40. New Reactions of Amino-Functionalized 3-Vinyl-1*H*-indoles and Tetrahydropyridin-4-yl Analogues with Dienophiles

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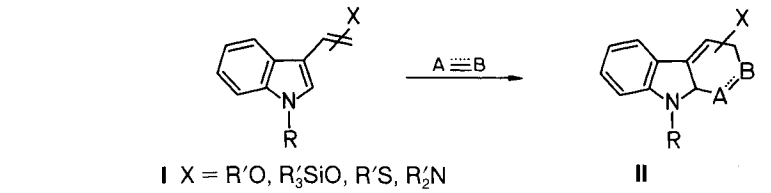
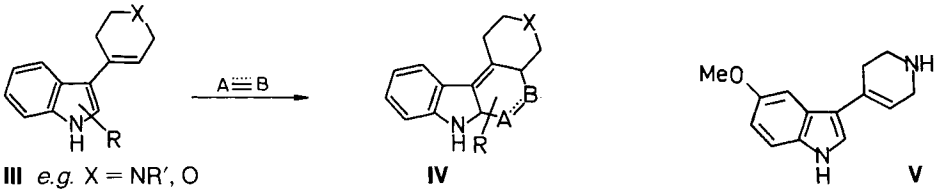
Reactions of 3-[2-(morpholin-4-yl)vinyl]-1*H*-indole (**1**), the 1,2-dihydro-9*H*-carbazole **2**, as well as the 3-(tetrahydropyridin-4-yl)-1*H*-indoles **3a** and **3b** with some carbo- and heterodienophiles are described. The scope and limitations of the synthetic utility of these amino- (or homoamino)-functionalized 3-vinyl-1*H*-indoles are reported and some MO calculations for the qualitative prediction of their reactivities are presented. The reactions gave rise to substitution products, redox products, *Diels-Alder* adducts, ene adducts, and *Michael*-type adducts (*Schemes 2* and *3*).

Introduction. – *Diels-Alder* reactions of 2- and 3-vinyl-1*H*-indoles as 4π-electron components are now well established as a versatile procedure for the regio- and stereoselectively controlled syntheses of [*b*]annellated indoles and/or carbazoles [1–5]. This methodology should also constitute an interesting concept for the synthesis of selectively heteroatom-functionalized carbazoles and [*b*]annellated indoles such as, *e.g.*, compounds **II** functionalized with alkoxy, alkylthio, or amino groups (to be synthesized from precursors **I**, see *Scheme 1*). Compounds of these types are currently of general interest as

Scheme 1



I X = R'O, R'_3SiO, R'S, R'_2N **II**



III *e.g.* X = NR', O **IV** **V**

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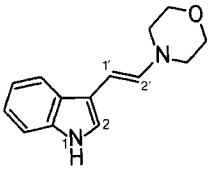
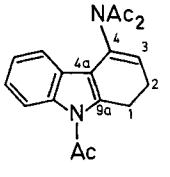
building blocks in alkaloid chemistry [6] and/or in the development of pharmacologically active lead compounds [7]. However, the *Diels-Alder* reactivity of heteroatom-functionalized 3-vinyl-1*H*-indoles **I** has only been sparsly explored in the areas of alkoxy- [8] [9], trialkylsilyloxy- [10], alkylthio- [11], or amino-functionalized [12] 3-vinyl-1*H*-indoles. Also, only little information on the scope and limitations of the *Diels-Alder* reactivity of 3-vinyl-1*H*-indoles of type **III** is available. The latter compounds possess the vinyl function integrated in a six-membered heterocyclic system [13a] (*Scheme 1*). The crucial *Diels-Alder* step with **III** should lead to heterocyclic annellated carbazoles of type **IV**, a class of compounds of special interest for the development of antitumor active DNA intercalators [14]. Furthermore, compounds of type **III** (X = NH, R'N) belong to an attractive group of lead structures with antidepressive activity [13b] and, in particular, compound **V** binds strongly to 5-hydroxytryptamine-1 receptors in the central nervous system exhibiting antagonistic effects. Hence, the synthetic elaboration of these types of 3-vinyl-1*H*-indoles and of their derivatives are also highly relevant for medicinal chemistry.

