Nitrogen Heterocycles. Part 7.[1] Some Reactions of 2-Anilinophthalimidine Derivatives †

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2-Anilino-3-benzyl-3-hydroxyphthalimidine (1) gives, on treatment with acids under various conditions, the methoxy-derivative (2), 2-anilino-3-benzylidenephthalimidine (3), 2-(*o*-carbamoylphenyl)-3-phenylindole (7), and 11-phenylisoindolo[2,1-*a*]indol-6-one (8). Compound (8) may be obtained also by pyrolytic rearrangement of (3). Pyrolysis of (1) affords 4-benzyl-3-phenylphthalizinium-3-olate (11), which can be transformed into a number of compounds, including the cycloadduct (12) with dimethyl but-2-ynedioate. Bromination of (3) gives 2-(*p*-bromoanilino)-3-benzylidenephthalimidine (5) and 3-bromo-2-(*p*-bromoanilino)-3-(α-bromobenzyl)-phthalimidine (16), which, by reaction with methanol or ethanol, affords the alkoxy-derivative [(17) or (18)]. Compounds (1) or (3), (5), (17), and (18) are converted by bases into the corresponding phthalazinones (19)—(22).

3-(α-BROMOBENZYLIDENE)PHTHALIMIDINE and some of its derivatives bearing appropriate *N*-substituents rearrange or cyclise under a variety of conditions.[1,2] We now report the results obtained with 2-anilino-3-benzyl-3-hydroxyphthalimidine (1), the adduct formed by reaction of 3-benzylidenephthalide with aniline, and of some compounds derived from it.

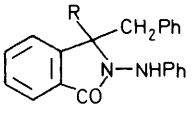
Treatment of compound (1) with hydrochloric acid in methanol at 0 °C gave the methoxy-derivative (2), mixed with a small amount of 2-anilino-3-benzylidenephthalimidine (3); the latter was obtained as the main product by heating (1) or (2) with acids in methanol. Acetylation of (3) gave 2-(*N*-acetylanilino)-3-benzylidenephthalimidine (4), which afforded the known[3] 2-(*N*-acetylanilino)phthalimide (6) on ozonolysis.

Although by analogy with the results obtained from other 3-benzylidenephthalimidine derivatives[4] and in view of the fact that a rather bulky *N*-substituent is present one could tentatively propose an *E*-configuration for (4), the spectral data of this compound [and those of (3) also] did not permit a sure attribution of configuration.

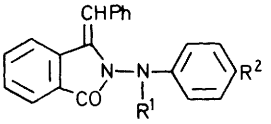
† Presented in part to the Tuscan Section of the Italian Chemical Society, Pisa, December 14, 1972; *Chimica e Industria*, 1973, **55**, 380.

[1] Part 6, A. Marsili, V. Scartoni, I. Morelli, and P. Pierangeli, *J.C.S. Perkin I*, 1977, 959.
[2] A. Marsili and V. Scartoni, *Gazzetta*, 1974, **104**, 165.
[3] F. D. Chattaway and W. Tesh, *J. Chem. Soc.*, 1920, **117**, 711.
[4] A. Marsili and V. Scartoni, *Gazzetta*, 1972, **102**, 806.

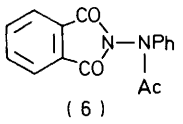
When compound (1) was refluxed with hydrobromic acid in acetic acid solution the two indole derivatives (7) and (8) were isolated. The latter was formed also by heating (3) at 300—350 °C. The formation of (7) is in agreement with the mechanism proposed for the Fischer indole synthesis,[5] the ammonia remaining bonded to the carbonyl group during the [3,3] sigmatropic rearrangement of the enehydrazide (3). The indoloisoindolone (8) is derived from (7) by pyrolytic cyclisation. Treatment of (8) with *p*-nitroperbenzoic acid led to *N*-(*o*-benzoylphenyl)phthalimide (9); compound (8) was formed also by photolysis of 3-(α-bromobenzylidene)-2-phenylphthalimidine (10).*



