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A Convenient Regiospecific Synthesis of New Conjugated Tetrazole Derivatives *via* the Reaction of Dienones with the Tetrachlorosilane-Sodium Azide Reagent and their NMR Structural Assignment

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Summary. Several new 1-aryl-, aralkyl-, and heteroaryl-5-(4-phenylbuta-1,3-dienyl)tetrazole derivatives and annulated tetrazole derivatives were efficiently and regiospecifically prepared in nearly quantitative yield *via* a facile one step reaction of dienones with a combination of tetrachlorosilane and sodium azide in acetonitrile under mild conditions. A complete structure assignment of three representative examples of the tetrazoles was achieved by advanced 2D NMR measurements including COSY, TOCSY, HSQC, HMBC, N*O*ESY, and R*O*ESY experiments.

Keywords. Tetrachlorosilane; Sodium azide; Dienyltetrazoles; Synthesis; NMR spectroscopy.

Introduction

Several tetrazole derivatives have recently received increased attention due to their wide medicinal and industrial applications [1–3]. 1,5-Disubstituted (1*H*)-tetrazoles have long been known for their pharmaceutical activity as stimulants or depressants of the central nervous system [4] and as anti-hypercholesteremics [5, 6]. The development of tetrazole containing non-peptide angiotensin II antagonists for the treatment of congestive heart failure [7, 8] has provided an impetus for the development of new synthetic methods for this class of compounds. The

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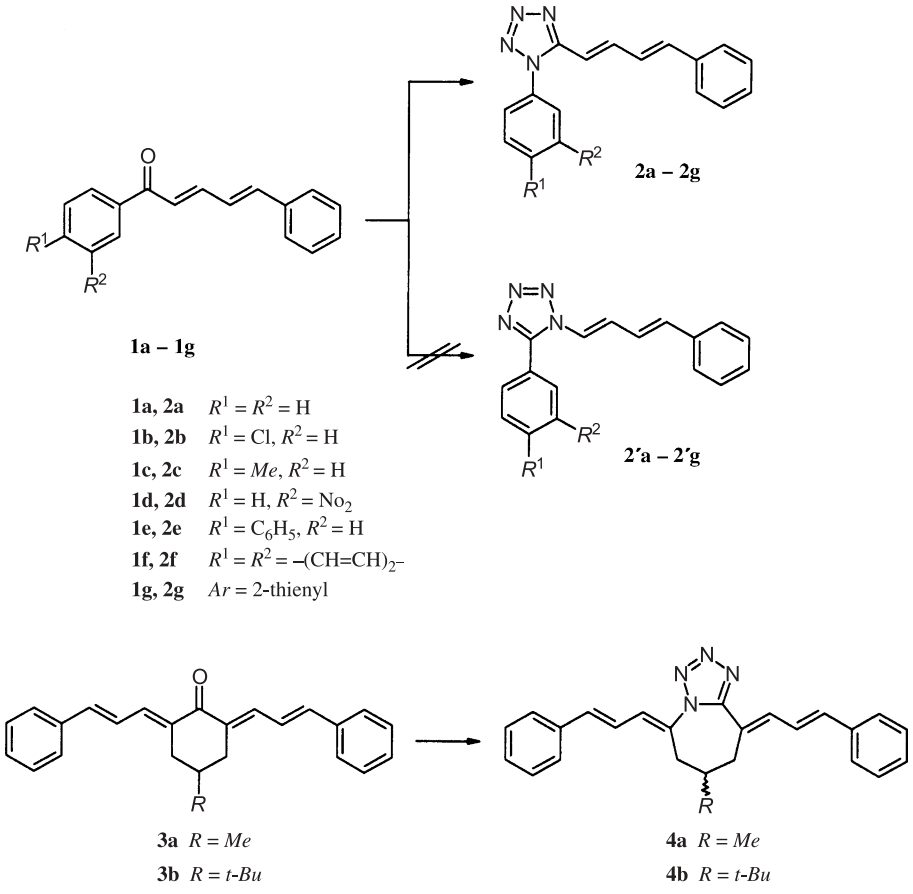
conventional synthesis of 1,5-disubstituted tetrazole derivatives includes the thermal addition of organic azides to electron deficient nitriles [9], thermolysis [10], photolysis [11] or *Lewis* acid induced decomposition [12] of geminal diazides, cyclization of *in situ* generated imidoyl azides [13], and alkylation of 5-substituted tetrazoles [14].

Recently, we have reported that the reaction of different molar ratios of tetrachlorosilane with sodium azide leads to the generation of a mixture of azidochlorosilanes of the general formula $Si(N_3)_nCl_{4-n}$ [15]. Shortly, thereafter, reports by *Herges* and *Starck* [16] have proven to be consistent with our results. A mixture of three equivalents of sodium azide and one equivalent of tetrachlorosilane, which has been found to consist mainly of triazidochlorosilane, has proved to be a suitable and improved reagent for the direct conversion of aldehydes to the corresponding nitriles [15]. It was also used for the efficient oxidation of aldehydes to acyl azides in the presence of activated manganese dioxide [17]. Ketones [18] and primary carboxylic acid amides [19] have been converted to the corresponding tetrazoles using this reagent combination in acetonitrile at ambient and reflux conditions. As part of investigations into the reactivity and potential of this reagent combination which provides an expedient source of azide the reaction of dienones with tetrachlorosilane and sodium azide was investigated as a possible route for the synthesis of 5-dienyltetrazole derivatives.

