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1,2,5-Oxadiazole (Furazan) Derivatives from Benzoylnitromethane and Dipolarophiles in the Presence of DABCO: Structure and Intermediates

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Furazan (1,2,5-oxadiazole) derivatives are obtained along with isoxazolines from the reaction of benzoylnitromethane with dipolarophiles in the presence of DABCO. Furazans are shown to derive from the intermediate dibenzoylfuroxan (3,4-dibenzoyl-1,2,5-oxadiazole-5-oxide) and dipolarophiles under hydrolytic conditions.

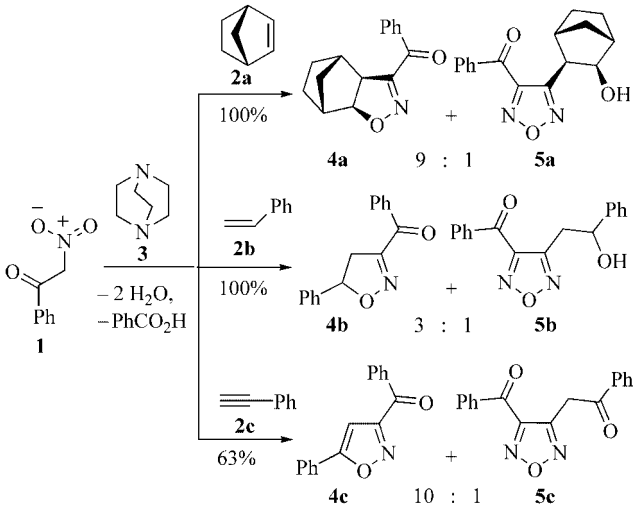
Introduction

We recently reported a new, mild and efficient procedure for the synthesis of isoxazolines starting from activated nitro compounds, mediated by tertiary diamines (e.g. DABCO). Evidence suggested that the dehydration step occurs from an intermediate nitronate-dipolarophile adduct H-bonded to the ammonium counterion of the diamine, while the corresponding nitrile oxide appears to have a minor role, if any, as a reaction intermediate.[1]

Besides the expected isoxazolines, minor side products have been isolated from benzoylnitromethane: these are neither isomeric with isoxazolines nor with dibenzoylfuroxan (dimer of the possible intermediate nitrile oxide). The elucidation of the structure and formation of these side products, which is reported here, might shed light on the entire process and show if they are derived from dibenzoylfuroxan. In previously known syntheses from nitro compounds, the presence of furoxans as side products alongside isoxazolines[2] has been assumed as a proof that nitrile oxides are reaction intermediates.[3]

Results and Discussion

From the reaction of benzoylnitromethane (**1**) and norbornene (**2a**) in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO, **3**), besides the adduct **4a** (Scheme 1) a minor amount of another product (**5a**) was isolated, together with benzoic acid; the starting material **1**, in excess, was also cleaved in part to benzoic acid and nitromethane. Compound **5a** was identified by standard spectroscopic techniques (ν_{OH} IR absorption, ^1H and ^{13}C NMR signals and mass spectrometry) and elemental analysis. Crystallographic analysis, carried out on compound **5a**, confirmed the ascribed structure (Figure 1).



Scheme 1.

The yield and the molar ratio between the products **4a** and **5a** depend on the amount of base and water employed.

Other dipolarophiles [styrene (**2b**) and phenylacetylene (**2c**)] also gave minor amounts of compounds **5b** and **5c**, besides the expected adducts **4b** and **4c**, similarly to **5a**. The elemental analysis and spectroscopic data are consistent with the depicted structures **5b** and **5c** (Scheme 1).

Since under these reaction conditions the 1:1 adduct **4a** is not converted into the furazan **5a**, we considered the possibility that the furazans **5a**–**5c** form from the furoxan **7** under these conditions. We therefore prepared this com-

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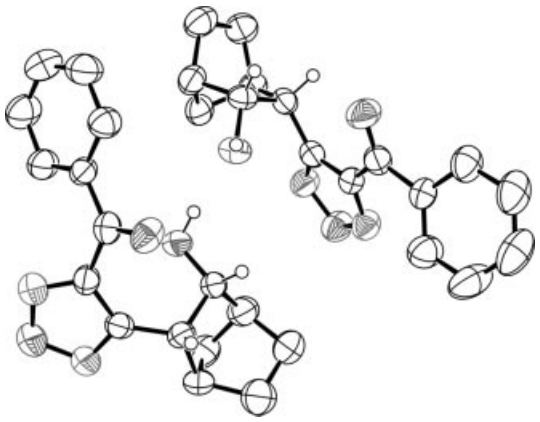