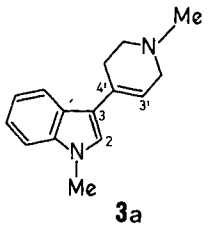
Thus, in continuation of our synthetic investigations on pericyclic reactions with vinylindoles [1–5] [7] [8], we now report new results as well as information on the scope and limitations of the *Diels-Alder* reactivity of the amino-functionalized 3-vinyl-1*H*-indoles **1** and **2** as well as of the 3-(1,2,3,6-tetrahydropyridin-4-yl)-1*H*-indoles **3a** and **3b** which are cyclic homoanalogous amino-functionalized 3-vinyl-1*H*-indoles. In addition, **1** and **2** possess the basic structural features (indole-C–C–NR_2 for **1** and indole-C–NR_2 for **2**) of many naturally occurring alkaloids such as those found in the *Aristotelia*, *Kopsia*, and *Aspidosperma* genera [16].



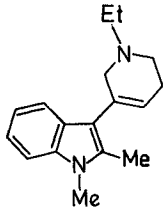
1



2



3a

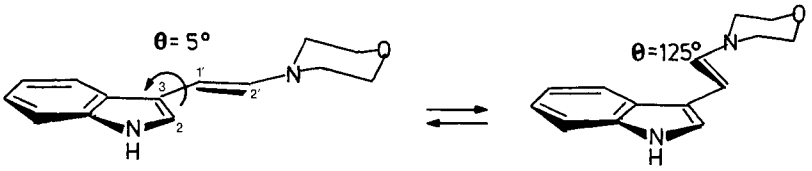


3b

Results and Discussion. – The (*E*)-3-[2-(morpholin-4-yl)vinyl]-1*H*-indole (**1**), prepared according to [16] in 100% yield from 1*H*-indole-3-acetaldehyde and morpholine, is a viscous yellow oil of low stability in the presence of acidic compounds and moisture. A bicycloannellation of **1** with cyclohexenone to yield a disubstituted bicyclo[2.2.2]-octanone in a polar, multistep process was reported [16]. Furthermore, according to π-VESCF MO calculations[2]), the 3-vinyl-1*H*-indole **1** contains an electron-rich butadiene-1,4-diamine unit (*E*(HOMO) = –8.70 eV) and, thus, should participate in a

[2]) The MMX program packet from *Serena Software Ltd.*, Bloomington, IN, was used. The π-VESCF MO version has been described [17]; the MMX molecular-mechanics program was established from the MM2 and MMP1 programs (*Allinger* QCPE 395 and QCPE 318) by *K. E. Gilbert* and *J. J. Gajewski*. All MO calculations were performed with full geometry optimization.

HOMO(diene)-LUMO(dienophile)-controlled *Diels-Alder* process with appropriate dienophiles. Additionally, MMX molecular-mechanics calculations[2]) predict that the s-*cis*-conformer **VI** (generated from rotation about C(3)–C(1′)) is more stable than the s-*trans*-conformer **VII** by *ca.* 5 kcal/mol. Conformational analyses according to the rigid-rotor approximation in the MMX program additionally reveal the global minimum conformation to be s-*cis* (see **VI**) with a torsional angle θ(C(2)–C(3)–C(1′)–C(2′)) of 5°. An activation barrier of 4.7 kcal/mol towards the s-*trans*-conformer **VII** as a local minimum (respective torsional angle 125°) exists. Nevertheless, a sufficient population of the s-*cis*-conformation **VI** should be present in the equilibrium mixture for the *Diels-Alder* step [19]. On the other hand, the HOMO coefficients c[2]) and the results of charge calculations[3]) generally predict a preferred attack of an electrophile (and hence also of an electrophilic dienophile) at the olefinic C(1′)-atom of the morpholino-enamine moiety (c(C(1′)) = −0.4475, c(C(2′)) = −0.3877, c(C(2)) = 0.3351, c(C(3)) = 0.3628[2]); sum of σ- and π-charges = −0.20 (at C(1′)) and 0.03 (at C(2′))[3])).



