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Isothiazoles. Part II[1]. Reaction of 3-Diethylamino-4-(4-methoxyphenyl)-isothiazole-1,1-dioxide with Sodium Azide.

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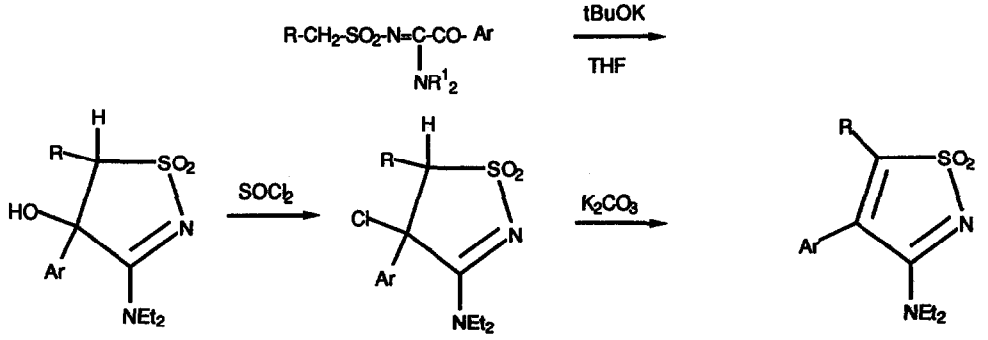
Abstract: 3-Diethylamino-4-(4-methoxyphenyl)-isothiazole-1,1-dioxide 1, was reacted with the azide ion in different solvents. Depending on reaction conditions 4-diethylamino-3a,6a-dihydro-3a-(4-methoxyphenyl)-1H-isothiazole-[4,5-d]-1,2,3-triazole-6,6-dioxide 3 and/or 4-diethylamino-1-[3-diethylamino-4,5-dihydro-4-(4-methoxyphenyl)-5-isothiazolyl-1,1-dioxide]-3a,6a-dihydro-3a-(4-methoxyphenyl)-1H-isothiazole-[4,5-d]-1,2,3- triazole-6,6-dioxide 4 were formed. When ethanol or acetone were used as reaction solvent the formation of the above compounds was accompanied by solvent addition forming 3-diethylamino-4,5-dihydro-4-(4-methoxyphenyl)-5-ethoxy-isothiazole-1,1-dioxide 2 and 3-diethylamino-4,5-dihydro-4-(4-methoxyphenyl)-5-(2-oxopropyl)-isothiazole-1,1-dioxide 6, respectively. Reaction mechanisms and structures of products are discussed.

As a part of our continuing research on the potentiality of N-sulfonylamidines as synthons in the chemistry of sulfur-containing heterocycles, we have recently developed a new synthetic pathway to substituted isothiazoles. More specifically, base-catalyzed cyclization of N-alkylsulfonylamidines of α–ketoacids results in the easy production of 3-dialkylamino-4,5-dihydro-4-hydroxy-isothiazole-1,1-dioxides. In these compounds the hydroxy group is readily replaced by chlorine on reaction with thionyl chloride. Then, hydrogen chloride elimination brought about by potassium carbonate offers a practical entry to 3-dialkylaminoisothiazole-1,1-dioxides (Scheme 1)[1].