Figure 1. X-ray crystal structure of **5a**.

pound from benzoylnitromethane (**1**) following a literature procedure[14] and submitted it to the same reaction conditions (DABCO, water and chloroform at 60 °C). Without the dipolarophile, benzoic acid was the sole identified product, whereas in the presence of the dipolarophiles norbornene (**2a**), styrene (**2b**) or phenylacetylene (**2c**) furoxan **7** was mainly converted into the furazans **5a** (70%) **5b** (50%), and **5c** (41%), respectively.

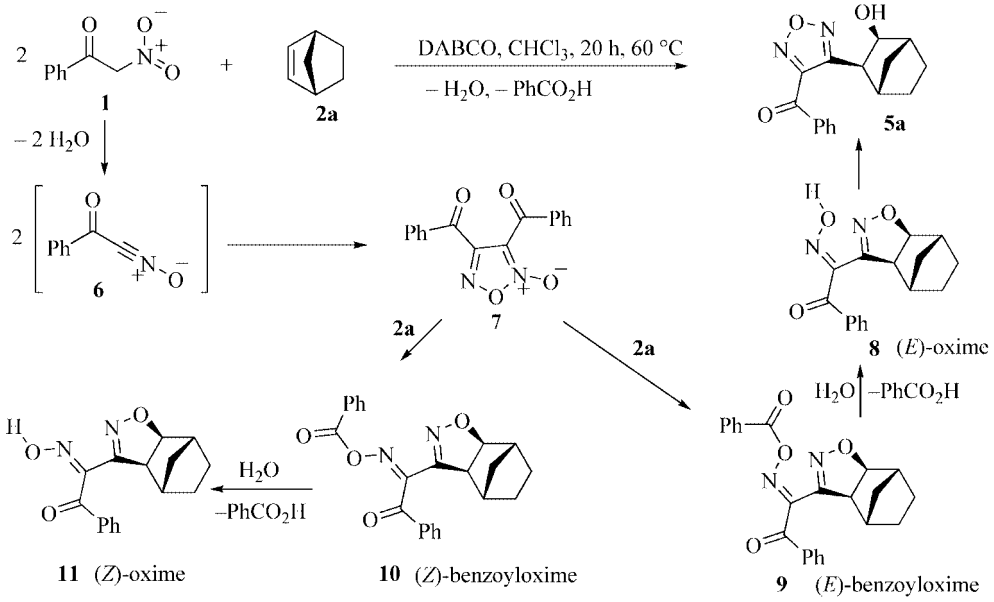
The reaction of dibenzoylfuroxan (**7**) with norbornene (**2a**) was also examined in more detail (Scheme 2). The above discussion refers to the reaction carried out with an excess of water (visible droplets): besides the furazan **5a**, minor amounts of benzoic acid, *O*-benzoyloxime (**10**) and oxime **11** were identified. If the reaction is carried out without added water, hydrolysis is only due to traces of water present in the medium: in this case, two oximes and two *O*-benzoyloximes were identified by column chromatography, in addition to the furazan **5a** (38%) and benzoic acid.

A comparison of the reported experiments suggests that the (*E*)-oxime **8** and the corresponding (*E*)-benzoyloxime **9**, which have a configuration suited for ring rearrangement to the furazan **5a**,[4] cannot accumulate as hydrolysis proceeds: therefore, only the corresponding (*Z*)-isomers **10** and **11** are obtained from the reaction with water in excess. The configuration thus ascribed to these compounds is supported by their NMR spectra: the chemical shifts of the bridgehead protons are consistent with those reported for the parent debenzoylated adducts obtained from the dimer of fulminic acid and norbornene.[5]

The benzoyloximes **9** and **10** are analogous to the adducts obtained (without stereochemical ascriptions) from furoxan **7** and other dipolarophiles on heating in boiling toluene or xylene.[6–9] These reactions were rationalised either by a furoxan cycloadduct undergoing rearrangement[6] or by a rearranged nitrile oxide isomer of **7**.[7] The latter gives either the cycloadducts with a dipolarophile or a furoxan dimer of **7** in the absence of a dipolarophile.[7] This dimer of **7** was never found in our experiments. Since the reactions reported here occur under much milder conditions, the process is possibly base-catalysed rather than a thermal one.

