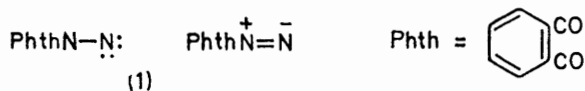


Reaction of Phthalimidonitrene with Furans

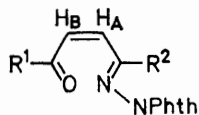
By D. W. Jones, Department of Organic Chemistry, The University, Leeds LS2 9JT

2,5-Dimethylfuran reacts with phthalimidonitrene to give the 2-phthaloylhydrazone of *cis*-hex-3-ene-2,5-dione. Monosubstituted furans including the 2-methyl, 2-methoxy-, 2-phenyl, and 2-methoxycarbonyl derivatives react similarly, as do 1,3-diphenylbenzo[*c*]furan and 4,7-dihydro-1,3-diphenylbenzo[*c*]furan. The product of the last reaction is readily converted into 2-amino-1,3-diphenylisoindole. Reaction of phthalimidonitrene with 1,4-diphenyl-2-benzopyran-3-one affords 2,3-diphenyl-1-phthalimidoindole through initial 1,2-addition.

THE oxidation of *N*-aminophthalimide is believed to produce phthalimidonitrene (1) which reacts with olefins,¹ acetylenes,² and sulphoxides³ in the expected ways. Nitrenes generally react with aromatic compounds,⁴ but, perhaps because of reduced electrophilicity associated with resonance as in structure (1), phthalimidonitrene does not react significantly with either benzene or anisole. We have already shown⁵ that more nucleophilic aromatic compounds like benzo[*b*]furan and benzo[*b*]thiophen react with the nitrene. We now describe the reaction of the nitrene (1) with simple furans.



When the nitrene (1) was generated in the presence of an excess of 2,5-dimethylfuran the phthaloylhydrazone (2) was readily isolated by direct crystallisation of the crude product. The gross structure (2) accords with the spectroscopic properties of the product (see Experimental section); the *cis*-stereochemistry is favoured by the

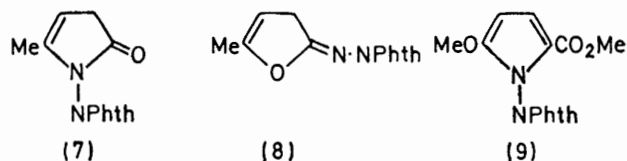


- (2) R¹ = R² = Me
 (3) R¹ = Me, R² = H
 (4) R¹ = CO₂Me, R² = H
 (5) R¹ = Ph, R² = H
 (6) R¹ = OMe, R² = H

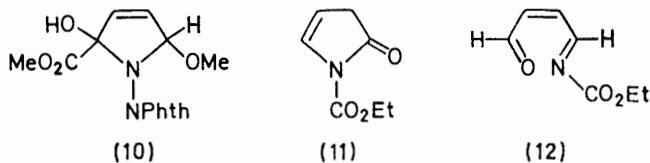
value of J_{AB} (12 Hz). Monosubstituted furans including the 2-methyl, 2-methoxycarbonyl, 2-phenyl, and 2-methoxy-derivatives react similarly, giving the hydrazones (3)–(6) respectively. Compounds (4) and (5) were converted into their *trans*-isomers by adsorption on silica gel. Comparison of the n.m.r. spectra of the *cis*- and *trans*-isomers confirmed the *cis*-stereochemistry of the initially formed products. Thus for the *cis*-isomer (4), the AB system appears at higher field (τ 2.79) and J_{AB} is smaller (11 Hz) than for the *trans*-isomer, in

which case the AB system is centred at τ 2.61 (J_{AB} 16 Hz). For the monosubstituted furans the isolated products correspond to initial nitrene attack at the 4,5-double bond. Thus the mass spectra of compounds (3) and (4) show strong $M - \text{COMe}$ and $M - \text{CO}\cdot\text{CO}_2\text{Me}$ peaks, respectively. Peaks corresponding to loss of the formyl radical expected⁶ for the isomers in which R¹ and R² are interchanged were very weak. For compound (5) the assigned structure is supported by carbonyl absorption at 1651 cm⁻¹, and for compound (6) the absence of low frequency carbonyl absorption precludes the formulation with R¹ and R² interchanged.

