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1,3-Dipolar Cycloadditions of Heterocycles 1. Cycloadditions of *C*-Benzoyl-*N*-Phenylnitrone to Furan[1]

Ľ. Fišera*, J. Kováč, J. Poliačiková, and **J. Leško**[a]

Department of Organic Chemistry, Slovak Technical University,
CS-880 37 Bratislava, Czechoslovakia

[a]Laboratory of Mass Spectrometry, Slovak Technical University,
CS-880 37 Bratislava, Czechoslovakia

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A frontier orbital treatment of furan suggests its possible reactivity in 1,3-dipolar cycloadditions with dipoles posessing low lying LUMO's, such as nitrones, especially those with electronwithdrawing substituents. By the reaction of *C*-benzoyl-*N*-phenylnitrone **1 a** with an excess of furan at 60° the monocycloadduct **2 a**, two biscycloadducts **4** and **5** and further reaction products of nitrone such as azoxybenzene **8**, diketoamide **9 a**, benzoanilide **10 a**, benzoic acid **11 a** and phenyl glyoxylic acid **12** were isolated. The cycloaddition of *C*-(4-bromobenzoyl)-*N*-phenylnitrone **1 b** with furan is also reported.

(Keywords: Cycloaddition of nitrone; 1,3-Dipolar cycloaddition; Frontier orbital treatment; Furan)

1,3-Dipolare Cycloaddition an Heterocyclen 1. Cycloaddition von C-Benzoyl-N-phenylnitron an Furan

Die Interpretation der Grenzorbitale von Furan deutete auf eine mögliche Reaktivität bezüglich 1,3-dipolarer Cycloaddition hin, die durch LU(1,3-Dipol)—HO(Furan)-Wechselwirkung bestimmt wird. Nitrone mit elektronenanziehenden Substituenten wurden ausgewählt. Bei der Reaktion des *C*-Benzoyl-*N*-phenyl-nitrons (**1 a**) mit großem Überschuß von Furan (bei 60°) wurden das Monocycloaddukt **2 a**, die zwei Biscycloaddukte **4** und **5**, sowie weitere Reaktionsprodukte des Nitrons erhalten: Azoxybenzol (**8**), Umlagerungsprodukt **9 a**, Benzanilid **10 a**, Benzoesäure (**11 a**) und Phenylglyoxalsäure (**12**). Die Cycloaddition von *C*-(4-Brombenzoyl)-*N*-phenylnitron (**1 b**) an Furan wurde ebenfalls durchgeführt.

Although the reactivity of furan in cycloaddition reactions[2] in which this compound acts as the π^4s component, is very well investigated, there are only a few data about its behaviour as a

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dipolarophile in 1,3-dipolar cycloaddition reactions, such as reactions of furan with nitriloxides[3] and nitrileimines[4].

The present paper starts a series dealing with 1,3-dipolar cycloaddition reactions of heterocycles namely of furan and its derivatives. Besides the synthetic meaning of these cycloadditions of furan and the overall insight on mechanism of 1,3-dipolar cycloadditions, it seems also of interest whether the reaction proceeds by the concerted[5] or a stepwise[6] process. If zwitterionic or biradical intermediates of sufficient life time were formed during the course of the cycloaddition reaction, it could be possible to expect a formation of the substituted product as a consequence of a retention of the aromatic heterocyclic system.

Only in the last years the PMO theory explained the reactivity of 1,3-dipoles and dipolarophiles and simultaneously afforded a key to the explanation of the regioselectivity of 1,3-dipolar cycloadditions[7]. *Sustmann*[8] classified cycloadditions into three types depending whether the dominant interaction is between the HOMO of the dipole and the LUMO of the dipolarphile or the LUMO of the dipole and the HOMO of the dipolarophile or where both these interactions are equally significant.