Conclusions

The side products of the reaction between benzoylnitromethane (**1**) and dipolarophiles [norbornene (**2a**), styrene (**2b**) and phenylacetylene (**2c**)] in the presence of DABCO (**3**) have been identified as furazan (1,2,5-oxadiazole) derivatives. The evidence reported here indicates that benzoylnitromethane (**1**) gives the dibenzoylfuroxan **7** as a key intermediate, which is the dimerisation product of the nitrile oxide **6**. The furoxan **7** then undergoes addition to the dipolarophile, hydrolysis and ring rearrangement to the final products (furazans and benzoic acid). With respect to the main 1:1 reaction between **1** and the dipolarophile,



Scheme 2.

this side reaction path requires a high concentration of both the base and water; however, enhanced hydrolysis causes decomposition of the starting material **1** and also of furoxan **7**. Therefore, for synthetic purposes in order to obtain furazanes it is convenient to prepare the furoxan in a separate step, in the absence of dipolarophile. Subsequent treatment of furoxan with dipolarophile and DABCO in the presence of an excess of water affords the corresponding furazans in fair yields.

Experimental Section

General: Melting points were measured on a Büchi 510 apparatus and are uncorrected. Chromatographic separations were performed on silica gel; R_f values refer to TLC carried out on 25-mm silica gel plates (Merck F254), with the same eluent indicated for the column chromatography unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded with a Mercuryplus 400 spectrometer (operating at 100.58 MHz for ^{13}C). The multiplicity of the ^{13}C NMR signals was determined by means of APT or HMQC experiments. Chemical shifts were determined relative to the residual solvent peak ($CHCl_3$: δ = 7.24 ppm for ^{1}H and δ = 77.0 ppm for ^{13}C). Mass spectra were obtained in EI mode at a 70 eV ionising voltage; relative percentages are shown in brackets. Commercially available benzoylnitromethane was used without further purification. IR spectra were recorded as solutions in spectroscopic grade $CHCl_3$, unless otherwise stated, using a Perkin–Elmer 881 spectrophotometer. Elemental analyses were obtained with an Elemental Analyser Perkin–Elmer 240C apparatus.

General Method for Reaction of Benzoylnitromethane (1) with Dipolarophiles: A solution of **1** (175 mg, 1.06 mmol), DABCO (24 mg, 0.212 mmol) and dipolarophile (0.424 mmol) in anhydrous and ethanol-free chloroform (1.4 mL) was stirred for 20 h in a sealed vessel (Schlenk) at 60 °C. The solvent was then removed and the residue dissolved in diethyl ether (15 mL) and washed with water (3 × 15 mL portions). The organic layer was dried (sodium sulfate) and concentrated, then the residue column chromatographed on silica gel.

Reaction of Benzoylnitromethane with Norbornene: After work-up, the residual oil was subjected to chromatographic purification (hexane/diethyl ether, 10:1). A first fraction (R_f = 0.31) containing the isoxazoline **4a** (white solid, 92 mg, 90%) was followed by a second fraction [$R_f < 0.1$; R_f (hexane/diethyl ether, 2:1) = 0.33] containing furazan **5a** (glassy solid, 12 mg, 10%).

Isoxazoline 4a: Colourless crystals, hexane, m.p. 49–50 °C. (ref.[10] 50–51 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09–1.16 (m, 1 H, norb-*H*), 1.18–1.24 (m, 1 H, norb-*H*), 1.29–1.36 (m, 1 H, norb-*H*), 1.38–1.44 (m, 1 H, norb-*H*), 1.49–1.62 (m, 2 H, norb-*H*), 2.58–2.61 (m, 1 H, norb-*H*), 2.62–2.66 (m, 1 H, norb-*H*), 3.51 (d, *J* = 8.4 Hz, 1 H, C*H*C=N), 4.64 (d, *J* = 8.4 Hz, 1 H, C*H*ON), 7.39–7.48 (m, 2 H, Ph-H_{para}), 7.52–7.59 (m, 1 H, Ph-H_{meta}), 8.11–8.14 (m, 2 H, Ph-H_{ortho}) ppm. ^{13}C NMR (100.58 MHz, $CDCl_3$): δ = 22.7 (t, Norb-*C*), 27.2 (t, Norb-*C*), 32.3 (t, Norb-*C*), 39.3 (d, Norb-*C*H), 43.1 (d, Norb-*C*H), 56.3 (d, *C*C=N), 89.4 (d, *C*ON), 128.2 (d, 2 C, Ar-*C*), 130.2 (d, 2 C, Ar-*C*), 133.3 (d, Ar-*C*), 136.4 (s, Ar-*C*), 158.2 (s, *C*=N), 186.7 (s, *C*=O) ppm. MS (EI): *m*/*z* (%) = 241 (36) [M$^+$], 212 (11), 174 (3), 105 (100), 77 (72). IR (KBr) = $\tilde{\nu}$ 2967, 2875, 1653 cm^{-1}. $C_{15}H_{15}NO_2$ (241.29): calcd. C 74.67, H 6.27, N 5.80; found C 74.46, H 5.99, N 5.72.