An attempt to convert compound (3) into its *trans*-isomer by adsorption on silica gel gave instead the pyrrolone (7). The n.m.r. spectrum of the product was very similar to that of α -angelica lactone, and led to two possible formulations (7) and (8). The correctness



of structure (7) was established by an independent synthesis of its dihydro-derivative by amination of 5-methyl-2-pyrrolidone and treatment of the product with phthalic anhydride. A related ring-closure of compound (4) to the pyrrole (9) occurred on treatment with methanolic hydrogen chloride. This reaction presumably involves dehydration of an initially formed methanol adduct (10). A similar mechanism would



account for the conversion (3) \rightarrow (7). The reaction of ethoxycarbonylnitrene with furan gives the pyrrolone

⁴ L. A. Paquette in 'Nonbenzenoid Aromatics,' ed. J. P. Snyder, vol. 1, Academic Press, New York, 1969, p. 249; R. A. Abramovitch and V. Uma, *Chem. Comm.*, 1968, 797; R. A. Abramovitch and E. F. V. Scriven, *ibid.*, 1970, 787; W. Lwowski and R. L. Johnson, *Tetrahedron Letters*, 1967, 891; F. D. Marsh and H. E. Simmons, *J. Amer. Chem. Soc.*, 1965, **87**, 3529.

⁵ D. W. Jones, *J.C.S. Perkin I*, 1972, 225.

⁶ Cf., H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1967, p. 141.

¹ D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *J. Chem. Soc. (C)*, 1970, 576; T. L. Gilchrist, C. W. Rees, and E. Stanton, *ibid.*, 1971, 988.

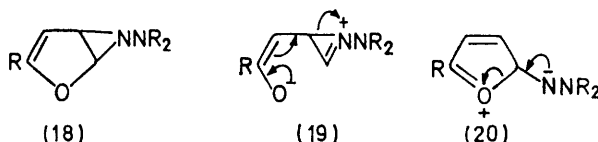
² D. J. Anderson, T. L. Gilchrist, and C. W. Rees, *Chem. Comm.*, 1969, 147.

³ D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *Chem. Comm.*, 1969, 146.

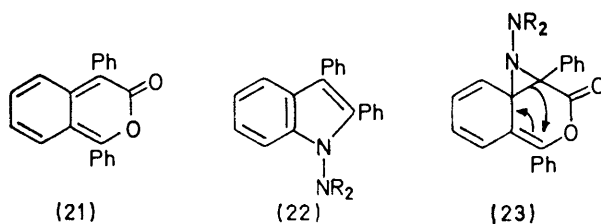
(11) or its conjugated isomer **7** rather than the compound (12) analogous to the hydrazones (2)—(6). It seems at least possible that the reaction of ethoxycarbonylnitrene with furan first gives compound (12), which undergoes ring-closure to (11) either under the reaction conditions (*ca.* 130°), or in the subsequent work-up. The conversion (12) → (11) is clearly related to the observed easy conversion (3) → (7). The reaction of phthalimidonitrene with furan produced an intractable product.

The conversion of furans into relatively stable derivatives of but-2-enal is, like the conversion into 2,5-dialkoxydihydrofurans,⁸ a reaction of potential synthetic utility. We illustrate one way in which the nitrene addition can be employed by a synthesis of 2-amino-1,3-diphenylisoindole (13), which on oxidative deamination might produce the potentially stable 1,2-diphenylbenzocyclobutene.⁹ It was first shown that phthalimidonitrene reacted smoothly with 1,3-diphenylbenzo[*c*]furan to give the phthaloylhydrazone (14), which however failed to give the isoindole (15) on attempted deoxygenation with triethyl phosphite.* The reaction of phthalimidonitrene with the readily available¹⁰ 4,7-dihydro-1,3-diphenylbenzo[*c*]furan (16) produced the hydrazone (17) by preferential attack on the furan system. With toluene-*p*-sulphonic acid in boiling benzene compound (17) gave the isoindole (15) in good yield. Hydrazinoly-

(2)—(6) include an initial 1,2-addition of the nitrene (1) to give a furoaziridine (18) related to the isolable product from benzo[*b*]furan,⁵ and subsequent C—O bond cleavage [to (19)] or C—N bond cleavage [to (20)]. These intermediate zwitterions could then proceed to the hydrazones in the indicated ways.