Results and Discussion

Treatment of 1,5-diphenyl-2,4-pentadiene-1-one (**1a**) with a mixture of two equivalents of tetrachlorosilane and six equivalents of sodium azide in dry acetonitrile at room temperature led to 1-phenyl-5-(4-phenylbuta-1,3-dienyl)-1*H*-tetrazole (**2a**) in excellent yield (Scheme 1). The structure of **2a** was deduced from both spectral and analytical data. The IR spectrum of **2a** showed the disappearance of the carbonyl stretching of the dienone and the appearance of a new strong absorption band at $\bar{\nu} = 1624\,cm^{-1}$ due to the new C=N bond and the MS spectrum showed the molecular ion peak at $m/z = 275$ ($[M+1]^+$) as the base peak. Moreover, as judged by the melting point, **2a** was identical with that prepared by *Buzilova* et al. [20]. To our knowledge, **2a** was the only reported dienyl substituted tetrazole derivative, which however has been prepared *via* a tedious, low overall yield, several step process, using the highly irritant *N*-substituted haloacidamides and haloalkyltetrazoles as starting materials [20, 21].

The general applicability of the reaction for the synthesis of dienyltetrazoles was demonstrated by using dienones with the $SiCl_4/NaN_3$ reagent to get the corresponding conjugated tetrazoles. In the systems studied, we aimed at the effect of electronic and steric factors on the rate of reaction as well as on the migrating aptitudes of the aryl and alkyl groups with respect to the phenyldienyl group. The reaction turned out to be general and quite efficient for a variety of dienones regardless whether the starting materials contained electron donating or electron withdrawing groups. Thus, activated and moderately deactivated dienones such as 1-(4-methylphenyl)-5-phenyl-2,4-pentadiene-1-one (**1c**) and 1-(4-chlorophenyl)-5-phenyl-2,4-pentadiene-1-one (**1b**) yielded the corresponding tetrazoles **2c** and **2b** in nearly quantitative yields. In addition, the relatively slower transformation of the



Scheme 1

strongly deactivated dienone derivative **1d** into the dienyl tetrazole derivative **2d** was observed in reasonable yield.

The present reaction works well also with moderately sterically hindered dienones. *E.g.*, 1-(4-biphenyl)-5-phenyl-2,4-pentadiene-1-one (**1e**) and 1-(2-naphthyl)-5-phenyl-2,4-pentadiene-1-one (**1f**) gave under the same reaction conditions the respective tetrazoles **2e** and **2f** in quite good yields. The heteroaryl dienone 1-(2-thienyl)-5-phenyl-2,4-pentadiene-1-one (**1g**) gave the corresponding tetrazole **2g**, but in lower yield, due to the relative tendency of the starting material to be polymerized under the reaction conditions (Scheme 1). Structures of the tetrazole derivatives **2** were based on analytical and spectral data.

The NMR structure elucidation of **2b** was performed as a representative example for all derivatives of **2** because hitherto the structure of such rearrangement products has not yet been proven unequivocally. In a $^1H/^1H$ TOCSY spectrum it was possible to distinguish between three separated ^1H systems, the butadienyl chain (system A), the *N*-linked 4-chlorophenyl ring (system B), and the unsubstituted phenyl ring (system C). The ^{13}C spectrum showed four peaks, typically for quarternary carbons at $\delta = 152.6$, 136.9, 136.1, and 132.4 ppm. Starting from these ^{13}C signals in the $^{13}C/^1H$ HMBC spectrum we found the characteristic $^{13}C/^1H$

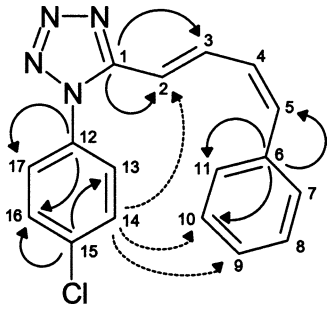
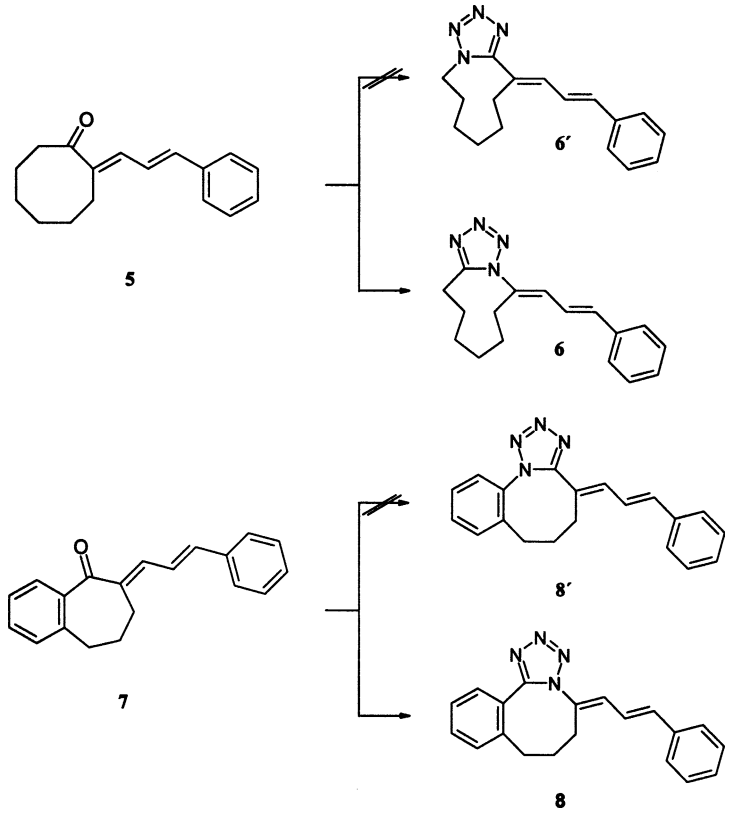


