Intermolecular Thermal Reaction of Arylnitrenes with Furans

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4-Methoxy-, 4-chloro-, and 4-nitro-phenylnitrenes have been thermally generated by decomposition of the corresponding aryl azides in the presence of furan and a series of 2-substituted and 2,5-disubstituted furans. 4-Nitrophenylnitrene has been shown to be capable of undergoing electrophilic addition to the furan ring both at the α- and β-position, whereas only evidence of α-attack has been provided by 4-chlorophenylnitrene. On the other hand, no evidence of electrophilic attack has been obtained with 4-methoxyphenylnitrene, which affords only products ascribable to the triplet nitrene. The formation of a number of products ultimately resulting from nitrene attack at the α-position of the furan ring followed by a ring-opening process and the general occurrence of 1-(4-nitrophenyl)- and 1-(4-chlorophenyl)-1,2,3-triazole from thermolysis of 4-nitro- or 4-chloro-phenyl azide in the presence of the furans examined is discussed.

In contrast to the reactions of nitrenes with aromatic compounds,[1] the corresponding reactions with furans have been little explored. Thermolysis of ethyl azidoformate in the presence of furan has been reported to give the pyrrolone (1) or its conjugate isomer (2).[2]

Generation of phthalimidonitrene in 2,5-dimethylfuran has been shown to yield the 2-phthaloylhydrazone (3b; X = Me) of *cis*-hex-3-ene-2,5-dione.[3] These reactions are believed to proceed *via* nitrene 1,2-addition to the diene system to give an intermediate aziridine (4a,b), which would then undergo ring opening ultimately leading to the pyrrolone (1) or (2) or the hydrazone (3b; X = Me), respectively (Scheme 1). Similar
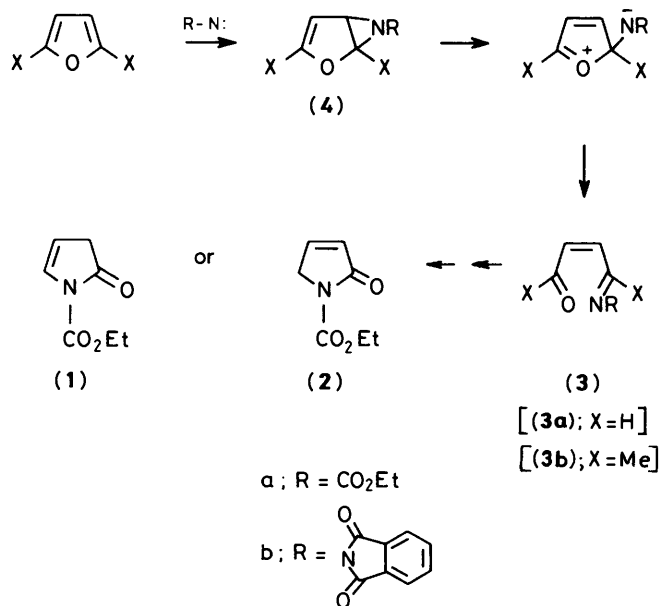

Scheme 1.

results have been obtained from reaction of phthalimidonitrene with 2-substituted furans.[3]

Only a few intramolecular reactions of arylnitrenes with furans have been so far reported. The nitrenes generated by reduction of 2-(2-nitrophenyl)furan with triethyl phosphite or by thermolysis of 2-(2-azidophenyl)furan exhibit insertion into

the adjacent furan β-hydrogen to give 4*H*-furo[3,2-*b*]indole,[4a] presumably by a mechanism analogous to that involved in the formation of carbazole from 2-nitrenobiphenyl.[1,4b] On the other hand, photolysis or pyrolysis of methyl 5-[2-(*o*-azidophenyl)ethyl]furan-2-carboxylates (5) surprisingly affords the pyrroloquinolines (6) in addition to the 2-(2-furyl)indoles.

