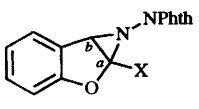
Mild thermal route to phthalimidonitrene and its reaction with activated benzenes to give 2*H*- and 3*H*-azepines; X-ray crystal structure analysis of an isolable 2*H*-azepine

David W. Jones* and Mark Thornton-Pett
School of Chemistry, The University of Leeds, Leeds LS2 9JT, UK

At 80 °C 1a-acetyl-1-phthalimido-1a,6b-dihydrobenzofuro[2,3-*b*]azirine **1** (X = Ac) transfers phthalimidonitrene to a series of traps: Me_2SO, 2-methoxynaphthalene, indene, methyl methacrylate, methyl crotonate, mesityl oxide, *cis*- and *trans*-stilbene and cyclohexene. Oxidation of *N*-aminophthalimide with lead tetraacetate in the presence of these traps gives the same major products (ref. 2*a*). With 1,3-dimethoxybenzenes, the reagent **1** (X = Ac) provides 2*H*- and 3*H*-azepines *e.g.* **25a** and **24a** as the major products with *N*-phthalimidoanilines *e.g.* **18** formed to a lesser extent. On the other hand $Pb(OAc)_4$ oxidation of *N*-aminophthalimide in the presence of 1,3-dimethoxybenzenes gives *N*-phthalimidoanilines and no detectable 2*H*- or 3*H*-azepines. Small quantities of acetic or benzoic acid present during the dissociation of **1** (X = Ac) in the presence of 1,3-dimethoxybenzenes cause marked increases in the formation of *N*-phthalimidoanilines compared with azepines. The unusually stable and isolable 2*H*-azepines **25** rearrange to 3*H*-azepines **24** only on heating and 5,7-dimethoxy-3-methyl-2-phthalimido-2*H*-azepine **25d** is characterised by X-ray crystal structure analysis.

We have described the preparation of the benzofuro[2,3-*b*]-azirine **1** (X = H) by oxidation of *N*-aminophthalimide **2** with lead tetraacetate in the presence of benzo[*b*]furan.[1] Upon heating compound **1** (X = H) at 110 °C it rearranged to compound



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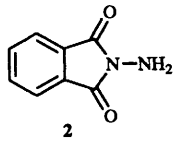

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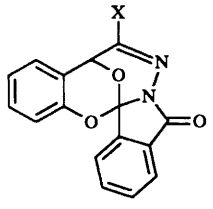

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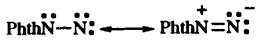

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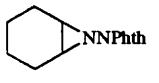

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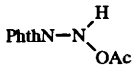

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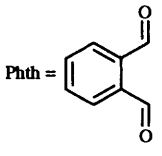
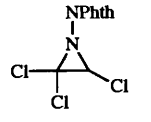


3 (X = H). To investigate the mechanism of this process we prepared **1** (X = Ac) from the commercially available 2-acetylbenzo[*b*]furan. Our purpose was to detect any accumulation of positive charge at the carbon labelled *a* in **1** at the rearrangement transition state by observing slower rearrangement in the presence of the electron withdrawing acetyl group. This objective was not realised as the thermolysis of compound **1** (X = Ac) in boiling benzene gave not only the expected rearrangement product **3** (X = Ac) but a larger quantity of 2-acetylbenzo[*b*]furan and some phthalimide. These products suggested initial breakdown of compound **1** (X = Ac) into 2-acetylbenzo[*b*]furan and phthalimidonitrene, although it was unclear just how phthalimidonitrene **4** gave phthalimide. This interpretation was confirmed when compound **1** (X = Ac) and cyclohexene were heated in boiling benzene. The cyclohexene–phthalimidonitrene adduct **5** was obtained in 45% yield. This product was identical to a sample of **5** prepared by the method of Anderson *et al.* by oxidation of compound **2** with lead tetraacetate in the presence of cyclohexene.[2a],†

In a similar way dissociation of **1** (X = Ac) in the presence of a series of alkenes gave the expected aziridines in the indicated (%) yield: indene (52), methyl methacrylate (56), methyl crotonate (32) and mesityl oxide (48). These yields are based on the nitrene source and refer to pure recrystallised products. Trapping with trichloroethene gave chloral (trichloroacetaldehyde) phthalylhydrazone the known rearrangement product of the expected aziridine **7**.[2a] Trapping with dimethyl sulfoxide gave



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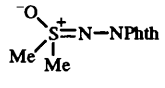

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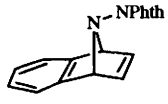

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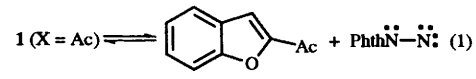
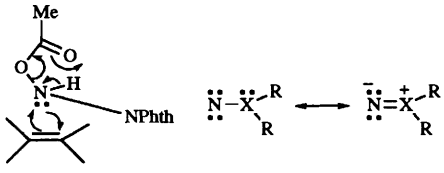
the sulfoximide **8** (41%). Evidence favouring the intervention of free phthalimidonitrene in these reactions is provided by stereospecific formation of aziridines from *cis*- and *trans*-stilbene and *cis*- and *trans*-4-methylpent-2-ene. Confirmatory evidence was obtained when we showed[2c] that a common intermediate was involved in the thermolysis of the series of compounds **1** (X = Ac, CO_2Me, COPh, $COBu^t$, CN) as well as the Rees sulfimide[3] (corresponding to sulfoximide **8**) and the Carpino compound **9**.[4] At the same time it was shown that nitrene formation from compound **1** (X = Ac) was reversible [eqn. (1)].

† Although originally thought to involve the nitrene **4** the oxidative route to **5** and related compounds *e.g.* **1** (X = Ac and H) apparently involves the *N*-acetoxyhydrazine **6** (ref. 2*b*, *c*).



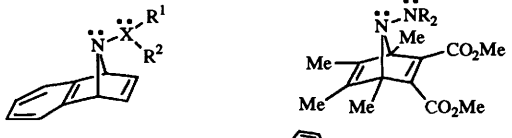
Dissociation of compound **1** (X = Ac) will be facilitated by the stability of both the aromatic product and the nitrene **4**, and could be further aided by the ability of carbon atoms *a* and *b* (see **1**) to sustain negative and positive charge, respectively. The importance of the last factor is indicated by the failure of the aziridine **1** (X = H)[1] to function as a nitrene source. Mechanisms for the exchange involving cleavage of one C–N bond in **1** (X = Ac) followed by reaction with the trap to give either a dipolar or a biradical intermediate are less likely. They are inconsistent with the stereospecificity of the reaction, the efficiency of both nucleophilic and electrophilic alkenes as traps and the evidence for a common intermediate in several fragmentation reactions.[2c] The *N*-acetoxyhydrazine **6** from lead tetraacetate oxidation of compound **2** may transfer the N–NPhth moeity to alkenes in the concerted manner depicted in **10** related to the Bartlett mechanism for peracid epoxidation of



