which had two one-proton singlets at δ 6.75 and 5.70 for the vinyl proton, H-10, and the bridgehead proton, H-4, respectively.

Bromine in chloroform converted the adduct (12) into the monobromo-derivative (13), with evolution of hydrogen bromide. The amide group [ν(C=O) 1 645 cm^{-1}] is retained in the product. Initial addition of one bromine molecule to the conjugated imine of (12) is apparently followed by displacement of HBr from the dibromo-intermediate (15).

Catalytic hydrogenation of the cycloadduct (12) over palladium–carbon (10%) gave the benzodiazocine (16), which showed amide ν(C=O) 1 650 cm^{-1} and amine ν(N–H) 3 350 cm^{-1}. The n.m.r. spectrum showed an exchangeable (D_2O) NH singlet at δ 4.35, a quartet at δ 4.05 for H-4, a two-proton multiplet at δ 3.10 for the 6-protons and a two-proton complex multiplet at δ 2.10 for the 5-protons. These assignments were confirmed by double-resonance experiments.



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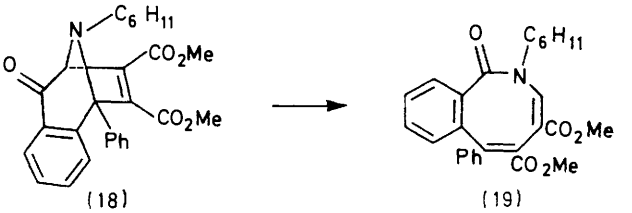
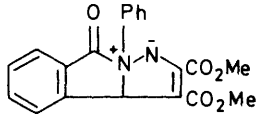


(18) (19)



(20)

Mechanisms of Formation of Isomeric Cycloadducts.—The conventional cycloadducts (4)—(8) are derived by

[8] R. M. Acheson, M. W. Foxton, and G. R. Miller, *J. Chem. Soc.*, 1965, 3200.

[9] N. Dennis, A. R. Katritzky, E. Lunt, M. Ramaiah, R. L. Harlow, and S. H. Simonsen, *Tetrahedron Letters*, 1976, 1569.

[10] R. L. Harlow and S. H. Simonsen, unpublished results.

cycloadditions of the dipolarophiles with the dipolar betaine (3). Lund [5] unambiguously established the betaine structure (3) by two-electron reduction to 3,4-dihydro-3-phenylphthalazin-1(2*H*)-one. The mechanisms of these rearrangements are not yet clear. The diazocines (9) and (12) could be derived from the normal cycloadducts (8) and (6) by electrocyclic reactions of the type (17); this is similar to the mechanism postulated by Padwa *et al.*[11] for the conversion of the adduct (18) into the azocine (19). The formation of the abnormal tricyclic derivatives (10) and (14) could be explained by 1,3-acyl shifts in (8) and (6), respectively. However, another possibility is that adducts of the type (8)—(10) are interconverted *via* the species (20), which by a 1,2-shift of the aryl group can yield (8), by electrocyclic ring opening can yield (9), and by 1,3-shift of the acyl group can give (10).

The foregoing work indicates the complexities of cycloaddition to diazinium betaines and provides evidence for subtle valence-bond isomerism processes in these compounds.

EXPERIMENTAL

M.p.s. were determined with a Reichert apparatus. Spectra were recorded with a Perkin-Elmer 257 grating i.r. spectrophotometer, a Hitachi–Perkin-Elmer RMU-6E mass spectrometer, a Unicam SP 800A u.v. spectrophotometer, and a Varian HA-100 n.m.r. spectrometer. Compounds were purified until they were observed as single spots on t.l.c. (Kieselgel PF 254; chloroform as eluant).

N-Anilinophthalimide.—Phenylhydrazine (2.10 g, 0.02 mol) in $CHCl_3$ (10 ml) was added to phthalic anhydride (2.96 g, 0.02 mol) in $CHCl_3$ (100 ml) and the mixture was kept at 20 °C for 3 h. The precipitated anilinophthalamic acid was filtered off, air dried, and heated at 160 °C in an oil-bath for 10 min with occasional stirring to give *N*-anilinophthalimide (3.5 g, 77%) as yellow needles, m.p. 180 °C (from EtOH) (lit.,[11] 156—185 °C) (Found: C, 70.8; H, 4.5; N, 11.6. Calc. for $C_{14}H_{10}N_2O_2$: C, 70.6; H, 4.2; N, 11.8%); $\nu_{max.}$ (Nujol) 1 785 and 1 730 cm^{-1}.