From the values determined for the frontier orbitals of furan, $E_{\mathrm{HOMO}} = -8.8\,\mathrm{eV}$ and $E_{\mathrm{LUMO}} = 2.1\,\mathrm{eV}$ [3a] we assumed that 1,3-dipolar cycloadditions of furan belonged to the second type in which both interactions are of equal significance. The HOMO of furan is determined by a value of its lowest vertical ionisation potential, $IP = 8.88\,\mathrm{eV}$ and the LUMO of furan was calculated by *Houk* et al. [3a]. *Compton* et al. [10] calculated E_{LUMO} for furan to be 0.527 eV using a semiempirical method based upon a variable β—γ modification of the *PPP* aproximation to the *Hartree-Fock* equation. With respect to the results of cycloadditions published[3,4] and ours discussed below, it seems that their calculated value of E_{LUMO} for furan is too low. Our conclusion is supported by the fact that cycloadditions of nitrile oxides and nitrile imines, both belonging to the second type of the HOMO—LUMO interactions, are successful. Therefore, cycloadditions of azomethine oxides (nitrones) have been chosen as models for investigation of the furan dipolarophility.

1,3-Dipolar cycloadditions of nitroneshave been reported with a variety of compounds, none however, was carried out with furan derivatives[11,12]. The reaction of *C*,*N*-diphenylnitrone with furan at room temp and also at 60 °C failed even at 140 °C in an autoclave. Only unreacted nitrone and resinous compounds were obtained. Also, the reaction of *C*-(4-nitrophenyl)-*N*-phenylnitrone with furan, 2-furancarbaldehyde and 2-furan carboxylic acid methyl ester failed.

The perturbation interaction diagram elaborated by us on the basis of determined energies of the frontier orbitals for *C*-phenyl-*N*-methyl nitrone[7c,13] and for furan can be used as a model in judgement of the cycloaddition of furan with nitrones. The rate of the reaction of *C*-phenyl-*N*-methyl nitrone with furan is controlled by the $LU_{1,3\text{-dipole}}$—HO_{furan} interaction. The reaction is facilitated by electronwithdrawing substituents on nitrone (a decrease of E_{LUMO}) and by electronreleasing substituents on furan ring (an increase of E_{HOMO}). Since the reactivity of *C*,*N*-diphenylnitrone and *C*-phenyl-*N*-methylnitrone[14] is the same order, on the basis of above mentioned considerations, *C*-benzoyl-*N*-phenylnitrone has been chosen. Its benzoyl group lowers the energy of the LUMO resulting in stabilisation of the transition state formed by the interaction of the $LU_{nitrone}$—HO_{furan} and faster reaction. *Huisgen*[14] found that *C*-benzoyl-*N*-phenylnitrone (**1a**) adds to crotonic acid ester 110 times faster than *C*,*N*-diphenylnitrone and, moreover, **1a** adds at room temp to ethylene[15] with which *C*,*N*-diphenylnitrone does not react even at 100 °C. The reaction of **1a** is very rapid with high regioselectivity; the *C*-acyl-adducts formed can easily be crystallized and characterized by spectra and by m.p′.s.

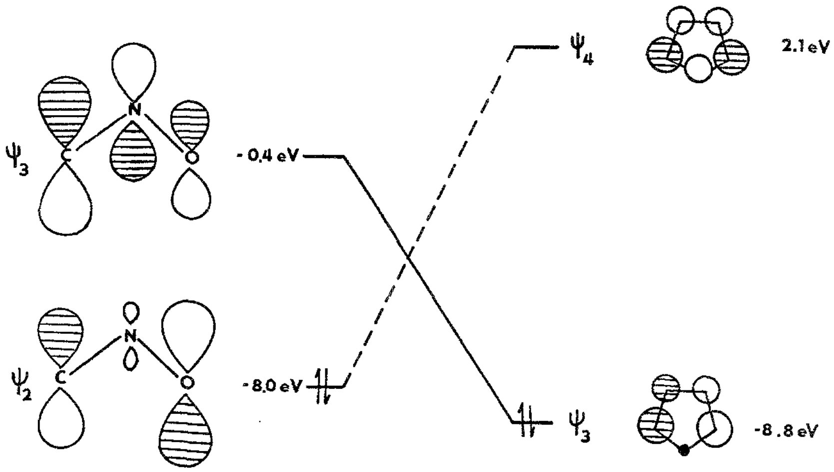
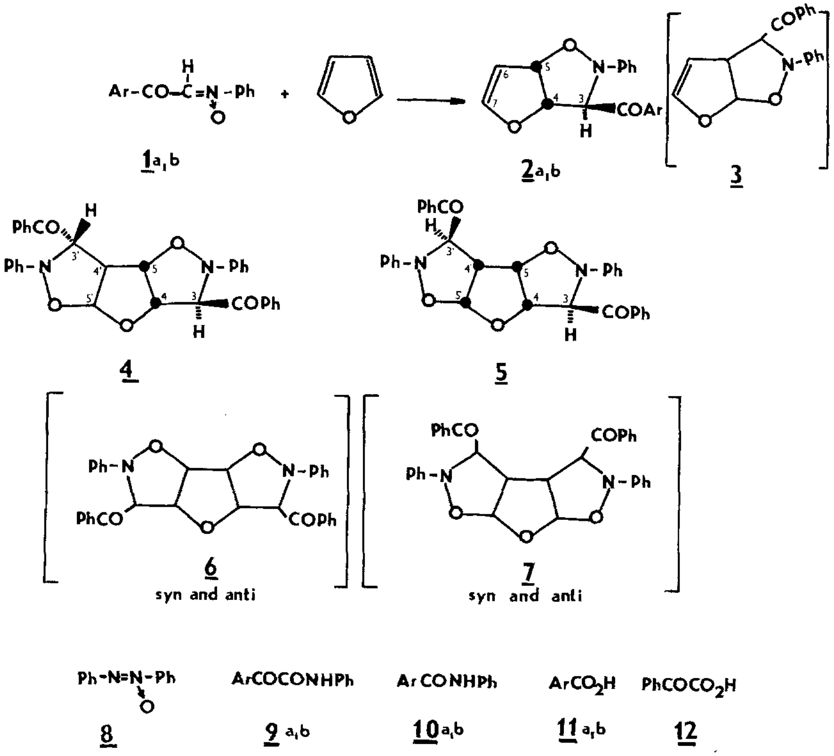