The compounds (6) are assumed to result from intramolecular addition of a nitrene intermediate to the 4,5-double bond of the furan ring, followed by ring-opening, ring closure to a pyrrole, and unusual oxygen elimination.[5]
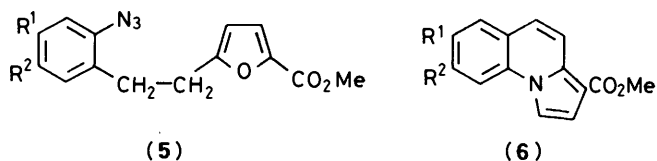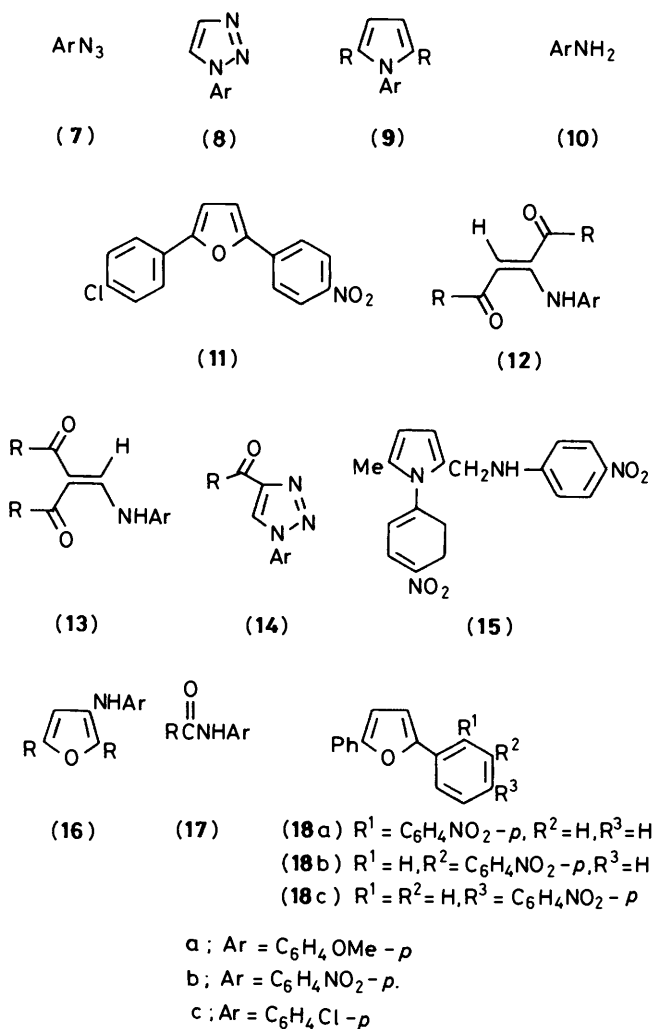

In this paper we report our results from a study of the thermal decomposition of 4-methoxy-, 4-nitro-, and 4-chloro-phenyl azides (7a—c) in the presence of furan, monosubstituted furans including the 2-methyl and 2-(4-chlorophenyl) derivatives, or 2,5-disubstituted furans including the 2,5-dimethyl and 2,5-diphenyl derivatives. This study was undertaken with the aim of exploring the intermolecular reactivity of thermally generated arylnitrenes towards furans.

Results and Discussion

The thermal decomposition of the aryl azides (7a—c) (0.2M in the appropriate oxygen-free furan) was generally carried out at 110 °C for 5 days. Control experiments showed that these reactions, when performed under more drastic thermal conditions (140—150 °C), exhibited similar chemical trends, but generally led to the formation of tars.

Thermolysis of 4-methoxyphenylazide (7a) in furan at 110 °C gave, after chromatography, 4-methoxyaniline (10a) (27%), 2,7-dimethoxyphenazine (4%), and 4,4'-dimethoxyazobenzene (5%) as the only identifiable products, attributable to hydrogen abstraction and coupling of triplet 4-methoxyphenylnitrene.[6] Similar results were obtained in the presence of 2,5-dimethylfuran.

No evidence of nitrene attack on the furan ring could be obtained. However, in furan 4-nitro- (7b) and 4-chloro-phenyl

ArN$_3$ (7)

(8)

(9)

ArNH$_2$ (10)

(11)

(12)

(13)

(14)

(15)

(16)

(17)

(18 a)   R^1 = C$_6$H$_4$NO$_2$-p, R^2=H,R^3=H

(18 b)   R^1 = H,R^2= C$_6$H$_4$NO$_2$-p,R^3=H

(18 c)   R^1 = R^2= H,R^3 = C$_6$H$_4$NO$_2$ - p

a ; Ar = C$_6$H$_4$OMe - p

b ; Ar = C$_6$H$_4$NO$_2$-p.

c ; Ar = C$_6$H$_4$Cl -p

azide (7c) gave very complex reaction mixtures, from which the triazole (8b) (24%) or the triazole (8c) (8%) together with 1-(4-chlorophenyl)pyrrole (9c; R = H) (6%), could be isolated respectively together with unknown products and tarry material (Scheme 2). The triazoles (8b) (15%) and (8c) (5%) were