Fig. 1. Structure **2b** including the most important $^{13}C/^{1}H$ HMBC correlations ($^{13}C\rightarrow{}^{1}H$) and $^{1}H/^{1}H$ R*O*ESY cross peaks ($^{1}H\dashrightarrow{}^{1}H$); the atom numbering is not in accord with the IUPAC numbering of the system, but was chosen with request to an unequivocal data handling

correlations, shown in Fig. 1. Thus, ^{13}C signals at 136.9 and 132.4 ppm are only correlated to protons of system B (H13, H14, H16, H17). Accordingly, they are assigned to C15 and C12, whereas the signal of C6 at 136.1 ppm correlates to protons of system A (H5) and system C (H7, H8, H10, H11). The most characteristic ^{13}C signal at 152.6 ppm, which has to be assigned to C1, shows correlations to system A only, in particular, to H2 and H3. Therefore, the 4-chlorophenyl ring has to be *N*-linked and the butadienyl chain is linked to the tetrazole carbon C1. Regarding the stereochemistry of structure **2b** we propose the (2*E*,4*Z*)-configuration shown in Fig. 1, based on *J*-coupling and N*O*E cross peaks. Coupling constants of $^{3}J_{H2,H3} = 15.4$ Hz and $^{3}J_{H4,H5} = 12.3$ Hz corroborated the respective (*E*)- and (*Z*)-configurations. Additionally, we found characteristic cross peaks in a $^{1}H/^{1}H$ R*O*ESY-spectrum (Fig. 1), which are in agreement with the proposed configuration. Unfortunately, it was not possible to discriminate the N*O*E cross peaks of H7, H11, H13, and H17 at 7.47 ppm due to their overlapping signals.

As deduced from the above mentioned data of **2b**, dienones of aryl methyl ketones give the anticipated tetrazoles **2a**–**2g** with preferable aryl migration rather than that of the bulky phenyldienyl group to yield **2′a**–**2′g**. This result is consistent with the reported preferable aryl migration with respect to the vinyl group [22], particularly to the styryl group [18, 23], which may be attributed to the steric factor as both possess an sp^2-hybridized carbon atom. As it is well known that the substituents in acetophenones have no effect on the course of such molecular rearrangements [24], it is reasonable that all above mentioned dienones of aryl methyl ketones (Scheme 1) undergo the same rearrangement with regioselective aryl migration. Of course, the tetraenone derivatives of 4-substituted cyclohexanones **3a** and **3b** gave the respective racemic tetrazoles **4a** and **4b**, but in lower yields (Scheme 1).

In contrast to the migration results for the systems **2** and **4**, the monocinnamylidenecyclooctanone **5** afforded the condensed tetrazole derivative **6** and not **6′** in moderate yield (Scheme 2). Beside the mass spectrum of **6** which showed the molecular ion peak at $m/z = 280$ ($[M+H]^+$) as well as the characteristic peak of tetrazole at $m/z = 252$ attributed to $[M–N_2]^+$, the structure of **6** was deduced by 1D and 2D NMR measurements. First of all, the ^{1}H spectrum showed no signals assignable to a methylene group linked to nitrogen ($\delta = 4.0$–4.6 ppm) [25]. On the other hand, there were three quaternary ^{13}C signals ($\delta = 156.3$, 136.4, and



Scheme 2

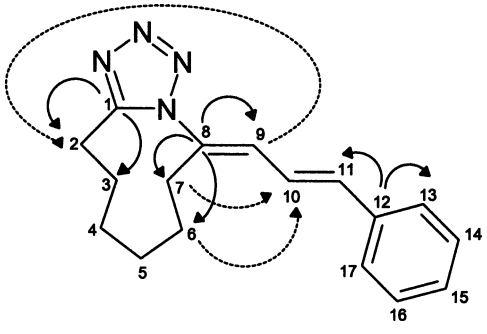


Fig. 2. Structure **6** including the most important $^{13}C/^{1}H$ HMBC correlations ($^{13}C \rightarrow {}^{1}H$) and $^{1}H/^{1}H$ N*O*ESY cross peaks ($^{1}H \dashrightarrow {}^{1}H$); the atom numbering is not in accord with the IUPAC numbering of the system, but was chosen with request to an unequivocal data handling

135.0 ppm), which were easily assigned by correlations to characteristic ^{1}H signals in the $^{13}C/^{1}H$ HMBC spectrum, shown in Fig. 2.