Furazan 5a: Colourless crystals, hexane/diethyl ether (1:2), m.p. 99–100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22–1.32 (m, 3 H, norb-*H*), 1.59–1.62 (m, 2 H, norb-*H*), 1.91 (dm, *J* = 10.4, 1 H, norb-*H*), 2.16–2.21 (m, 1 H, norb-*H*), 2.92–2.99 (m, 1 H, norb-*H*), 3.29 (dd, *J* = 1.6 and 7.0 Hz, 1 H,C*H*CN), 4.14 (d, *J* = 7.0 Hz, 1 H, C*H*OH), 7.48–7.53 (m, 2 H, Ph-H_{para}), 7.62–7.68 (m, 1 H, Ph-H_{meta}), 8.10–8.16 (m, 2 H, Ph-H_{ortho}) ppm. ^{13}C NMR (100.58 MHz, $CDCl_3$): δ = 24.4 (t, Norb-*C*), 28.6 (t, Norb-*C*), 33.9 (t, Norb-*C*), 39.3 (d, Norb-*C*), 44.9 (d, Norb-*C*), 45.6 (d, Norb-*C*), 75.6 (d, *C*OH), 128.7 (d, 2 C, Ar-*C*), 130.4 (d, 2 C, Ar-*C*), 134.6 (d, Ar-*C*), 135.7 (s, Ar-*C*), 151.6 (s, *C*=N), 155.1 (s, *C*=N), 185.8 (s, *C*=O) ppm. MS (EI): *m*/*z* (%) = 284 (4) [M$^+$], 267 (40) [M – OH]$^+$, 239 (3), 188 (8), 105 (100) [(PhCO)$^+$], 77 (57). IR (KBr) = $\tilde{\nu}$ 3484, 3375, 2932, 2867, 1672, 1657, 1597, 1451 cm^{-1}. $C_{16}H_{16}N_2O_3$ (284.31): calcd. C 67.59, H 5.67, N 9.85; found C 67.61, H 5.65, N 10.00.

Reaction of Benzoylnitromethane with Styrene: After work-up, the residual oil was subjected to chromatographic purification with hexane/diethyl ether (10:1). A first fraction (R_f = 0.24) containing the isoxazoline **4b** (80 mg, 75%) was followed by a second fraction [$R_f < 0.1$; R_f (hexane/diethyl ether, 2:1) = 0.23] containing the furazan **5b** (31 mg).

Isoxazoline 4b: Light-yellow oil (ref.[11] light yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.38 (dd, *J* = 8.8 and 17.8 Hz, 1 H, 4-H), 3.77 (dd, *J* = 11.4 and 17.8 Hz,1 H, 4-H), 5.76 (dd, *J* = 8.8 and 11.4 Hz, 1 H, 5-H), 7.29–7.41 (m, 5 H, Ar-*H*), 7.48 (m, 2 H, Ar-*H*), 7.61 (m, 1 H, Ar-*H*), 8.24 (m, 2 H, COPh-H_{ortho}) ppm. ^{13}C NMR (100.58 MHz, $CDCl_3$): δ = 41.8 (t, *C*-4), 84.2 (d, *C*-5), 125.9 (d, 2 C, Ar-*C*), 128.4 (d, 2 C, Ar-*C*), 128.6 (d), 128.8 (d, 2 C, Ar-*C*), 130.3 (d, 2 C, Ar-*C*), 133.6 (d), 135.7 (s, Ar-*C*), 139.7 (s, Ar-*C*), 157.4 (s, *C*=N), 186.2 (s, *C*OPh) ppm. MS (EI): *m*/*z* (%) = 251 (25) [M$^+$], 234 (12), 205 (4), 204 (4), 105 (100) [(PhCO)$^+$], 77 (55). IR: $\tilde{\nu}$ = 3068, 3030, 2926, 2857, 1672, 1652, 1599, 1581,1572 cm^{-1}. $C_{16}H_{13}NO_2$ (251.28): calcd. C 76.48, H 5.21, N 5.57; found C 76.50, H 5.29, N 5.44.