(7b,c)————
i ————→ (8b,c) + (9c; R = H)
ii ————→ (8b,c) + (10b,c)
iii (7b) ————→ (8b) + (10b) + (11)
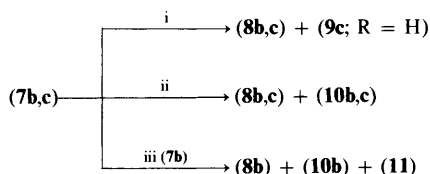
Scheme 2. *Reagents and conditions:* i, furan, 110 °C, 5 days (7b) or 140 °C, 20 h (7c); ii, 2-methylfuran, 110 °C, 5 days; iii, 2-(4-chloro-phenyl)furan, 110 °C, 4 days

also obtained from the azides (7b and c) in 2-methylfuran, along with the arylamines (10b and c) (18 and 20%) and large amounts of unidentifiable material (Scheme 2). Moreover, 4-nitrophenyl azide (7b) in 2-(4-chlorophenyl)furan similarly gave the triazole (8b) and the aniline (10b) in comparable yields (23 and 25% respectively) together with minor amounts of 2-(4-chloro-phenyl)-5-(4-nitrophenyl)furan (11) (10%) (Scheme 2).

From these findings, it appeared at first that the azides (7b and c) rather than the corresponding nitrenes might have been primarily involved in the thermal reaction with the above

furans. The general formation of the triazoles (8b and c) suggested that 1,3-dipolar cycloaddition of the azides (7b and c) to the 2,3- (or 4,5-) double bond of the appropriate furan should have occurred. Subsequent elimination of a ketocarbene unit [RC(O)CH; R = H, Me, or C$_6$H$_4$Cl-p] from the resulting dihydrotriazole adducts might have afforded the triazoles (8b,c) formally by a retro-1,3-dipolar cycloaddition. However, the rate of decomposition of the azide (7b) in furan, 2-methyl-, or 2-(4-chlorophenyl)-furan appeared to remain virtually unchanged (and be comparable to that in benzene), as was indicated by the fact that these reactions gave comparable amounts of unchanged azide after the same reaction time (see Experimental section). These findings suggested that the azide (7b) and presumably (7c) should actually lead to the initial formation of nitrene intermediates.
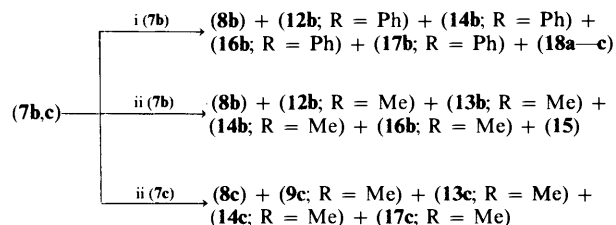
General evidence for arylnitrene attack on the furan ring was obtained by subsequent study of the thermolyses of the azides (7b and c) in 2,5-diphenyl- and/or 2,5-dimethyl-furan. These reactions allowed us to rule out the mechanism initially envisioned for the formation of the triazoles (8b and c), since these compounds could also be produced under such circumstances.

The azide (7b) in 2,5-dimethylfuran gave, after column chromatography, (i) triazole (8b) (16%); (ii) (Z)-3-(4-nitro-phenylamino)hex-3-ene-2,5-dione (12b; R = Me) (9%); (iii) 3-[(4-nitrophenylamino)methylene]pentane-2,4-dione (13b; R = Me) (6%); (iv) the 4-acetyltriazole (14b; R = Me) (7%); (v) the pyrrole (15) (10%); and (vi) 2,5-dimethyl-3-(4-nitrophenyl-amino)furan (16b; R = Me) (6%), contaminated with some dione (12b; R = Me) (Scheme 3).

The amine (16b; R = Me) was found to be very sensitive to air; the oxidation product (12b; R = Me) was formed fairly rapidly on exposure to air at room temperature or during chromatographic separation. This behaviour is consistent with the chemical behaviour previously observed with the relatively rare furylamines.[7]

As with azide (7b), 4-chlorophenyl azide (7c) in 2,5-dimethylfuran gave the corresponding triazole (8c) (7%), the pentanedione (13c; R = Me) (5%), and the 4-acetyltriazole (14c; R = Me) (4%). This reaction also afforded 1-(4-chlorophenyl)-2,5-dimethylpyrrole (9c; R = Me) (13%) and some 4-chloro-acetanilide (17c; R = Me) (3%), but no evidence of formation of the compound (16c; R = Me), the arylaminofuran analogue of (16b; R = Me), nor of its possible oxidation product (12c; R = Me) was provided (Scheme 3).