10 **11a** **11b**

alkenes. A similar one step transfer of N–NPhth from **1** (X = Ac) is inconsistent with the test for a common intermediate involving the electronically and sterically diverse range of nitrene source listed earlier.[2c]

Following our original observations on compound **1** (X = Ac)[5] which followed photochemical generation of phthalimidonitrene from the sulfoximide **8**[6a] as well as aziridines carrying at least one conjugating group,[6b] several reports of dissociation reactions which probably lead to nitrenes have appeared. For easy dissociation the nitrene should be stabilised by an adjacent heteroatom *e.g.* as shown in **11a** ⟷ **11b**. As the importance of octet structure **11b** increases with increased donor character in the groups R attached to X, formation of the nitrene by dissociation becomes easier. Thus, phthalimidonitrene is produced from compound **12** (=**9**) at 105 °C but a lower

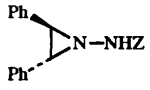


12 X = N, R^1, R^2 = Phth
13 X = N, R^1 = H, R^2 = C(O)OCH$_2$
14 X = S; R^1 = • •, R^2 = nitrophenyl

15

temperature (55 °C) suffices for fragmentation of compound **13** where the presence of only one carbonyl reduces the availability of the lone pair of electrons on X.[4,7] Similarly the sulfur stabilised nitrene from compound **14** is more easily extruded as the number of nitro groups on the phenyl ring is reduced.[8] The adducts **15** from *N*-aminopyrroles and dimethyl acetylenedicarboxylate extrude aminonitrenes[9] at ≈30 °C the ease of dissociation increasing in the order: N–NH$_2$ < N–NHMe < N–NMe$_2$. Indeed dialkylated species of this type can be stable in solution.[10]

Substituents on the carbon atoms of the aziridine ring also exert considerable influence on the ease of nitrene extrusion. Conjugating groups may stabilise the transition state of a concerted cheletropic elimination or alternatively stabilise one centre of a biradical or zwitterion intermediate. Such groups have been shown to labilise 1-phthalimidoaziridines to photochemical dissociation as mentioned above.[6b] In some cases *trans*-aziridines which permit greater conjugation of the substituents fragment more readily than their *cis*-counterparts *e.g.* *trans*-aziridines **16**[4,7] and **17**[11] decompose more rapidly than their *cis*-isomers.



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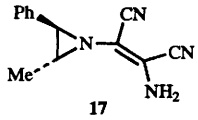

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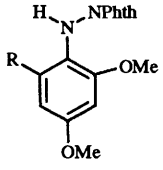
On the basis of available evidence it is not possible to distinguish between one and two step mechanisms for dissociation of compound **1** (X = Ac). Since the dissociation is reversible [eqn. (1)][1] and related additions are highly stereoselective, microscopic reversibility would suggest a one step cheletropic extrusion from **1** (X = Ac). Nevertheless some caution is urged by the work of Lahti[12] who proposes a two-step mechanism with a zwitterionic intermediate for the dissociation of *trans*-aziridine **16** (Z = H) and its *cis* isomer.

In summary compound **1** (X = Ac) is a readily prepared convenient source of phthalimidonitrene produced by mild thermolysis (80 °C) under conditions suitable for the preparation of products sensitive to acid, oxidation and UV light. The reaction of phthalimidonitrene with activated aromatic compounds described below is one example where the presence of acetic acid has a marked influence on reaction course.

Reaction of phthalimidonitrene with activated aromatic compounds

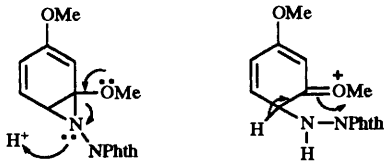
At a time when *N*-aminophthalimide and lead tetraacetate were believed to produce phthalimidonitrene **4** rather than the acetoxyhydrazine **6** these reactants were brought together in the presence of benzene and anisole but no isolable products derived from these aromatic compounds were observed. Use of the more reactive 1,3-dimethoxybenzene gave the product **18** of



18 R = H
19 R = OMe
20 R = CH$_2$CN

21

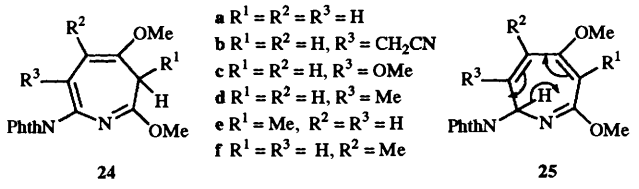
apparent C–H insertion by the nitrene. Use of a large excess of 1,3-dimethoxybenzene presumably reduced the tendency of the reactive product **18** to undergo further reaction with the electrophilic species generated, and **18** could be isolated in 37% yield based upon **2**. The arylhydrazine **18** could arise by attack upon *N*-acetoxyhydrazine **6** which acts as a 'source' of the nitrenium ion **21**, or alternatively by attack upon free **21** produced from **6**. Again **6** could transfer N–NPhth to 1,3-dimethoxybenzene in a concerted process depicted in **10** and akin to alkene epoxidation. The aziridinobenzene **22** might be expected to undergo aziridine ring cleavage, particularly in the presence of the acetic acid resulting from the lead tetraacetate oxidation. This would lead **22** (see arrows in structure) to **23** which would give the observed product **18** upon proton loss **23** (see arrows in structure). Indeed traces of acid are thought to be important in determining the product distribution in the reactions of nitrenes



22 23

with aromatic compounds.[13] Rapid ring opening of the type shown in the structure of **22** (arrows) could explain the apparent absence of the azepines that would be formed by electrocyclic ring opening of **22**. Oxidation of *N*-aminophthalimide in the presence of 1,3,5-trimethoxybenzene and 3,5-dimethoxyphenylacetonitrile likewise gave the benzene derivatives **19** and **20**, respectively and no isolable azepines.

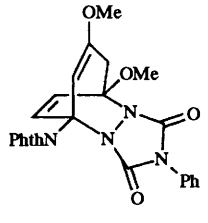
In contrast to these results the nitrene source **1** (X = Ac) and 1,3-dimethoxybenzene in refluxing benzene (16–18 h) gave mostly the 3*H*-azepine **24a**; the 400 MHz ^{1}H NMR spectrum of



a $R^1 = R^2 = R^3 = H$
b $R^1 = R^2 = H$, $R^3 = CH_2CN$
c $R^1 = R^2 = H$, $R^3 = OMe$
d $R^1 = R^2 = H$, $R^3 = Me$
e $R^1 = Me$, $R^2 = R^3 = H$
f $R^1 = R^3 = H$, $R^2 = Me$