Fig. 1. Interaction diagram of *C*-phenyl-*N*-methylnitrone with furan

By the reaction of nitrone **1a** with an excess of furan at 60 °C in a glass autoclave for 4 h, followed by preparative-TLC treatment a white crystalline compound, m.p. 126-128 °C was obtained. Its mass spectrum showed an M^+ at *m*/e 293 and fragment peaks at *m*/e 225 (nitrone **1a**) and *m*/e 68 (furan) among other peaks, all confirming that the 1:1 adduct formed is a product of cycloaddition and not a product of substitution. Also, its UV spectrum (λ_{max} = 247 nm) is consistent with UV spectra of izoxazolidine derivatives. Theoretically, two regioisomers **2** and **3** (Scheme 1) can be formed.

Scheme 1



All cycloadditions of nitrones suggest that by every frontier interaction the other regioisomer is preferentially formed[7,13]. On the basis of calculations the highest atomic orbital coefficients were found to be in the LUMO at the terminal electrophilic carbon and in the HOMO at oxygen, respectively. The highest atomic orbital coefficients in the HOMO and also in the LUMO were found to be always at α—C.

In Table 1 values of atomic orbital coefficients for the hypothetical nitrone $H_2C{=}N{<}^{H}_{O}$[7b], furan[16] and 2,3-dihydrofuran[16] calculated according to the CNDO/2 method are listed. Since the orientation of reactants is controlled by the overlap of molecular orbitals having the highest atomic orbital coefficients by the dominant $LU_{nitrone}$—HO_{furan}

Tab. 1. *Eigenvectors and eigenvalues of the frontier orbitals*

	$H_2C{=}\overset{H}{\underset{|}{N}}\rightarrow O$			furan			2,3-dihydrofuran		
	C_C	C_N	C_O	C_O	C_2	C_3	C_O	C_2	C_3
HOMO	— 0.654	— 0.155	0.740	0.0	0.586	0.394	— 0.502	0.455	0.590
LUMO	— 0.618	0.674	— 0.406	— 0.359	0.558	— 0.350	— 0.164	0.718	— 0.648

interaction the adduct **2** is unambiguosly formed and by the second $HO_{nitrone}$—LU_{furan} interaction the adduct **3** could be formed.