Finally, 4-nitrophenyl azide (7b) in 2,5-diphenylfuran displayed a chemical trend comparable to that observed with 2,5-dimethylfuran. This reaction gave the triazole (8b) (15%), the 3-arylaminofuran (16b; R = Ph) (5%) and the dione (12b; R = Ph) (9%), together with the 4-benzoyltriazole (14b; R = Ph) (1%) and some 4'-nitrobenzanilide (17b; R = Ph) (4%). As with (16b; R = Me), the aminofuran (16b; R = Ph) underwent ready conversion into the dione (12b; R = Ph) in the presence of air. In this case an unresolved mixture of the arylation products (18a—c) (10%) was also obtained (Scheme 3). A

(7b,c)————
i (7b) ————→ (8b) + (12b; R = Ph) + (14b; R = Ph) + (16b; R = Ph) + (17b; R = Ph) + (18a—c)
ii (7b) ————→ (8b) + (12b; R = Me) + (13b; R = Me) + (14b; R = Me) + (16b; R = Me) + (15)
ii (7c) ————→ (8c) + (9c; R = Me) + (13c; R = Me) + (14c; R = Me) + (17c; R = Me)

Scheme 3. *Reagents and conditions:* i, 2,5-diphenylfuran, 110 °C, 5 days; ii, 2,5-dimethylfuran, 110 °C, 5 days

similar mixture of the isomers (18a—c) was produced by homolytic arylation of 2,5-diphenylfuran by 4-nitrophenyl radicals generated by diazotization of 4-nitroaniline (10b) under aprotic conditions.[8]

The general evidence obtained in this work allows a number of conclusions to be drawn. Furans are readily attacked by the strongly electrophilic 4-nitro- and 4-chloro-phenylnitrenes, but appear to be sluggish in reactivity towards the weakly electrophilic 4-methoxyphenylnitrene. Electrophilic nitrene attack at the 2- (or 5-) position of the furan ring would give an intermediate zwitterion (19); ring cleavage of (19) to the imino compound (20) and recyclization would lead to compound (21), from which the pyrroles (9c; R = H or Me) could be ultimately formed by formal oxygen elimination (Scheme 4).

The pyrrole (15) could, in principle, result from further reaction of the dimethylpyrrole (9b; R = Me), which might be initially formed by a route similar to that proposed for the pyrroles (9c; R = H or Me). In fact, formal insertion of

(9c; R = H, Me)

Scheme 4. *Reagents:* i, (7b), $-N_2$; ii, (7b) or (7c), $-N_2$; iii, O_2; iv, H_2O; v, (7b) and/or (7c)

4-nitrophenylnitrene into a methyl C–H bond of (9b; R = Me) might account for the pyrrole (15). However, our failure to observe any dimethylpyrrole (9b; R = Me) suggests that this compound is unlikely to be the actual precursor of the pyrrole (15).

The mechanism suggested for the pyrrole formation is essentially consistent with previous reports of related reactions of nitrenes with furans and thiophenes.[2–5,9]

Indirect evidence for the possible occurrence of the imino-ketones (20), and thus presumably for the intermediates (19) and (21), was provided by the reaction of the azides (7b and c) with the diones (22; R = Me or Ph). We have observed[10] that 4-nitrophenyl azide (7b) smoothly adds to the C=C double bond of the dione (22; R = Ph) at 110 °C to give an intermediate dihydrotriazole, from which the 4-benzoyltriazole (14b; R = Ph) and the enaminodione (12b; R = Ph) are ultimately formed in comparable yield together with minor amounts of the dione (13b; R = Ph). Similarly, the hex-3-ene-2,5-dione (22; R = Me) reacts with the azides (7b and c) to afford the 4-acetyltriazoles (14b and c; R = Me), the hexenediones (12b and c; R = Me), and the pentanediones (13b and c; R = Me) to an extent dependent upon the starting azide (7b,c).[10]

These results suggest that the 4-acyltriazoles (14b; R = Me or Ph and 14c; R = Me), the compounds (13b and c; R = Me), and (at least in part) the hexenediones (12b; R = Me or Ph), resulting from the decomposition of the azides (7b and c) in the presence of 2,5-diphenyl- and/or 2,5-dimethyl-furan, are due to further reaction of the diones (22; R = Me or Ph) produced to some extent by hydrolysis of the corresponding iminoketones (20b and c) (Scheme 4). This view is supported by the fact that we could isolate trace amounts of (Z)-1,4-diphenylbut-2-ene-1,4-dione (22; R = Ph) from the reaction of the azide (7b) in 2,5-diphenylfuran.

Unfortunately, the mechanism of formation of the triazoles (8b and c) remains obscure. Our findings would suggest that the furan ring is converted into some reactive species, probably arising from initial α-attack of a nitrene intermediate, which would bear a C=C double bond located between the C-3 and C-4 carbon atoms of the original furan ring. 1,3-Dipolar cycloaddition of the azide present to such a double bond would give an intermediate dihydrotriazole, from which the triazoles (8b and c) would ultimately result by a facile aromatization process.