Furazan 5b: Gummy solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.48 (d, *J* = 6.3 Hz, 2 H, CH_2*C*N), 5.15 (t, *J* = 6.3 Hz, 1 H, C*H*OH), 7.18–7.40 (m, 5 H, Ar-*H*), 7.42–7.60 (m, 2 H, Ar-*H*), 7.61–7.74 (m, 1 H, Ar-*H*), 8.10–8.20 (m, 2 H, Ar-*H*) ppm. ^{13}C NMR (100.58 MHz, $CDCl_3$): δ = 33.2 (t, CH_2CN), 72.4 (d, C*H*OH), 125.5 (d, 2 C, Ar-*C*), 128.0 (d, Ar-*C*), 128.5 (d, 2 C, Ar-*C*), 128.6 (d, 2 C, Ar-*C*), 130.4 (d, 2 C, Ar-*C*), 134.7 (d, Ar-*C*), 135.4 (s, Ar-*C*), 142.4 (s, Ar-*C*), 151.0 (s, *C*=N), 153.0 (s, *C*=N), 184.7 (s, CO) ppm. MS (EI): *m*/*z* (%) = 294 (<1) [M$^+$], 293 (11) [M – H]$^+$, 277 (1) [M – OH]$^+$, 276 (2) [M – H_2O]$^+$, 189 (7), 107 (67), 105 (100) [(PhCO)$^+$], 79 (39), 77 (77). IR: $\tilde{\nu}$ = 3067, 3032, 2930, 1667 (C=O), 1599, 1580 cm^{-1}. $C_{17}H_{14}N_2O_3$ (294.30): calcd. C 69.38, H 4.79, N 9.52; found C 69.00, H 4.73, N 9.76.

Reaction of Benzoylnitromethane with Phenylacetylene: After work-up, the residual oil was subjected to chromatographic purification with hexane/diethyl ether (13:1). A first fraction (R_f = 0.30) containing the isoxazole **4c** (60 mg, 57%) was followed by a second fraction (R_f = 0.17) containing the furazan **5c** (8 mg, 6%).

Isoxazole 4c: White solid, m.p. 84–85 °C (89–90 °C;[12] 84.5–85 °C[13]). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.03 (s, 1 H, 4-H), 7.42–7.50 (m, 5 H, Ar-*H*), 7.60–7.63 (m, 1 H, Ar-*H*), 7.80–7.83 (m, 2 H, Ph-H_{ortho}), 8.32–8.38 (m, 2 H, COPh-H_{ortho}) ppm. ^{13}C NMR (100.58 MHz, $CDCl_3$): δ = 100.2 (d, *C*-4), 126.0 (d, 2 C, COPh-C_{ortho}), 126.7 (s, COPh-C_{ipso}), 128.5 (d, 2 C, Ph-C_{meta}), 129.1 (d, 2 C, COPh-C_{meta}), 130.6 (d, 2 C, Ph-C_{ortho}), 130.7 (d, COPh-C_{para}), 134.0 (d, Ph-C_{para}), 135.7 (s, Ph-C_{ipso}), 162.4 (s, *C*-3), 170.7 (s, *C*-5), 185.7 (s, C=O) ppm. MS (EI): *m*/*z* (%) = 249 (17) [M$^+$], 105 (100) [(PhCO)$^+$], 77 (94). IR: $\tilde{\nu}$ = 1662 (C=O), 1450 cm^{-1}. $C_{16}H_{11}NO_2$ (249.27): calcd. C 77.10, H 4.45, N 5.62; found C 77.50, H 4.81, N 5.56.