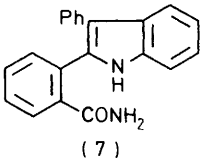
(1) R = OH
(2) R = OMe



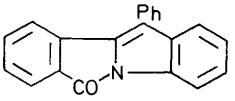
(3) R^1 = H, R^2 = H
(4) R^1 = Ac, R^2 = H
(5) R^1 = H, R^2 = Br



(6)



(7)



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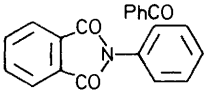

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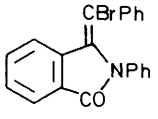
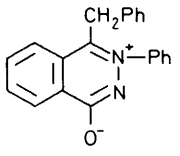
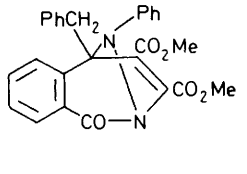


(10)

When solutions of compound (1) in acetic acid or in cyclohexanone were heated at reflux, conversion into the betaine (11) (4-benzyl-3-phenylphthalazinium-1-olate) took place. This thermal rearrangement of 2-anilino-3-hydroxyphthalimidines has been described before.[6] The 1,3-dipolar character of (11) was confirmed by reaction with dimethyl butynedioate to obtain the cycloadduct (12), in agreement with Katritzky's findings for similar compounds.[7] In addition, the betaine (11) underwent the following transformations: with acetic anhydride it gave the acetate (13) [also obtained directly from (1) with acetic anhydride], which was ozonolysed to the acetoxyphthalazinone (14); † methanolic hydrogen bromide



(11)



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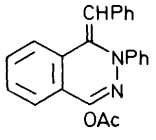
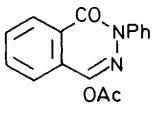
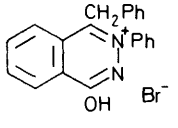


(13)



(14)



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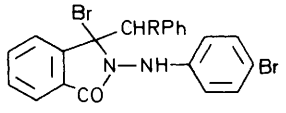
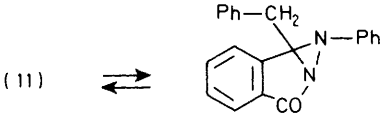


(16) R = Br
(17) R = OMe
(18) R = OEt

caused conversion into the hydroxyphthalazinium bromide (15); hydrochloric acid at 180 °C transformed (11) into (8); and photolysis in methanol led to compound (2).

The last two reactions suggest that the betaine (11) is in equilibrium with the diaziridine (23),‡ which could



(11) (23)

either rearrange to (3), and hence to (8), or react with methanol to give (2).

Treatment of (3) with an equimolar amount of bromine in chloroform afforded the *p*-bromoanilino-derivative (5); this compound easily added one further molecule of bromine to give the unstable tribromo-derivative (16), also obtainable from (3) and 2 mol. equiv. of bromine. When (16) was treated with methanol or ethanol, or else when (3) was brominated in the presence of these two alcohols, the stable 3-(α-alkoxybenzyl)-3-bromo-2-(*p*-bromoanilino)phthalimidines (17) and (18) were obtained.

We have shown previously [1,2,4] that bromination of 3-benzylidenephthalimidine and *N*-aralkyl-3-benzylidenephthalimidines leads to products [3-(α-bromobenzylidene)phthalimidines] derived from a substitution reaction at vinylic carbon. In the case of compound (5) [formed from (3) by aryl substitution] only addition of

* Work in progress in this laboratory.

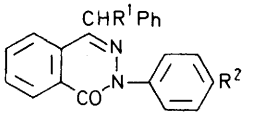
† An *N*-acetyl isomer of (14) has been described.[3] Attempted preparation of this compound from 2,3-dihydro-2-phenylphthalazine-1,4-dione and acetic anhydride led, however, to (14).

‡ Equilibria of this kind, involving valence-bond tautomerism, have been discussed recently (see N. Dennis, A. R. Katritzky, and H. Wilde, *J.C.S. Perkin I*, 1976, 2338, and references cited therein).

[5] M. K. Eberle and L. Brzechffa, *J. Org. Chem.*, 1976, **41**, 3775.
[6] H. Lund, *Tetrahedron Letters*, 1965, 3973.
[7] N. Dennis, A. R. Katritzky, and M. Ramaiah, *J.C.S. Perkin I*, 1976, 2281.