VI rotation barrier from **VI** to **VII**: 4.7 kcal/mol **VII**

Therefore, we have now experimentally examined the reactions of **1** with a variety of dienophiles such as *N*-phenylmaleimide (**4**), methyl propynoate (**5**), and *4*-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (**6**; *Scheme 2*). In spite of numerous variations of the reaction conditions, we were not able to effect a *Diels-Alder* reaction. In the reactions with **4** and **5**, only the simple *N*-substituted morpholine derivatives **7a** and **7b** were obtained. The yields of these products (49 and 50%, resp.) reveal that the major portion of **7a** and **7b** results directly from the reaction of **1** with **4** and **5**, respectively, since the starting material contained morpholine to less than 10% (^{1}H-NMR analysis), a contamination originating from the laborious synthesis of **1**. As the mechanistic rationale, we suggest, on the basis of a related reaction of *N*-alkylmorpholines, methyl propynoate, and CH-acidic compounds [21], the following process (*Scheme 2*): Attack of the morpholine N-atom of **1** at an electrophilic center of the carbodienophile A ≡ B gives a betaine which reacts with a further molecule of **1** (now serving as an NH-acidic partner), probably by way of an intermediary complex **VIII**, in a cleavage process to furnish **7a** and **7b** as well as the dimeric 3-vinyl-1*H*-indole **IX**. The latter compound should be highly susceptible to polymerization (TLC shows the presence of numerous polymeric products but provides no indications concerning structure **IX**).

We then investigated the scope and limitations of the predictable *Diels-Alder* reactivity of the cyclic indolyl-enimide **2** which contains a conformatively fixed s-*cis*-butadiene

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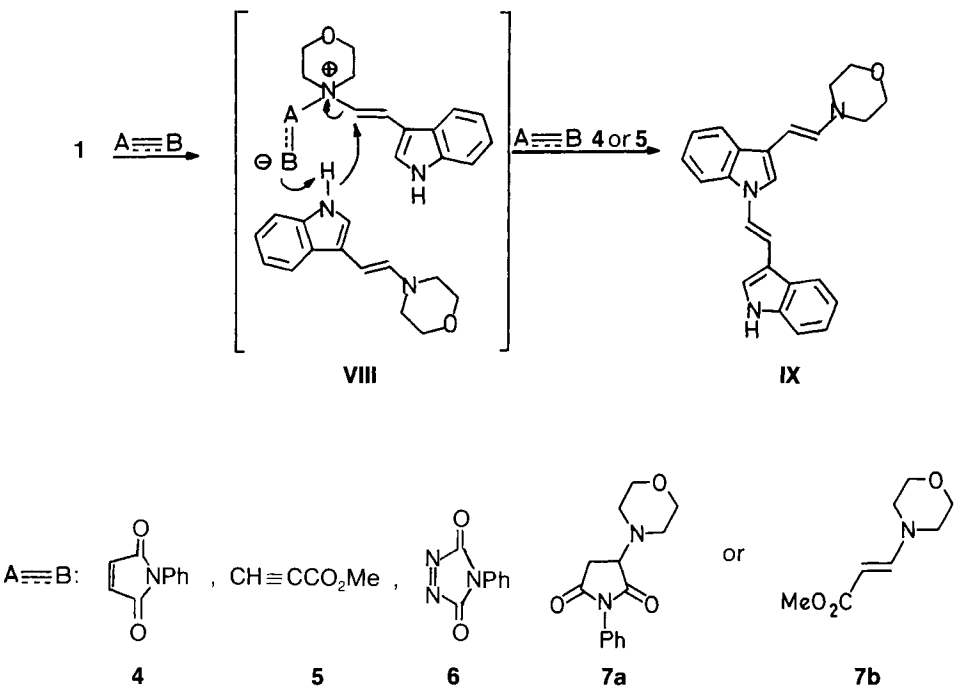
[3]) The σ- and π-charges were calculated according to [18]. The molecular-modeling program packet SYBYL from *Evans & Sutherlands*, *Tripos Assoc. Inc.*, St. Louis, MO, was used. A geometry optimization was performed with the implemented force-field program MAXIMIN 2 before charge calculations were carried out.