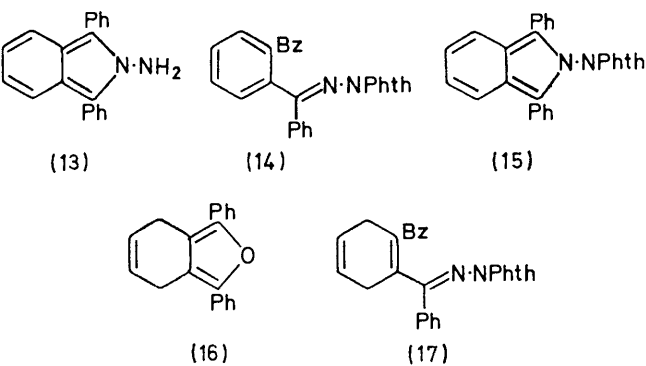
Whilst it is difficult entirely to exclude an initial orbital symmetry-allowed¹² 1,4-addition of the nitrene to the furans, such a mechanism would conflict with the experimental finding of almost exclusive 1,2-addition of *singlet* nitrenes to 1,3-dienes.¹³ Our own results with phthalimidonitrene confirm the preference for 1,2-addition. Thus the stabilised *o*-quinonoid compound (21),



a reactive diene which had shown no tendency to undergo 1,2-addition,¹⁴ reacted with the nitrene (1) to give the indole (22), and no trace of the isoindole (15), the expected product of 1,4-addition and decarboxylation. The formation of compound (22) is rationalised by assuming initial 1,2-addition to give (23), which then undergoes a 1,3-shift (arrows) and decarboxylation. The structure of compound (22) was proved by hydrazinolysis to 1-amino-2,3-diphenylindole which was prepared from 2,3-diphenylindole and mesityloxyamine. The reaction of 1-amino-2,3-diphenylindole with phthalic anhydride gave back the indole (22).

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. Unless otherwise specified i.r. spectra refer to Nujol mulls, u.v. spectra to ethanolic solutions, and n.m.r. spectra to solutions in deuteriochloroform measured with a Varian A60A spectrometer. Mass spectra were obtained with an A.E.I. MS902 instrument. Petroleum refers to light petroleum, b.p. 60—80°, and chromatography on silica to short column chromatography¹⁵ over Kieselgel G (Merck). The phrase 'work-up in the usual way' refers to dilution



sis of compound (15) produced the desired 2-aminoisoindole (13). Oxidation of the amine (13) provided no evidence for the intermediacy of 1,2-diphenylbenzocyclobutene, and a ring-expanded product analogous to that recently obtained by the oxidation of aminoindazoles¹¹ was not formed; a considerable amount of starting material remained after treatment with 1 mol. equiv. of the oxidising agent and preferential attack of the reagent on the quinonoid system seems likely.

Likely mechanisms for the formation of the hydrazones

* Prolonged boiling of *o*-dibenzoylbenzene with triethyl phosphite gives 1,3-diphenylbenzo[*c*]furan. When the reaction is conducted at 230°, 1,4-diphenyl-naphthalene is the main product (unpublished results).

⁷ K. Hafner and W. Kaiser, *Tetrahedron Letters*, 1964, 2185.

⁸ N. Elming, *Adv. Org. Chem.*, 1960, **2**, 67.

⁹ Cf. M. P. Cava and M. J. Mitchell, 'Cyclobutadiene and Related Compounds,' Academic Press, New York and London, 1967, p. 193.

¹⁰ R. Adams and M. H. Gold, *J. Amer. Chem. Soc.*, 1940, **62**, 56.

¹¹ D. J. C. Adams, S. Bradbury, D. C. Horwell, M. Keating, and C. W. Rees, *Chem. Comm.*, 1971, 828.

¹² M. J. S. Dewar, *Angew. Chem. Internat. Edn.*, 1971, **10**, 761, provides a full account of this and related additions.

¹³ A. Mishra, S. N. Rice, and W. Lwowski, *J. Org. Chem.*, 1968, **33**, 481; A. G. Anastassiou, *J. Amer. Chem. Soc.*, 1968, **90**, 1527; R. S. Atkinson and C. W. Rees, *Chem. Comm.*, 1967, 1230, 1232.

¹⁴ J. M. Holland and D. W. Jones, *J. Chem. Soc. (C)*, 1970, 530.

