

Synthesis and Properties of Dichlorovinyl Derivatives of Tetrazoles

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Abstract—1-Substituted 1*H*-tetrazole-5-thiols and 5-substituted 1*H*-tetrazoles easily reacted with trichloroethylene to form the corresponding *S*- and *N*-dichlorovinyl derivatives, respectively. In the case of 5-substituted 1*H*-tetrazoles, the reaction led to a mixture of 1- and 2-dichlorovinyltetrazoles. 5-Substituted-2-dichlorovinyltetrazoles are characterized by low thermal stability, but easily enter into the polymerization reaction.

Keywords: 1-substituted 1*H*-tetrazole-5-thiols, 5-substituted 1*H*-tetrazoles, trichloroethylene, dichlorovinyl derivatives

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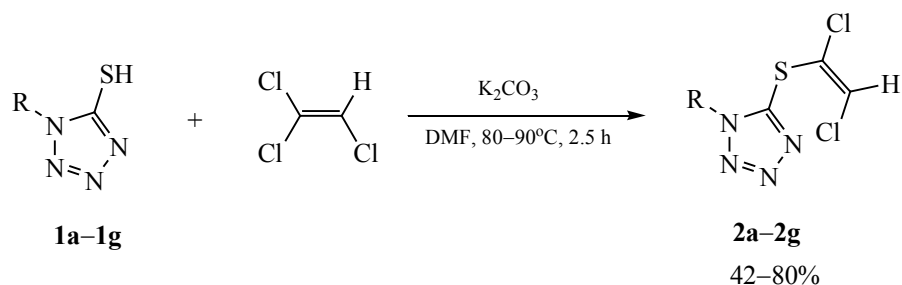
Vinyl derivatives of (thio)tetrazoles attract attention as starting materials for the synthesis of high molecular weight compounds, biologically active substances, and functional materials [1–5]. Vinyltetrazole-based polymers are components of promising energy-intensive materials, gas separation membranes, nonwoven filter materials for medicine, and other composite materials [1, 2].

To date, the problem of synthesizing unsubstituted vinyltetrazoles has been successfully solved. Although the known methods for the preparation of these compounds are multistage, they make it possible to obtain the corresponding vinyl derivatives in good yields [2, 6]. In contrast, almost all known methods for the preparation of substituted vinyltetrazoles can be reduced to two main groups: the functionalization of previously obtained vinyltetrazoles using metal-catalyzed cross-coupling [7] and the addition reaction of thiotetrazoles to the activated triple bond C≡C [8]. Both of these reaction groups make it possible to obtain only a limited range of the products, with aromatic substituents in the first case and, usually, with electron-withdrawing carboxyl or keto groups in the second. As for the vinyl chloride derivatives of tetrazoles, no method for their preparation has been proposed to date.

One of the simple ways to introduce a chlorovinyl group could be nucleophilic substitution of halogen at the double bond; however, such reactions are hindered due to the low reactivity of substituted vinyl chlorides. At the same time, with an increase in the number of chlorine atoms, the reactivity increases significantly, and trichloroethylene can already react with strong nucleophiles to form halogen substitution products [9]. Since 1-substituted tetrazole-5-thiols and 5-substituted tetrazoles are rather strong nucleophiles, it can be expected that their reaction with trichloroethylene will lead to dichlorovinylthio- and dichlorovinyltetrazoles. Taking into account the prospects for the use of these compounds, the study of this reaction is an urgent task.

1-Substituted 1*H*-tetrazole-5-thiols were found to react with trichloroethylene at 80–90°C in the presence of K₂CO₃ in DMF to form dichlorovinyl derivatives in good yields (Scheme 1). It should be noted that we have previously shown that 1-substituted 1*H*-tetrazole-5-thiols easily enter into the copper-catalyzed cross-coupling reaction with aryl halides [10], however, in the case of trichloroethylene, the addition of copper compounds did not have any effect on the reaction course.

Scheme 1.



R = Ph (**a**), (2-CHF₂O)C₆H₄ (**b**), 1-naphthyl (**c**), Bn (**d**), PhCH₂CH₂ (**e**), *c*-Hex (**f**), Me (**g**).