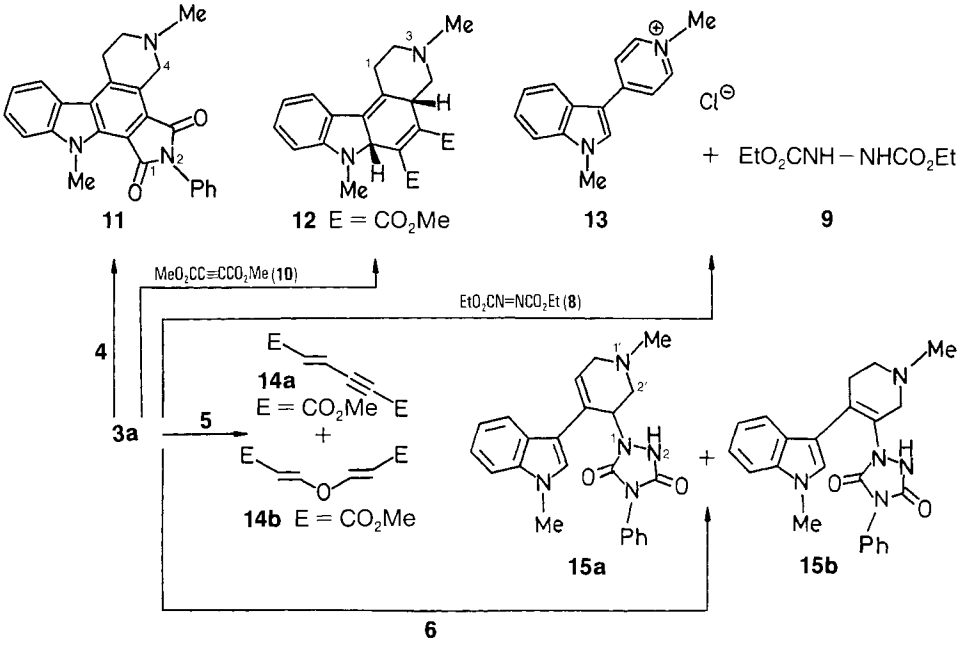
Scheme 2



diamine unit. Compound **2** was prepared in a multi-step sequence according to the procedure described in [12]. Some successful *Diels-Alder* reactions of the *N*-phenylsulfonyl derivative of **2** with carbodienophiles under highly specific conditions such as, *e.g.*, at room temperature with molecular sieves as catalyst and a reaction time of 2–6 weeks, have been reported [12]. On the basis of π-VESCF MO[2]) and charge calculations[3]), compound **2** should also be able to participate in [4 + 2] π-cycloadditions as both frontier-molecular-orbital- and charge-controlled processes (E(HOMO) = −10.56 eV; c(HOMO; C(9a)) = −0.4168, c(C(4a)) = −0.4294, c(C(4)) = 0.3167, c(C(3)) = 0.4372[2]); sum of σ- and π-charges +0.15 (at C(9a)), −0.16 (at C(4a)), +0.10 (at C(4)), and −0.26 (at C(3))[3])). On the other hand, compound **2** is highly susceptible to polymerization and to hydrolysis. In spite of several variations of the reaction conditions (lower temperature, strictly anhydrous reaction medium, inert-gas atmosphere, and the presence of a mild catalyst such as, *e.g.*, highly activated molecular sieves), *Diels-Alder* reactions were not observed with maleimide **4**, propynoate **5**, or triazoledione **6**. In the reaction with diethyl azodicarboxylate (**8**; see *Scheme 3*), only a redox process took place, and the hydrazine **9** was the only stable product that could be isolated to date.