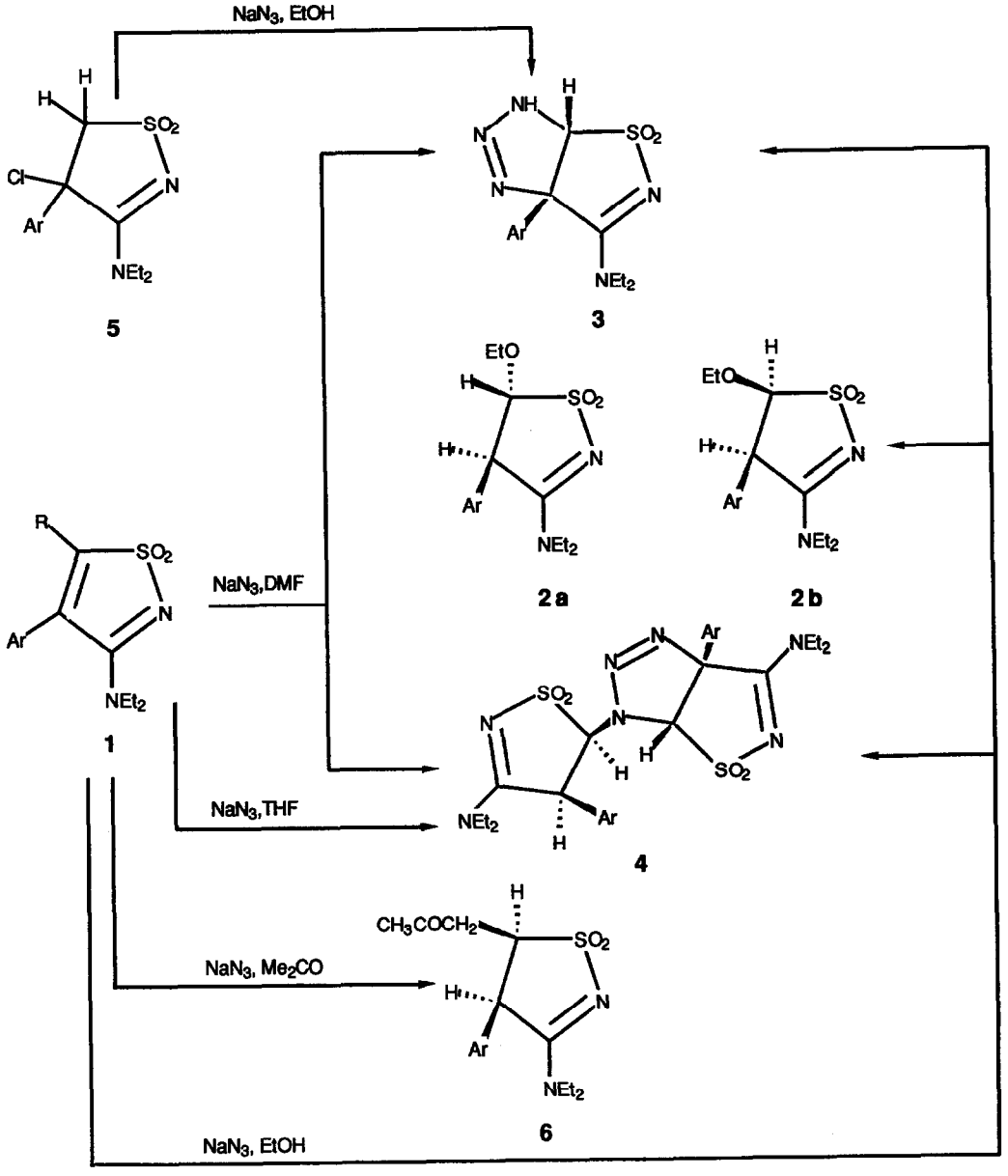
Scheme 1

All these heterocycles include in their ring the N-sulfonylamidine moiety. This class of compounds occurs only occasionally in the chemical literature [2-3]. Notwithstanding they are uncommon, these compounds are of general interest because valuable pharmacological properties are associated with some structurally related 3-aminobenzothiazole-1,1-dioxides [4-5]. The chemical reactivity of 3-aminoisothiazole-1,1-dioxides is yet unexplored. From a formal point of view they can be classified as cyclic N-sulfonylamidines and/or cyclic α,β-unsaturated sulfones. According to this latter feature, reactivity with nucleophiles at the C-4, C-5 bond can be expected. However, since it appeared that in the present case the electron withdrawing effect of the SO_2 group could be overwhelmed or simply balanced by that of the N-sulfonylamidine moiety a study of the regioselectivity of the reactions with nucleophiles was deemed useful. This paper reports on the reactions of 3-diethylamino-4-(4-methoxyphenyl)-isothiazole-1,1-dioxide **1** with the azide ion.