24 25

the product mixture indicated a **24a**:**18** ratio of *ca.* 12. Similar products, **24b** and **24c**, respectively, were obtained from 3,5-dimethoxyphenylacetonitrile and 1,3,5-trimethoxybenzene. Differences from the behaviour of 1,3-dimethoxybenzene itself are the increased quantity of **20** relative to azepine **24b** (**24b**:**20**, 1.7:1) from the phenylacetonitrile and the isolation of an isomeric azepine (17% yield) in addition to **24c** (19% yield) from 1,3,5-trimethoxybenzene. The latter proved to be the 2*H*-azepine **25c** a logical precursor *via* the 1,5-hydrogen shift shown in **25** (arrows) of the 3*H*-azepine **24c**. Indeed **25c** became the major product (40% yield) when the nitrene source **1** (X = Ac) and 1,3,5-trimethoxybenzene were allowed to react together for a shorter time (5 h). Moreover several related 2*H*-azepines **25** could be isolated together with their 3*H*-isomers **24** using this shorter reaction time. In this way we prepared **25a**, **25c**, **25d**, **25e** and **25f**. The NMR spectra of the 3*H*-azepines **24** (Experimental section) provided good evidence for the proposed structures. Thus, the spectrum of **24a** showed the methylene protons as a singlet (δ 2.98) and the vinyl protons as doublets (J 6.5 Hz) at δ 6.06 and 5.45. In the spectrum of the derived phenyltriazoledione adduct **26** the methylene protons appear as an AB-system



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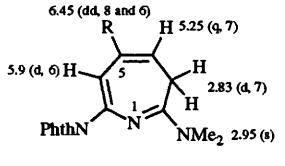
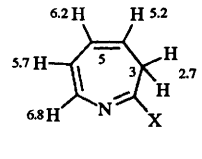
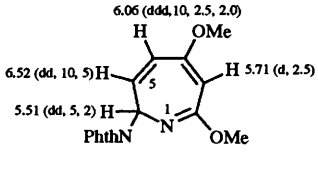


27 R = H
28 R = Me



29 X = NHPh



25a

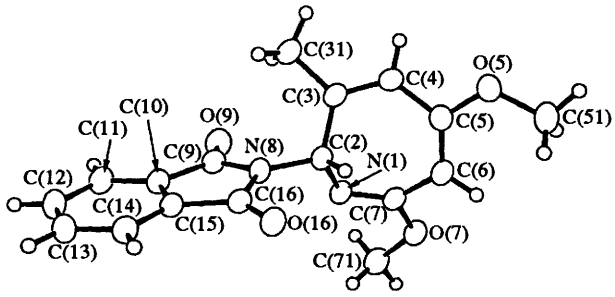


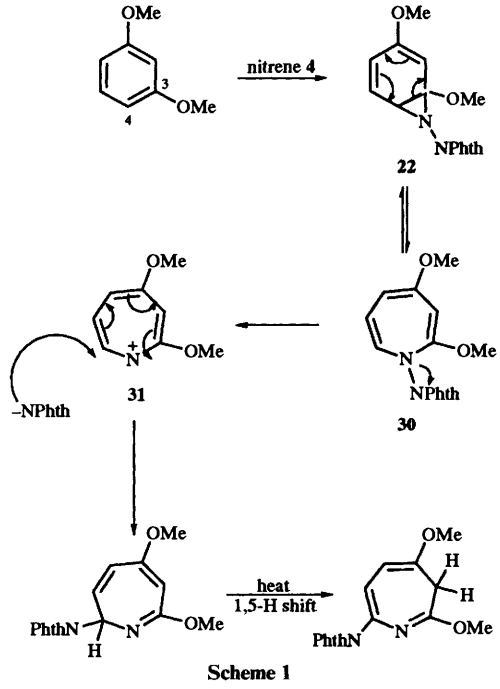
Fig. 1 Structure of compound **25d** as determined by X-ray crystallography. Ellipses for non-hydrogen atoms are at the 50% probability level whilst, in the interests of clarity, hydrogen atoms are drawn as small circles of arbitrary radius.

centred at δ 3.26 (J_{AB} 19 Hz) and the vinyl protons as doublets (J 10 Hz) at δ 6.94 and 6.16. Further ^{1}H NMR evidence was sought by preparation of methyl derivatives the spectra of which showed the appropriate features including *e.g.* the appearance of the C–Me resonance as a singlet in **24d** (absence of allylic coupling), and as a doublet (J_{vic} 7 Hz) in **24e**. Although no isolable product was obtained upon lead tetraacetate oxidation of **2** in the presence of *N*,*N*-dimethylaniline, the 3*H*-azepine **27** was obtained in a modest (14%) yield using the nitrene source **1** (X = Ac). The NMR spectrum of **27** is appended to structure **27** in the form δ value (multiplicity, J values) and clearly shows the presence of the $-CH_2-CH{=}CH-CH{=}C<$ structural fragment. In the homologue from *N*,*N*-4-trimethylaniline the 5-H resonance is replaced by a methyl signal as a br singlet at δ 1.95, the C-4 proton resonance is a triplet (J 7 Hz) and the 6-H resonance is a singlet. The δ and J values for the known 3*H*-azepine **29** and the related 2-methoxy derivative[14] are in good agreement with those of **27**; the shifts for **29** are appended to structure **29**. Like our 3*H*-azepines, the previously known compounds show equivalence of the methylene protons associated with rapid inversion between two boat like conformers and there is no discernable allylic coupling ($J_{3H,5H} \approx 0$).

Since 2*H*-azepines lacking special stabilising features such as annulation of a benzene ring are usually non-isolable our assignment of the 2*H*-azepine structures **25** to our products requires comment. The ^{1}H NMR spectrum of **25a** is appended to that structure in the form δ value (multiplicity, J Hz) and fully agrees with the assigned structure. Moreover derivatives with a methyl group replacing hydrogen at C-5 and C-6 were prepared and showed the expected changes in their spectra *e.g.* **25f** with a methyl at C-4 shows methyl resonance as a triplet due to approximately equal allylic and homoallylic coupling to 3-H and 2-H, respectively: other changes are detailed in the Experimental section.

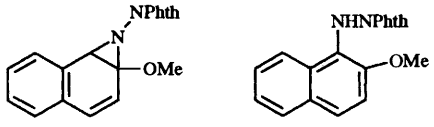
Conversion of the 2*H*-azepines into their 3*H*-isomers provides evidence of structure. Thus **25a** gives **24a** upon melting and **25c** is converted (albeit incompletely) into **24c** upon heating in boiling benzene (16 h). Finally the 2*H*-azepine structure was unequivocally established for **25d** by an X-ray crystal structure analysis shown in Fig. 1.