Electrophilic attack at the β-position of the furan ring may be expected to take place effectively when both α-positions are blocked.[11] In fact, evidence of β-attack is provided by the reaction of 4-nitrophenylnitrene with 2,5-dimethyl- and 2,5-diphenyl-furan, indicated by the formation of both the 3-arylaminofurans (16b; R = Me, Ph) and the diones (12b; R = Me or Ph), at least in part resulting from their oxidation (Scheme 4). However, no evidence of β-attack has been provided by 4-chlorophenylnitrene with 2,5-dimethylfuran. This may be due to the lower electrophilic power of 4-chloro-compared with 4-nitro-phenylnitrene.

The p-nitrophenylation products (11) and (18a—c) arising from thermolysis of the azide (7b) in the presence of 2-(4-chlorophenyl)furan and 2,5-diphenylfuran, respectively probably result from homolytic aromatic substitution by 4-nitrophenyl radicals. Such substitution is known to take place exclusively at the α-positon,[8,12] no substitution of the furan ring having been observed with a 2,5-disubstituted furan.[12]

There is a precedent for homolytic aromatic p-nitrophenyl-ation occurring on pyrolysis of the azide (7b); in 1,3,5-trimethoxybenzene at 140 °C compound (7b) afforded a small amount of 2,4,6-trimethoxy-4'-nitrobiphenyl.[13] This product has been assumed to result from homolytic arylation of the sym-trimethoxybenzene by p-nitrophenyl radicals arising from the homolytic cleavage of $p\text{-}NO_2C_6H_4N_3 \rightarrow p\text{-}NO_2C_6H_4 \cdot + N_3 \cdot$.

In our opinion *p*-nitrophenyl radicals are unlikely to be formed by the homolytic cleavage of the azide (**7b**), since these radicals are not generally produced on pyrolysis of (**7b**).[1,4b,13] We believe that these radicals (if actually formed) would arise from another unknown route, in which the aromatic substrate present possibly plays a determining role.

Experimental

Furan, 2-methylfuran, and 2,5-dimethylfuran were commercial products. 2-(4-Chlorophenyl)furan[14a] and 2,5-diphenyl-furan[14b] were prepared according to the literature. The aryl azides (**7a—c**) were prepared from the corresponding anilines by procedure A of Smith and Brown.[15] Reaction products such as 4,4-dimethoxyazobenzene,[16] 2,7-dimethoxyphenazine,[16] the anilines (**10a—c**), the triazoles (**8b**)[17a] and (**8c**),[17b] the benzoyltriazole (**14b**; R = Ph),[18] the pyrroles (**9c**; R = H)[19a] and (**9c**; R = Me),[19b] the enaminodiones (**12b**; R = Me)[20a] and (**12b**; R = Ph),[20b] and (*Z*)-1,4-diphenylbut-2-ene-1,4-dione (**22**; R = Ph)[21] were each identified by spectral comparison with authentic samples independently prepared or commercially available. Column chromatography was carried out on Merck silica gel (0.040—0.063 particle size) by gradual elution with light petroleum (b.p. 40—70 °C), diethyl ether–light petroleum mixtures (up to 100% diethyl ether) and finally with acetone.

^{1}H N.m.r. spectra were recorded at 60 or 300 MHz for solutions in $CDCl_3$ with Me_4Si as internal standard and i.r. spectra were recorded on a Perkin-Elmer 257 spectrometer. All m.p.s were measured on a Köfler apparatus and are uncorrected.

Thermal Decomposition of the Aryl Azides (**7a—c**). *General Procedure.*—A degassed 0.2M solution of the appropriate aryl azide (**7**) in freshly distilled furan, 2-methylfuran, 2,5-dimethyl-furan, or benzene (15 ml) was heated at 110 °C for 5 days in a sealed tube. The excess of solvent was distilled off and the residue subjected to column chromatography. The decomposition of 4-nitrophenyl azide (**7b**) in the presence of 2-(4-chlorophenyl)- or 2,5-diphenyl-furan was similarly carried out by treating the azide (**7b**) (2.45 mmol) with a ten-fold molar excess of the furan derivative.

In all cases, yields of identified products from the decomposition of the azides (**7a—c**) are based on reacted azide.