RESULTS AND DISCUSSION

Reaction of **1** with a suspension of NaN_3 in ethanol at room temperature produced quickly and in overall quantitative yield a mixture of four products, i. e., **2a**, **2b**, **3**, **4** in a ratio of 72 : 12 : 9 : 7 (Scheme 2). This ratio was established by HPLC. A chromatographic separation afforded, as pure products, **2a** and **3** which were identified as described later. The formation of product **3** containing the isothiazolo-[4,5-d]-triazole ring is rationalized by assuming a nucleophilic addition of the azide ion to the C-4, C-5 bond of the starting substance followed by ring closure (Scheme 3). This reaction, though not surprising at first, appeared to be rather unprecedented. In fact, a good documentation exists on the chemical literature of the reactions of electron-poor alkenes with hydrazoic acid. Saturated azides are invariably formed in satisfactory yields [6]. As far as the use of azide ion is concerned, it appears that this reaction has been applied only to alkynes or to electron-poor alkenes bearing a leaving group. In the former case α-vinylazides, in some instances able to cyclize to aromatic 1,2,3-triazoles, are produced through addition [7]. In the second instance the reaction results in addition-elimination producing vinylazides or triazoles [8]. In the case of the reported reactions which use hydrazoic acid as reactant and an alcohol as solvent, no participation of the solvent itself has been observed. This is expected because the reaction medium is essentially acidic. However, when sodium azide in ethanol is used it appears that it is a sufficiently strong base to produce in the reaction medium a reactive concentration of ethoxide ion which successfully competes with azide for the electron-poor double bond of the substrate. In good agreement with the above, another case of addition of the conjugate base of the solvent has been reported for the reaction of β-chloro-α-phenylcinnamaldehyde with NaN_3/MeOH [9]. A further confirmation of this situation has been obtained by titration of a saturated solution (30%) of sodium azide in ethanol. Two experiments using as titrating agent hydrochloric acid and silver nitrate demonstrated the equilibrium: $N_3^- + EtOH \rightleftharpoons HN_3 + EtO^-$. Though qualitative, the data recorded at room temperature show that the ratio is about 4 : 1 (N_3^-/EtO^-). Considering the quantitative outcome of the reaction of **1** with NaN_3/EtOH it has to be assumed that the reaction of EtO^- is faster [10] and this is confirmed by the observation, in separate experiments, that the formation of both **2** and **3** are irreversible reactions, at least under the conditions adopted. In agreement with the above picture, the reaction of **1** with an ethanolic solution of hydrazoic acid (only a trace amount of sodium azide was used as catalyst) produced the triazoline **3** *essentially* free from by-products. Similarly, compound **2a** was formed as the sole reaction product (in mixture with a minor amount of the cis-isomer **2b**) when **1** was reacted with ethanol containing a catalytic amount of sodium