We also focused on the stereochemistry of structure **6** and propose the (8*E*,10*E*)-configuration shown in Fig. 2. Thus, $^{3}J_{H10,H11}$ was found in the 1D spectrum to amount to 15.3 Hz, whereas the (*E*)-configuration on C8/C9 is given

by strong N*O*E cross peaks (Fig. 2). For a (*Z*)-configuration on C8/C9 we would await a weaker cross peak H6/H10 and at least a weak cross peak H10/H2, which could not be observed.

In addition, a further support to the conclusion from the above results was derived from the ready migration of exocyclic vinyl groups with respect to the alkyl analogs [26]. The IR spectrum of **6** showed a higher frequency absorption band for C=N at $\bar{\nu} = 1665\,\mathrm{cm}^{-1}$. However, some strained tetrazole derivatives have been reported to exhibit higher frequency stretching bands for C=N [25, 27].

Even dienones of carbocyclic aromatic ketones, such that of the benzosuberone **7** smoothly gave the annulated tetrazole **8** in excellent yield with regioselective migration of the phenyldienyl group instead of the phenyl group to yield **8′** (Scheme 2). This was deduced from elemental and spectral analysis and, in particular, from 2D NMR spectroscopy. In a $^1H/^1H$ TOCSY spectrum it was possible to recognize four different spin systems (A = condensed phenyl ring, B = unsubstituted phenyl ring, C = aryl bridge, D = butadienyl chain). Linking of these spin systems could be achieved by $^{13}C/^1H$ correlations from HMBC-spectra, in particular of five quarternary carbons ($\delta = 152.1$, 139.3, 136.6, 134.6, and 125.1 ppm), as shown in Fig. 3. Unfortunately, there was no correlation from C11 at 134.6 ppm to spin system D (only to H9 and H10 of system C), but the connection could be shown by a correlation from C12 to H10.

The most important correlation was from C1 at 152.1 ppm to H3 ($\delta = 7.80$ ppm) in spin system A. This confirmed the linkage of the condensed phenyl ring to the tetrazole carbon, because in case of *N*-linkage an estimated correlation from C1 to H10 or H12 would occur with much higher probability. Concerning the stereochemistry of **8** we propose again a (11*E*, 13*E*)-configuration (Fig. 3), characterized by a coupling constant $^3J_{\mathrm{H13,H14}} = 15.1$ Hz and some N*O*E cross peaks (Fig. 3) which should not occur for a (11*Z*, 13*E*)-configuration (in particular H9/H20).

Because the phenyl group is usually considered a better migrating group than the vinyl group [18, 22, 23], the observed result of a dichotomy of regioselective migration may be interpreted in the light of the advantageous migratory aptitude of the exocyclic vinyl group [26, 28].

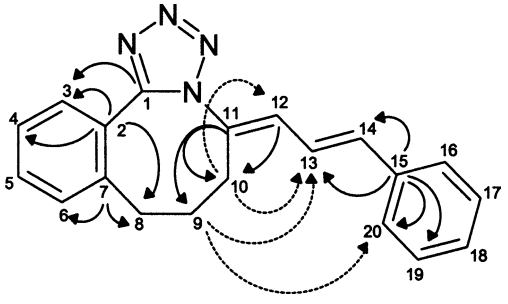
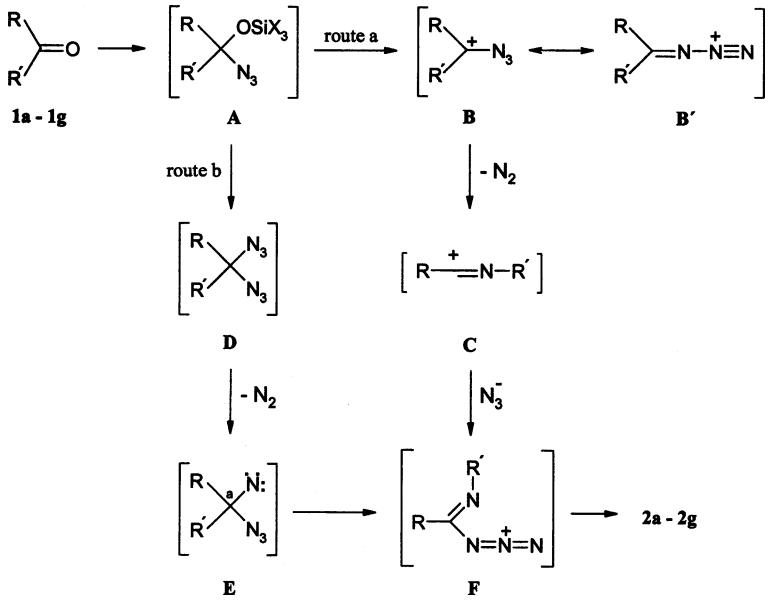