1-Oxido-3-phenylphthalazinium (3).—$NaBH_4$ (0.1 g, 0.02 mol) in $[CH_2]_4O$ (3 ml) was added quickly and with vigorous stirring to *N*-anilinophthalimide (0.238 g, 0.001 mol) in $[CH_2]_4O$ (8 ml) and distilled water (0.5 ml) at 20 °C. After 2 h, the excess of $NaBH_4$ was decomposed with a large excess of Me_2CO. The solution was stirred for 0.5 h more, filtered, and evaporated under vacuum. The oily residue was heated at 120—130 °C for 15 min to give a solid which was dissolved in hot EtOH (5 ml). Ether (50 ml) was then added to give 1-oxido-3-phenylphthalazinium (3) (0.172 g, 75%) as needles, m.p. 204—205 °C (from EtOH) (lit.,[5] 210 °C) (Found: C, 76.3; H, 4.7; N, 12.5. Calc. for $C_{14}H_{10}N_2O$: C, 75.7; H, 4.5; N, 12.6%); $\nu_{max.}$ (Nujol) 1 600 (C=C) and 1565 ($\overset{+}{C}-\overset{-}{O}$) cm^{-1}; δ ($CDCl_3$) 7.40—8.0 (8 H, m, aromatic), 8.28 (1 H, m, *peri*-H), and 8.60 (1 H, s, H-4); *m/e* 222.

3,4-Dihydro-3,10-endo-diphenyl-2,4-ethanophthalazin-1(2H)-one (4).—1-Oxido-3-phenylphthalazinium (0.11 g, 5×10^{-4} mol), styrene (10 ml), and hydroquinone (3—4 crystals) were heated in an oil-bath at 120° C for 5 h. Unchanged styrene was removed under vacuum. The solid residue crystallised from EtOH to give the *adduct* (4) (0.140 g, 65%) as needles, m.p. 154 °C (Found: C, 80.9; H, 5.8; N, 8.3. $C_{22}H_{18}N_2O$ requires C, 81.0; H, 5.6; N, 8.6%); $\nu_{max.}$ (Nujol) 1 700 (αβ-unsaturated ketone C=O), 1 600 (C=C), 1 490, 1 350, 1 260, 1 100, and 1 065 cm^{-1}; δ ($CDCl_3$) 7.3 (4 H, m, aromatic), 5.10 (1 H, dd, H-4, $J_{4,9\text{-}endo}$ 1, $J_{4,9\text{-}exo}$ 6 Hz), 4.70 (1 H, dd, H-10-*exo*, $J_{9\text{-}endo,10\text{-}exo}$ 5, $J_{9\text{-}exo,10\text{-}exo}$ 8.5 Hz), and 2.84 (2 H, m, H-9-*endo* and H-9-*exo*, $J_{9\text{-}endo,9\text{-}exo}$ 12.5 Hz); *m/e* 326.

3,4-Dihydro-3,9,10-triphenyl-2,4-ethenophthalazin-1(2H)-one (5).—The betaine (3) (0.111 g, 5×10^{-4} mol), diphenylacetylene (0.134 g, 0.001 5 mol), and *o*-dichlorobenzene (8 ml) were heated under reflux for 18 h. The solvent was removed under vacuum and the residue crystallised from light petroleum (b.p. 40—60 °C) to give the *adduct* (5) (0.172 g, 86%), as yellow needles, m.p. 214 °C (Found: C, 84.8; H, 5.3; N, 5.6. $C_{28}H_{20}N_2O$ requires C, 84.0; H, 5.0; N, 7.0%); $\nu_{max.}$ (Nujol) 1 715 (C=O), 1 600 (C=C), 1 530, 1 500, 1 270, 1 290, 1 140, and 830 cm^{-1}; $\lambda_{max.}$ (EtOH) 350 (ε 9×10^3), 297 (12×10^3), 280 (12.8×10^3), 250 (20×10^3), and 207 nm (37×10^3); δ ($CDCl_3$) 7.95—7.2 (19 H, m, aromatic) and 5.72 (1 H, s, H-4); *m/e* 400.