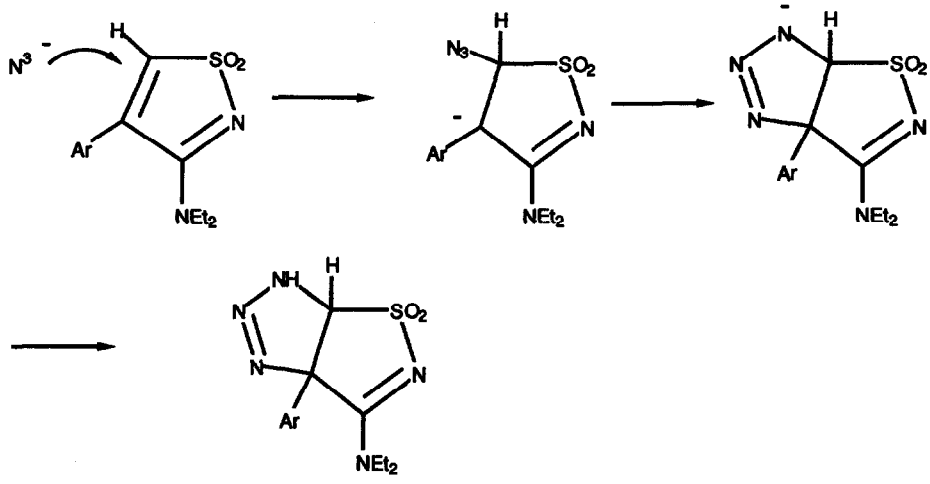
ethoxide. No reaction was observed in absence of ethoxide. An alternative and on the whole shorter access to the triazoline derivative **3** was found in the direct reaction of 4-chloro-4,5-dihydroisothiazole-1,1-dioxide **5**



Scheme 2

with sodium azide in ethanol. As said in the introduction, compound **5** is the precursor of **1** which is obtained

by reacting **5** with a base such as potassium carbonate. It was expected that sodium azide could act both as base and as nucleophile. Notwithstanding the presence of ethanol a high yield of **3** was obtained, practically no **2**



3

Scheme 3

being formed. This result, too, fits the above mechanistic picture. Since hydrogen chloride is eliminated the reaction medium is not basic, thus ruling out the possibility of addition of the conjugated base of the solvent. The ability of the double bond of **1** to add nucleophilic reactants is further confirmed by the obtention of compound **4**. The formation of **4** is rationalized by assuming the addition of the anion of **3**, formed as the first reaction product, to the starting substrate. Only the trans isomer was formed as confirmed by structural assignement (see later). The formation path of compound **4** was confirmed by reacting isolated **3** with **1**. The reaction was possible only in presence of a catalytic amount of sodium azide, thus evidencing the participation of the anion of **3**. The ability of the solvent to be involved in the reaction between sodium azide and the isothiazole **1** was further observed when the reaction was performed in acetone. Two main products were formed and isolated by chromatography, i. e., **4** and **6**, the latter clearly deriving from the reaction of the acetone enolate produced by the catalytic action of sodium azide. In this case only trace amounts of the triazoline **3** could be detected. Probably a greater amount of **4** is produced with respect to the reaction in ethanol because ethanol is more acidic than acetone and extensively protonates the anion of **3** making it unreactive as nucleophile and producing the highly competitive ethoxide ion.

The reaction was also tested using solvents unable to produce conjugated bases. By reacting **1** with a suspension of NaN_3 in tetrahydrofuran only **4** was obtained in appreciable yield. By performing the reaction in DMF a mixture of **3** and **4** was formed (ratio about 2 : 1, HPLC) . This different outcome is explained by considering that in THF a very low concentration of NaN_3 exists owing to the bad solubility of the salt. Accordingly, the anion of **3**, as soon as formed, successfully competes with azide for the substrate **1**. Instead,

in DMF, NaN_3 is readily soluble, allowing for an ample availability of the azide ion which makes the formation of 3 very quick and complete, thus excluding its reaction with the starting compound.

A last comment is necessary on the regioselectivity of the reaction. Apparently, a single position is reactive with nucleophilic reagents, i.e. position 5, as evidenced by the formation of compounds 2, 4 and 6. Very likely the same regiochemistry is valid for the first interaction between 1 and N_3^-, eventually leading to the cyclic product. This demonstrates that the driving force of the reaction resides more in the extensively conjugated anionic intermediate produced when C-5 is attacked by a nucleophile than in the electron withdrawing effect of the SO_2 group itself.

STRUCTURAL DETERMINATION OF COMPOUNDS 2, 3, 4, 6.