A likely mechanism for the formation of the 2*H*- and 3*H*-azepines is given in Scheme 1 for 1,3-dimethoxybenzene. Attack of the nitrene upon the more electron-rich C-3–C-4 bond of 1,3-dimethoxybenzene affords a benzofuro[2,3-*b*]azirine intermediate **22** which, in the absence of acid could undergo electrocyclic ring-opening to the 1*H*-azepine **30**. Heterolysis of the N–N bond in **30** could be driven by a degree of 8π electron antiaromaticity in 1*H*-azepines as well as by formation of the aromatic azatropylium cation **31** and the rather stable phthalimide anion. Recombination of these species at C-7 of the 2,4-dimethoxyazatropylium species **31** is probably dictated by the greater charge at this carbon than at any other atom present



Scheme 1

save the nitrogen. Hückel calculations give a charge of 0.3812 at C-7, 0.4289 at the nitrogen and 0.3570 at C-2. Finally 1,5-hydrogen shift converts the 2*H*- into 3*H*-azepines. In the presence of acids the benzofuro[2,3-*b*]azirine **22** might be expected to be diverted to the benzene derivative **18** (arrows in **22** and **23**; preceding page). Indeed the ratio of azepine **24a** to benzene **18** changed from 12:1 in favour of **24a** to 1.53:1 in favour of **18** upon carrying out the nitrene transfer in the presence of acetic acid; benzoic acid produced a similar effect. For 2,6-dimethoxytoluene the benzene:azepine ratio changes from 1:1 in the absence of acetic acid to 25:1 in its presence (see Experimental section). When valence tautomerism in the intermediate benzofuro[2,3-*b*]azirine is inhibited by benzannulation, as in **32**, derived from 2-methoxynaphthalene, only the



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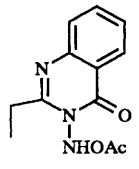

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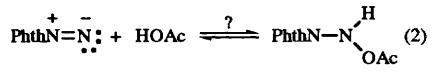
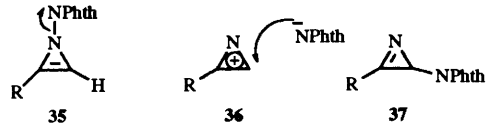
formal insertion product **33** is produced. Although the effect of added acetic acid was predicted on the mechanistic basis outlined above, a second explanation is possible. The nitrene **4** and acetic acid could combine to give the *N*-acetoxyhydrazine **6** which could then act as a source of the electrophilic nitrenium cation **21**. Although *N*-acetoxyaminoquinazolinone **34** fails to exchange either its amino proton or OAc group with CD_3CO_2D at −20 °C [2b] the occurrence of the equilibrium shown in eqn. (2) for acetoxyhydrazine **6** at 80 °C is possible, and certainly the capture of nitrene **4** by acetic acid is likely. Our further experiments will seek evidence for such reactions.



Finally we draw attention to the considerable analogy between the mechanism for azepine formation (Scheme 1) proposed here and the route proposed by Anderson *et al.*[15] for the formation of 2*H*-azirines upon oxidation of *N*-aminophthalimide in the presence of acetylenes; anti-aromatic 1*H*-azirines **35** are the expected intermediates which may undergo heterolysis of the N–N bond to an aromatic azacyclopropenyl cation **36**



35 36 37

and phthalimide anion. Recombination then gives the observed 2*H*-azirine products **37**.

Experimental

Mps were determined with a Kofler hot-stage apparatus and are uncorrected. Infrared spectra were recorded on a Philips PU 8706 infrared spectrophotometer, and referenced to a peak at 1601 cm^{-1} of polystyrene. ^1H NMR spectra were determined in $CDCl_3$, with tetramethylsilane as internal standard with a Varian A60A spectrometer (60 MHz) or a Bruker 90 Mz instrument. Coupling constants (*J*) are in Hz. Mass spectra were obtained on an A.E.I. MS902 instrument. Chromatography on silica refers to short-column chromatography over Kieselgel G60 (Merck).[16] Ether refers to diethyl ether and light petroleum (petroleum) to the fraction bp 60–80 °C.

1a-Acetyl-1-phthalimidoamino-1a,6b-dihydro-1*H*-benzofuro-[2,3-*b*]azirine 1 (X = Ac)

Finely ground *N*-aminophthalimide (1.25 g), dichloromethane (20 cm^3) and benzofuran (1.5 g) were cooled to 0–5 °C in an ice-bath, and lead tetraacetate (3.5 g; dried by pressing between filter papers) was added in small portions over 10–15 min with stirring. The product was diluted with water, and the organic layer was dried ($MgSO_4$) and evaporated under reduced pressure at room temperature. Trituration of the product with benzene, filtration of the cooled mixture, and washing the product with a little cold benzene gave compound **1** (X = Ac) as very pale yellow solid (1.75–2.2 g) mp 139–141 °C (decomp.). The analytical sample was prepared from benzene–petroleum using the minimum of heating and dried at 20 °C in high vacuum, mp 136–140 °C (decomp.) (Found: C, 67.3; H, 3.8; N, 8.85. $C_{18}H_{12}N_2O_4$ requires C, 67.5; H, 3.8; N, 8.75%); δ(60 MHz) 2.58 and 2.68 (relative intensity 3.5:1, 3 H, s, $COCH_3$ in invertomers), 5.08 and 5.32 (relative intensity 3.5:1, 1 H, s, benzylic H in invertomers) and 6.7–8.0 (8 H, m, ArH); ν_{max}(Nujol)/cm^{-1} 1598, 1618, 1720 and 1770.

Thermolysis of the benzofuro[2,3-*b*]azirine 1 (X = Ac)

The foregoing benzofuro[2,3-*b*]azirine (1.59 g) in benzene (30 cm^3) was boiled under reflux (18 h), and the product chromatographed on silica in ether–benzene (1:19) to give first 2-acetylbenzofuran (370 mg) followed by the *rearrangement product* **3** (X = Ac) (330 mg), mp, 167–170 °C (from benzene–petroleum) (Found: C, 67.55; H, 3.85; N, 8.55%); δ 2.45 (3 H, s), 6.26 (1 H, s), 6.7–8.15 (8 H, m, ArH); ν_{max}(Nujol)/cm^{-1}, 1592, 1614, 1681 and 1761. When treated with hydrogen in ethyl acetate (5 cm^3) over Adams catalyst (20 mg) for 18 h the rearrangement product **3** (X = Ac) gave a dihydro derivative mp 170–172 °C (Found: C, 66.9; H, 4.35; N, 8.95. $C_{18}H_{14}N_2O_4$ requires C, 67.1; H, 4.4; N, 8.7%); δ 1.41 (3 H, d, *J* 7), 3.2 (1 H,

br, OH), 4.77 (1 H, br m, C*H*OH), 5.86 (1 H, s, benzylic methine) and 6.7–8.2 (8 H, m, ArH); ν_{max}(Nujol)/cm^{-1} 3400 and 1740.

Thermolysis of benzofuro[2,3-*b*]azirine 1 (X = Ac) in the presence of traps

The nitrene precursor **1** (X = Ac), the trap and benzene in the stated quantities were boiled under reflux for the stated time. After evaporation on a rotary evaporator at *ca.* 45 °C the product was examined by TLC and NMR spectroscopy and pure products isolated by short-column chromatography on silica with the solvent system stated.