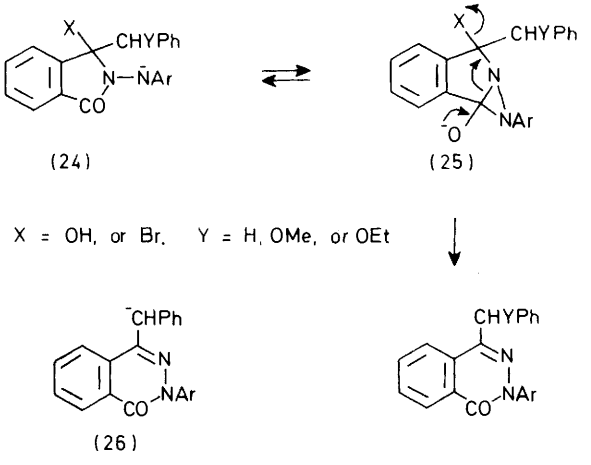
bromine to the double bond has been observed. If one considers the electrophilic step of the bromination process,[8] which in these compounds involves two benzylic carbon atoms, a carbocation at C-3 may be stabilised by electron-releasing substituents at the ring nitrogen; therefore proton elimination may occur. On the other hand, the electron-withdrawing *p*-bromoanilino-substituent of (5) must exert a destabilising effect on such a carbocation, thus favouring initial electrophilic attack at C-3 and completion of the reaction by attack of either bromide or alkoxide ions at the exocyclic benzylic carbon.

The action of ethanolic potassium hydroxide on (1) and (3) led to the known [9] phthalazinone (19); analogously, treatment of (5), and of (17) and (18), with base caused



(19) $R^1 = R^2 = H$
(20) $R^1 = H$, $R^2 = Br$
(21) $R^1 = OMe$, $R^2 = Br$
(22) $R^1 = OEt$, $R^2 = Br$

conversion into the phthalazinone derivatives (20)—(22), respectively. This base-catalysed transformation probably involves an anionic intermediate such as (24), which could rearrange through the tautomeric hydroxydiaziridine anion (25). In the case of (3) and (5), the rearrangement mechanism is probably analogous, the last step being protonation of a carbanion such as (26).



(24) (25)

X = OH, or Br. Y = H, OMe, or OEt

(26)

Compounds (1), (2), (3), and (8) were tested both for anti-inflammatory and analgesic activity (*in vivo*) and for antibacterial activity (*in vitro*). Whereas (2) and (8) were inactive, (1) showed inhibiting action on *Streptococcus pyogenes haemolyticus*, and (3) analgesic activity. None of these compounds was considered interesting enough for further study.

EXPERIMENTAL

M.p.s were determined with a Kofler apparatus; i.r. spectra were recorded for Nujol mulls with a Perkin-Elmer 137 spectrophotometer; u.v. spectra were determined for solutions in 95% ethanol with a Zeiss PMQ II spectrophotometer; n.m.r. spectra were recorded for solutions in $CDCl_3$ (unless otherwise indicated) with a JEOL C-60 HL spectrometer (Me_4Si as internal standard).

2-Anilino-3-benzyl-3-hydroxyphthalimidine (1).—Phenylhydrazine (19 ml) in ethanol (20 ml) was added in portions to a hot solution of 3-benzylidenephthalide (20 g) in ethanol (40 ml). The mixture was refluxed for 1 h, then left overnight at room temperature. The precipitate (1) (17.4 g) crystallised from methanol as *prisms*, m.p. 188—190 °C (Found: C, 76.15; H, 5.45; N, 8.2. $C_{21}H_{18}N_2O_2$ requires C, 76.35; H, 5.5; N, 8.5%), $\nu_{max.}$ 3 333 (OH, NH) and 1 669 cm^{-1} (CO), δ 3.1 (1 H, m, OH), and 3.02, 3.25, 3.52, and 3.75 (2 H, ABq, CH_2). Addition of water to the mother liquor caused precipitation of a further crop (4.4 g).