¹⁵ B. J. Hunt and W. Rigby, *Chem. and Ind.*, 1967, 1868.

with dichloromethane, washing with water, drying (MgSO_4), and evaporation under reduced pressure on a water-bath.

Reaction of 2-Methylfuran with Phthalimidonitrene.—Lead tetra-acetate (3.65 g) was added in portions during 10 min to a stirred mixture of the furan (3 ml), dichloromethane (20 ml), and *N*-aminophthalimide (1.25 g) maintained at 0–5°. T.l.c. of the crude product indicated that the phthaloylhydrazone (3) was the only product. After work-up in the usual way chromatography on silica and elution with ether–benzene (1:4) gave 5-methyl-1-phthalimidopyrrol-2(3H)-one (7) (380 mg), m.p. 177–178° (from benzene–petroleum) (Found: C, 64.6; H, 4.3; N, 11.45%; M^+ , 242.068. $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_3$ requires C, 64.5; H, 4.2; N, 11.6%; M , 242.069), τ 1.9–2.32 (4H, m, aromatic), 4.7–4.95 (1H, m, =CH), 6.7–6.95 (2H, m, CH_2), and 8.03–8.25 (3H, m, Me), ν_{max} 1660, 1720, 1738, and 1785 cm^{-1} . Continued elution with the same solvent gave *cis*-4-oxopent-2-enol 1-phthaloylhydrazone (3) (615 mg), m.p. 156–157° (from benzene) (Found: C, 64.45; H, 4.25; N, 11.6%), τ –0.01 to –0.19 (1H, four lines of X part of a virtually coupled ABX system, CHO), 1.9–2.35 (4H, m, aromatic), 3.35 (AB system, J_{AB} ca. 10 Hz), and 7.65 (3H, s, Me), ν_{max} 1602, 1680, 1724, 1760, and 1780 cm^{-1} .

Conversion of the Phthaloylhydrazone (3) into the Pyrrolone (7) on Silica Gel.—The phthaloylhydrazone (110 mg) was adsorbed on a silica gel column made up in benzene–ether (1:1). Elution of the column after 18 h gave the pyrrolone (7) (59 mg), m.p. 177–181°, identical (mixed m.p. and i.r. spectrum) with the compound previously obtained.

Catalytic Reduction of the Pyrrolone (7).—The pyrrolone (100 mg), Adams catalyst (20 mg), and ethyl acetate (5 ml) were shaken in hydrogen for 2.5 h. Filtration, evaporation, and crystallisation of the product, first from benzene–petroleum and then from methanol, gave 5-methyl-1-phthalimido-2-pyrrolidone, m.p. 160–163° (Found: C, 64.1; H, 4.9; N, 11.65. $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_3$ requires C, 63.9; H, 4.95; N, 11.5%), τ 2.0–2.4 (4H, m, aromatic), 4.95 (1H, m, HCN), 5.2–8.4 (4H, complex m), and 8.75 (3H, d, J 7 Hz, Me), ν_{max} 1700, 1730, and 1780 cm^{-1} .

5-Methyl-1-phthalimido-2-pyrrolidone.—5-Methyl-2-pyrrolidone (1 g), 50% sodium hydride–liquid paraffin (0.5 g), and dry dimethylformamide (3 ml) were heated in an oil-bath at 80–90° in a dry nitrogen atmosphere (16 h). The product was diluted with dimethylformamide (3 ml) and cooled to 0°, and mesityloxyamine¹⁶ (from 4 g of its hydrochloride) was added. After 1 h at 0° and 4 h at room temperature, xylene (25 ml) and phthalic anhydride (3 g) were added, and the mixture was boiled under reflux (2 h). The crude product was diluted with dichloromethane, washed with 2*N*-sodium hydroxide solution and water, dried (MgSO_4), and evaporated; the product crystallised from benzene–petroleum to give the title compound (223 mg), m.p. 161–162°, identical (mixed m.p. and i.r. spectrum) with the sample obtained previously.

