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One-pot regioselective vinylation of tetrazoles: preparation of 5-substituted 2-vinyl-2*H*-tetrazoles

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ABSTRACT

The one-pot regioselective preparation of 5-aryl/alkyl-2-vinyl-2*H*-tetrazoles from 5-substituted tetrazoles via a very simple procedure using 1,2-dibromoethane and triethylamine without the need of any catalyst is described. The mechanism of this reaction is also discussed.

The preparation of tetrazoles and their derivatives has been the subject of intense investigation in recent years, especially due to the use of 5-substituted-1*H*-tetrazoles as an isosteric replacement for the carboxylic acid moiety in pharmaceutical chemistry.[1] The most significant representatives of biologically active compounds containing the tetrazole ring are the antihypertensive angiotensin II receptor antagonists named sartanes.[1] Moreover, tetrazoles have found widespread use as ligands in coordination chemistry, as components of explosives and in the photographic industry.[2] The synthesis of 5-substituted tetrazoles via cycloaddition of an azide anion to the corresponding nitrile is well described in the literature. All the synthetic approaches fall within three main categories: those that use tin, aluminium or silicon-containing compounds as donors of azide anions,[3] those that use Lewis acids,[4] and finally those that proceed in acidic media or are acid-catalyzed.[5,6]

The simplest preparation of 1,5- and 2,5-disubstituted tetrazoles is based on alkylation or arylation of 5-substituted tetrazoles. The main disadvantage of this method is the lack of regioselectivity. The product obtained is usually a mixture of both isomers in an approximately 1:1 ratio and these isomers are extremely difficult to separate. Attempts to influence the regioselectivity by modification of the reaction conditions have mostly failed.[7] The synthesis of 1,5-disubstituted tetrazoles by different methods, starting mainly from the corresponding amides, is well described.[8] However, there are only a few methods for the selective synthesis of 2,5-disubstituted tetrazoles from 5-substituted tetrazoles, such as the palladium- and copper-catalyzed arylation with diaryliodonium salts.[9] The majority of these methods take advantage of a bulky substituent, with preferential reaction at position 2 of the tetrazole (reviewed in Koldobskii et al.[10]).

Although several methods for the preparation of 5-substituted 2-vinyl-2*H*-tetrazoles have been published, all have substantial disadvantages. The first method is direct vinylation of tetrazole using vinyl acetate in the presence of mercuric acetate. The major drawback lies in the toxicity of the mercuric substances along with relatively low yields.[11] Another possibility is the dehydration of 5-aryl-2-(2-hydroxyethyl)-2*H*-tetrazoles or dehydrohalogenation of 5-aryl-2-(2-chloroethyl)-2*H*-tetrazoles. However, the preparation of these intermediates leads to both 1,5- and 2,5-isomers in various ratios, which must be separated chromatographically.[12] Although a mild copper-catalyzed vinylation of various azoles has been described, it was unsuccessful in the case of tetrazoles.[13] An unexpected formation of vinyltetrazoles was observed during the preparation of tetrazole macrocycles. However, this reaction was not regioselective and the obtained yields of both 1- and 2-vinyl derivatives were low (10%), even after long reaction times (24–120 h).[14]

We have developed a new, one-pot, regioselective method for the preparation of 2-vinyltetrazoles. We found that the reaction of 5-phenyl-1*H*-tetrazole (**1a**) with 1,2-dibromoethane and triethylamine in a 1:1:2 molar ratio in acetonitrile led to the preferential formation of 5-phenyl-2-vinyl-2*H*-tetrazole (**2a**) (Scheme 1). Tetrazole 1,1-, 1,2- and 2,2-dimers, that is, 1,1-bis(5-phenyl-1*H*-tetrazol-1-yl)ethane (**3a**), 1-[2-(5-phenyl-2*H*-tetrazol-2-yl)ethyl]-5-phenyl-1*H*-tetrazole (**3b**), and 2,2-bis(5-phenyl-2*H*-tetrazol-2-yl)ethane (**3c**), were formed as side products (Fig. 1). Increasing the amount