Compounds **2a** and **2b** were identified mainly on the basis of their ^{1}H-NMR spectra . For both compounds a typical AX-system is associated with H-4 and H-5. The low value of the coupling constant (J=1 Hz) for **2a** is evidence of the trans configuration [11] . The cis isomer shows expectedly a greater coupling constant of 8.2 Hz. Similarly the identity of compound **6** is confirmed by MS and ^{1}H-NMR spectra, which display signals in agreement with the proposed structure. A coupling constant of 9 Hz between H-4 and H-5 is indication that in this case the cis isomer was formed. The triazoline structure of **2** is demonstrated in the ^{1}H-NMR spectrum by signals at 4.60 ppm and 9.10 ppm (exchangeable with D_2O) associated with H-6a and N-H, respectively. A definitive structure proof was obtained by single crystal X-ray analysis which allowed also to identify the tautomer existing in the crystalline phase (Fig. 1) .

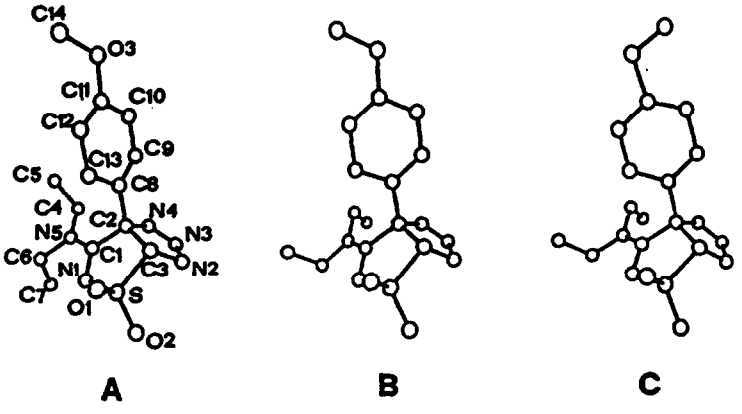


Figure 1

The asymmetric unit of 3 contains an unusual number (3) of independent molecules, which have slightly different stereochemistry. In particular, Fig. 1 shows that the local conformation of the methoxy and the diethylamino residues are quite different in the three cases. Any attempt to describe the crystal structure in a

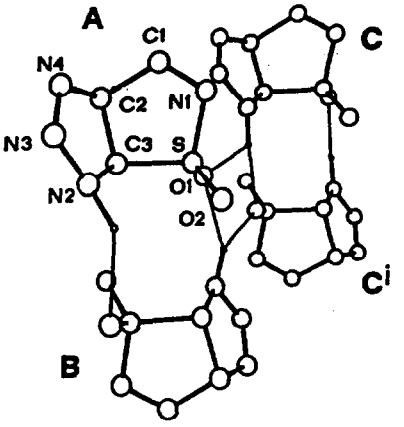


Figure 2

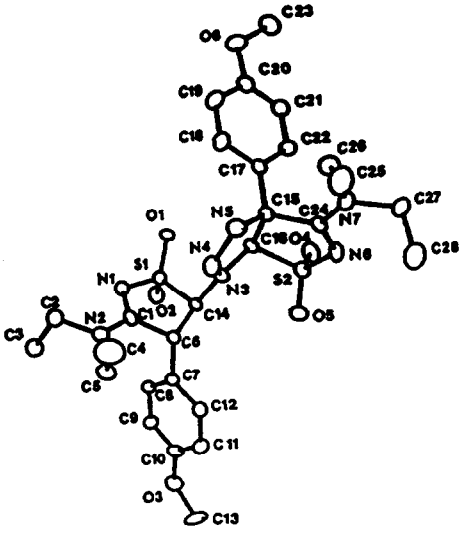


Figure 3

higher symmetry space group, according to ref. 12 and 13 failed. An apparent higher symmetry is reached by the moieties constituted by the two condensed penta-atomics rings. Figure 2 shows that the molecule A is nearly centrosymmetric to molecule B, and that the molecules C and C^i (i = -x, 1-y, 2-z) can be obtained by translation of A and B. This space arrangement is stabilized by a network of weak hydrogen-bonds.The structure of **4** was inferred from analytical and spectral data, mainly ^{1}H-NMR spectra showing signals in the 4.90-5.15 ppm region associated with the protons (C-4 and C-4', C-5') linked to the ring carbons. However, a definitive proof of the structure of compound **4**, including configurational assignement, was obtained only by single crystal X-ray analysis (Fig. 3).