Fig. 3. Structure **8** including the most important $^{13}C/^1H$ HMBC correlations ($^{13}C \rightarrow {}^1H$) and $^1H/^1H$ R*O*ESY cross peaks ($^1H \dashrightarrow {}^1H$); the atom numbering is not in accord with the IUPAC numbering of the system, but was chosen with request to an unequivocal data handling



Scheme 3

A plausible mechanism for the formation of the conjugated tetrazole derivatives **2a**–**2g**, **4**, **6**, and **8** is shown in Scheme 3. It is likely that the dienyl tetrazoles are formed *via* two competing routes a and b. The reaction involves the formation of the siloxy azide intermediate (A) *via* 1,2-addition of the *in situ* generated silicon(IV) azide chloride $Si(N_3)_nCl_{4-n}$ to the carbonyl group of **1**, followed by subsequent formation of the *gem*-diazide (D) (route b). The latter intermediate undergoes rearrangement with predominant migration of the aryl group rather than the phenyldienyl group giving the imidoyl azide (F), followed by cyclization to the tetrazole derivatives **2a**–**2g**. We think that the migrating aptitude of the phenyl group is higher than that of the phenyldienyl group, possibly due to the more extended conjugation in the latter. This would facilitate the developing positive charge on C_a, (intermediate E), and thus enhance the synchronous formation of C=N and migration of the phenyl ring.

In route a the intermediate (A) collapses to generate a carbenium ion (B), which undergoes a *Beckmann* type rearrangement by loosing a molecule of nitrogen followed by regiospecific 1,2-migration of the aryl group from the carbonyl carbon to the adjacent nitrogen to give the iminocarbenium ion (intermediates C). In this ion the positive charge is stabilized by the extended conjugation in the phenyldienyl group. Trapping of (C) by azide anion leads to the imidoyl azide intermediates (F) which then cyclize to the tetrazoles **2a**–**2g**. The equilibrium between imidoyl azide and tetrazole has been well established [29]. The tetrazole form exists predominantly around room temperature. However, the IR spectra of the products showed absorption bands for C=N and N=N of the tetrazole ring and the absence of the absorption band of the azido group of imidoyl azide ($\bar{\nu} \sim 2160 - 2120\,cm^{-1}$). According to these results 1,5-disubstituted tetrazoles were obtained in a regiospecific manner with the regioselective migrations described above.

In conclusion, the tetrazole formation according to the afore mentioned methodology tolerates a variety of functional groups on the aromatic ring in the dienones. Thus, chloro-, methyl-, and nitro-containing dienones gave the corresponding tetrazoles in good to excellent yield. In addition, the reaction tolerates mono- and bis-dienyl derivatives of cyclic and benzo-fused cyclic ketones to give several highly interesting annulated tetrazole derivatives.

Experimental

Melting points were determined by using the *Griffin* capillary melting point apparatus and were uncorrected. Infrared spectra were recorded on a Mattson FTIR spectrometer 5000. The mass spectra were recorded on GC-MS QP-1000 Ex Shimadzu (Japan) and Fisons MD 800 mass spectrometer. Ultraviolet spectra were recorded on a Unicam UV/Vis UV2 spectrometer. ^{1}H NMR and ^{13}C NMR were recorded on Bruker FT NMR (300, 400 MHz), Bruker Avance DPX 200 MHz, and Bruker Avance DRX 500 MHz spectrometer. 2D NMR experiments were performed on a 500 MHz spectrometer using standard pulse sequences as provided by the manufacturer. Typical 90° hard pulse durations were 8 µs (^{1}H) and 18 µs (^{13}C), 90° pulses in decoupling experiments were set to 100 µs. HSQC and HMBC experiments were optimized for coupling constants of 140 Hz for single quantum correlations and 10 Hz for multi-bond correlations. N*O*ESY mixing times and R*O*ESY spin lock were set to 200 ms, TOCSY experiments used MLEV mixing sequences with 22.55 µs 90° pulses. All ketones used for the preparation of dienones were of commercial grade and used as such. Tetrachlorosilane was used as obtained from Aldrich. Acetonitrile was dried by refluxing over P_2O_5 followed by distillation. Column and preparative thin layer chromatography were carried out using Merck silicagel 60 GF-254 (230–400 mesh). Analytical TLC was performed on aluminum sheets (Merck, silicagel 60 F-254, thickness 0.2 mm). The dienones **1a**–**1g** [30–36], **3a**, **3b**, **5**, and **7** [37, 38] were prepared according to literature methods.

General Procedure for the Reaction of Dienones **1a**–**1g**, **3a**, **3b**, **5**, *and* **7** *with Tetrachlorosilane-Sodium Azide*

Tetrachlorosilane (1.2 cm^3, 10 mmol) was added to a mixture of 5 mmol of dienone **1a**–**1g**, **3a**, **3b**, **5**, or **7** and 1.95 g of sodium azide (30 mmol) in 15 cm^3 of acetonitrile. The mixture was stirred at ambient temperature until TLC showed disappearance of the starting material, then poured onto 100 cm^3 of ice water and extracted with 2 × 50 cm^3 of ethyl acetate. The extracts were washed with H_2O, dried over anh. $MgSO_4$, and evaporated under vacuum. The crude products were purified either by crystallization from ethyl acetate (**2a**–**2c**, **2e**, **2f**, and **8**) or by column chromatography (**2d**, **2g**, **4a**, **4b**, and **6**) using a mixture of pet. ether ethyl acetate.