Cyclohexene–phthalimidonitrene adduct 5. Cyclohexene (2 cm^3, 9.7 mmol), benzofuro[2,3-*b*]azirine **1** (X = Ac) (400 mg, 1.25 mmol) and benzene (10 cm^3) were refluxed (16 h). Chromatography with benzene–ether (13:1) gave the cyclohexene–phthalimidonitrene adduct **5** (135 mg, 45%), mp 132–134 °C (from benzene–petroleum) identical with an authentic sample [2a] (NMR spectrum).

Indene–phthalimidonitrene adduct. Indene (0.5 g, 4.3 mmol), benzofuro[2,3-*b*]azirine **1** (X = Ac) (0.2 g, 0.62 mmol) and benzene (5 cm^3) were boiled under reflux (18 h). The reaction mixture was concentrated to one third of its volume and then a small seed of the indene–phthalimidonitrene adduct [2a] was introduced whereupon the indene adduct crystallised in nearly pure form (90 mg, 52%). This adduct decomposed upon attempted chromatography on silica with benzene–ether (19:1).

Reaction of benzofuro[2,3-*b*]azirine with *trans*-stilbene. *trans*-Stilbene (0.5 g, 5.5 mmol), benzofuro[2,3-*b*]azirine **1** (X = Ac) (100 mg, 0.31 mmol) and benzene (7 cm^3) were refluxed (16 h). Chromatography with benzene–ether (39:1) gave the known [2a] *trans* 1-phthalimido-2,3-diphenylaziridine (25 mg, 24%).

***cis*-Stilbene–phthalimidonitrene adduct.** *cis*-Stilbene (0.4 g, 2.2 mmol), benzofuro[2,3-*b*]azirine **1** (X = Ac) (320 mg, 1.0 mmol) and benzene (10 cm^3) were boiled under reflux (5 h). The 60 MHz ^{1}H NMR spectrum of the crude product indicated the absence of the *trans*-stilbene adduct. Chromatography with benzene–ether (39:1) gave the *cis*-stilbene–phthalimidonitrene adduct (47.5 mg, 14%) identical with authentic material prepared by the method of Anderson *et al.* [2a]

Methyl crotonate–phthalimidonitrene adduct. Methyl crotonate (1 cm^3, 9.4 mmol), the benzofuro[2,3-*b*]azirine **1** (X = Ac) (200 mg, 0.625 mmol) and benzene (5 cm^3) were refluxed (16 h). Chromatography with benzene–ether (19:1) gave the methyl crotonate–phthalimidonitrene adduct (52 mg, 32%) identical to a sample prepared by the method of Anderson *et al.* [2a]

Methyl methacrylate–phthalimidonitrene adduct. Methyl methacrylate (1.2 cm^3, 9.4 mmol), the benzofuro[2,3-*b*]azirine **1** (X = Ac) (200 mg, 0.625 mmol) and benzene (5 cm^3) were refluxed (16 h). Chromatography with benzene–ether (19:1) gave the known methyl methacrylate–phthalimidonitrene adduct [2a] (70 mg, 56%).

Dimethyl sulfoxide–phthalimidonitrene adduct. Dimethyl sulfoxide (2 cm^3, 28.2 mmol), the benzofuro[2,3-*b*]azirine **1** (X = Ac) (200 mg, 0.625 mmol), and benzene (5 cm^3) were refluxed (16 h). The product was diluted with CH_2Cl_2 and washed with water, dried ($MgSO_4$), and evaporated. The crude product in a little benzene deposited the dimethyl sulfoxide–phthalimidonitrene adduct **8** (60 mg, 41%) identical with an authentic sample prepared by the method of Anderson *et al.* [2a]

2-methoxy-*N*-phthalimido-1-naphthylamine 33. 2-Methoxynaphthalene (1 g, 6.3 mmol), the benzofuro[2,3-*b*]azirine **1** (X = Ac) (200 mg, 0.625 mmol) and benzene (10 cm^3) were boiled under reflux (16 h). Chromatography with benzene–ether (17:3) gave 2-*methoxy*-N-*phthalimido*-1-*naphthylamine* **33** (70 mg, 35%), mp 138–141 °C (from ethanol) (Found: C, 71.5; H, 4.35; N, 8.55. $C_{19}H_{14}N_2O_3$ requires C, 71.7; H, 4.4; N, 8.8%); δ($CDCl_3$; 60 MHz) 4.06 (3 H, s), 7.15–8.2 (10 H, m) and 7.03 (1 H, s, exch. D_2O, NH).

Reaction of benzofuro[2,3-*b*]azirine 1 with 1,3-dimethoxybenzene. (*a*) 1,3-Dimethoxybenzene (6 cm^3, 43.47 mmol), the benzofuro[2,3-*b*]azirine **1** (X = Ac) (630 mg, 1.97 mmol) and benzene (24 cm^3) were boiled under reflux (18 h). Chromatography with benzene–ether (9:1) gave 2,4-*dimethoxy*-7-*phthalimido*-3H-*azepine* **24a** (173 mg, 29.5%), mp 181–183 °C (from methanol) (Found: C, 64.45; H, 4.75; N, 9.55. $C_{16}H_{14}O_4N_2$ requires C, 64.4; H, 4.7; N, 9.4%); δ(60 MHz; $CDCl_3$) 2.98 (2 H, s), 3.68 (3 H, s), 3.70 (3 H, s), 5.45 (1 H, d, *J* 7), 6.06 (1 H, d, *J* 7) and 7.56–8.10 (4 H, m, ArH); ν_{max}(Nujol)/cm^{-1} 1390, 1630, 1720 and 1772.

This azepine **24a** (30 mg) and 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (30 mg) in benzene (1 cm^3) were kept at 20 °C (16 h) with exclusion of light. The *adduct* **26** (25 mg) that separated was filtered washed with a little cold benzene and recrystallised from CH_2Cl_2–MeOH with minimal heating (as the adduct dissociates readily), mp 180–182 °C (decomp.) (Found: C, 61.0; H, 4.0; N, 14.7. $C_{24}H_{19}O_6N_5$ requires C, 60.9; H, 4.05; N, 14.8%); δ (60 MHz; $CDCl_3$) 3.0 (1 H, d, *J* 18), 3.54 (1 H, d, *J* 18), 3.60 (3 H, s), 3.80 (3 H, s), 6.18 (1 H, d, *J* 10), 7.45 (5 H, br s) and 7.55–8.1 (4 H, m).