Reaction of 2,5-Dimethylfuran with Phthalimidonitrene.—Lead tetra-acetate (6.8 g) was added in portions during 10 min to a stirred mixture of the furan (1 g), dichloromethane (35 ml), and *N*-aminophthalimide (2.5 g) at 0–5°. After work-up in the usual way the product was triturated with benzene and filtered to remove phthalimide (250 mg), and the mother liquor was diluted with petroleum to give *cis*-hex-3-ene-2,5-dione 2-phthaloylhydrazone (2) (1.1 g), m.p. 110–112° (from benzene–petroleum) (Found: C, 65.4; H, 4.7; N, 10.95. $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3$ requires C, 65.6; H, 4.7; N, 10.9%), τ 2.0–2.4 (4H, m, aromatic), 3.75 (AB system,

J_{AB} 12 Hz), 7.56 (3H, s, Me), and 7.8 (3H, s, Me), ν_{max} 1592, 1638, 1690, 1713, and 1780 cm^{-1} .

Reaction of Methyl 2-Furoate with Phthalimidonitrene.—Lead tetra-acetate (3.65 g) was added in portions during 10 min to a stirred ice-cold mixture of methyl 2-furoate (2.5 ml), dichloromethane (20 ml), and *N*-aminophthalimide (1.25 g). Work-up in the usual way and trituration with benzene gave an insoluble and unstable solid (120 mg) which was discarded. The residual liquor on addition of petroleum deposited methyl *cis*-2,5-dioxopent-3-enoate 5-phthaloylhydrazone (4) (330 mg), m.p. 165–172° (from benzene–petroleum) (Found: C, 58.8; H, 3.65; N, 9.65. $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_5$ requires C, 58.7; H, 3.5; N, 9.8%), τ –0.24 (1H, d, J 8 Hz, CH=N), 1.9–2.3 (4H, m, aromatic), 2.79 (AB system, J_{AB} 11, J_{AX} 8 Hz), and 6.05 (3H, s, Me), ν_{max} 1610, 1690, 1723, 1730, 1750, and 1780 cm^{-1} . A further quantity (100 mg) was obtained by crystallisation of the residue from the evaporated parent liquor from methanol over 3 days. The methanolic mother liquor later deposited a yellow solid (230 mg). The i.r. spectrum indicated this was a mixture of compound (4) and its *trans*-isomer. When this experiment was repeated with less methyl furoate (1.5 g) the quantity of benzene-insoluble product increased (220 mg). Chromatography of the residue over silica and elution with ether–benzene (1:4) then gave the *trans*-isomer (440 mg), m.p. 192–194° (from chloroform–ethanol) (Found: C, 58.8; H, 3.6; N, 9.65%), τ 0.51 (1H, d, J 8.5 Hz), 1.9–2.3 (4H, m, aromatic), 2.61 (AB system, J_{AB} 16, J_{AX} 8.5 Hz), and 6.04 (3H, s, Me), ν_{max} 1670, 1720, 1748, and 1778 cm^{-1} .

Reaction of the Phthaloylhydrazone (4) with Methanolic Hydrogen Chloride.—A brisk stream of hydrogen chloride was passed through a solution of the *cis*-phthaloylhydrazone (190 mg) in dichloromethane (5 ml) and methanol (5 ml) until the initial yellow colour faded (<1 min). Evaporation of most of the solvent gave methyl 5-methoxy-1-phthalimidopyrrole-2-carboxylate (9) (150 mg), m.p. 215–217° (from chloroform–methanol) (Found: C, 59.9; H, 4.05; N, 9.2. $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_5$ requires C, 60.0; H, 4.0; N, 9.3%), τ 1.9–2.3 (4H, m, aromatic), 3.0 (1H, d, J 4 Hz), 4.48 (1H, d, J 4 Hz), 6.14 (3H, s, CO_2Me), and 6.34 (3H, s, OMe), ν_{max} 1700, 1732, 1765, and 1805 cm^{-1} .

Reaction of 2-Phenylfuran with Phthalimidonitrene.—Lead tetra-acetate (1.82 g) was added in portions during 10 min to a stirred ice-cold mixture of 2-phenylfuran (1.25 g), dichloromethane (12 ml), and *N*-aminophthalimide (625 mg). Work-up in the usual way and crystallisation of the product from benzene–petroleum gave *cis*-4-phenylbut-2-enedial 1-phthaloylhydrazone (5) (0.79 g), m.p. 149–152° (from benzene) (Found: C, 70.75; H, 4.0; N, 9.4. $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3$ requires C, 71.0; H, 3.95; N, 9.2%), τ [(CD_3)₂SO] 1.02 (1H, d, J 9 Hz), 1.67–2.5 (10H, m, aromatic and B part of an AB system), and 3.1 (1H, A part of AB system, J_{AB} 11.5, J_{AX} 8.5 Hz), ν_{max} 1652, 1702, 1712, 1750, and 1770 cm^{-1} .