EXPERIMENTAL

IR spectra were recorded on a PYE Unicam SP3-200 S Philips spectrophotometer. ^{1}H-NMR spectra (ppm, tetramethylsilane as internal standard, $CDCl_3$ as solvent): Bruker AC 200.

TLC: ready-to-use silica gel plates. Column chromatography: silica gel with the eluant indicated. Melting points: not corrected. M.S.: Varian Mat INCOS 50 instrument. Acid-base and argentometric titrations were performed on a Metrohm 670 titroprocessor. HPLC were carried out on a Shandon Hypersil column (250x4.6 mm) with a Millipore Water 441 instrument, detector λ = 254 nm. CH_2Cl_2 was used as eluant with 0.1% isopropanol and 0.5% CH_3CN with a flow rate of 2 ml/min.

1 and **4** are known products and were prepared according to published procedures [1].

X-RAY DATA:

Crystal structures of 3 and 4 : data for **4**, where different from **3** are given in square brackets.

(a) Crystal data. Crystal size: 0.15x0.20x0.10 [0.60x0.50x0.20] mm. Cell dimensions refined by least squares fitting of 25 centered reflections monitored in the range 25°<θ<45° [30°<θ<40°]. $C_{14}H_{19}N_5O_3S$ [$C_{28}H_{37}N_7O_6S_2$], M_r = 337.40 [631.77], triclinic [monoclinic], space group P-1 [$P2_1/n$], a = 10.727(1) [12.434(1)], b = 12.639(1) [10.921(1)], c = 17.921(2) [24.725(4)] Å, α = 98.98(8) [90.0], β = 92.22(10) [111.43(1)], γ = 94.66(9) [90.0]°, V = 2388.4(5) [3125.1(7)] Å^3, Z = 6 [4], F(000) = 1068 [1336], D_k = 1.407 [1.343] g.cm^{-3}, μ = 19.7 [19.4] cm^{-1}.

(b) Data collection and processing. CAD4 diffractometer, Cu Kα graphite monochromated radiation (λ = 1.54184 Å). ω-2θ scan, scan speed 3.3°. min $^{-1}$, scan width (0.7+0.14tgθ) [0.85+0.14tgθ]°, aperture (1.6+0.5tgθ) [1.8+0.5tgθ] mm; 9086 [6244] hk+1 reflections measured to $(\sin\theta/\lambda)_{max}$ = 0.6095 Å^{-1}. Orientation control monitored after each 500 reflections; standard reflections measured every 7200 s of scanning time. Lp, empirical absorption[14] (transmission minimum = 63.52 [40.32]%, maximum = 99.30 [98.57]%) and decay corrections (maximum decay = 27.4 [58.2]%) applied. Among 8046 [5977] unique reflections 3432 [3212] considered as observed (I>2σ(I)). R_{int} after merging for P-1 [$P2_1/n$] space group 0.033 [0.022].

(c) Structure solution and refinement. Atomic scattering factors with anomalous dispersion coefficents from International Tables for X-Ray Crystallography [15]. Calculation performed with SDP[16] on the MICROVAX-3100 computer at CGS-Pavia. Structure solved by direct methods (MULTAN[17]). Refinement by full-matrix least-squares. Non-hydrogen atoms refined anisotropically. Positions of hydrogen atoms revealed from difference Fourier map and not refined. Weighting function (w = F_o/394 if F_o<394, w = 394/F_o if F_o>394, $(F_o)_{max}/3$ = 394) [w = F_o/ 578 if F_o<578, w = 578/F_o if F_o>578, ($F_o)_{max}/3$ = 578] keeps

$\Sigma w(\Delta F)^2$ uniform over ranges of $\sin\theta/\lambda$ and $|F_o|$.
Refinement converged to R = 0.092 [0.070] and $R_w = \{[\Sigma w (F_o-F_c)^2]/[\Sigma w F_o^2]\}^{1/2} = 0.088$ [0.040], $(\text{shift/error})_{max} = 0.05$ [0.04], S = 1.18 [1.09], excursion in final difference Fourier map within 0.28 [0.21] and -0.25 [-0.18] e.Å^{-3}.