In an earlier report, the synthesis and only superficially investigated *Diels-Alder* reactions of 3-(tetrahydropyridin-4-yl)-1*H*-indoles were reported [13a], and the problem of the polymerization reactivity of this class of dienes was mentioned. We have now extended these studies to include the scope and limitations of the reactivity of compounds **3a** and **3b** in *Diels-Alder* reactions with maleimide **4**, propynoate **5**, triazoledione **6**, azodicarboxylate **8**, and dimethyl acetylenedicarboxylate (**10**; *Scheme 3*). Compounds **3a**

Scheme 3



and **3b** are easily prepared in yields of 45 and 56% according to [20]. On the basis of MMX calculations [17], the s-*cis*-conformation of **3** is energetically preferred and, in the same manner, the MO values are useful for the prediction of a [4 + 2] cycloaddition (**3a**: E(HOMO) = −9.78 eV, c(HOMO; C(2)) = −0.3818, c(C(3)) = −0.4093, c(C(3′)) = 0.4873, c(C(4′)) = 0.3750[2]); sum of σ- and π-charges +0.67 (at C(2)), −0.02 (at C(3)), −0.15 (at C(3′)), −0.04 (at C(4′))[3]). However, in our hands, new *Diels-Alder* reactions of **3a** were only realized with **4** and **10** to furnish the cycloadducts **11** and stereoselectively **12** (*Scheme 3*). In the reaction of **3a** with azodicarboxylate **8**, a redox process took place, and the pyridinium chloride **13** [13a] could be isolated as a highly stable product in addition to compound **9**. On the other hand, the less dienophilic propynoate **5** did not react with **3a** to a cycloadduct; instead, the dienophile underwent dimerization and addition of H_2O (probably from the solvent) to give the unexpected products **14a** and **14b** which have already been reported in [21]. The tertiary amine function in **3a** should catalyse this reaction, as has been demonstrated by reactions of other tertiary amines with **5** [21][4]). Nevertheless, **3a** did react with triazoledione **6** under exclusively kinetically controlled conditions (−78°) to furnish the ene adduct **15a** (major product) and the *Michael*-type adduct **15b** (unseparable 3:2 mixture). At room temperature, **6** induced immediate polymerization of **3a**. In summary, the 'polyfunctionalized' reactivity pattern of **3a** is reflected in the electron-rich diene system, the allylic system, and the oxidizable tetrahydropyridine moiety.

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[4]) See [21] for the mechanistic rationale.

The 3-(tetrahydropyridin-4-yl)-1*H*-indole **3b** is electronically closely related to compound **3a**; however, in our hands, **3b** reacted with the dienophiles **4–6**, **8**, and **10** to yield only products which could not be fully characterized. The polymerization reactivity is strongly enhanced in comparison to that of **3a**. Only in the reaction with triazoledione **6**, a crude product could be isolated whose MS revealed a 1:1 ratio of the reactants. However, the ^{1}H-NMR spectrum of the not unequivocally identified product ruled out the formation of a *Diels-Alder* product.

The pyrido-annellated compounds **11** and **12** obtained represent annellation variants of the antitumor active ellipticines [22], while compounds of the types **13**, **15a**, and **15b** possess structural features of some serotonine receptor antagonists [13b]. Hence, pharmacological screening of all products will be carried out.

The constitutions and configurations presented for the compounds described here are based above all on 200-MHz ^{1}H-NMR characterization methods including some NOE measurements.

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Experimental Part

General. All reactions must be performed in highly pure, anh. solvents under inert-gas atmospheres. For reaction conditions, see the *Table*. Flash chromatography (FC): silica gel *60* (*Merck*, 0.040–0.063 mm particle size); eluent petroleum ether (40–60°)/AcOEt. M.p.: *Büchi SMP-20*; not corrected. ^{1}H-NMR and ^{13}C-NMR spectra: *Bruker-WM-200* and *Bruker-WM-400* spectrometers; δ [ppm] scale, coupling constants J in Hz, TMS as internal standard. EI-MS (70 eV): *Varian MAT 7*, data given as m/z (%). C,H,N Analyses: *Carlo Erba Strumentazione 1106* apparatus.