(*b*) 1,3-Dimethoxybenzene (1 cm^3, 7.24 mmol), the benzofuro[2,3-*b*]azirine **1** (X = Ac) (300 mg, 0.94 mmol) and benzene (5 cm^3) were refluxed (5 h). Chromatography of the product with benzene–ether (19:1) gave 5,7-*dimethoxy*-2-*phthalimido*-2H-*azepine* **25a** (20 mg, 18%), mp 165–168 °C (from $CHCl_3$–MeOH, dried 1 h 70 °C, then 24 h at 20 °C) (Found: C, 64.3; H, 4.5; N, 9.6%); δ(60 MHz; $CDCl_3$) 3.59 (3 H, s), 3.70 (3 H, s), 5.51 (1 H, dd, *J* 5 and 2, 2-H), 5.71 (1 H, d, *J* 2.5, 6-H), 6.06 (1 H, ddd, *J* 10, 2.5 and 2, 4-H), 6.52 (1 H, dd, *J* 10 and 5, 3-H) and 7.6–8.1 (4 H, m); ν_{max}(Nujol)/cm^{-1} 1585, 1615, 1632, 1652, 1710, 1725, 1772 and 1779. After heating in boiling benzene (48 h) this product gave the 3*H*-azepine prepared in (*a*) above.

(*c*) 1,3-Dimethoxybenzene (2 cm^3, 14.5 mmol), the benzofuro[2,3-*b*]azirine **1** (X = Ac) (200 mg, 0.625 mmol), benzene (8 cm^3) and benzoic acid (20 mg, 0.164 mmol) were refluxed (16 h). Chromatography with benzene–ether (9:1) gave 2,4-*dimethoxy*-N-*phthalimidoaniline* **18** (26 mg, 14.8%), mp 180–181 °C (from EtOH) [Found: C, 64.4; H, 4.55; N, 9.25; M (osmometer) 291. $C_{16}H_{14}N_2O_4$ requires *M*, 298]; δ(60 MHz; $CDCl_3$) 3.9 (3 H, s), 3.9 (3 H, s), 6.3 (1 H, dd, *J* 8.5 and 2.5, 5-H), 6.41–6.7 (2 H, m, 3-H and 6-H) and 7.40–8.0 (4 H, m); ν_{max}(Nujol)/cm^{-1} 1601, 1619, 1715, 1778 and 3310; the 400 MHz ^{1}H NMR spectrum of the total product of a similar reaction run in the presence of acetic acid indicated an aromatic: 3*H*-azepine ratio of 1.53:1. In the absence of acetic acid this ratio was 0.083:1.

Reaction of benzofuro[2,3-*b*]azirine 1 with 1,3,5-trimethoxybenzene. (*a*) 1,3,5-Trimethoxybenzene (2 g, 11.9 mmol), the benzofuro[2,3-*b*]azirine **1** (X = Ac) (300 mg, 0.94 mmol) and benzene (8 cm^3) were refluxed (17 h). Chromatography of the product with benzene–ether (9:1) gave first 3,5,7-*trimethoxy*-2-*phthalimido*-2H-*azepine* **25c** (54 mg, 17%), mp 140–142 °C (from MeOH) (Found: C, 62.25; H, 5.0; N, 8.75. $C_{17}H_{16}N_2O_5$ requires C, 62.2; H, 4.9; N, 8.5%); δ(60 MHz; $CDCl_3$) 3.59 (3 H, s), 3.66 (3 H, s), 3.70 (3 H, s), 5.15 (1 H, dd, *J* 2.5 and 1, 4-H), 5.5 (1 H, d, *J* 2.5, 2-H), 5.78 (1 H, d, *J* 1, 6-H) and 7.6–8.0 (4 H, m); ν_{max}(Nujol)/cm^{-1} 1560, 1630, 1715 and 1779. Continued elution of the column gave 2,4,6-*trimethoxy*-7-*phthalimido*-3H-*azepine* **24c** (57 mg, 18.6%), mp 179–180 °C (from ethanol) (Found: C, 62.1; H, 4.85; N, 8.5%); δ(60 MHz; $CDCl_3$) 3.0 (2 H, s), 3.52 (3 H, s), 3.68 (6 H, s), 5.44 (1 H, s) and 7.58–8.0 (4 H, m); ν_{max}(Nujol)/cm^{-1} 1575, 1625, 1718, 1755 and 1780.

(*b*) 1,3,5-Trimethoxybenzene (5 g, 29.76 mmol), the benzofuro[2,3-*b*]azirine **1** (X = Ac) (1.5 g, 4.69 mmol) and benzene (25 cm^3) were refluxed (5 h). Chromatography of the product with benzene then benzene–ether (9:1) gave 3,5,7-trimethoxy-2-

phthalimido-2*H*-azepine **25c** (620 mg, 40.2%) identical with the sample prepared in (*a*) above. With 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (44 mg) in benzene (5 cm^3) this 2*H*-azepine gave after 18 h an *adduct* (120 mg) mp 161–163 °C (from benzene–petroleum) (Found: 60.1; H, 4.0; N, 14.15. $C_{17}H_{16}O_5N_2$ requires C, 59.6; H, 4.2; N, 13.9%); δ(60 MHz; $CDCl_3$) 3.57 (3 H, s), 3.64 (3 H, s), 3.82 (3 H, s), 4.82 (1 H, d, *J* 2), 5.13 (1 H, d, *J* 2), 6.30 (1 H, s) and 7.20–8.1 (9 H, m); ν_{max}(Nujol)/cm^{-1} 1675, 1710, 1718, 1740 and 1780.

Reaction of benzofuro[2,3-*b*]azirine 1 with 3,5-dimethoxyphenylacetonitrile. 3,5-Dimethoxyphenylacetonitrile (2 g, 12.26 mmol), the benzofuro[2,3-*b*]azirine **1** (X = Ac) (300 mg, 0.94 mmol) and benzene (8 cm^3) were refluxed (16 h). Chromatography of the product with benzene–ether (9:1) gave first 6-*cyanomethyl*-2,4-*dimethoxy*-7-*phthalimido*-3H-*azepine* **24b** (70 mg, 22.4%), mp 231–232 °C (from $CHCl_3$–EtOH) (Found: C, 64.1; H, 4.5; N, 12.5. $C_{18}H_{15}N_3O_4$ requires C, 64.1; H, 4.5; N, 12.5%); δ(60 MHz; $CDCl_3$) 3.04 (2 H, s), 3.36 (2 H, s), 3.70 (3 H, s), 3.72 (3 H, s), 5.47 (1 H, s) and 7.65–8.1 (4 H, m); ν_{max}(Nujol)/cm^{-1} 1565, 1618, 1628, 1704, 1712, 1758 and 1778. Continued elution of the column gave 2-*cyanomethyl*-4,6-*dimethoxy*-N-*phthalimidoaniline* **20** (40 mg, 12.8%), mp 175–176 °C (from methanol) (Found: C, 64.0; H, 4.5; N, 12.1%); δ(60 MHz; $CDCl_3$) 3.76 (3 H, s, OMe), 3.89 (5 H, s, OMe and CH_2CN), 6.48 [3 H, s, ArH and NH (exch. D_2O)] and 7.54–7.8 (4 H, m); ν_{max}(Nujol)/cm^{-1} 1492, 1500, 1604, 1615, 1715, 1750, 1752 and 3305.