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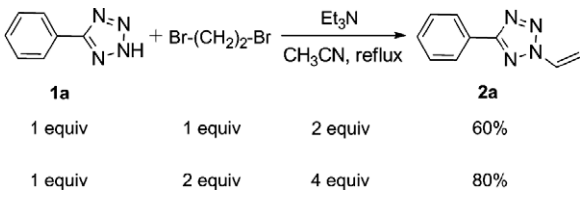


Scheme 1.

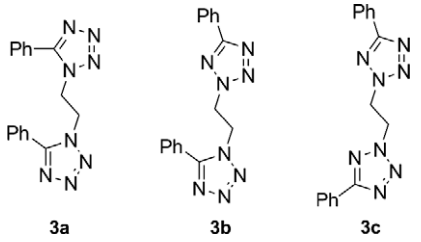


Figure 1. Tetrazole dimers **3a–c**, side products of the reaction.

of 1,2-dibromoethane and triethylamine increased the yield of the product **2a** and decreased the yield of the dimers **3a–c**. Surprisingly, 5-phenyl-1-vinyl-1*H*-tetrazole was formed in only a trace amount.

This result encouraged us to investigate the reaction mechanism. Alkylation of 5-substituted tetrazoles is a well known process. Thus, the alkylation of 5-substituted 1*H*-tetrazole with 1,2-dibromoethane would furnish an approximate 1:1 ratio of regioisomers and the subsequent elimination would yield both 1- and 2-vinyl derivatives of 5-substituted 1*H*-tetrazole. Also, an increasing amount of both the alkylating agent and base would not significantly affect the ratio of 1- and 2-substituted isomers. Therefore, alkylation of the tetrazole with 1,2-dibromoethane is unlikely to be the first step of this reaction. However, this mechanism may well explain the formation of the tetrazole dimers **3a–c**.

The requirement of a twofold molar amount of the base relative to 1,2-dibromoethane suggests that the elimination step of the reaction proceeds via a quaternary ammonium salt by a mechanism similar to Hofmann elimination. This hypothesis was verified by the reaction of tetrazole **1a** with 1,2-dibromoethane in the presence of different organic bases. The reaction with diisopropylethylamine as the base proceeded similarly to the reaction with triethylamine, that is, vinyl derivative **2a** was formed as the main product. The same reaction using pyridine led to a mixture of quaternary ammonium salts, and no vinyl derivative **2a** was detected in the reaction mixture.

Thus, it is likely the reaction proceeds via the following pathway (Scheme 2). In the first step, triethylamine reacted with 1,2-dibromoethane to form (2-bromoethyl)triethylammonium bromide, which reacted with tetrazole **1a** producing triethyl-2-(5-phenyl-2*H*- tetrazol-2-yl)ethylammonium bromide. Substitution at position 2 of the tetrazole ring is probably directed by the steric requirements of (2-bromoethyl)triethylammonium bromide. Under the reaction conditions, triethyl-2-(5-phenyl-2*H*-tetrazol-2-yl)ethylammonium bromide underwent spontaneous elimination to produce vinyl derivative **2a**.

In order to confirm the proposed reaction mechanism, we attempted to prepare the putative intermediate (2-bromoethyl)triethylammonium bromide by reaction of 1,2-dibromoethane with triethylamine according to the procedure described previously.[15] Surprisingly, only triethylammonium bromide was recovered from the reaction mixture when using various temperatures and solvents. Thus, commercially available (2-bromoethyl)trimethylammonium bromide was used to evaluate the proposed reaction mechanism. On reaction with potassium 5-phenyl-1*H*-tetrazolate in *N*,*N*-dimethylformamide, the quaternary ammonium intermediate trimethyl-2-(5-phenyl-2*H*-tetrazol-2-yl)ethylammonium bromide (**4**) was obtained, isolated and characterized.[16] Formation of vinyl derivative **2a** as a side product also occurred during this reaction.