3,4,5,6-Tetrahydro-2,4-diphenyl-2,3-benzodiazocin-1(2H)-one (16).—Compound (12) (0.160 mg, 5×10^{-4} mol) in ethyl acetate (50 ml) was hydrogenated over Pd–C (10%) (50 mg) at atmospheric pressure until uptake ceased. The solvent was removed under vacuum and the product was separated by preparative t.l.c. (silica gel; $CHCl_3$). Elution with chloroform gave a major *product* (16) (130 mg, 80%) as needles, m.p. 158 °C (from EtOH) (Found: C, 79.2; H, 6.0; N, 8.5. $C_{22}H_{20}N_2O$ requires C, 80.5; H, 6.1; N, 8.5%); $\nu_{max.}$ (Nujol) 3 350 (N–H) and 1 650 cm^{-1} (amide C=O); δ ($CDCl_3$) 6.82—7.72 (14 H, m, aromatic), 4.35 (1 H, s, NH), 4.05 (1 H, q, H-4), 3.10 (2 H, m, H-6), and 2.10 (2 H, m, H-5); $\lambda_{max.}$ (EtOH) 265 (ε 1.6×10^4) and 214 nm (3.8×10^4); *m/e* 328. A (fast-moving) second compound (10 mg, 12%) was also eluted; it gave needles, m.p. 97—98 °C (from EtOH); $\nu_{max.}$ (Nujol) 1 650 cm^{-1}; δ ($CDCl_3$) 7.6—7.0 (m, aromatic), 2.7 (3 H, m), and 1.98 (1 H, m); *m/e* 224.

Reaction of 1-Oxido-3-phenylphthalazinium with Phenylacetylene.—(a) *Solvent xylene.* The betaine (3) (0.111 g, 5×10^{-4} mol), phenylacetylene (0.102 g, 0.001 mol), and xylene (10 ml) were heated under reflux (150 °C) for 12 h. Solvent was removed under vacuum and the residue was separated on preparative t.l.c. (Kieselgel PF 254). Elution with $CHCl_3$ gave *2,4-diphenyl-2,3-benzodiazocin-1(2H)-one* (12) (0.129 g, 75%) as needles, m.p. 145—146 °C (from EtOH) (Found: C, 81.1; H, 5.0; N, 8.6. $C_{22}H_{16}N_2O$ requires C, 81.5; H, 5.0; N, 8.6%); $\nu_{max.}$ (Nujol) 1 650 cm^{-1} (amide C=O); $\lambda_{max.}$ (EtOH) 300 (ε 3.6×10^3), 228 (5.6×10^4), and 215 nm (6.6×10^4); δ ($CDCl_3$) 7.80—7.0 (1 H, m, aromatic), 6.60 (1 H, d, H-5, $J_{5,6}$ 11 Hz); δ ($CDCl_3$) [with 5 mg $Pr(fod)_3$ to 15 mg substrate] 7.80—7.20 (11 H, m, aromatic), 7.15 (1 H, d, H-6, $J_{5,6}$ 11 Hz), 5.96 (1 H, d, H-5), 3.81 (2 H, m, *N*-phenyl *ortho*-protons), and 3.22 (1 H, m, H-10); *m/e* 324. Further elution gave *3,4-dihydro-3,10-diphenyl-2,4-ethenophthalazin-1(2H)-one* (6) (0.017 g, 10%) as yellow needles, m.p. 220 °C (from EtOH) (Found: C, 81.3; H, 5.0; N, 8.6. $C_{22}H_{16}N_2O$ requires C, 81.5; H, 5.0; N, 8.6%); $\nu_{max.}$ (Nujol) 1 710 cm^{-1} (α,β-unsaturated C=O); $\lambda_{max.}$ (EtOH) 245 (ε 4.8×10^4) and 207 nm (5.2×10^4); δ ($CDCl_3$) 7.2—8.0 (14 H, m, aromatic),

[11] A. Padwa, P. Sackman, E. Shefter, and E. Vega, *J.C.S. Chem. Comm.*, 1972, 680.

6.02 (1 H, d, H-9, $J_{4,9}$ 9 Hz), and 4.74 (1 H, d, H-4); *m/e* 324.