Table. *Experimental Details of the Reactions of* **1** *and* **3a** *with Dienophiles*

3-Vinyl-1*H*-indole	Dienophile[a])	Solvent	Temperature [°]	Reaction time	Product[a])	Yield	
						[mg]	[%]
1 [16]	**4**	CH_2Cl_2	20°	2 h	**7a**[b])	82	49
1	**5**	CH_2Cl_2	20°	2 h	**7b**[b])	63	58
3a [20]	**4**	toluene	110°	3 h	**11**[c])[d])	218	42
3a	**10**	toluene	110°	3 h	**12**[b])	72	15
3a	**8**	CH_2Cl_2	20°	1 h	**13**[c])	180	61
3a	**5**	toluene	20°	11 h	**14a/14b**[b])	159 + 29	74 + 12
3a	**6**	CH_2Cl_2	–78°	15 min	**15a/15b**[c]) (3:2)	459	87

[a]) See *Schemes 2* and *3*.
[b]) Product purified by FC.
[c]) Product precipitated.
[d]) See [13a].

3-(Morpholin-4-yl)-1-phenylpyrrolidine-2,5-dione (**7a**) [23]. Prepared from **1** (150 mg, 0.63 mmol) and *N*-phenylmaleimide (**4**; 109 mg, 0.063 mmol) in CH_2Cl_2 (50 ml). FC with petroleum ether/AcOEt 4:1. M.p. 175° (Et_2O). ^{1}H-NMR ($CDCl_3$): 2.55–2.65 (*m*, 1 CH_2N); 2.82 (*dd*, ^3J = 20, 4, H_α–C(4)); 2.85–2.95 (*m*, 1 CH_2N); 3.00 (*dd*, ^3J = 20, 9, H_β–C(4)); 3.60 (*t*, ^3J = 6, CH_2OCH_2); 3.90 (*dd*, ^3J = 9, 4, H_α–C(3)); 7.25 (*d*, ^3J = 8, 2 arom. H); 7.35 (*t*, ^3J = 8, 1 arom. H); 7.45 (*t*, ^3J = 8, 2 arom. H). EI-MS: 260 (25, $M^{+\cdot}$), 227 (100), 114 (48). HR-MS: 260.2998 ($C_{14}H_{16}N_2O_3$, calc. 260.2952).

(E)-Methyl 3-(Morpholin-4-yl)prop-2-enoate (**7b**) [24]. Prepared from **1** (150 mg, 0.63 mmol) and methyl propynoate (**5**; 53 mg, 0.63 mmol) in CH_2Cl_2 (50 ml). FC with petroleum ether/AcOEt 4:1. M.p. 68° (Et_2O). ^{1}H-NMR ($CDCl_3$): 3.20 (*t*, ^3J = 6, CH_2NCH_2); 3.60 (*s*, MeO); 3.65 (*t*, ^3J = 6, CH_2OCH_2); 4.70 (*d*, ^3J = 12, 1 olef. H); 7.40 (*d*, ^3J = 12, 1 olef. H). EI-MS: 171 (82, $M^{+\cdot}$), 140 (100, $[M - MeO]^+$). HR-MS: 171.1901 ($C_8H_{13}NO_3$, calc. 171.1977).

*Diethyl Hydrazine-*N,N'*-dicarboxylate* (**9**). Physical data in full agreement with those cited in [24] for the same compound.