The qualitative evidence for the reliability of the perturbed interaction diagram, namely that the product obtained in 21% yield has a structure **2a**, was obtained from its ^{1}H-NMR spectrum. The ^{1}H-NMR spectrum of **2a** shows two groups of multiplets with the ratio of protons 10:5. The first multiplet in the lower field (δ, 7.18–8,16 ppm, 10 H) was assigned to the signals of aromatic protons of the benzyoyl and phenyl groups. The assignment of the second multiplet to the signals of protons of the dihydrofuran skeleton an izoxazolidine group was only possible with the aid of shift reagents and by INDOR techniques. The value of the coupling constant of signals of bridged hydrogens ($J_{4,5} = 7.0$ Hz) clearly suggests that the hydrogens are in a *cis*-arrangement and confirms the *cis*-stereospecifity of the concerted 1,3-dipolar cycloaddition also for the reaction of nitrone **1a** with furan. Therefore, the adduct has the structure **2a**. If adduct **3** would have been formed, its ^{1}H-NMR spectrum should show a significant doublet with $J \sim 7$ Hz for the bridged 5-H proton in the neighbourhood of the heteroatoms. The signals of the bridged 4-H proton and the proton in the neighbourhood of the carbonyl group appear as a doublet and singlet, respectively. The *anti* arrangement of bridge protons of the dihydrofuran skeleton with izoxazolidine 3-H protons was deduced from the zero value of the coupling constants $J_{3,4}$. This conclusion is also supported by a comparison with the *Karplus* equation as well as with bis adducts formed by the reaction of benzene nitrile oxide with furan[3a] and cyclopentadiene[17] both having an *anti* arrangement of protons. The 4-H and 5-H bridge protons in the neighbourhood of the double bond of the dihydrofuran part are coupled with olefinic protons ($J_{5,6} = 2.5$ Hz and $J_{5,7} < 1$ Hz) whilst these coupling constants are approximately equal to those of 2,3-dihydrofuran[18]. As a consequence of equal coupling constants the signal of the 6-H proton appears to be a triplet.

The further reaction product with lower R_F (compared with **2a**) is a yellow crystalline compound **9a** (obtained in 12% yield). Its mass spectrum showed an M^+ at *m*/e 225 equal to that of the starting nitrone. By their mutual comparison it appears that these compounds are not identic. **9a** showed in its IR spectrum a band at 3,450 cm^{-1} belonging to the NH vibrations as supported by the presence of the NH proton in the ^{1}H-NMR spectrum. Therefore, **9a** has a structure of diketoamide formed by an rearrangement of the nitrone. This rearrangement is very often observed in a series of nitrones and is catalysed by *Lewis* acids and also by UV radiation[19]. *Kroehnke*[20] obtained **9a** by the action of Ac_2O on **1a** in 88% yield.

The third compound isolated (**8**, m.p. 35–36 °C) has the highest R_F value. Its elemental analysis showed a higher content of nitrogen (14.31%) as expected for products of cycloaddition or the products of the rearrangement of nitrone. The ^{1}H-NMR spectrum and the mass spectrum of **8** pointed towards azoxybenzene, as proved additionally by its UV spectrum and mixed m.p. with a standard. Its formation can be explained by the presence of water in furan which hydrolysed nitron **1a** to phenylhydroxylamine which in turn gives azoxybenzene by disproportionation.

$$\mathbf{1a} \xrightarrow{H_2O} Ph\mathrm{COCHO} + Ph\mathrm{NHOH} \longrightarrow Ph\mathrm{N{=}N(O)}Ph$$

Gore and *Hughes*[21] obtained *p*-hydroxyazobenzene in 20% yield by the reaction of *C*,*N*-diphenylnitrone with 98% H_2SO_4. According to the mechanism suggested by these authors a hydrolysis of nitrone to phenylhydroxylamine is considered from which azoxybenzene is formed, which in turn affords *p*-hydroxyazobenzene by the *Wallach* transformation. When commercial furan was employed in our experiments, azoxybenzene was formed in 60% yield (assuming that for one molecule of azoxybenzene two molecules of nitrone are necessary). However, by using furan redestilled above Na the yield of azoxybenzene was drastically decreased (9%). Since by the reaction of nitrone with furan no *bis* adducts were found, the excess of furan was decreased and the reaction performed in absolute toluene at 60 °C for 18 h in an autoclave. After 10 day's at room temp in the dark a white crystalline compound **4** was precipitated, which was filtered off and the filtrate chromatographed on a column and subsequently by preparative TLC. **4** showed an UV spectrum typical for the spectra of izoxazolidines and its ^{1}H-NMR spectrum exhibited signals for aromatic and tetrahydrofuran protons the 20:6 ratio of which points out to a bis adduct. Theoretically, from mono adduct **2a** four bis adducts (**4**, **5**, $\mathbf{6}_{syn}$ and $\mathbf{6}_{anti}$) and from the mono adduct **3** further two bis adducts ($\mathbf{7}_{syn}$ and $\mathbf{7}_{anti}$) can be formed.