1-Phenyl-5-(4-phenylbuta-1,3-dienyl)-1H-tetrazole (**2a**, $C_{17}H_{14}N_4$)

Reaction time 12 h; Yield 93%; Mp 160–161°C (Ref. [20] 160–162°C); TLC: $R_f = 0.65$ (pet. ether: ethyl acetate = 6:1); ^{1}H NMR (300 MHz, *DMSO*-d_6): $\delta = 7.80 - 7.54$ (m, 7H), 7.41 − 7.22 (m, 5H), 7.09 (d, $J = 15$ Hz, =CH), 6.56 (d, $J = 15$ Hz, =CH) ppm; CI-MS (solid probe, CH_4 3.5): $m/z = 275$ ($[M + H]^+$); IR (KBr): $\bar{\nu} = 3057$, 3020 (=CH), 1628 (C=N), 1593 (C=C), 1497, 1442, 1292, 1110, 986, 755, 689 cm^{-1}; UV/Vis ($CHCl_3$): $\lambda_{max}(\varepsilon) = 323$ (15900) nm (dm$^3 \cdot$ mol$^{-1} \cdot$ cm^{-1}).

(1E,3Z)-1-(4-Chlorophenyl)-5-(4-phenylbuta-1,3-dienyl)-1H-tetrazole (**2b**, $C_{17}H_{13}ClN_4$)

Reaction time 13 h; Yield 91%; Mp 204°C; TLC: $R_f = 0.62$ (pet. ether:ethyl acetate = 6:1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.77$ (dd, $J = 15.4$, 9.3 Hz, H3), 7.61 (d, $J = 8.6$ Hz, ar-H14, ar-H16), 7.47 (2d, $J = 8.6$, 7.1 Hz, ar-H7, ar-H11, ar-H13, ar-H17), 7.37 (t, $J = 7.1$ Hz, ar-H8, ar-H10), 7.32 (d, $J = 7.1$ Hz, ar-H9), 6.93 (d, $J = 12.3$ Hz, H5), 6.92 (dd, $J = 12.3$, 9.3 Hz, H4), 6.37 (d, $J = 15.4$ Hz, H2) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 152.6$ (C1), 142.1 (C3), 140.4 (C5), 136.9 (C15), 136.1 (C6), 132.4 (C12), 130.5 (C14, C16), 129.4 (C9), 129.1 (C8, C10), 127.4 (C7, C11), 126.7 (C4), 126.6 (C13, C17), 110.0 (C2) ppm – atom numbering for the ^{1}H and ^{13}C spectra refers to Fig. 1; CI-MS (solid probe, CH_4 3.5): $m/z = 309$ ($[M + H]^+$); IR (KBr): $\bar{\nu} = 3057$, 3023 (CH=), 1624 (C=N), 1497, 1445, 1410, 1285, 1090, 897, 826, 751, 688 cm^{-1}; UV/Vis ($CHCl_3$): $\lambda_{max}(\varepsilon) = 313$ (20400) nm (dm$^3 \cdot$ mol$^{-1} \cdot$ cm^{-1}).

1-(4-Methylphenyl)-5-(4-phenylbuta-1,3-dienyl)-1H-tetrazole (**2c**, $C_{18}H_{16}N_4$)

Reaction time 12 h; Yield 95%; Mp 169°C; TLC: $R_f = 0.66$ (pet. ether:ethyl acetate = 6:1); ^{1}H NMR (300 MHz, *DMSO*-d_6): $\delta = 7.70 - 7.46$ (m, 5H), 7.42 – 7.20 (m, 6H), 7.08 (d, $J = 15$ Hz, =CH), 6.56 (d, $J = 15$ Hz, =CH), 2.42 (s, CH_3); IR (KBr): $\bar{\nu} = 3066$, 3025 (CH=), 2917, 2860 (CH_3), 1622 (C=N), 1515, 1489, 1448, 1096, 994, 817, 752, 694 cm^{-1}; UV ($CHCl_3$): $\lambda_{max}(\varepsilon) = 328$ (16700) nm ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$).

1-(3-Nitrophenyl)-5-(4-phenylbuta-1,3-dienyl)-1H-tetrazole (**2d**, $C_{17}H_{13}N_5O_2$)

Reaction time 21 h; Yield 81%; Mp 208–209°C; TLC: $R_f = 0.85$ (pet. ether:ethyl acetate = 4:1); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.47$ (m, 1H), 7.86 (m, 2H), 7.41 (m, 7H), 6.96 (d, $J = 8.5$ Hz, 2H), 6.39 (d, $J = 15$ Hz, 1H) ppm; IR (KBr): $\bar{\nu} = 3099$, 2924, 2855, 1621 (C=N), 1534, 1491, 1445, 1350 (NO_2), 1103, 1001, 884, 800, 736, 692 cm^{-1}; UV/Vis ($CHCl_3$): $\lambda_{max}(\varepsilon) = 331$ (16900) nm ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$).