5,6,7,12-Tetrahydro-5,12-dimethyl-2-phenylpyrido[3,4-c]pyrrolo[3,4-a]carbazole-1,3(2H,4H)-dione (**11**). Prepared from **3a** (300 mg, 1.32 mmol) and **4** (230 mg, 1.32 mmol) in toluene (60 ml). Isolation of **11** was achieved by direct crystallization from the reaction mixture. M.p. 257° (petroleum ether/$CHCl_3$). ^{1}H-NMR ($CDCl_3$): 2.60 (*s*, Me–N(5)); 2.80 (*t*, ^3J = 5.8, CH_2(7)); 3.50 (*t*, ^3J = 5.8, CH_2(6)); 4.15 (*s*, CH_2(4)); 4.37 (*s*, Me–N(12)); 7.00–7.50 (*m*, 8 arom. H); 8.20 (*d*, ^3J = 8, H–C(8)). EI-MS: 395 (15, $M^{+\cdot}$), 57 (100). Anal. calc. for $C_{25}H_{21}N_3O_2$ (395.47): C 75.90, H 5.35, N 10.63; found: C 75.77, H 5.40, N 10.21.

(±)-Dimethyl 2,3,4,4aβ,6aβ,7-Hexahydro-3,7-dimethyl-1H-pyrido[3,4-c]carbazole-5,6-dicarboxylate (**12**). Prepared from **3a** (300 mg, 1.32 mmol) and dimethyl acetylenedicarboxylate (**10**; 375 mg, 2.64 mmol) in toluene (60 ml). FC with petroleum ether/AcOEt 5:1. M.p. 115° (petroleum ether). ^{1}H-NMR ($CDCl_3$): 2.00–2.10 (*m*, 1 H, CH_2(1) or CH_2(2)); 2.30–2.40 (*m*, 1 H, CH_2(1) or CH_2(2)); 2.80 (*s*, Me–N(3)); 2.80–2.90 (*m*, 1 H, CH_2(1) or CH_2(2)); 2.95–3.10 (*m*, CH_2(1) or CH_2(2)); 3.30 (*s*, Me–N(7)); 3.75 (*s*, MeO); 3.90 (*s*, MeO); 5.20 (*dd*, ^3J = 8, ^2J = 16, H_β–C(4)); 5.30 (*dd*, ^3J = 10, ^2J = 16, H_α–C(4)); 6.45 (*dd*, ^3J = 8, ^3J = 10, H_β–C(4a)); 6.80 (*s*, H_β–C(6a)); 7.00 (*t*, ^3J = 8, H–C(10)); 7.15 (*t*, ^3J = 8, H–C(9)); 7.30 (*d*, ^3J = 8, H–C(8)); 7.60 (*d*, ^3J = 8, H–C(11)). EI-MS: 368 (67, $M^{+\cdot}$), 309 (100), 144 (56). Anal. calc. for $C_{21}H_{24}N_2O_4$ (368.44): C 68.46, H 6.57, N 7.60; found: C 68.09, H 6.21, N 7.81.

1-Methyl-4-(1'-methyl-1'H-indol-3'-yl)pyridinium Chloride (**13**). Prepared from **3a** (300 mg, 1.32 mmol) and diethyl azodicarboxylate (**8**; 230 mg 1.32 mmol) in CH_2Cl_2 (60 ml). The precipitate was crystallized from EtOH. M.p. 230°. ^{1}H-NMR ((D_6)DMSO): 3.90 (*s*, Me–C(1')); 4.20 (*s*, Me–C(1)); 7.35 (*s*, H–C(2')); 7.37 (*d*, ^3J = 7.8, H–C(7')); 7.70 (*dd*, ^3J = 7.8, 8.0, H–C(5') or H–C(6')); 8.20 (*dd*, ^3J = 7.8, 8.0, H–C(6') or H–C(5')); 8.30 (*d*, ^3J = 7.75, H–C(3), H–C(5)); 8.60–8.80 (*m*, H–C(4'), H–C(2), H–C(6)). ^{13}C-NMR ((D_6)DMSO, *J*-modulated spin-echo experiment): 33.4 (*q*); 46.0 (*q*); 109.5 (*s*); 111.5 (*d*); 119.8 (*d*); 120.7 (*d*); 122.4 (*d*); 123.1 (*d*); 124.6 (*s*); 135.7 (*d*); 138.2 (*s*); 144.3 (*d*); 150.2 (*s*). Anal. calc. for $C_{15}H_{15}ClN_2$ (258.75): C 69.63, H 5.83, N 10.83; found: C 68.29, H 5.78, N 10.59.