(b) *Solvent* o-*dichlorobenzene*. The betaine (3) (0.888 g, 0.004 mol) and phenylacetylene (0.410 mg, 0.004 mol) in *o*-dichlorobenzene were heated under reflux for 12 h. Solvent was removed under vacuum and the residue was separated on preparative t.l.c. Elution with chloroform gave compound (6) (0.300 g, 23.0%). Further elution gave a second isomer 3,4-*dihydro*-3,9-*diphenyl*-2,4-*ethenophthalazin*-1(2H)-*one* (7) (0.10 g, 7.0%) as yellow needles, m.p. 195—196 °C (from EtOH) (Found: C, 81.7; H, 5.2; N, 8.8. $C_{22}H_{16}N_2O$ requires C, 81.0; H, 4.9; N, 8.6%); $\nu_{max.}$ (Nujol) 1 715 (amide C=O) and 1 600 cm^{-1} (C=C); δ ($CDCl_3$) 8.0—6.9 (14 H, m, aromatic), 6.75 (1 H, s, H-10), and 5.70 (1 H, s, H-4); *m/e* 324. A third compound (0.10 g, 7%) was isolated as yellow needles, m.p. 90—91 °C (from EtOH) (Found: C, 74.8; H, 5.4; N, 7.8. Calc. for $C_{22}H_{16}N_2O_2,H_2O$: C, 73.7; H, 5.0; N, 7.8%); $\nu_{max.}$ (Nujol) 1 710 cm^{-1}; δ ($CDCl_3$) 7.1—8.0 (m) and 5.3 (1 H, s); *m/e* 340.

Dimethyl 1,2-*Dihydro*-1-*oxo*-2-*phenyl*-2,3-*benzodiazocine*-4,5-*dicarboxylate* (9).—1-Oxido-3-phenylphthalazinium (3) (0.222 g, 0.001 mol) and dimethyl acetylenedicarboxylate (DMAD) (0.217 g, 0.001 5 mol) were heated under reflux in $CHCl_3$ (10 ml) for 12 h. Solvent was removed under vacuum and the residue was crystallised from EtOH to give the *cycloadduct* (9) (0.314 g, 85%) as needles, m.p. 150 °C (Found: C, 65.6; H, 4.5; N, 7.7%); $\nu_{max.}$ (Nujol) 1 730 (unsaturated ester C=O), 1 650 (amide C=O), and 1 600 cm^{-1} (C=C); $\lambda_{max.}$ (EtOH) 350 (ε 1 × 10^3), 285sh (6.9 × 10^3), 245 (1.4 × 10^4), and 210 nm (2.3 × 10^4): δ ($CDCl_3$) 8.24 (1 H, s, H-6), 7.6—7.2 (9 H, m, aromatic), 3.82 (3 H, s, CH_3), and 3.73 (3 H, s, CH_3); *m/e* 364.

Dimethyl 1,2,3,4-*Tetrahydro*-1-*oxo*-3-*phenyl*-2,4-*ethenophthalazine*-9,10-*dicarboxylate* (8).—The betaine (3) (0.222 g, 0.001 mol) and DMAD (0.217 g, 0.001 mol) were heated under reflux in xylene (10 ml) for 12 h. The solvent was removed under vacuum and the residue crystallised from EtOH to give the *cycloadduct* (8) (0.290 g, 80%) as pale yellow needles, m.p. 176—177 °C (Found: C, 65.2; H, 4.5; N, 7.7. $C_{20}H_{16}N_2O_5$ requires C, 65.9; H, 4.4; N, 7.7%); $\nu_{max.}$ (Nujol) 1 755 (saturated ester C=O), 1 715 (C=O), and 1 600 cm^{-1} (C=C); δ ($CDCl_3$) 8.0—7.0 (9 H, m, aromatic), 6.26 (1 H, s, H-4), 3.84 (3 H, s, CH_3), and 3.80 (3 H, s, CH_3); *m/e* 364.

Dimethyl 1,3a,4,8b-*Tetrahydro*-4-*oxo*-1-*phenylindeno*-[1,2-c]*pyrazole*-3,3a-*dicarboxylate* (10).—The betaine (3) (0.222 g, 0.001 mol) and DMAD (0.217 g, 0.001 mol) were heated under reflux in xylene (10 ml) for 12 h. The solvent was removed under vacuum and the product was crystallised from EtOH to give the *cycloadduct* (10) (0.300 mg, 83%) as yellow needles, m.p. 190 °C (Found: C, 65.0; H, 4.9; N, 7.5. $C_{20}H_{16}N_2O_5$ requires C, 65.9; H, 4.4; N, 7.7%); $\nu_{max.}$ (Nujol) 1 750 (saturated ester C=O), 1 735 (unsaturated ester C=O), 1 705 (ring C=O), and 1 600 cm^{-1} (C=C); $\lambda_{max.}$ (EtOH) 240 (ε 1.2 × 10^4), 290 (5.7 × 10^3), 243 (2 × 10^4), and 208 nm (3.2 × 10^4); δ ($CDCl_3$) 7.0—8.0 (9 H, m, aromatic), 6.28 (1 H, s, H-8b), 3.84 (3 H, s, CO_2Me), and 3.90 (3 H, s, CO_2Me); *m/e* 364.