Caramella and *Houk*[3a] determined on the basis of the IP values reported for analogous enol ethers the energy of the HOMO and LUMO for 2,3-dihydrofuran to be 8.5 eV and 2.4 eV, respectively. We [22] have determined the IP value for the compound **2a** (IP = 8.05 eV) from its charge transfer complex with tetracyano-ethylene, which means that a further 1,3-dipolar cycloaddition to the adduct **2a** is governed by the $\mathrm{LU}_{\mathrm{nitrone}}$—$\mathrm{HO}_{\mathrm{dihydrofuran}}$ **2a** interaction.

On the other hand, the highest atomic orbital coefficient for dihydrofuran was found to be at the β-carbon atom (Table 1) leading to the reverse orientation as observed for furan. On the basis of given qualitative considerations a formation of bis adducts **6** and **7** can be excluded. Moreover, their highly symmetrical structure should be manifest in the ^{1}H-NMR spectra. However, in the ^{1}H-NMR spectrum four significant dublets are observed suggesting the structure of the *anti* bisadduct to be **4**. Its yield was 24%.

An *anti* arrangement of the couple of the tetrahydrofuran bridge protons is deduced from the zero value of the coupling constant $J_{4,5}$. In contrast to the monoadduct **2a** the signals of izoaxazolidine 3-H and 3′-H protons appeared as weakly split doublets, both having coupling constants < 1 Hz corresponding to their *anti* arrangement with respect to the tetrahydrofuran protons.

From the filtrate according to the mentioned procedure the following compounds were obtained: **8** (9%), mono adduct **2a** (26%), **9a** (4%), the benzanilide **10a** (8%) and **5** (15%). Compound **10a** is probably formed by decarbonylation of **9a** caused by the action of silicagel.

Elemental analysis of compound **5** (%N, 5.44), its UV spectrum typical of izoxazolidine derivatives and ^{1}H-NMR spectrum suggest that this compound is a *syn* bisadduct. The *syn* arrangement of protons of the tetrahydrofuran skeleton is responsible for the „splitting" of the 5-H and 4′-H protons. The value of the coupling constant $J_{3,4}$ and $J_{3',4'}$ (both < 1 Hz) confirm the *anti* arrangement of tetrahydrofuran and izoxazolidine protons. Since further products having the lowest R_F values, benzoic acid **11a** (4%) and phenyl glyoxylic acid **12** (4%) were isolated and identified. The rest ($\sim$ 10–14%, calculated on nitrone) contained resinous compounds.

The reaction of *C*-(4-bromobenzoyl)-*N*-phenylnitrone (**1b**) with furan has also been investigated under the same conditions as those with nitrone **1a**. From the reaction mixture mainly products of decomposition of nitrone **1b** were isolated: azoxybenzene (26%), *p*-bromobenzoic acid **11b** (26%) and *p*-bromobenzanilide **10b** (11%) and a small amount of **9b** (< 1%). Their structure was determined by mass spectrometry and by mixed m.p. As a product of cycloaddition **2b** was obtained having the equal stereochemistry as the adduct **2a**.

Totally, 65% of nitrone **1a** reacted with furan by 1,3-dipolar cycloaddition giving cycloadducts where as the byproducts had their origin in side reactions of nitrone. *Huisgen* et al. [15] have not reported side reactions of nitrone **1a**. Butadiene (with IP = 9.08 eV[16] on the basis of the $\mathrm{LU_{nitrone}}$—$\mathrm{HO_{dipolarophile}}$ energy differences) should have a somewhat lower reactivity than furan.

Butadiene, however reacted with nitrone **1a** even at roomtemp. (20 h) quantitatively giving a cycloadduct. In our case the resonance energy of furan has to be overcome and therefore the reaction is slower and side reactions of nitrone can take place. Besides, the formed mono adduct **2a** of the dihydrofuran type is more reactive than furan itself and therefore corresponding bis adducts are the main reaction products. Their formation can be inhibited by carrying out the reaction with large excess of furan.