Conversion of the *cis*-Phthaloylhydrazone (5) into its *trans*-Isomer on Silica Gel.—The foregoing *cis*-phthaloylhydrazone (150 mg) was applied to a silica gel column made up in ether–benzene (1:4). After 6 h elution of the column with the same solvent gave the *trans*-isomer (70 mg), m.p. 165–171° (from benzene–petroleum) (Found: C, 70.8; H, 3.95; N, 9.4%), τ –0.32 (1H, d, J 9 Hz), 1.68–2.38 (9H, m, aromatic), and 2.48 (AB system, J_{AB} 12, J_{AX} 9 Hz), ν_{max} 1651, 1728, 1750, and 1774 cm^{-1} .

Reaction of 2-Methoxyfuran with Phthalimidonitrene.—

¹⁶ L. A. Carpino, *J. Amer. Chem. Soc.*, 1960, **88**, 3133.

Lead tetra-acetate (1.82 g) was added in portions during 10 min to a stirred ice-cold mixture of the furan (1 g), dichloromethane (15 ml), and *N*-aminophthalimide (625 mg). After work-up in the usual way the product crystallised from benzene-petroleum to give *cis*-4-methoxybut-2-enedial 1-phthaloylhydrazone (6) (180 mg), m.p. 190–194° (from benzene) (Found: C, 60.5; H, 4.05; N, 10.95). $C_{13}H_{10}N_2O_4$ requires C, 60.5; H, 3.9; N, 10.85%, τ -0.52 (1H, d, *J* 10 Hz), 1.8–2.15 (4H, m, aromatic), 2.95 (1H, dd, *J* 11.5 and 10.0 Hz), 3.6 (1H, d, *J* 11.5 Hz), and 6.1 (3H, s, Me), ν_{max} . 1645, 1736, and 1785 cm^{-1} .

Reaction of 1,3-Diphenylbenzo[c]furan with Phthalimidonitrene.—The furan (200 mg), *N*-aminophthalimide (700 mg), and dichloromethane (40 ml) were stirred at 0° while lead tetra-acetate (2 g) was added in portions during 15 min. The product was evaporated to dryness and applied in chloroform to two thick-layer silica gel plates. Development with ether-benzene (1:4) and isolation of the dark zone (u.v. lamp) by extraction with chloroform gave *o*-dibenzoylbenzene monophthaloylhydrazone (14), m.p. 178–180° (from chloroform-ethanol) (Found: C, 77.9; H, 4.25; N, 6.4%; M^+ , 430.130). $C_{28}H_{18}N_2O_3$ requires C, 78.1; H, 4.2; N, 6.5%; M , 430.132, ν_{max} . 1570, 1595, 1662, 1720, 1745, and 1778 cm^{-1} . After being heated with hydrochloric acid-acetic acid this product gave *o*-dibenzoylbenzene, identical (mixed m.p. and i.r. spectrum) with authentic material.

Reaction of 4,7-Dihydro-1,3-diphenylbenzo[c]furan with Phthalimidonitrene.—The furan (5.44 g), *N*-aminophthalimide (3.24 g), and dichloromethane (68 ml) were stirred at 0–5° while lead tetra-acetate (9.1 g) was added in portions during 10 min. Work-up in the usual way and crystallisation of the crude product from benzene gave 1,2-dibenzoyl-cyclohexa-1,4-diene monophthaloylhydrazone (17) (6.38 g), m.p. 197–201° (Found: C, 77.8; H, 4.7; N, 6.65). $C_{28}H_{20}N_2O_3$ requires C, 77.75; H, 4.6; N, 6.5%, τ [(CD₃)₂SO] 2.0–3.0 (14H, m, aromatic), 4.16 (2H, m, olefinic), and 7.0 (4H, m, allylic), ν_{max} . 1660, 1715, and 1778 cm^{-1} .