2-Anilino-3-benzyl-3-methoxyphthalimidine (2).—Concentrated hydrochloric acid (8 ml) was added to a stirred solution of (1) (5.4 g) in methanol (150 ml) at 0 °C. After 90 min the precipitate (2) (3.5 g) was removed, and crystallised from benzene–hexane as *prisms*, m.p. 168—170 °C (Found: C, 76.85; H, 6.1; N, 7.9. $C_{22}H_{20}N_2O_2$ requires C, 76.7; H, 5.85; N, 8.15%), $\nu_{max.}$ 3 289 (NH) and 1 701 cm^{-1} (CO), δ [$(CD_3)_2SO$] 2.9 (3 H, s, CH_3), 3.02, 3.25, 3.47, and 3.70 (2 H, ABq, CH_2), and 8.25 (1 H, s, NH). Addition of water to the filtrate, extraction with ether, and evaporation afforded a residue (1.5 g) consisting of mainly (2) and a little (3).

2-Anilino-3-benzylidenephthalimidine (3).—(a) *From compound* (1). Concentrated hydrochloric acid (20 ml) and (1) (30 g) in methanol (180 ml) were refluxed for 15 min. The solid (3) (21 g) formed at room temperature crystallised from chloroform–methanol as yellow *platelets*, m.p. 192—194 °C (Found: C, 80.75; H, 5.1; N, 8.65. $C_{21}H_{16}N_2O$ requires C, 80.75; H, 5.15; N, 8.95%), $\nu_{max.}$ 3 290 (NH) and 1 695 cm^{-1} (CO), $\lambda_{max.}$ 275 (log ε 4.05) and 331 nm (4.13).

(b) *From compound* (2). A solution of compound (2) (0.5 g) in methanol (9 ml) and concentrated hydrochloric acid (1 ml) was refluxed for 10 min and cooled to obtain (3) (0.4 g).

N-(N-Acetylanilino)-3-benzylidenephthalimidine (4).—Compound (3) (0.5 g) in acetic anhydride (5 ml) was refluxed for 10 h. Evaporation and treatment of the residue with methanol afforded (4) (0.5 g) as *prisms*, m.p. 152—154 °C (Found: C, 77.75; H, 5.25; N, 7.85. $C_{23}H_{18}N_2O_2$ requires C, 77.95; H, 5.1; N, 7.9%), $\nu_{max.}$ 1 718 and 1 695 cm^{-1} (CO), $\lambda_{max.}$ 266sh (log ε 4.07) and 329 nm (4.16), δ 2.2 (3 H, s, CH_3) and 6.77 (1 H, s, olefinic H). When (4) (0.2 g) in ethanol (3 ml) containing 10% sodium hydroxide (2 ml) was heated for 10 min at reflux, dilution with water gave compound (3) (0.12 g).

N-(N-Acetylanilino)phthalimide (6).—A stream of oxygen–ozone was bubbled for 3 h into a solution of compound (4) (0.5 g) in methanol (30 ml) and dichloromethane (100 ml) at −70 °C. The solution was treated with dimethyl sulphide in ether at 0 °C, and after 20 h at room temperature was evaporated. The oily residue crystallised from ethanol–water to afford compound (6) (0.2 g), m.p. 201—203 °C (lit.,[3] 198 °C).

2-(o-Carbamoylphenyl)-3-phenylindole (7) *and 11-Phenylisoindolo[2,1-a]indol-6-one* (8).—A solution of compound (1) (2.0 g) in 3 : 1 acetic acid–concentrated hydrobromic acid (8 ml) was heated at 100 °C for 1 h. After cooling, the precipitate (8) (0.6 g) was removed and crystallised from methanol

[8] R. C. Fahey, *Topics Stereochem.*, 1968, **3**, 237.
[9] J. Ephraim, *Ber.*, 1893, **26**, 1376.

as yellow *needles*, m.p. 223—226 °C (Found: C, 85.3; H, 4.65; N, 4.6. $C_{21}H_{13}NO$ requires C, 85.4; H, 4.45; N, 4.75%), $\nu_{max.}$ 1 721 cm^{-1} (CO). The filtrate was carefully diluted with water; after several hours compound (7) (0.2 g) was collected and crystallised from benzene–light petroleum as *needles*, m.p. 196—197 °C (Found: C, 80.5; H, 5.25; N, 8.65. $C_{21}H_{16}N_2O$ requires C, 80.75; H, 5.15; N, 8.95%), $\nu_{max.}$ 3 225 and 3 460 (NH) and 1 640 and 1 670 cm^{-1} (CO).