Acid-base and argentometric titrations: A suspension of NaN_3 (110 mg, 1.69 mmol) in ethanol (15 ml), was stirred for 2 h at room temperature. After centrifugation and filtration, two samples (0.4 ml each) were drawn; one was titrated with HCl 0.01 N and the other with $AgNO_3$ 0.01N.

Reaction of 1 with NaN_3 in ethanol: equimolecular amounts of **1** and NaN_3 were suspended in the reaction solvent and stirred at room temperature until disappearance of **1** (TLC eluant: ethyl acetate/cyclohexane 6:4). The reaction mixture was evaporated under reduced pressure and water was added. The residue was extracted with CH_2Cl_2, washed twice with water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the solid residue chromatographed on silica gel (eluant petroleum ether containing increasing amounts of diethyl ether). Products **2a** and **3** were then crystallized with CH_2Cl_2/diethyl ether.
3: Yield: 12%. M.p.: 178°C. Calcd.: C 49.85% H 5.64% N 20.77% Found: C 50.08% H 5.79% N 20.55%. ^{1}H-NMR: 0.80 (t, J=7 Hz, 3H, CH_3); 1.25 (t, J=7 Hz, 3H, CH_3); 3.40-3.60 (m, 2H, CH_2); 3.60-3.70 (m, 2H, CH_2); 3.80 (s, 3H, OCH_3); 4.65 (s, 1H, H-6a); 7.00 (AB system, J=8 Hz, 2H, Aryl-H); 7.15 (AB system, J=8 Hz, 2H, Aryl-H); 9.2 (s, 1H, N-H).
2a: Yield: 70%. M.p.: 90°C. Calcd.: C 56.47% H 7.06% N 8.23% Found: C 55.99% H 7.01% N 8.60%. ^{1}H-NMR: 0.85 (t, J=7 Hz, 3H, CH_3); 1.22 (t, J=7.1 Hz, 3H, CH_3); 1.27 (t, J=7 Hz,3H, CH_3); 2.90-3.20 (m, 2H, CH_2N); 3.25-3.45, 3.60-3.80 (2m, 1+ 1H, CH_2N); 3.60-3.80, 4.10-4.30 (2m, 1 + 1H, CH_2N); 3.80 (s, 3H, OCH_3); 4.10-4.30 (m, 1H, H-4); 4.50 (d, J=1 Hz, 1H, H-5); 6.90 (AB system, J=8 Hz, 2H, Aryl-H); 7.2 (AB system, J=8 Hz, 2H, Aryl-H).
Products **2b** and **4** were obtained in mixture and any attempt to purify them failed.