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Experimental

All melting points are uncorrected. IR spectra were measured using a Zeiss (Jena) IR spectrophotometer in CCl_4 solution or KBr technique. UV spectra were taken on a UV VIS spectrophotometer in CH_3OH solution. ^1H-NMR spectra were determined in $CDCl_3$ (except of compound **4**) using a Tesla BS 487 C spectrometer (80 MHz), with Me_4Si as internal standard. The mass spectra were measured on MS 902 S apparatus with direct inlet system. Energy of ionization was 70 eV, trap current 100 μA, temp. of the ion source 70–110 °C. *C*-Benzoyl-*N*-phenylnitrone (**1a**) and *C*-(4-Bromobenzoyl)-*N*-phenylnitrone (**1b**) were prepared from nitrosobenzene and phenacyl-pyridiniumbromide or 4-bromophenacylpyridiniumbromide acording to ref. [15]. Furan was the commercial product and was carefully distilled over Na. Column chromatography and preparative TLC were performed with silicagel and silicagel LSL_{254} (Lachema) 45 g pro 20 × 20 cm plate, 2 mm thickness, respectively, eluent chloroform—*n*-heptane 8:2.

Cycloaddition of **1a** *to Furan*

A mixture of **1a** (5 g, 22.2 mmol), furan (20 ml) and abs. toluene (10 ml) was kept in a glass autoclave at 60 °C for 18 h and 10 days at 25 °C. The white crystalline bis adduct **4** was filtered off, and the filtrate was evaporated under reduced pressure, leaving a oil residue.

(1) Bis adduct **4**:

1.4 g (24%), m.p. 180–183 °C from *Et*OH. (Found: C 74.05, H 4.98, N 5.38. $C_{32}H_{26}N_2O_5$ (518,56). Calc.: C 74.11, H 5.05, N 5.40.

^1H-NMR (δ, d_6DMS): 7.02–8.01 (aromatic ring protons, m, 20 H), 5.73 (5′-H, $J_{4'\text{-}5'} = 5.4$ Hz, 1 H), 5.24 and 5.32 (3-H and 3′-H, d, $J_{3\text{-}4}$ and $J_{3'\text{-}4'} < 1$ Hz, 2 H), 4.96 (4-H, d, $J_{4-5} = 5.0$ Hz, $J_{3-4} < 1$ Hz, 1 H), 4.58 (5-H, d, $J_{4-5} = 5.0$ Hz, 1 H), 4.27 (4′-H, d, d, $J_{4'\text{-}5'} = 5.4$ Hz, $J_{3'\text{-}4'} < 1$ Hz, 1 H).

UV (*Me*OH): $\lambda_{max} = 2.47$ nm ($\log \varepsilon = 4.64$).

IR (KBr): $\nu_{CO} = 1{,}699\ cm^{-1}$. MS: M^+—77 (*m*/e 441), base peak 77 (C_6H_5).

Column chromatography and preparative TLC gave following products:

(2) Azoxybenzene **8**:

0.2 g (9%), m.p. and mixed m.p. 35–36 °C from *n*-hexane. (Found: N 14.31. $C_{12}H_{10}N_2O$ (198.22). Calc.: N 14.13.

($CDCl_3$) 7.37–8.43 (aromatic ring protons, m).

UV (*Me*OH): $\lambda_{max} = 233$ nm ($\log \varepsilon = 4.13$), 238 (4.07), 260 (4.05), 323 (4.34).

MS: M^+ 198 ($C_{12}H_{10}N_2O$), base peak 77.

(3) Mono adduct **2a**:

2.1 g (26%), m.p. 126-128 °C from CH_2Cl_2—*n*-hexane. (Found: C 73.58, H 5.18, N 4.76. $C_{18}H_{15}NO_3$ (293.30). Calc.: C 73.71, H 5.15, N 4.78.

NMR ($CDCl_3$): 7.18-8.16 (aromatic ring protons, m, 10 H), 6.05 (7-H, q, $J_{6-7} = 2.5$ Hz, $J_{5-7} < 1$ Hz, 1 H), 5.91 (4-H, d, $J_{4-5} = 7.0$ Hz, $J_{3-4} = 0$ Hz, 1 H), 5.68 (3-H, s, 1 H), 5.57 (5-H, o, $J_{4-5} = 7.0$ Hz, $J_{5-6} = 2.5$ Hz, $J_{5-7} < 1$ Hz, 1 H), 5.13 (6-H, d, d, $J_{5-6} = 2.5$ Hz, $J_{6-7} = 2.5$ Hz, 1 H).