Other Preparations of Compound (8).—(a) *From compound* (7). Compound (7) (1.0 g) was heated at 300—350 °C for 15 min. After cooling, extraction of the crude product with chloroform, evaporation, and treatment of the residue with methanol afforded (8) (0.7 g).

(b) *From compound* (3). Pyrolysis of (3) (1.1 g) and work-up as described above yielded (8) (0.9 g). Alternatively, a solution of compound (3) (2 g) in acetic acid (30 ml) and concentrated hydrobromic acid (10 ml) was heated at 100 °C for 2 h. The usual work-up afforded (8) (1.1 g).

(c) *From compound* (4). A suspension of (4) (0.2 g) in acetic acid (3 ml) and concentrated hydrobromic acid (1 ml) was heated for 2 h at 100 °C. Dilution with water afforded (8) (0.08 g).

(d) *From* 3-(α-*bromobenzylidene*)-2-*phenylphthalimidine* (10). A solution of (10) (1 g) in benzene (100 ml) was irradiated for 20 h at room temperature with a 70 W high-pressure mercury lamp (Hanau TQ 81) equipped with an immersion well system (Pyrex glass). The residue from evaporation crystallised from methanol to give (8) (0.5 g).

N-(o-*Benzoylphenyl*)*phthalimide* (9).—A solution of (8) (0.36 g) and *p*-nitroperbenzoic acid (0.6 g) in chloroform (20 ml) was kept at room temperature for 4 days. The precipitated *p*-nitrobenzoic acid was filtered off, and the filtrate was washed with 2N-sodium carbonate and evaporated. The residue (9) (0.2 g) crystallised from methanol as *prisms*, m.p. 203—205 °C (Found: C, 77.0; H, 4.15; N, 4.15. $C_{21}H_{13}NO_3$ requires C, 77.05; H, 4.0; N, 4.3%), $\nu_{max.}$ 1 669, 1 724, and 1 812 cm^{-1} (CO). The same product (0.5 g) was obtained by refluxing for 30 min a mixture of phthalic anhydride (0.4 g) and *o*-aminobenzophenone (0.3 g) in acetic acid (5 ml).

4-*Benzyl*-3-*phenylphthalazinium*-1-*olate* (11).—(*a*) A suspension of compound (1) (1 g) in acetic acid (5 ml) was refluxed until a clear solution was obtained (10 min). Addition of water (10 ml) and an excess of 10% sodium hydroxide caused precipitation of (11) (0.6 g), which crystallised from methanol–ether as *prisms*, m.p. 214—216 °C (Found: C, 80.65; H, 5.3; N, 8.75. $C_{21}H_{16}N_2O$ requires C, 80.75; H, 5.15; N, 8.95%), $\nu_{max.}$ 1 613 cm^{-1} (CO), $\lambda_{max.}$ 260infl. (log ε 4.17) and 344 nm (3.98), δ 4.45 (2 H, s, CH_2).

(*b*) Compound (1) (0.5 g) in cyclohexanone (5 ml) was refluxed for 30 min. Evaporation and crystallisation of the oily residue gave (11) (0.3 g).

Dimethyl 5-*Benzyl*-2,5-*dihydro*-1-*oxo*-10-*phenyl*-2,5-*imino*-1H-2-*benzazepine*-3,4-*dicarboxylate* (12).—A mixture of (11) (0.5 g) and dimethyl butynedioate (0.5 ml) in benzene (5 ml) was refluxed for 10 h. The precipitate (12) (0.05 g) crystallised from methanol as yellow *neeales*, m.p. 171—173 °C (Found: C, 71.1; H, 4.7; N, 6.45. $C_{27}H_{22}N_2O_5$ requires C, 71.35; H, 4.9; N, 6.15%), $\nu_{max.}$ 1 664 and 1 721 cm^{-1} (CO), δ 3.78 (6 H, s, CH_3), and 4.15, 4.37, 4.60, and 4.82 (2 H, ABq, CH_2). Evaporation of the mother liquor and treatment of the residue with methanol afforded (12) (0.05 g).