Furazan 5c: Colourless, needle-shaped crystals, m.p. 107–108 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.84 (s, 2 H, CH_2COPh), 7.46–7.56 (m, 4 H, Ar-*H*), 7.59–7.70 (m, 2 H, Ar-*H*), 7.96–8.01 (m, 2 H, Ph-H_{ortho}), 8.21–8.24 (m, 2 H, COPh-H_{ortho}) ppm. ^{13}C NMR (100.58 MHz, $CDCl_3$): δ = 33.8 (t, *C*H_2CO), 128.3 (d, 2 C, Ph-C_{ortho}), 128.7 (d, 2 C, Ar-*C*), 128.8 (d, 2 C, Ar-*C*), 128.9 (s, Ar-*C*), 130.5 (d, 2 C, COPh-C_{ortho}), 133.9 (d, Ar-*C*), 134.6 (d, Ar-*C*), 135.5 (s, Ar-*C*), 150.8 (s, *C*=N), 151.5 (s, *C*=N), 184.7 (s, *C*O), 193.0 (s, CH_2*C*O) ppm. MS (EI): *m*/*z* (%) = 292 (<1) [M$^+$], 105 (100) [(PhCO)$^+$], 77 (75). IR: $\tilde{\nu}$ = 1692 (C=O), 1667 (C=O) cm^{-1}. $C_{17}H_{12}N_2O_3$ (292.92): calcd. C 69.86, H 4.14, N 9.58; found C 70.15, H 4.02, N 9.40.

Reaction of Isoxazoline 4a with DABCO: A solution of **1** (175 mg, 1.06 mmol), DABCO (24 mg, 0.212 mmol) and isoxazoline **4a** (102 mg, 0.424 mmol) in anhydrous and ethanol-free chloroform (1.4 mL) was stirred for 20 h in a sealed vessel (Schlenk) at 60 °C. The solvent was then removed and the NMR analysis of the residue showed the presence of only starting materials. Repetition of this reaction in the presence of water gave the same result.

Reaction of 7 with Dipolarophiles

Preparation of the Furoxan 3,4-Dibenzoyl-1,2,5-oxadiazole 2-Oxide (7): Furoxan **7** was prepared from benzoylnitromethane following a procedure described previously.[14] White solid m.p. 83–84 °C (ethanol) (ref.[14] 84–85 °C; ref.[15] 83–85 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.60 (m, 4 H), 7.60–7.78 (m, 2 H), 7.86 (d, *J* = 11.6 Hz, 2 H), 8.19 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100.58 MHz, $CDCl_3$): δ = 111.5 (s, *C*=N$^+$O$^-$), 128.8 (d, 2 C, Ar-*C*), 129.0 (d, 2 C, Ar-*C*), 129.5 (d, 2 C, Ar-*C*), 130.4 (d, 2 C, Ar-*C*), 133.6 (s, 2 C, Ar-*C*), 135.1 (d, Ar-*C*), 135.3 (d, Ar-*C*), 154.1 (s, *C*=N), 180.1 (s, *C*OPh), 181.4 (s, *C*OPh) ppm. MS (EI): *m*/*z* (%) = 294 (<1) [M$^+$], 178 (9), 129 (12), 105 (100) [(PhCO)$^+$], 77 (87). IR (KBr): $\tilde{\nu}$ = 3070, 1662, 1611, 1474, 1451, 1332 cm^{-1}. $C_{16}H_{10}N_2O_4$ (294.26): calcd. C 65.31, H 3.43, N 9.52; found C 65.01, H 3.19, N 9.33.

Reaction of 7 with Norbornene and DABCO. Isolation of Benzoyloxime and Oxime Intermediates: A solution of **7** (74 mg, 0.25 mmol), DABCO (28 mg, 0.25 mmol) and norbornene (24 mg, 0.25 mmol) in chloroform (0.7 mL) was stirred for 20 h in a sealed vessel (Schlenk) at 60 °C. The solvent was then removed and the residue dissolved in diethyl ether (15 mL) and washed with brine (3 × 15 mL portions) then with 1 M NaOH (3 × 15 mL portions) and brine again (3 × 15 mL portions). The organic layer was dried (sodium sulfate) and concentrated. The reaction was repeated twice in the same conditions. The combined residues were column chromatographed on silica gel (hexane/diethyl ether, 10:1) to afford a first fraction (R_f = 0.15) containing the (*Z*)-oxime **11** (8 mg, 4%), a second fraction [R_f < 0.10; R_f (hexane/diethyl ether, 2:1) = 0.33] containing the furazan **5a** (80 mg, 38%), a third fraction [R_f < 0.10; R_f (hexane/diethyl ether, 2:1) = 0.17] containing the benzoyloximes (*E*)-**9** and (*Z*)-**10** (12 mg, 4%) and a last fraction [R_f < 0.10; R_f (hexane/diethyl ether, 2:1) = 0.14] containing the (*E*)-oxime **8** (5 mg, 2%).