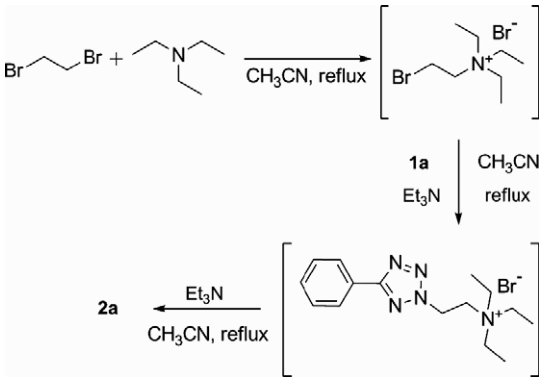
Compound **4** readily and quantitatively decomposed to vinyl tetrazole **2a** in boiling acetonitrile in the presence of triethylamine, thereby confirming the suggested mechanism for the vinylation (Scheme 3).

We subsequently studied the effects of various solvents on the yields of vinyl tetrazole **2a**. It was found that the reaction proceeded in high yields almost regardless of the solvent used, which is another advantage of this method (Table S1—Supplementary data). However, to prevent increased formation of dimers, the order of addition of the reagents is important. It is necessary to maintain an excess of dibromoethane in the reaction mixture. The utility of this method was demonstrated by the preparation of several new 5-aryl-2-vinyl-2*H*-tetrazoles **2a–h** (Table 1).[17,18]

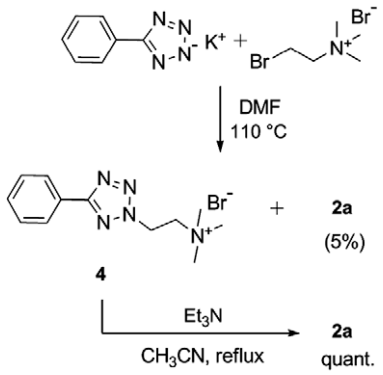
Moreover, 5-alkyl-2*H*-tetrazoles can also be converted into the corresponding 5-alkyl-2-vinyl-2*H*-tetrazoles in moderate yields (**2i–k**; Table 1).[17,18] The lower yields can be attributed to the higher nucleophilicity of 5-alkyl-2*H*-tetrazoles leading to easier formation of tetrazole dimers, and to less steric hindrance from the 5-alkyl groups. The low isolated yield of methyl derivative **2k** (21%) was due to the volatility of the product, however, examination of the NMR spectra of the reaction mixture revealed that the 2-vinylation proceeded in 53% yield, similar to the other alkyl derivatives.

Another advantage of this method is that the relatively lipophilic products can be easily isolated by column chromatography, because they have markedly higher R_f values than other components of the reaction mixture.

In conclusion, we have developed a one-pot regioselective method for the preparation of 5-substituted 2-vinyl-2*H*-tetrazoles

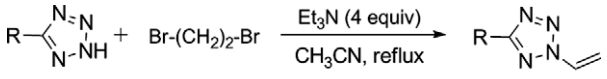


Scheme 2.



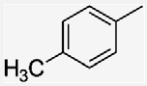
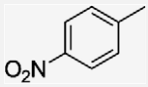
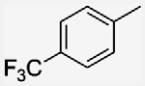
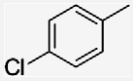
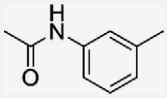
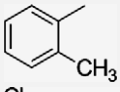
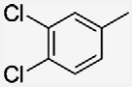
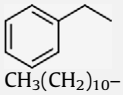
Scheme 3.