Dimethyl But-1-en-3-yne-1,4-dicarboxylate (**14a**) [21] *and Dimethyl 3,3'-Oxybis[prop-2-enoate]* (**14b**) [21]. Prepared from **3a** (300 mg, 1.32 mmol) and **5** (111 mg, 1.32 mmol) in CH_2Cl_2 (60 ml). Purification by FC (petroleum ether/AcOEt 8:1). The physical data of **14a** and **14b** are in full accord with the data in [21] for the same compounds.

14a: M.p. 52° (petroleum ether). ^{1}H-NMR ($CDCl_3$): 3.75 (*s*, 2 MeO); 6.73 (*q*, ^3J = 15.4, 2 olef. H). EI-MS: 168 (100, $M^{+\cdot}$), 137 (80, $[M-MeO]^+$), 106 (61, $[M - 2\,MeO]^+$).

14b: M.p. 123° (petroleum ether). ^{1}H-NMR ($CDCl_3$): 3.75 (*s*, 2 MeO); 5.15 (*d*, ^3J = 12, 2 H, H–C(2)); 7.55 (*d*, ^3J = 12, 2 H, H–C(3)). EI-MS: 186 (28, $M^{+\cdot}$), 155 (32, $[M - MeO]^+$).

4-Phenyl-1-[1',2',3',6'-tetrahydro-1'-methyl-4'-(1''-methyl-1''H-indol-3''-yl)pyridin-3'-yl]-1,2,4-triazolidine-3,5-dione (**15a**) *and 4-Phenyl-1-[1',2',5',6'-tetrahydro-1'-methyl-4'-(1''-methyl-1''H-indol-3''-yl)pyridin-3'-yl]-1,2,4-triazolidine-3,5-dione* (**15b**). Prepared from **3a** (300 mg, 1.32 mmol) and 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (**6**; 232 mg, 1.32 mmol) in CH_2Cl_2 (70 ml). Products **15a**/**15b** were isolated from the crude mixture by crystallization from AcOEt. The 3:2 mixture **15a**/**15b** could not be separated even by MPLC without decomposition.

15a: ^{1}H-NMR ($CDCl_3$): 2.45 (*s*, Me–N(1')); 2.70 (*d*, ^3J = 2.8, 1 H–C(2')); 2.80 (*d*, ^3J = 3.2, 1 H–C(2')); 3.45 (*d*, ^3J = 4.5, 1 H–C(6')); 3.51 (*d*, ^3J = 4.5, 1 H–C(6')); 3.75 (*s*, Me–N(1'')); 5.25 (*m*, H–C(3')); 6.50 (*dd*, ^3J = 4.5, H–C(5')); 7.00–7.50 (*m*, 9 H, H–C(2''), H–C(5''), H–C(6''), H–C(7''), Ph); 7.80 (*d*, ^3J = 8, H–C(4'')); 8.9 (*s*, 1 H, NH).

15b: ^{1}H-NMR ($CDCl_3$): 2.15 (*s*, Me–N(1')); 2.70–2.80 (*m*, 1 H–C(5')); 2.80 (*d*, ^3J = 15, 2.1, 1 H–C(5')); 3.05 (*d*, ^3J = 8.5, 15, 1 H–C(6')); 3.20 (*m*, 1 H–C(6')); 3.60 (*s*, CH_2(2')); 7.00–7.50 (*m*, 10 H, H–C(2''), H–C(4''), H–C(5''), H–C(6''), H–C(7''), Ph); 8.9 (*s*, 1 H, NH).

15a/**15b** (3:2 mixture): EI-MS: 401 (10, $M^{+\cdot}$), 255 (100), 226 (21, $[M - 6]^+$). HR-MS: 401.4399 ($C_{23}H_{22}N_4O_2$, calc. 401.4721).

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