UV (*Me*OH): $\lambda_{max} = 247$ nm ($\log \varepsilon = 4.33$).

IR (KBr): ν(CO) = 1,693 cm^{-1}.

MS: M^+ 293 ($C_{18}H_{15}NO_3$).

(4) Bis adduct **5**:

0.9 g (15%), m.p. 155-157 °C from benzene—*n*-hexane. (Found: C 74.28, H 5.01, N 5.44. $C_{32}H_{26}N_2O_5$ (518.56). Calc.: C 74.11, H 5.05, N 5.40.

NMR ($CDCl_3$): 6.82-8.02 (aromatic ring protons, m, 20 H), 5.88 (5'-H), d, $J_{4'-5'} = 6.0$ Hz, 1 H), 5.51 (4-H, d, $J_{4-5} = 5.0$ Hz, 1 H), 5.10 and 5.28 (3-H and 3'-H, d, J_{3-4} and $J_{3'-4'} < 1$ Hz, 2 H), 4.62-4.88 (5-H, m, 1 H), 3.78-4.00 (4'-H, m, 1 H).

UV (*Me*OH): $\lambda_{max} = 248$ nm ($\log \varepsilon = 4.63$).

IR (KBr): ν(CO) = 1,694 cm^{-1}.

(5) Diketoamide **9a**:

0.6 g (12%), m.p. 55-57 °C.

IR ($CHCl_3$): $\nu_{NH} = 3{,}450$ cm^{-1}.

MS: M^+ 225 ($C_{16}H_{11}NO_2$), 121, 120, 105 ($Ph\text{—}\overset{+}{C}{\equiv}O$), 92 ($Ph\overset{+}{N}H$) 91 and 77.

(6) Benzanilide **10a**:

0.35 g (8%), m.p. and mixed m.p. 163 °C, M^+ 197 ($C_{15}H_{11}NO$).

(7) Benzoic acid **11a**:

0.11 g, (4%) m.p. and mixed m.p. 122 °C. M^+ 122 ($C_7H_6O_2$).

(8) Phenyl glyoxylic acid **12**:

0.05 g (1%), m.p. 66 °C. M^+ 150 ($C_8H_6O_3$).

Cycloaddition of **1b** *to Furan*

1b (2 g, 6.57 mmol) and furan (20 ml) yielded the following products after column chromatography:

(1) *p*-Bromobenzoic acid **11b**:

0.35 g (26%), m.p. and mixed m.p. 254 °C. M^+ 202, 200 ($C_7H_5BrO_2$).

(2) Azoxybenzene **8**:

(26%).

(3) *p*-Bromobenzanilide **10b**:

0.2 g (11%), m.p. and mixed m.p. 197 °C. M^+ 277, 275 ($C_{15}H_{10}BrNO$).

(4) Mono adduct **2b**:

0.6 g (16%), m.p. 150-152 °C from CH_2Cl_2—*n*-hexane. Found C 57.91, H 3.91, Br 21.97, N 4.11. $C_{18}H_{14}BrNO_3$ (372.21). Calc.: C 58.08, H 3.79, Br 21.47, N 3.76.

NMR ($CDCl_3$): 7.17-7.96 (aromatic ring protons, m, 9 H), 6.05 (7-H, d, $J_{6-7} = 2.5$ Hz, 1 H), 5.93 (4-H, d, $J_{4-5} = 6.5$ Hz, 1 H), 5.72 (3-H, s, 1 H), 5.56 (5-

H, d, d, $J_{4-5} = 6.5$ Hz, $J_{5-6} = 2.0$ Hz, 1 H), 5.15 (6-H, q, $J_{6-7} = 2.5$ Hz, $J_{5-6} = 2.0$ Hz, 1 H).

UV (*Me*OH): $\lambda_{max} = 250$ nm ($\log \varepsilon = 4.25$).

IR (KBr): ν(CO) = 1,690 cm^{-1}.

MS: M^+ 373, 371 ($C_{18}H_{14}BrNO_3$).

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