(*Z*)-Oxime 11: Gummy solid. ^{1}H NMR: δ = 1.10–1.70 (m, 6 H), 2.49–2.54 (m, 1 H), 2.62–2.6 (m, 1 H), 3.24 (d, *J* = 8.4 Hz, 1 H, C*H*CN), 4.74 (d, *J* = 8.4 Hz, 1 H, C*H*ON), 7.34–7.67 (m, 3 H, Ar-*H*), 7.80–7.94 (m, 2 H, Ar-*H*) ppm. MS (EI): *m*/*z* (%) = 284 (<1) [M$^+$], 105 (100) [(PhCO)$^+$], 77 (38).

Benzoyloximes 9 and 10: Gummy solid. ^{1}H NMR (*Z* isomer): δ = 1.11–1.34 (m, 3 H), 1.40–1.68 (m, 3 H), 2.63–2.67 (m, 1 H), 2.88–2.99 (m, 1 H), 3.64 (d, *J* = 8.0 Hz, 1 H, C*H*CN), 4.71 (d, *J* = 8.4 Hz, C*H*ON, 1 H), 7.27–7.33 (m, 2 H, Ar-*H*), 7.44–7.55 (m, 3 H, Ar-*H*), 7.58–7. 69 (m, 3 H, Ar-*H*), 7.86–7.92 (m, 2 H, Ar-*H*) ppm; (*E* isomer): δ = 1.11–1.34 (m, 3 H), 1.40–1.68 (m, 3 H), 2.54–2.57 (m, 1 H), 2.60–2.64 (m, 1 H), 3.73 (d, *J* = 8.4 Hz, 1 H, C*H*CN), 4.71 (d, *J* = 8.4 Hz, C*H*ON, 1 H), 7.44–7.55 (m, 4 H, Ar-*H*), 7.58–7. 69 (m, 2 H, Ar-*H*), 8.01–8.11 (m, 4 H, Ar-*H*) ppm. ^{13}C NMR (100.58 MHz, $CDCl_3$) (*Z* isomer): δ = 22.6 (t), 27.3 (t), 32.5 (t), 39.0 (d), 43.3 (d), 55.1 (d, *C*HCN), 90.2 (d, *C*HON), 128.6 (d, 2 C, Ar-*C*), 129.1 (d, 2 C, Ar-*C*), 129.2 (s, 2 C, Ar-*C*), 129.6 (d, 2 C, Ar-*C*), 133.8 (s, Ar-*C*), 133.9 (s, Ar-*C*), 134.9 (d, Ar-*C*), 154.2 (s, C=N), 157.4 (s, C=N), 162.5 (s, NO*C*=O), 188.4 (s, NC*C*=O) ppm; one aromatic carbon not detected; (*E* isomer): δ = 22.9 (t), 27.2 (t), 32.2 (t), 39.9 (d), 42.8 (d), 57.8 (d, *C*HCN), 90.0, (d, *C*HOH), 128.8 (d, 2 C Ar-*C*), 128.9 (d, 2 C, Ar-*C*), 129.9 (d, 2 C, Ar-*C*), 130.5 (d, 2 C, Ar-*C*), 134.0 (s, Ar-*C*), 134.6 (d, Ar-*C*), 151.6 (s, C=N), 153.6 (s, C=N), 163.1 (s, NO*C*=O), 187.1 (s, NC*C*=O) ppm; two aromatic carbons not detected. MS (EI): *m*/*z* (%) = 388 (2) [M$^+$], 105 (100) [(PhCO)$^+$], 77 (51). IR: $\tilde{\nu}$ = 2968, 2878, 1759, 1689, 1598, 1451 cm^{-1}.

(*E*)-Oxime 8: Gummy solid. ^{1}H NMR: δ = 1.10–1.68 (m, 6 H), 2.53–2.63 (m, 1 H), 2.66–2.77 (m, 1 H), 3.40 (d, *J* = 8.6 Hz, 1 H, C*H*CN), 4.60 (d, *J* = 8.6 Hz, C*H*ON, 1 H), 7.34–7.67 (m, 3 H, Ar-*H*), 7.80–7.92 (m, 2 H, Ar-*H*) ppm. ^{13}C NMR (100.58 MHz, $CDCl_3$): δ = 22.6 (t), 27.3 (t), 32.4 (t), 39.2 (d), 43.1 (d), 55.7 (d, *C*HCN), 88.9 (d, *C*HON), 128.8 (d, 2 C, Ar-*C*), 129.1 (d, 2 C, Ar-*C*), 133.3 (s, Ar-*C*), 134.3 (d, Ar-*C*), 151.1 (s, C=N), 154.0 (s, C=N), 190.3 (s, C=O) ppm. MS (EI): *m*/*z* (%) = 284 (42) [M$^+$], 267 (2) [M – OH]$^+$, 239 (15), 179 (23), 105 (100) [(PhCO)$^+$], 77 (84). IR: $\tilde{\nu}$ = 3564, 2965, 2878, 1685, 1598 (cm^{-1}).