1,3-Diphenyl-2-phthalimidoisoindole.—The foregoing phthaloylhydrazone (800 mg), toluene-*p*-sulphonic acid (25 mg), and benzene (20 ml) were boiled under reflux (2 h). The resulting red-brown crystals were filtered off, washed with ethanol, and recrystallised from chloroform-ethanol to give 1,3-diphenyl-2-phthalimidoisoindole (15) (550 mg), m.p. 197–201° (Found: C, 81.0; H, 4.45; N, 6.75). $C_{28}H_{18}N_2O_2$ requires C, 81.2; H, 4.35; N, 6.8%, τ 2.1–3.2, ν_{max} . 1734 and 1778 cm^{-1} , λ_{max} . 364 nm (ϵ 14,690).

2-Amino-1,3-diphenylisoindole.—1,3-Diphenyl-2-phthalimidoisoindole (4.6 g) in ethanol (250 ml) was boiled under reflux with hydrazine hydrate (5 g) for 5 h. After evaporation of ethanol the product was taken up in dichloromethane; the solution was filtered, washed with 2*N*-sodium hydroxide solution and water, dried (MgSO₄), and evap-

orated. Crystallisation of the product from chloroform-ethanol gave 2-amino-1,3-diphenylisoindole (13) (1.68 g) as yellow rods, m.p. 125–129° (Found: C, 84.15; H, 5.65; N, 10.0). $C_{20}H_{16}N_2$ requires C, 84.5; H, 5.7; N, 9.85%, τ 2.5 (10H, m, Ph), 2.8 (AA'BB' pattern), and 5.44 (2H, s, NH₂), ν_{max} . 3285 and 3300 cm^{-1} , λ_{max} . 375 nm (ϵ 8168). This product deteriorates rapidly in the presence of light and air but can be stored in the dark in the crystalline state.

Reaction of Phthalimidonitrene with 1,4-Diphenyl-2-benzopyran-3-one.—The title compound (745 mg), *N*-aminophthalimide (810 mg), and dichloromethane (15 ml) were stirred at 0° while lead tetra-acetate (2.21 g) was added in portions during 10 min. After work-up in the usual way the product was chromatographed on silica. Benzene-light petroleum (4:1) eluted a yellow band (55 mg), which afforded yellow needles of 2,3-diphenyl-1-phthalimidoinole (22), m.p. 185–187° (from chloroform-ethanol) (Found: C, 80.9; H, 4.25; N, 6.7). $C_{28}H_{18}N_2O_2$ requires C, 81.1; H, 4.4; N, 6.8%, ν_{max} . 1755 and 1795 cm^{-1} . The n.m.r. spectrum showed the presence of aromatic protons only.

This product (20 mg), ethanol (3 ml), and hydrazine hydrate (100 mg) were boiled under reflux (1 h). After evaporation of ethanol the product was subjected to thick-layer chromatography on silica. Benzene-light petroleum (4:1) developed a blue fluorescent band (u.v. lamp) which after extraction with chloroform and recrystallisation from methanol gave 1-amino-2,3-diphenylindole (10 mg), m.p. 146–148° (Found: C, 84.5; H, 5.65; N, 9.85%), identical (mixed m.p. and i.r. spectrum) with the product obtained later.

1-Amino-2,3-diphenylindole.—2,3-Diphenylindole¹⁷ (520 mg) and sodium methoxide (85 mg) were stirred in dry dimethylformamide (5 min). Mesityloxyamine (473 mg) was then added while the mixture was stirred in ice. After stirring at 0° for 4 h the solvent was evaporated off under reduced pressure on a water-bath; the product was diluted with sodium hydroxide solution (2*N*), and extracted with ether. The extract was dried (MgSO₄) and evaporated and the solid product recrystallised from methanol to give 1-amino-2,3-diphenylindole (270 mg), m.p. 146–148°.

2,3-Diphenyl-1-phthalimidoinole.—1-Amino-2,3-diphenylindole (71 mg), phthalic anhydride (500 mg), and xylene (10 ml) were boiled under reflux (2 h). The product was diluted with dichloromethane; the solution was washed with sodium hydroxide solution (2*N*) and water, dried (MgSO₄), and evaporated to give 2,3-diphenyl-1-phthalimidoinole (61 mg), m.p. 185–187° (from chloroform-ethanol), identical (mixed m.p. and i.r. spectrum) with the product previously prepared.

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¹⁷ S. Bodfors, *Ber.*, 1925, **58**, 775.