Reaction of 1 with NaN3 in acetone: equimolecular amounts of **1** and NaN_3 were stirred in acetone at room temperature, with a drop of water just to dissolve the inorganic azide. After about 24 h the solvent was evaporated under reduced pressure and water was added. The residue was extracted with CH_2Cl_2, washed twice with water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the solid residue chromatographed on silica gel (eluant cyclohexane/ethyl acetate 6:4) yielding **4** and **6**. **4** was then crystallized with diethyl ether and **6** with CH_2Cl_2/diethyl ether.
4: Yield: 60%. M.p.: 152-154°C. Calcd.: C 53.23% H 5.86% N 15.52% Found: C 53.32% H 5.88% N 15.17%. ^{1}H-NMR: 0.95 (t, J=7 Hz, 3H, CH_3); 1.10 (t, J=7 Hz, 3H, CH_3); 1.20-1.40 (m, 6H, CH_3); 3.05-3.20, 3.20-3.70 (2m, 6H, CH_2N); 3.70-4.00 (m, 2H, CH_2N); 3.8 (s, 6H, OCH_3);4.95 (s, 1H, H-6a); 5.10 (s, 1H, H$^{4'}$or H$^{5'}$); 5.15 (s, 1H, H$^{4'}$or H$^{5'}$); 6.90 (AB system, J=8 Hz, 2H, Aryl-H); 6.95 (AB system, J=8.4 Hz, 2H, Aryl-H); 7.15 (AB system, J=8.4 Hz, 2H, Aryl-H); 7.30 (AB system, J=8 Hz, 2H, Aryl-H).
6: Yield: 10%; M.S. 352; ^{1}H-NMR: 0.85 (t, J=7 Hz, 3H, CH_3); 1.20 (t, J= 7 Hz, 3H, CH_3); 1.90 (s, 3H, CH_3CO); 2.30 (dd, $J_{gem.}$=19.7 Hz., $J_{vic.}$=11.5 Hz, 1H, CH_2CO); 3.00 (dd, $J_{gem.}$=19.7 Hz, $J_{vic.}$=2.8 Hz, 1H, CH_2CO); 3.05-3.25 (m, 2H, CH_2N); 3.30-3.50, 3.60-3.80 (2m, 1 + 1H, CH_2N); 3.80 (s, 3H, OCH_3);

4.00 (ddd, $J_{H\text{-}4/H\text{-}5}$=9 Hz, J=2.8 Hz, J=11.5 Hz, 1H, H-5); 4.65 (d, J=9 Hz, 1H, H-4); 6.85 (AB system, J = 8 Hz, 2H, Aryl-H); 6.90-7.15 (broad signal, 2H, Aryl-H).

Reaction of 1 with NaN_3 in THF: equimolecular amounts of **1** and NaN_3 were stirred in THF at room temperature, with enough water just to dissolve the inorganic azide. After about 24 h the solvent was evaporated under reduced pressure and water was added. The residue was extracted with CH_2Cl_2, washed twice with water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the solid residue chromatographed on silica gel (eluant cyclohexane/ethyl acetate 2:8). **4** was then crystallized with CH_2Cl_2/diethyl ether. Yield: 30%.

Reaction of 5 with NaN_3 : equimolecular amounts of **5** and NaN_3 were suspended in ethanol and stirred under reflux until disappearance of **5** (TLC eluant: ethyl acetate/cyclohexane 4:6). The reaction solvent was evaporated and water was added. The residue was extracted in CH_2Cl_2 washed twice with water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the solid residue was crystallized with CH_2Cl_2/diethyl ether yielding pure **3**. Yield: 70%

Reaction of 1 with hydrazoic acid : an ethanol solution of HN_3 freshly prepared from equimolecular amounts of NaN_3 and HCl, was dropped in a stirred solution of **1** in ethanol and a catalytic amount of NaN_3 was added. The formation of **3** was detected by TLC (eluant ethyl acetate/cyclohexane 4:6).

Reaction of 3 with 1 in ethanol: equimolecular amounts of **1** and **3** with a trace of NaN_3 were stirred in ethanol at room temperature for about 24 h (TLC eluant ethyl acetate/cyclohexane 4:6). The reaction was elaborated as usual, giving after crystallization with CH_2Cl_2/diethyl ether pure **4**. Yield 80%.

Reaction of 1 with NaN_3 in DMF: equimolecular amounts of **1** and NaN_3 were stirred in DMF at room temperature until disappearance of **1** (about 1h, TLC eluant ethyl acetate/cyclohexane 4:6). After evaporation of the solvent the residue was analyzed with HPLC showing the formation of both **3** and **4** in a ratio 2:1.

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