Table 1
Preparation of 5-substituted 2-vinyl-2*H*-tetrazoles



1 equiv 2 equiv

1a-k **2a-k**

Product	R-	Time (h)	Yield (%)
2a		4	80
2b		4	75
2c		4	79
2d		4	86
2e		5	84
2f		4	77
2g		4.5	78
2h		4.5	88
2i		4	53
2j	$CH_3(CH_2)_{10}$–	4	54
2k		4	53/21[a]

[a] NMR/isolated yield.

via a simple procedure without a metal catalyst or organocatalyst. The resulting 5-substituted 2-vinyl-2*H*-tetrazoles can undergo transformation of the double bond and can be used to prepare 3-substituted pyrazoles.[12c]

Acknowledgements

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Supplementary data

Supplementary data (general experimental details, copies of NMR spectra, Table S1) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.01.021.

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16. *Preparation of trimethyl-2-(5-phenyl-2H-tetrazol-2-yl)ethylammonium bromide* (**4**): Potassium 5-phenyl-1*H*-tetrazolate (3.4 mmol) and (2-bromoethyl)trimethylammonium bromide (3.4 mmol) were added to 5 ml of *N,N*-dimethylformamide. The reaction mixture was stirred at 110 °C for 4 h, then cooled to room temperature and the resulting solid was filtered, washed with $CHCl_3$ (10 ml) and dried. The solid was dispersed in boiling ethanol (96%, 15 ml), KBr was removed by filtration, the ethanolic filtrate was cooled and the product crystallized by the addition of Et_2O. Yield: 60%, mp 228–229 °C; ^{1}H NMR (300 MHz, D_2O) δ: 8.02–8.08 (m, 2H), 7.54–7.62 (m, 3H), 5.37 (t, *J* = 6.2 Hz, 2H), 4.21 (t, *J* = 6.2 Hz, 2H), 3.26 (s, 9H) ppm; ^{13}C NMR (75 MHz, D_2O) δ: 164.9, 130.9, 128.8, 126.3, 125.3, 62.7, 53.2, 46.7 ppm; Anal. Calcd for $C_{12}H_{18}BrN_5$: C, 46.16; H, 5.81; N, 22.43. Found: C, 45.77; H, 5.84; N, 22.43.
17. *General method for the preparation of 5-substituted 2-vinyl-2H-tetrazoles*: 1,2-Dibromoethane (6 mmol) in MeCN (1.5 ml) was stirred at reflux. Then, a solution of 5-substituted tetrazole (3 mmol) and Et_3N (12 mmol) in MeCN (2.5 ml) was added dropwise over 2 h. The mixture was heated at reflux for an additional 2–3 h (overall reaction time is given in Table 1). The reaction was monitored by TLC (mobile phase: hexane/Et_2O). MeCN was removed under reduced pressure, and the residue was dissolved in $CHCl_3$ (30 ml) and washed with H_2O (3 × 25 ml). The organic solution was dried over Na_2SO_4 and the solvent was evaporated. The product was obtained by column chromatography.
18. *Data for compounds* **2a–2k:** *5-Phenyl-2-vinyl-2H-tetrazole* (**2a**). Mobile phase: hexane/Et_2O, 15:1. Yield: 80%; mp 41 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.17–8.23 (m, 2H), 7.47–7.62 (m, 4H), 6.27 (dd, *J* = 15.6 and 1.5 Hz, 1H), 5.40 (dd, *J* = 8.8 and 1.5 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.9, 130.6, 129.8, 128.9, 127.0, 126.9, 108.4 ppm; Anal. Calcd for $C_9H_8N_4$: C, 62.78; H, 4.68; N, 32.54. Found: C, 62.55; H, 4.78; N, 32.64.