1-*Acetoxy*-4-*benzylidene*-3,4-*dihydro*-3-*phenylphthalazine* (13).—(*a*) Compound (1) (1 g) in acetic anhydride (5 ml) was refluxed for 1 h. After cooling, addition of ether–light petroleum caused separation of (13) (0.55 g), which crystallised from ethanol–light petroleum as *needles*, m.p. 183—184 °C (Found: C, 77.8; H, 5.25; N, 8.1. $C_{23}H_{18}N_2O_2$ requires C, 77.95; H, 5.1; N, 7.9%), $\nu_{max.}$ 1 695 and 1 724 cm^{-1} (CO), $\lambda_{max.}$ 262 (log ε 4.26), 287 (4.21), and 325sh nm (4.04), δ 2.57 (3 H, s, CH_3) and 6.70—8.15 (15 H, vinylic and aromatic).

(*b*) Compound (11) (0.25 g) in acetic anhydride (1.2 ml) was refluxed for 1 h. After cooling, addition of light petroleum–ether caused separation of (13) (0.2 g). When a suspension of (13) (0.2 g) in acetic anhydride (3 ml) and concentrated hydrobromic acid (1 ml) was heated at 100 °C for 2 h, and treated with water (10 ml) and 10% sodium hydroxide, compound (11) (0.16 g) was formed.

4-*Acetoxy*-2-*phenylphthalazin*-1(2H)-*one* (14).—Compound (13) (0.5 g) was submitted to ozonolysis as described for (4) to give the *phthalazinone* (14) (0.2 g), m.p. 132—134 °C (Found: C, 68.65; H, 4.1; N, 10.0. $C_{16}H_{12}N_2O_3$ requires C, 68.6; H, 4.3; N, 10.0%), $\nu_{max.}$ 1 672 and 1 779 cm^{-1} (CO).

4-*Benzyl*-1-*hydroxy*-3-*phenylphthalazinium Bromide* (15).—A solution of compound (11) (1 g) in methanol (5 ml) was treated with an excess of methanolic hydrogen bromide at room temperature. Addition of ether afforded (15) (1.1 g), which crystallised from methanol–ether as *needles*, m.p. 220—225 °C (Found: C, 63.9; H, 4.35; N, 7.2. $C_{21}H_{17}BrN_2O$ requires C, 64.15; H, 4.35; N, 7.1%), δ (CF_3CO_2H) 4.9 (2 H, s, CH_2). Alternatively, compound (13) (1 g) in methanol (5 ml) was treated with an excess of methanolic hydrogen bromide and worked-up as described above to obtain (15) (1 g).

Conversion of Compound (11) *into* (8).—A suspension of (11) (1 g) in 2N-hydrochloric acid (10 ml) was heated at 180 °C for 6 h in a sealed glass tube. After cooling the insoluble material crystallised from methanol to give (8) (0.5 g).

Photolysis of Compound (11).—A solution of (11) (0.5 g) in methanol (100 ml) was irradiated for 4 h at room temperature as described for the conversion of (10) into (8). Concentration of the mixture gave (2) (0.4 g).

3-*Benzylidene*-2-(p-*bromoanilino*)*phthalimidine* (5).—To a stirred solution of (3) (3.1 g) in ethanol-free chloroform (40 ml) a solution of bromine (0.53 ml) in chloroform (5 ml) was added dropwise at 0 °C. The usual work-up and crystallisation of the residue from chloroform–methanol afforded (5) (2.7 g) as pale yellow *plates*, m.p. 246—248 °C (Found: C, 64.25; H, 4.0. $C_{21}H_{15}BrN_2O$ requires C, 64.45; H, 3.85%), $\nu_{max.}$ 1 698 (CO) and 3 279 cm^{-1} (NH).