Decomposition of 4-Methoxyphenyl Azide (**7a**).—(a) *In furan.* Chromatography gave (i) unchanged azide (**7a**) (0.1 mmol, 3%); (ii) 4,4′-dimethoxyazobenzene (0.07 mmol, 5%); (iii) *p*-anisidine (**10a**) (0.8 mmol, 27%); (iv) 2,7-dimethoxyphenazine (0.06 mmol, 4%); (v) a mixture of unidentified products (60 mg); and (vi) tarry material (250 mg).

(b) *In 2,5-dimethylfuran.* Chromatography gave (i) unchanged azide (**7a**) (0.05 mmol, 1.5%); (ii) a mixture of unidentified products (70 mg); (iii) *p*-anisidine (**10a**) (1.2 mmol, 41%); and (iv) tarry material (150 mg).

Decomposition of 4-Nitrophenyl Azide (**7b**).—(a) *In benzene.* Chromatography gave (i) unchanged azide (**7b**) (1.65 mmol, 55%); (ii) 4-nitroaniline (**10b**) (0.28 mmol, 21%); and (iii) tarry material (100 mg).

(b) *In furan.* Chromatography gave (i) unchanged azide (**7b**) (0.34 mmol, 11%); (ii) 1-(4-nitrophenyl)-1,2,3-triazole (**8b**) (0.64 mmol, 24%); (iii) a mixture of unidentified products (102 mg); and (iv) tarry material (200 mg).

(c) *In 2-methylfuran.* Chromatography gave (i) unchanged azide (**7b**) (0.5 mmol, 17%); (ii) 4-nitroaniline (**10b**) (0.51 mmol, 20%); the triazole (**8b**) (0.38 mmol, 15%); (iii) a mixture of unidentified products (105 mg); and (iv) tarry material (190 mg).

(d) *In 2-(4-chlorophenyl)furan.* Chromatography gave (i) unchanged azide (**7b**) (0.73 mmol, 30%); (ii) 2-(4-*chlorophenyl*)-5-(4-*nitrophenyl*)*furan* (**11**) (0.165 mmol, 10%), m.p. 178—

179 °C; $v_{max.}$(solid film) 1 598, 1 510, and 1 328 cm^{-1}; *m/z* 299 (M^+, 100%), 269, 253, 225, 218, 189, and 139; δ_H(300 MHz) 6.8 (1 H, d, *J* 3.5 Hz), 6.98 (1 H, d, *J* 3.5 Hz), 7.42 (2 H, d, *J* 9 Hz), 7.7 (2 H, d, *J* 9 Hz), 7.85 (2 H, d, *J* 9 Hz), and 8.28 (2 H, d, *J* 9 Hz) (Found: C, 64.25; H, 3.3; N, 4.7. $C_{16}H_{10}ClNO_3$ requires C, 64.1; H, 3.35; N, 4.65%). The same compound (**11**) was independently obtained in 40% yield by diazotization of 4-nitroaniline (**10b**) with pentyl nitrite in ethyl acetate in the presence of 2-(4-chlorophenyl)furan according to a known procedure.[8]

Further elution gave (iii) the aniline (**10b**) (0.42 mmol, 25%); (iv) the triazole (**8b**) (0.40 mmol, 23%); (v) a mixture of unidentified products; and (vi) tarry material.

(e) *In 2,5-dimethylfuran.* Chromatography gave (i) unchanged azide (**7b**) (0.5 mmol, 17%); (ii) 2,5-*dimethyl*-3-(4-*nitrophenyl-amino*) *furan* (**16b**; R = Me), contaminated by some enamino-dione (**12b**; R = Me) (0.15 mmol, 6%); $v_{max.}$($CHCl_3$) 3 430 cm^{-1} (NH); δ_H(300 MHz) 2.15 (3 H, s), 2.28 (3 H, s), 5.78 (1 H, br s), 5.85 (1 H, s), 6.59 (2 H, d, *J* 9 Hz), and 7.99 (2 H, d, *J* 9 Hz) [Found: M^+, 232.0886 (100%). $C_{12}H_{12}N_2O_3$ requires *M*, 232.0878]; *m/z* 231, 186, 171, 143, and 116.

This compound (**16b**; R = Me) was found to be converted fairly rapidly into the enaminodione (**12b**; R = Me) on exposure to air.