5-p-Tolyl-2-vinyl-2H-tetrazole (**2b**): Mobile phase: hexane/Et_2O, 10:1. Yield: 75%; mp 40–41 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.08 (d, *J* = 8 Hz, 2H), 7.54 (dd, *J* = 15.6 and 8.8 Hz, 1H), 7.31 (d, *J* = 8 Hz, 2H), 6.25 (dd, *J* = 15.6 and 1.5 Hz, 1H), 5.37 (dd, *J* = 8.8 and 1.5 Hz, 1H), 2.42 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.9, 140.9, 129.8, 129.6, 127.0, 124.1, 108.2, 21.5 ppm; Anal. Calcd for $C_{10}H_{10}N_4$: C, 64.50; H, 5.41; N, 30.09. Found: C, 64.09; H, 5.45; N, 30.45.
5-(4-Nitrophenyl)-2-vinyl-2H-tetrazole (**2c**): Mobile phase: hexane/Et_2O, 4:1. Yield: 79%; mp 128–129 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.28–8.48 (m, 4H), 7.59 (dd, *J* = 15.6 and 8.8 Hz, 1H), 6.32 (dd, *J* = 15.6 and 1.7 Hz, 1H), 5.48 (dd, *J* = 8.8 and 1.7 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ: 163.0, 149.0, 132.8, 129.6, 127.9, 124.2, 109.5 ppm; Anal. Calcd for $C_9H_7N_5O_2$: C, 49.77; H, 3.25; N, 32.25. Found: C, 49.82; H, 3.52; N, 32.09.
5-[4-(Trifluoromethyl)phenyl]-2-vinyl-2H-tetrazole (**2d**): Mobile phase: hexane/Et_2O, 10:1 Yield: 86%; mp 44 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.32 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.58 (dd, *J* = 15.6 and 8.8 Hz, 1H), 6.31 (dd, *J* = 15.6 and 1.6 Hz, 1H), 5.45 (dd, *J* = 8.8 and 1.6 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ: 163.7, 132.4 (q, *J* = 32.8 Hz), 130.3, 129.7, 127.3, 125.9 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.3 Hz), 109.1 ppm; Anal. Calcd for $C_{10}H_7F_3N_4$: C, 50.01; H, 2.94; N, 23.33. Found: C, 49.99; H, 2.82; N, 23.05.
5-(4-Chlorophenyl)-2-vinyl-2H-tetrazole (**2e**): Mobile phase: hexane/Et_2O, 15:1. Yield: 84%; mp 81–82 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.13 (d, *J* = 8.7 Hz, 2H), 7.55 (dd, *J* = 15.6 and 8.8 Hz , 1H), 7.47 (d, *J* = 8.7 Hz, 2H), 6.27 (dd, *J* = 15.6 and 1.6 Hz, 1H), 5.41 (dd, *J* = 8.8 and 1.6 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.0, 136.7, 129.7, 129.2, 128.3, 125.4, 108.7 ppm; Anal. Calcd for $C_9H_7ClN_4$: C, 52.31; H, 3.41; N, 27.11. Found: C, 52.29; H, 3.34; N, 27.2.
N-[3-(2-Vinyl-2H-tetrazol-5-yl)phenyl]acetamide (**2f**): Mobile phase: Et_2O/hexane, 4:1. Yield: 77%; mp 153–154 °C; ^{1}H NMR (300 MHz, CD_3SOCD_3) δ: 10.18 (m, 1H), 8.41–8.45 (m, 1H), 7.89 (dd, *J* = 15.5 and 8.7 Hz, 1H), 7.70–7.80 (m, 2H), 7.45–7.52 (m, 1H), 6.18 (dd, *J* = 15.5 and 1.5 Hz, 1H), 5.56 (dd, *J* = 8.7 and 1.5 Hz, 1H), 2.07 (s, 3H) ppm; ^{13}C NMR (75 MHz, CD_3SOCD_3) δ: 168.8, 164.2, 140.3, 130.5, 130.0, 126.9, 121.3, 117.0, 109.7, 24.2 ppm; Anal. Calcd for $C_{11}H_{11}N_5O$: C, 57.63; H, 4.84; N, 30.55. Found: C, 57.49; H, 5.04; N, 30.47.
5-o-Tolyl-2-vinyl-2H-tetrazole (**2g**): Mobile phase: hexane/Et_2O, 20:1. Yield: 78%; isolated as an oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.06–8.11 (m, 1H), 7.58 (dd, *J* = 15.6 and 8.8 Hz, 1H), 7.29–7.43 (m, 3H), 6.27 (dd, *J* = 15.6 and 1.5 Hz, 1H), 5.39 (dd, *J* = 8.8 and 1.5 Hz, 1H), 2.67 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.3, 137.7, 131.4, 130.2, 129.8, 129.6, 126.0, 125.9, 108.3, 21.7 ppm; HRMS (EI): *m*/*z* calcd for $C_{10}H_{10}N_4$ $[M]^+$: 186.0905; found: 186.0908.
5-(3,4-Dichlorophenyl)-2-vinyl-2H-tetrazole (**2h**): Mobile phase: hexane/Et_2O,