Reaction of benzofuro[2,3-*b*]azirine 1 with 3,5-dimethoxytoluene. (*a*) 3,5-Dimethoxytoluene (2 g, 11.9 mmol), the benzofuro[2,3,-*b*]azirine **1** (X = Ac) (300 mg, 0.94 mmol) and benzene (8 cm^3) were refluxed (16 h). Chromatography of the product with benzene–ether (9:1) gave 2,4-*dimethoxy*-6-*methyl*-7-*phthalimido*-3H-*azepine* **24d** (80 mg, 27.4%), mp 201–203 °C (from MeOH) (Found: C, 65.4; H, 5.15; N, 9.1. $C_{17}H_{16}N_2O_4$ requires C, 65.4; H, 5.2; N, 9.0%); δ(60 MHz; $CDCl_3$) 1.86 (3 H, s), 2.95 (2 H, s), 3.64 (3 H, s), 3.65 (3 H, s), 5.29 (1 H, s) and 7.62–8.0 (4 H, m); ν_{max}(Nujol)/cm^{-1} 1572, 1628, 1703, 1715, 1756 and 1775.

(*b*) 3,5-Dimethoxytoluene (1 cm^3, 13.16 mmol), the benzofuro[2,3-*b*]azirine **1** (X = Ac) (330 mg, 1.03 mmol) and benzene (5 cm^3) were boiled under reflux (5 h). Chromatography of the product with benzene–ether (19:1) gave first 5,7-*dimethoxy*-3-*methyl*-2-*phthalimido*-2H-*azepine* **25d** (50 mg, 15.5%), mp 155–160 °C with resolidification and remelting at 198–200 °C (from methanol) (Found: C, 65.4; H, 5.15; N, 8.8%); δ(60 MHz; $CDCl_3$) 2.02 (3 H, br s, $w_{\frac{1}{2}} \approx 3.5$ Hz), 3.67 (3 H, s), 3.72 (3 H, s), 5.64 (1 H, d, *J* 2.5), 5.74 (1 H, br s, $w_{\frac{1}{2}} \approx 4$ Hz, 6-H?), 5.93 (1 H, br, $w_{\frac{1}{2}} \approx 7$ Hz, H-4?) and 7.65–8.1 (4 H, m); ν_{max}(Nujol)/cm^{-1} 1575, 1614, 1631, 1650, 1695, 1711, 1725, 1773 and 1779.

Continued elution of the column gave the 3*H*-azepine prepared in (*a*) above (68 mg, 21.2%).

Reaction of benzofuro[2,3-*b*]azirine 1 with 2,4-dimethoxytoluene. 2,4-Dimethoxytoluene (1 g, 6.58 mmol), the benzofuro[2,3-*b*]azirine **1** (X = Ac) (560 mg, 1.75 mmol) and benzene (8 cm^3) were refluxed (5 h). Chromatography of the product with benzene–ether (19:1) gave the major product 5,7-*dimethoxy*-4-*methyl*-2-*phthalimido*-2H-*azepine* **25f** (55 mg, 10.1%), mp 154–156 °C (from MeOH) (Found: C, 65.8; H, 5.35; N, 9.2%); δ(60 MHz; $CDCl_3$) 1.88 (3 H, t, *J* ≈ 1), 3.61 (3 H, s), 3.74 (3 H, s), 5.46 (1 H, dq, *J* 6 and ≈1), 5.68 (1 H, s), 6.25 (1 H, dq, *J* 6 and ≈1) and 7.6–8.1 (4 H, m).

Reaction of benzofuro[2,3-*b*]azirine 1 with 2,6-dimethoxytoluene. (*a*) 2,6-Dimethoxytoluene (1 g, 6.58 mmol), the benzofuro[2,3-*b*]azirine **1** (X = Ac) (330 mg, 1.03 mmol) and benzene (5 cm^3) were refluxed (5 h). Chromatography of the product with benzene–ether (19:1) gave first 2,4-*dimethoxy*-3-*methyl*-7-*phthalimido*-3H-*azepine* **24e** (35 mg, 10.85%) mp 183–185 °C (from MeOH) (Found: C, 65.2; H, 5.25; N, 9.0%); δ(60 MHz; $CDCl_3$) 1.36 (3 H, d, *J* 7.5), 2.8 (1 H, q, *J* 7.5), 3.66 (3 H, s), 3.69 (3 H, s), 5.46 (1 H, br d, *J* 7.5, 5-H), 6.03 (1 H, d, *J* 7.5, 4-H) and 7.6–8.1 (4 H, m).

Continued elution gave a compound tentatively identified as 2,4-*dimethoxy*-3-*methyl*-5-*phthalimido*-3H-*azepine* (15 mg, 4.65%), mp 197–199 °C (from MeOH) (Found: C, 65.1; H, 4.9; N, 8.65%); δ(90 MHz; $CDCl_3$) 1.55 (3 H, d, *J* 7), 3.60 (3 H, s), 3.70 (3 H, s), 5.4 (1 H, d, *J* 7), 6.89 (1 H, d, *J* 7) and 7.7–8.0 (4 H, m); the resonance for the proton at C-3 is partly concealed by the strong methoxy resonances at δ 3.6–3.7.

Continued elution of the column gave 2,4-*dimethoxy*-3-*methyl*-N-*phthalimidoaniline* (50 mg, 15.5%), mp 168–170 °C (from MeOH) (Found: C, 65.65; H, 4.95; N, 9.15%); δ(60 MHz; $CDCl_3$) 2.19 (3 H, s), 3.75 (3 H, s), 3.93 (3 H, s), 6.53 (2 H, apparent s), 6.63 (1 H, exch. D_2O, NH) and 7.68–8.1 (4 H, m).

The ^1H NMR spectrum of the crude product from this reaction showed the isolated azepines were the only azepines present. The product mixture was unchanged after heating in boiling benzene (18 h) (^1H NMR spectrum).

(*b*) 2,6-Dimethoxytoluene (1.5 g, 9.87 mmol), the benzofuro[2,3-*b*]azirine **1** (X = Ac) (320 mg, 1 mmol), benzene (5 cm^3) and acetic acid (120 mg, 2 mmol) were refluxed (16 h). The ^1H NMR spectrum of the crude product indicated the absence of the foregoing 5-phthalimidoazepine and the presence of the 7-phthalimido-3*H*-azepine and the *N*-phthalimidoaniline in a ratio of 1:2.5.