Further elution gave (iii) *the pyrrole* (**15**) (0.13 mmol, 10%), m.p. 157—158 °C; $v_{max.}$(KBr) 3 350 cm^{-1} (NH); δ_H(300 MHz) 2.05 (3 H, s), 4.13 (2 H, d, *J* 5.5 Hz), 4.34 (1 H, br s), 6.02 (1 H, br d, *J* 3 Hz), 6.24 (1 H, br d, *J* 3 Hz), 6.41 (2 H, d, *J* 9 Hz), 7.40 (2 H, d, *J* 9 Hz), 8.01 (2 H, d, *J* 9 Hz), and 8.31 (2 H, d, *J* 9 Hz) (Found: M^+, 352.1179. $C_{18}H_{16}N_4O_4$ requires *M*, 352.1165); *m/z* 350, 215 (100%), 169, 168, 167, 154, 138, and 65; (iv) (*Z*)-3-(4-nitrophenylamino)hex-3-ene-2,5-dione (**12b**; R = Me) (0.23 mmol, 9%); and (v) 4-*acetyl*-1-(4-*nitrophenyl*)-1,2,3-*triazole* (**14b**; R = Me) (0.17 mmol, 7%), m.p. 233—234 °C; $v_{max.}$(solid film) 1 700 cm^{-1} (C=O); *m/z* 232 (M^+), 204, 189 (100%), 174, 162, 143, 79, and 43; δ_H(60 MHz) 2.18 (3 H, s), 8.07 (2 H, d, *J* 9 Hz), 8.53 (2 H, d, *J* 9 Hz), and 8.67 (1 H, s) (Found: C, 51.55; H, 3.5; N, 24.05. $C_{10}H_8N_4O_3$ requires C, 51.7; H, 3.45; N, 24.15%). The same compound (**14b**; R = Me) was independently obtained in 72% yield by treating the azide (**7b**) with but-3-yn-2-one in benzene according to the procedure of Vereshchagin *et al.*[18] This reaction also afforded the isomeric 5-*acetyl*-1-(4-*nitrophenyl*)-1,2,3-*triazole* (16%), m.p. 160—162 °C; $v_{max.}$(solid film) 1 695 cm^{-1} (C=O); *m/z* 232 (M^+), 189 (100%), 162, 161, 143, 76, and 43; δ_H(60 MHz) 2.67 (3 H, s), 7.77 (2 H, d, *J* 9 Hz), 8.37 (1 H, s), and 8.46 (2 H, d, *J* 9 Hz). Further elution gave (vi) 3-[(4-*nitrophenylamino*)*methylene*]*pentane*-2,4-*dione* (**13b**; R = Me) (0.15 mmol, 6%), m.p. 202—204 °C; $v_{max.}$(KBr) 3 330 (NH), 1 645 (C=O), and 1 595 cm^{-1} (C=O); *m/z* 248 (M^+, 100%), 233, 191, 145, 112, and 43; δ_H(60 MHz) 2.43 (3 H, s), 2.57 (3 H, s), 7.23 (2 H, d, *J* 9 Hz), 8.23 (2 H, d, *J* 9 Hz), 8.15 (1 H, d, *J* 13 Hz), and 12.73 (1 H, br d, *J* 13 Hz) (Found: C, 57.95; H, 4.9; N, 11.2. $C_{12}H_{12}N_2O_4$ requires C, 58.05; H, 4.85; N, 11.3%); (vii) the triazole (**8b**) (0.39 mmol, 16%); (viii) a mixture of unidentified products (124 mg); and (ix) tarry material.

(f) *In 2,5-diphenylfuran.* Chromatography gave (i) unchanged azide (**7b**) (0.97 mmol, 40%); (ii) a mixture (0.044 mmol, 3%) of two isomeric compounds in the ratio 75:25 (M^+, 341 as indicated by g.l.c. and mass spectroscopy) which were probably 2-(4′-nitrobiphenyl-2-yl)- and 2-(4′-nitrobiphenyl-3-yl)-5-phenylfuran (**18a**) and (**18b**); (iii) 2-(4′-*nitrobiphenyl-4-yl*)-5-*phenylfuran* (**18c**) (0.103 mmol, 7%), m.p. 192—194 °C; $v_{max.}$(KBr) 1 600, 1 512, 1 348, and 835 cm^{-1}; δ_H(300 MHz) 6.77 (1 H, d, *J* 3.6 Hz), 6.83 (1 H, d, *J* 3.6 Hz), 7.25—7.5 (3 H, m), 7.67 (2 H, d, *J* 9 Hz), 7.76 (4 H, dd), 7.85 (2 H, d, *J* 9 Hz), and 8.31 (2 H, d, *J* 9 Hz) [Found: M^+, 341.1057 (100%). $C_{22}H_{15}NO_3$ requires *M*, 341.1058]; *m/z* 294, 264, 251, 189, 105, and 77. Aprotic diazotization of the aniline (**10b**) in the presence of 2,5-diphenylfuran[8] gave a comparable mixture of the three isomeric