15:1. Yield: 88%; mp 116–117 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.29 (d, J = 2 Hz, 1H), 8.02 (dd, J = 8.4 and 2 Hz, 1H), 7.50–7.62 (m, 2H), 6.28 (dd, J = 15.6 and 1.7 Hz, 1H), 5.43 (dd, J = 8.8 and 1.7 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ: 163.0, 134.9, 133.4, 131.0, 129.6, 128.8, 126.8, 126.1, 109.1 ppm; Anal. Calcd for $C_9H_6Cl_2N_4$: C, 44.84; H, 2.51; N, 23.24. Found: C, 44.96; H, 2.77; N, 23.35.

5-Benzyl-2-vinyl-2H-tetrazole (**2i**): Mobile phase: hexane/Et_2O, 10:1. Yield: 53%; isolated as an oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.46 (dd, J = 15.7 and 8.8 Hz, 1H), 7.20–7.40 (m, 5H), 6.16 (dd, J = 15.7 and 1.5 Hz, 1H), 5.33 (dd, J = 8.8 and 1.5 Hz, 1H), 4.28 (s, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.5, 136.3, 129.7, 128.8, 128.7, 126.9, 108.3, 31.8 ppm; HRMS (EI): m/z calcd for $C_{10}H_{10}N_4$ $[M]^+$: 186.0905; found: 186.0904.

5-Undecyl-2-vinyl-2H-tetrazole (**2j**): Mobile phase: hexane/Et_2O, 15:1. Yield: 54%; isolated as an oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.46 (dd, J = 15.7 and 8.8 Hz, 1H), 6.14 (dd, J = 15.7 and 1.5 Hz, 1H), 5.31 (dd, J = 8.8 and 1.5 Hz, 1H), 2.90 (t, J = 7.7 Hz, 2H), 1.74–1.85 (m, 2H), 1.20–1.40 (m, 16H), 0.87 (t, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.9, 129.8, 107.8, 31.9, 29.6, 29.4, 29.3, 29.2, 29.1, 27.9, 25.4, 22.6, 14.1 ppm; HRMS (ESI): m/z calcd for $C_{14}H_{27}N_4$ $[M+H]^+$: 251.2230; found: 251.2229.

5-Methyl-2-vinyl-2H-tetrazole (**2k**): Mobile phase: hexane/Et_2O, 4:1. Yield: 53% (by NMR) / 21% (isolated); isolated as a volatile liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.46 (dd, J = 15.7 and 8.8 Hz, 1H), 6.15 (dd, J = 15.7 and 1.5 Hz, 1H), 5.32 (dd, J = 8.8 and 1.5 Hz, 1H), 2.55 (3H, s) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ: 162.9, 129.7, 107.9, 10.9 ppm; HRMS (ESI): m/z calcd for $C_4H_7N_4$ $[M+H]^+$: 111.0665; found: 111.0663.