3-*Bromo*-2-(p-*bromoanilino*)-3-(α-*bromobenzyl*)*phthalimidine* (16).—Compound (3) (2.0 g) was treated with 2 mol. equiv. of bromine under the same conditions as described for (5). An amorphous unstable solid (1.9 g) was obtained, which was purified by precipitation from benzene solution with hexane and dried (P_2O_5) *in vacuo* (Found: Br, 43.25. Calc. for $C_{21}H_{15}Br_3N_2O$: Br, 43.5%).

3-(α-*Alkoxybenzyl*)-3-*bromo*-2-(p-*bromoanilino*)*phthalimidines* (17) *and* (18).—The phthalimidine (3) or (5) was treated with bromine (2 or 1 mol. equiv., respectively), and to the stirred solution was added an excess of methanol or ethanol. After 30 min the usual work-up afforded a residue, which was crystallised from benzene–hexane. Yields varied from 80 to 90%. Compound (17) formed *needles*, m.p. 174—175 °C (Found: C, 52.8; H, 3.8. $C_{22}H_{18}Br_2N_2O_2$ requires C, 52.6; H, 3.6%), $\nu_{max.}$ 1 715 (CO) and 3 300 cm^{-1} (NH), δ 3.02 (3 H, s, CH_3), 5.75 (1 H, s, CH), and 6.25 (1 H, s, NH). Compound (18) gave *needles*. m.p. 172—174 °C (Found: C, 54.3; H, 3.65. $C_{23}H_{20}Br_2N_2O_2$ requires C, 53.5; H, 3.9%), $\nu_{max.}$

1 712 (CO) and 3 300 cm^{-1} (NH), δ 1.08 (3 H, t, CH_3, *J* 6.7 Hz), 3.3 (2 H, q, CH_2, *J* 6.7 Hz), 5.67 (1 H, s, CH), and 5.71 (1 H, s, NH).

4-*Benzyl*-2-*phenylphthalazin*-1(2H)-*one* (19).—This compound (0.9 g), m.p. 170 °C (lit.,[10] 171 °C), was obtained by refluxing for 1 h compound (1) or (3) (1.0 g) with ethanolic 10% potassium hydroxide (10 ml) and diluting the solution with water.

4-*Benzyl*-2-(p-*bromophenyl*)*phthalazin*-1(2H)-*one* (20).—This compound (0.6 g) was obtained by treatment of compound (5) (1.0 g) with potassium hydroxide as described for (19). Crystallisation from chloroform–methanol gave *leaflets*, m.p. 108—110 °C (Found: C, 64.7; H, 3.6. $C_{21}H_{15}BrN_2O$ requires C, 64.45; H, 3.85%), $\nu_{max.}$ 1 658 cm^{-1} (CO), δ 4.35 (2H, s, CH_2). Alternatively, a mixture of *o*-phenylacetylbenzoic acid (2.4 g), *p*-bromophenylhydrazine (1.8 g), and ethanol (20 ml) was refluxed for 1 h. Dilution with water caused separation of (20) (2.0 g).

4-(α-*Alkoxybenzyl*)-2-(p-*bromoanilino*)*phthalazin*-1(2H)-*ones* (21) *and* (22).—A suspension of compound (17) or (18) (0.5 g) was refluxed for 30 min with ethanolic 10% potassium hydroxide (10 ml). Addition of water to the resulting solution caused separation of (21) or (22), which crystallised from benzene–hexane. Yields varied from 40 to 50%. Compound (21) gave *needles*, m.p. 180—182 °C (Found: C, 62.45; H, 4.1. $C_{22}H_{17}BrN_2O_2$ requires C, 62.7; H, 4.05%), $\nu_{max.}$ 1 664 cm^{-1} (CO), δ 3.56 (3 H, s, CH_3) and 5.65 (1 H, s, CH). Compound (22) formed *prisms*, m.p. 113—115 °C (Found: C, 63.6; H, 4.5. $C_{23}H_{19}BrN_2O_2$ requires C, 63.45; H, 4.4%), $\nu_{max.}$ 1 669 cm^{-1} (CO), δ 1.3 (3 H, t, CH_3, *J* 6.7 Hz), 3.75 (2 H, q, CH_2, *J* 6.7 Hz), and 5.76 (1 H, s, CH).

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