Reaction of 7 with Norbornene and DABCO in an Excess of Water: In a duplicate experiment, water was added (0.2 mL). A solution of furoxan **7** (74 mg, 0.25 mmol), DABCO (56 mg, 0.50 mmol) and norbornene (23.6 mg, 0.25 mmol) in chloroform/water (7:2; 0.9 mL) was stirred for 20 h in a sealed vessel (Schlenk) in an oil bath at 60 °C. The solvent was then removed and the residue dissolved in diethyl ether (15 mL) and washed with brine (3 × 15 mL portions), 1 M NaOH (3 × 15 mL portions) and brine again (3 × 15 mL portions). The organic layer was dried with sodium sulfate and concentrated. The residue was column chromatographed on silica gel (hexane/diethyl ether, 10:1) to afford a first fraction containing traces of (*Z*)-oxime **11**, a second fraction containing **5a** (50 mg, 70%) and a third fraction containing the benzoylated (*Z*)-oxime **10** (6 mg, 6%).

Reaction of 7 with Styrene: A solution of **7** (74 mg, 0.25 mmol), DABCO (56 mg, 0.50 mmol) and styrene (26 mg, 0.25 mmol) in chloroform/water (7:2; 0.9 mL) was stirred for 20 h in a sealed vessel (Schlenk) in an oil bath at 60 °C. The solvent was then removed and the residue dissolved in diethyl ether (15 mL) and washed with brine (3 × 15 mL portions), 1 M NaOH (3 × 15 mL portions) and brine again (3 × 15 mL portions) and then dried with sodium sulfate. After filtration, concentration in vacuo afforded 37 mg (50%) of furazan **5b** as a gummy solid.

Reaction of 7 with Phenylacetylene: A solution of **7** (74 mg, 0.25 mmol), DABCO (56 mg, 0.50 mmol) and phenylacetylene (26 mg, 0.25 mmol) in chloroform/water (7:2; 0.9 mL) was stirred for 20 h in a sealed vessel (Schlenk) in an oil bath at 60 °C. The solvent was then removed and the residue dissolved in diethyl ether (15 mL) and washed with brine (3 × 15 mL portions), 1 M NaOH (3 × 15 mL portions) and brine again (3 × 15 mL portions) and then dried with sodium sulfate. After filtration, concentration in vacuo afforded 30 mg (41%) of furazan **5c** as a yellow solid.

X-ray Structural Analysis of Compound 5a: $C_{32}H_{32}N_4O_6$, *M* = 568.62, triclinic, space group $P\bar{1}$, *a* = 10.681(2), *b* = 10.925(2), *c* =

13.491(3) Å, α = 104.31(2)°, β = 92.56(2)°, γ = 111.82(2)°, V = 1399.7(5) Å^3, Z = 2, D_c = 1.349, μ = 0.094 mm^{-1}, $F(000)$ = 600. 12191 Reflections were collected in the range 4.03° < θ < 33.70°; 8594 were independent, the parameters were 420 and the final R index was 0.0513 for reflections having $I > 2\sigma(I)$.

In Figure 1 we can see that there are two independent molecules in the asymmetric unit. They are not equivalent from a crystallographic point of view, so we obtain a cell which contains the two independent molecules.

Analysis was carried out with a Oxford Diffraction KM4 Xcalibur2 diffractometer at room temperature. Graphite-monochromated Mo-K_α radiation (40 mA/–40 kV) and a KM4 CCD/SAPPHIRE detector were used for cell parameter determination and data collection. The integrated intensities, measured using the ω-scan mode, were corrected for Lorentz and polarisation effects.[16] The substantial redundancy in data allows empirical absorption corrections (SADABS)[17] to be applied using multiple measurements of symmetry-equivalent reflections. The structure was solved by direct methods of SIR97[18] and refined by full-matrix least-squares on F^2 with SHELXL97.[19] The non-hydrogen atoms were refined anisotropically whereas hydrogen atoms were assigned in calculated positions and refined as isotropic.

CCDC-280587 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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