1-(1,1′-Biphenyl-4-yl)-5-(4-phenylbuta-1,3-dienyl)-1H-tetrazole (**2e**, $C_{23}H_{18}N_4$)

Reaction time 15 h; Yield 87%; Mp 205°C; TLC: $R_f = 0.5$ (pet. ether:ethyl acetate = 6:1); ^{1}H NMR (300 MHz, *DMSO*-d_6): $\delta = 8.01 - 7.90$ (m, 3H), 7.80 – 7.68 (m, 5H), 7.60 – 7.40 (m, 5H), 7.32 – 7.25 (m, 3H), 7.10 (d, $J = 15$ Hz, =CH), 6.63 (d, $J = 15$ Hz, =CH) ppm; IR (KBr): $\bar{\nu} = 3052$, 3028, 2926 (=CH), 1624 (C=N), 1520, 1487, 1447, 1407, 1096, 999, 844, 760, 693 cm^{-1}; UV/Vis ($CHCl_3$): $\lambda_{max}(\varepsilon) = 330$ (14700) nm ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$).

1-(2-Naphthyl)-5-(4-phenylbuta-1,3-dienyl)-1H-tetrazole (**2f**, $C_{21}H_{16}N_4$)

Reaction time 17 h; Yield 84%; Mp 154°C; TLC: $R_f = 0.3$ (pet. ether:ethyl acetate = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.08$ (d, $J = 8$ Hz, 1H), 7.96 (m, 3H), 7.78 (m, 1H), 7.65 (m, 2H), 7.56 (dd, $J = 8$, 2.1 Hz, 1H), 7.43 (m, 2H), 7.30 (m, 4H), 6.89 (m, 1H), 6.45 (d, $J = 16$ Hz, =CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 152.5$, 141.4, 139.7, 135.9, 133.5, 132.9, 131.0, 129.0, 128.8, 128.6, 128.4, 128.0, 128.0, 127.8, 127.1, 126.6, 124.3, 122.3, 110.4 ppm; EI-MS (m/z, %): 324 (M^+, 28), 296 ($M^+ - N_2$, 26), 295 ($M^+ - HN_2$, 47), 220 ($M^+ - C_6H_4N_2$, 18), 219 ($M^+ - C_6H_5N_2$, 100), 193 (16), 168 ($M^+ - C_{10}H_8N_2$, 15), 141 (27), 127 (40); IR (KBr): $\bar{\nu} = 3052$, 3021 (=CH), 2923, 2855, 1623 (C=N), 1512, 1488, 1445, 1421, 1106, 994, 860, 815, 747, 691 cm^{-1}; UV/Vis ($CHCl_3$): $\lambda_{max}(\varepsilon) = 242$ (16700) nm ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$).

5-(4-Phenylbuta-1,3-dienyl)-1-thien-2-yl-1H-tetrazole (**2g**, $C_{15}H_{12}N_4S$)

Reaction time 16 h; Yield 43%; Mp 138°C; TLC: $R_f = 0.55$ (pet. ether:ethyl acetate = 5:1); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.75$ (m, 1H), 7.45 – 7.19 (m, 8H), 6.95 (m, 2H), 6.46 (d, $J = 15.6$ Hz, =CH) ppm; EI-MS (m/z, %): 281 ($M^+ + 1$, 38), 280 (M^+, 72), 252 ($M^+ - N_2$, 83), 251 ($M^+ - HN_2$, 100), 225 (22), 219 (12), 175 ($M^+ - C_6H_5N_2$, 36), 154 (20), 128 (28); IR (KBr): $\bar{\nu} = 3104$, 3023 (=CH), 1624 (C=N), 1549, 1489, 1454, 1397, 1095, 997, 846, 753, 691 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 246 (16200) nm ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$).

7-Methyl-5,9-bis(3-phenylprop-2-enylidene)-6,7,8,9-tetrahydro-5H-tetrazolo[1,5-a]azepine (**4a**, $C_{25}H_{24}N_4$)

Reaction time 17 h; Yield 46%; Mp 237–239°C; TLC: $R_f = 0.45$ (pet. ether:ethyl acetate = 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.60 - 6.80$ (m, 16H), 2.83 (m, CH_2), 2.50 (m, CH_2), 1.20 (m, CH_3),

0.80 (m, CH) ppm; IR (KBr): $\bar{\nu} = 3026$ (=CH–), 2955, 2925, 2865 (CH_3, CH_2), 1618 (C=N–), 1492, 1452, 1412, 1100, 971, 762, 692 cm^{-1}.

7-tert-Butyl-5,9-bis(3-phenylprop-2-enylidene)-6,7,8,9-tetrahydro-5H-tetrazolo[1,5-a]azepine(**4b**, $C_{28}H_{30}N_4$)

Reaction time 18 h; Yield 44%; Mp 202°C; TLC: $R_f = 0.6$ (pet. ether:ethyl acetate = 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.65 - 6.70$ (m, 16H), $3.11 - 2.94$ (m, CH_2), $2.80 - 2.50$ (m, CH_2), 1.32 (m, CH), 1.11 (s, $3CH_3$) ppm ; EI-MS (m/z, %): 422 (M^+, 0.1), 394 (M^+–N_2, 26), 368 (6), 337 (M^+–$C_4H_9N_2$, 28), 317 (13), 278 (M^+–$C_9H_8N_2$, 34), 194 (24), 156 (100), 141 (69); IR (KBr): $\bar{\nu} = 3066$, 3029 (=CH–), 2956, 2925, 1618 (C=N), 1491, 1449, 1368, 1100, 966, 749, 694 cm^{-1}.