Reaction of benzofuro[2,3-*b*]azirine 1 with *N*,*N*-dimethylaniline. *N*,*N*-Dimethylaniline (2 cm^3, 15.8 mmol), the benzofuro[2,3-*b*]azirine **1** (X = Ac) (100 mg, 0.31 mmol) and benzene (10 cm^3) were refluxed (14 h). Chromatography of the product with ether–benzene (2:3) gave 2-*dimethylamino*-7-*phthalimido*-3H-*azepine* **27** (12 mg, 13.8%) mp 144–145 °C (from benzene–petroleum) (Found: C, 68.1; H, 5.3; N, 15.1. $C_{16}H_{15}N_3O_2$ requires C, 68.3; H, 5.4; N, 14.9%); δ(60 MHz; $CDCl_3$) 2.86 (2 H, d, *J* 7.5, 3-H), 5.26 (1 H, q, *J* 7.5, 4-H), 5.92 (1 H, *J* 5.5, 6-H), 6.47 (1 H, dd, *J* 7.5 and 5.5, 5-H) and 7.1–8.0 (4 H, m).

Reaction of benzofuro[2,3-*b*]azirine 1 with 4-dimethylaminotoluene. 4-Dimethylaminotoluene (3 g, 22.2 mmol), the benzofuro[2,3-*b*]azirine **1** (X = Ac) (660 mg, 2.06 mmol) and benzene (8 cm^3) were refluxed (16 h). Chromatography of the product with benzene–ether (3:2) gave 2-*dimethylamino*-5-*methyl*-7-*phthalimido*-3H-*azepine* **28** (75 mg, 12.34%), mp 188–191 °C (from ethanol) Found: C, 68.85; H, 6.0; N, 14.4. $C_{17}H_{17}N_3O_2$ requires C, 69.1; H, 5.8; N, 14.2%); δ(60 MHz; $CDCl_3$) 1.98 (3 H, br s, $w_{\frac{1}{2}} \approx 3$ Hz), 2.80 (2 H, br d, *J* 7.5), 2.99 (6 H, s), 5.08 (1 H, br t, *J* 7.5), 5.85 (1 H, s) and 7.6–8.0 (4 H, m); ν_{max}(Nujol)/cm^{-1} 1536, 1573, 1615, 1705, 1758 and 1776.

Oxidation of *N*-aminophthalimide in the presence of 1,3-dimethoxybenzene derivatives

(*a*) Lead tetraacetate (365 mg, dried by pressing between filter papers) was added portionwise over 10–15 min to a stirred, cold (ice-bath) mixture of *N*-aminophthalimide (125 mg, 0.77 mmol) in dichloromethane (8 cm^3) containing 1,3-dimethoxybenzene (2 cm^3, 14.5 mmol). The reaction mixture was diluted with CH_2Cl_2, washed with water, dried ($MgSO_4$) and then evaporated. The residue was chromatographed with benzene–diethylether (9:1). This gave crude substitution product (85 mg, 37%) further purified by crystallisation from ethanol and identical (IR spectrum) with the product **18** prepared as above. No evidence from TLC or ^1H NMR (60 MHz) was obtained for azepine products in the products of either this reaction or similar reactions performed at 80 °C, or in the presence of tetracyanoethene.

(*b*) Lead tetraacetate (365 mg), *N*-aminophthalimide (125 mg) and 1,3,5-trimethoxybenzene (2 g) were allowed to react as in the foregoing experiment and after a similar work-up the crude product was chromatographed with benzene–diethylether

(4:1) to give 2,4,6-*trimethoxy*-N-*phthalimidoaniline* **22** (130 mg, 51.4%), mp 145–147 °C (from MeOH) (Found: C, 62.2; H, 4.95; N, 8.75. $C_{17}H_{16}N_2O_5$ requires C, 62.2; H, 4.9; N, 8.5%); δ(60 MHz; $CDCl_3$) 3.76 (6 H, s), 3.78 (3 H, s), 6.16 (2 H, s), 6.5 (1 H, s, NH) and 7.58–8.0 (4 H, m); ν_{max}(Nujol)/cm^{-1} 1604, 1690, 1718, 1730, 1759, 1780 and 3340.

(*c*)*N*-Aminophthalimide (125 mg), lead tetraacetate (365 mg), and 2,6-dimethoxytoluene were allowed to react together in CH_2Cl_2 (10 cm^3) as in the preceding experiments. Following similar aqueous work-up the product was chromatographed with benzene–ether (19:1) or merely recrystallised from ethanol to give 2,4-dimethoxy-3-methyl-*N*-phthalimidoaniline (50 mg, 62%) identical with the sample prepared above. TLC and ^{1}H NMR failed to reveal any other products in the crude reaction mixture.

Crystal data for compound 25d

$C_{17}H_{16}N_2O_4$, $M = 312.32$, triclinic, $a = 7.6958(6)$, $b = 8.2095(7)$, $c = 12.3022(14)$ Å, $\alpha = 89.088(6)$, $\beta = 79.045(10)$, $\gamma = 79.835(5)°$, $V = 750.97(12)$ Å^3 [by least squares refinement of 2θ values of 40 reflections ($70.0° < 2\theta < 80.0°$, $\lambda = 1.5418$ Å) scanned either side of the beam stop to eliminate systematic errors], T/K 173, space group $P\bar{1}$ (no. 2), $Z = 2$, $D_x = 1.38$ g cm^{-3}, $F(000) = 328$. Colourless prism, crystal used had approximate dimensions of 0.51 × 0.27 × 0.17 mm.

Data collection and processing. Stoe STADI4 diffractometer, ω/θ mode with ω scan width of 1.05 + α-doublet splitting, scan speeds 1.0–8.0 deg min^{-1}, graphite monochromated Cu-Kα radiation; 2432 unique reflections measured ($4.0 < 2\theta < 130.0°$, $\pm h \pm k + l$); L_p correction and an empirical absorption correction (*via* ψ-scans). Three intensity control reflections measured every hour of exposure time indicated no significant crystal decay.

Structure analysis and refinement. Direct methods (for all non-hydrogen atoms),[17] full-matrix least squares refinement[18] (based on F_o^2) using all reflections with all non-hydrogen atoms anisotropic, hydrogen atoms constrained to idealised positions with fixed isotropic U (Å^2) values nU_{eq} of the parent non-hydrogen atom [$n = 1.5$ for methyl and 1.2 for all others]. Extinction correction [$F_c' = kF_c(1 + 0.001xF_c^2\lambda^3)^{-\frac{1}{4}}$, $x = 0.0103(13)$]; $R_1(=\Sigma||F_o| - |F_c||/\Sigma|F_o|) = 0.0405$, $wR_2\{= (\Sigma[w(F_o - F_c^2)^2]/\Sigma[wF_o^4])^{\frac{1}{2}}\} = 0.1291$ $\{w^{-1} = [\sigma^2(F_o^2) + (0.0675P)^2 + 0.2959\ P]$ where $P = (F_o^2 + 2F_c^2)/3\}$ for 212 parameters; R_1 calculated with 2130 data with $I > 2.0\sigma(I)$, wR_2 calculated using all reflections. A flat final difference synthesis (ρ_{min}, $\rho_{max} = -0.178$ and 0.211 e Å^3, respectively) contained no features of chemical significance. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.‡

‡ For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1995, Issue 1.

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Paper 4/06754A
Received 4*th November* 1994
Accepted 5*th January* 1995