compounds (**8a**—**c**). Further elution gave (iv) 3-(4-nitrophenyl-amino)-2,5-diphenylfuran (**16b**; R = Ph) (0.073 mmol, 5%), contaminated by some enaminodione (**12b**; R = Ph); $v_{max.}$(CHCl$_3$) 3 430 cm^{-1} (NH) (Found: M^+, 356.1151. C$_{22}$H$_{16}$N$_2$O$_3$ requires M, 356.1161); m/z 307, 251, 221, 205, 105 (100%), and 77. This compound was converted into the enaminodione (**12b**; R = Ph) on exposure to air for a few hours. Continued elution gave (v) (Z)-2-(4-nitrophenylamino)-1,4-diphenylbut-2-ene-1,4-dione (**12b**; R = Ph) (0.13 mmol, 9%); (vi) 4'-nitrobenzanilide (**17b**; R = Ph) (0.062 mmol, 4%);[22] (vii) the triazole (**8b**) (0.22 mmol, 15%); (viii) 4-benzoyl-1-(4-nitrophenyl)-1,2,3-triazole (**14b**; R = Ph) (1%); (ix) trace amounts of (Z)-1,4-diphenylbut-2-ene-1,4-dione (**22**; R = Ph); and (x) a mixture of unidentified products (100 mg).

Decomposition of 4-Chlorophenyl Azide (**7c**).—(*a*) *In furan*. This reaction was carried out at 140 °C for 20 h. Chromatography gave (i) unchanged azide (**7c**) (0.015 mmol, 5%); (ii) 1-(4-chlorophenyl)pyrrole (**9c**; R = H) (0.17 mmol, 6%); (iii) 1-(4-chlorophenyl)-1,2,3-triazole (**8c**) (0.23 mmol, 8%); (iv) a mixture of unidentified products (90 mg); and (v) tarry material (325 mg).

(*b*) *In 2-methylfuran*. Chromatography gave (i) unchanged azide (**7c**) (0.6 mmol, 20%); (ii) 4-chloroaniline (**10c**) (0.43 mmol, 18%); (iii) the triazole (**8c**) (0.12 mmol, 5%); (iv) a mixture of unidentified products (140 mg); and (v) tarry material (170 mg).

(*c*) *In 2,5-dimethylfuran*. Chromatography gave (i) unchanged azide (**7c**) (0.45 mmol, 15%); (ii) 1-(4-chlorophenyl)-2,5-dimethylpyrrole (**9c**; R = Me) (0.33 mmol, 13%); (iii) 4-acetyl-1-(4-chlorophenyl)-1,2,3-triazole (**14c**; R = Me) (0.10 mmol, 4%), m.p. 167—168 °C; $v_{max.}$(KBr) 1 695 cm^{-1} (C=O); δ_H(60 MHz) 2.73 (3 H, s), 7.43 (2 H, d, J 9 Hz), 7.65 (2 H, d, J 9 Hz), and 8.40 (1 H, s) (Found: M^+, 221.0349. C$_{10}$H$_8$ClN$_3$O requires M, 221.0356); m/z 193, 178 (100%), 151, 111, 75, and 43. This compound (**14c**; R = Me) was independently obtained in 66% yield by treating the azide (**7c**) with but-3-yn-2-one.[18] This reaction also gave the isomeric 5-acetyl-1-(4-chlorophenyl)-1,2,3-triazole (15%), m.p. 142—144 °C; $v_{max.}$(KBr) 1 705 cm^{-1} (C=O); δ_H(60 MHz) 2.52 (3 H, s), 7.33 (4 H, br s), and 8.15 (1 H, s) (Found: M^+ 221.0351); m/z 178 (100%), 150, 111, 73, and 43.

Further elution gave (iv) 3-[(chlorophenylamino)methylene]-pentane-2,4-dione (**13c**; R = Me) (0.13 mmol, 5%), m.p. 145—147 °C; $v_{max.}$(KBr) 3 440 cm^{-1} (NH), 1 620, and 1 572 cm^{-1}; δ_H(60 MHz) 2.35 (3 H, s), 2.52 (3 H, s), 7.03 (2 H, d, J 9 Hz), 7.33 (2 H, d, J 9 Hz), 8.10 (1 H, d, J 13 Hz), and 12.6 (1 H, br d, J 13 Hz) [Found: M^+, 237.05615 (100%). C$_{12}$H$_{12}$ClNO$_2$ requires M, 237.055 65]; m/z 222, 204, 180, 112, 95, and 43; (v) 1-(4-chlorophenyl)-1,2,3-triazole (**8c**) (0.18 mmol, 7%); (vi) 4-chloro-acetanilide (**17c**; R = Me)[23] (0.08 mmol, 3%); (vii) a mixture of unidentified products (96 mg); and (viii) tarry material (192 mg).

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