(2E,5E)-5-(3-Phenylprop-2-enylidene)-6,7,8,9,10,11-hexahydro-5H-tetrazolo[1,5-a]azonine (**6**, $C_{17}H_{20}N_4$)

Reaction time 22 h; Yield 47%; Mp 94°C; TLC: $R_f = 0.4$ (pet. ether:ethyl acetate = 5:1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.49$ (d, $J = 7.4$ Hz, ar-H13, ar-H17), 7.39 (t, $J = 7.4$ Hz, ar-H14, ar-H16), 7.34 (d, $J = 7.4$ Hz, ar-H15), 7.03 (dd, $J = 15.3$, 11.1 Hz, H10), 6.79 (d, $J = 15.3$ Hz, H11), 6.41 (d, $J = 11.1$ Hz, H9), 3.13 (t, $J = 6.1$ Hz, 2H2), 2.86 (t, $J = 6.1$ Hz, 2H7), 1.83 (m, 2H3), 1.52 (m, 2H6), 1.46 (m, 2H4), 1.42 (m, 2H5) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 156.3$ (C1), 138.8 (C11), 136.4 (C12), 135.0 (C8), 131.3 (C9), 129.2 (C15), 129.1 (C14, C16), 127.3 (C13, C17), 121.5 (C10), 30.8 (C7), 25.8 (C5), 25.6 (C3), 25.0 (C4), 24.1 (C6), 23.3 (C2) ppm – atom numbering for the ^{1}H and ^{13}C spectra refers to Fig. 2; EI-MS (m/z, %): 281 (M^+1, 67), 280 (M^+, 25), 252 (M^+–N_2, 59), 251 (M^+–HN_2, 28), 175 (M^+–$C_6H_5N_2$, 27), 156 (100), 141 (28), 115 (71); IR (KBr): $\bar{\nu} = 3415$, 3030, 2934, 2861, 1665, 1614, 1500, 1428, 1100, 975, 751, 693 cm^{-1}; UV/Vis ($CHCl_3$): $\lambda_{max}(\varepsilon) = 298$ (15900) nm ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$).

(2E,5E)-5-(3-Phenylprop-2-enylidene)-5,6,7,8-tetrahydrotetrazolo[5,1-a]benz[g]azocine (**8**, $C_{20}H_{18}N_4$)

Reacion time 14 h; Yield 87%; Mp 187–189°C; TLC: $R_f = 0.5$ (pet. ether:ethyl acetate = 5:1); ^{1}H NMR (500 MHz, *DMSO*-d_6): $\delta = 7.80$ (d, $J = 7.7$ Hz, ar-H3), 7.63 (d, $J = 7.7$ Hz, ar-H16, ar-H20), 7.60 (d, $J = 7.7$ Hz, ar-H4), 7.47 (t, $J = 7.7$ Hz, ar-H5), 7.42 (d, $J = 7.7$ Hz, ar-H6), 7.37 (t, $J =$ 7.7 Hz, ar-H17, ar-H19), 7.32 (d, $J = 11.4$ Hz, H12), 7.31 (d, $J = 7.7$ Hz, ar-H18), 7.25 (dd, $J = 15.1$, 11.4 Hz, H13), 6.97 (d, $J = 15.1$ Hz, H14), 2.73 (t, $J = 5.8$ Hz, 2H10), 2.69 (t, $J = 6.1$ Hz, 2H8), 1.91 (m, $J = 5.8$, 6.1 Hz, 2H9) ppm; ^{13}C NMR (125 MHz, *DMSO*-d_6): $\delta = 152.1$ (C1), 139.3 (C2), 137.0 (C14), 136.6 (C15), 134.6 (C11), 132.1 (C4), 130.5 (C3), 129.9 (C6), 128.7 (C17, C19), 128.3 (C18), 126.9 (C16, C20), 126.8 (C5), 125.1 (C7), 123.4 (C12), 122.3 (C13), 31.1 (C8), 30.4 (C9), 23.8 (C10) ppm – atom numbering for the ^{1}H and ^{13}C spectra refers to Fig. 3; CI-MS (solid probe, CH_4 3.5): $m/z = 315$ ($[M + H]^+$); EI-MS (m/z, %): 315 ($M^+ + 1$, 27), 314 (M^+, 36), 286 (M^+–N_2, 100), 285 (M^+–HN_2, 88), 257 (27), 209 (M^+–$C_6H_5N_2$, 24), 195 (53), 155 (88); IR (KBr): $\bar{\nu} = 3030$, 3020, 2941, 2922, 1611, 1597, 1487, 1462, 1439, 1388, 1304, 1284, 1088, 968, 778, 755, 695 cm^{-1}; UV/Vis ($CHCl_3$): $\lambda_{max}(\varepsilon) = 333$ (17300) nm ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$).

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