Thermal Conversion of the Cycloadduct (8) *into the Isomer* (10).—The cycloadduct (8) (0.364 g, 0.001 mol) was heated in an oil-bath at 170—180 °C for 5 h. The product was crystallised from EtOH to yield the isomer (10) (0.350 g, 99%), m.p. 190—191 °C (mixed m.p. with authentic sample 190 °C).

Thermal Conversion of the Cycloadduct (9) *into the Isomer* (10).—The cycloadduct (9) (0.364 g, 0.001 mol) was heated in an oil-bath at 190 °C for 3 h. The product crystallised from EtOH to give the isomer (10) (0.350 g, 99%), m.p. and mixed m.p. 190 °C.

6-*Bromo*-2,4-*diphenyl*-2,3-*benzodiazocin*-1(2H)-*one* (13).—A solution of bromine (0.03 g, 2 × 10^{-4} mol) in $CHCl_3$ (5 ml) was added with stirring to a solution of compound (12) (0.054 g, 1.7 × 10^{-4} mol) in $CHCl_3$ (10 ml). After 2 h the solvent was removed under vacuum. The residue was crystallised from EtOH to give the *bromo-derivative* (13) (10 mg, 15.3%) as needles, m.p. 184—185 °C (Found: C, 64.7; H, 3.8; N, 7.2; Br, 19.5. $C_{22}H_{15}BrN_2O$ requires C, 65.5; H, 3.7; N, 7.0; Br, 19.9%); $\nu_{max.}$ (Nujol) 1 645 (amide C=O) and 1 460 cm^{-1}; $\lambda_{max.}$ (EtOH) 280 sh (ε 11.4 × 10^3), 247sh (21.4 × 10^3), and 207 nm (36 × 10^3); δ ($CDCl_3$) 7.3—8(m); *m/e* 444.

Dimethyl 1,2,3,3a,4,8b-*Hexahydro*-4-*oxo*-1-*phenylindeno*-[1,2-c]*pyrazole*-3,3a-*dicarboxylate* (11).—Compound (10) (0.121 g, 3.3 × 10^{-4} mol) in ethyl acetate (100 ml) was hydrogenated over Pd–C (10%). The mixture was filtered and the solvent removed under vacuum. The residue was crystallised from EtOH to give the *product* (11) (0.04 g, 33.3%) as light green needles, m.p. 165—166 °C (Found: C, 65.6; H, 5.0; N, 7.5. $C_{20}H_{18}N_2O_5$ requires C, 65.6; H, 5.0; N, 7.7%); $\nu_{max.}$ (Nujol) 3 520 (N–H), 1 750 (saturated ester C=O), 1 700 (ketone, C=O), and 1 600 cm^{-1} (C=C); $\lambda_{max.}$ (EtOH) 345 (ε 4.1 × 10^3), 300sh (1.1 × 10^3), 237 (2.3 × 10^3), and 207 nm (5.9 × 10^3); δ [$(CD_3)_2SO$] 7.25—7.5 (9 H, m, aromatic), 6.32 (1 H, s, H-8b), 6.0 (1 H, d, H-3, $J_{NH,\ H\text{-}3}$ 6 Hz), 3.68 (3 H, s, CH_3), and 3.70 (3 H, s, CH_3); δ [$(CD_3)_2SO$–D_2O] 6.32 (1 H, s, H-8b), 5.86 (1 H, s, H-3), 3.68 (3 H, s, CH_3), and 3.70 (3 H, s, CH_3).

3a,8b-*Dihydro*-1,3-*diphenylindeno*[1,2-c]*pyrazol*-4(1H)-*one* (14).—Sublimation of compound (12) at 200 °C and 0.1 mmHg produced the isomer (14) as greenish-yellow crystals, m.p. 228 °C.

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