The synthesized 1-substituted dichlorovinylthio-tetrazoles are stable compounds. For compound **2c** (R = 1-naphthyl), we managed to grow single crystals suitable for X-ray diffraction analysis. The crystallographic data (Table 1, Fig. 1) confirmed the expected structure of the synthesized compound. It crystallizes in the monoclinic space group *C2/c*, with one molecule in an asymmetric cell and eight molecules in a unit cell. The chlorine atoms of the vinyl fragment are in the *trans*-position. The tetrazole ring is significantly unfolded relative to the naphthyl substituent, with a dihedral angle between the root-mean-square planes of these fragments of 86.58(3)°. Although there are no hydrogen bonds in the crystal structure of compound **2c**, it is stabilized by π - π -stacking interactions with the participation of π -systems of naphthyl fragments of neighboring molecules.

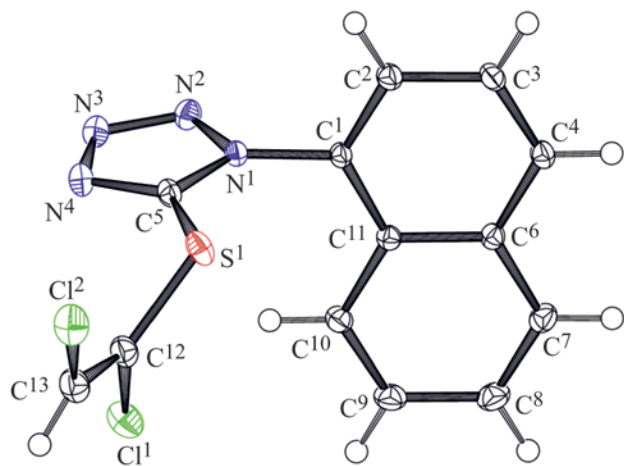


Fig. 1. General view of compound **2c** in crystal (CCDC 2090214).

We found that the reaction of 5-phenyl-1*H*-tetrazole with trichloroethylene in DMF in the presence of K₂CO₃ at a temperature below 80–90°C gives rise to 1-dichlorovinyl-5-phenyltetrazoles with a yield of 25–35%, as well as a significant amount of resinification products. This reaction outcome was found to be due to the fact that 2-dichlorovinyltetrazoles have low thermal stability and decompose upon heating. Indeed, when the reaction is carried out in DMSO in the presence of KOH, the temperature can be lowered to 40°C. As a result, a mixture of 1- and 2-dichlorovinyltetrazoles is formed within 1–2 h with a total yield of 43–74%. Under these conditions, we obtained a series of 1- and 2-dichlorovinyltetrazoles with various substituents at position 5 of the tetrazole ring (Scheme 2). The ratio of 1- and 2- isomers varies from 1.3 : 1 to 1 : 2, respectively.

In contrast to the corresponding 1-isomers and dichlorovinylthiotetrazoles, 2-dichlorovinyltetrazoles isolated in pure form have low stability and decompose when stored at room temperature, but can be stored for a long time at –18°C. The addition of radical initiators causes rapid polymerization of 5-substituted 2-dichlorovinyltetrazoles, which makes these compounds promising monomers for the preparation of functional materials.

In summary, trichloroethylene is a convenient and available substrate for the preparation of dichlorovinylthiotetrazoles, 1- and 2-dichlorovinyltetrazoles. 2-Dichlorovinyltetrazoles can be used as starting compounds for the synthesis of high molecular weight compounds.

EXPERIMENTAL

¹H and ¹³C NMR spectra were recorded on a Bruker Avance III HD 400 NanoBay spectrometer (400 and 100 MHz, respectively) in CDCl₃ solution, the internal

standard was the residual signals of the solvent. IR spectra were recorded on a Shimadzu FTIR-8400S spectrometer from KBr pellets. Elemental analysis was performed on a LECO CHNS-932 analyzer. The purity and individuality of the obtained compounds were monitored by TLC on Merck Silicagel UV-254 plates. Melting points were determined on a Kofler table. All starting materials and solvents were of reagent or analytical grade.

Single crystal X-ray diffraction analysis of compound **2c** was performed on a SMART Apex II X-ray diffractometer (Bruker AXS GmbH, Germany) using MoK_α radiation (graphite monochromator). The structure was solved by direct methods using the SIR2014 program [11] and refined using F^2 by full-matrix least squares in the anisotropic approximation for non-hydrogen atoms using the SHELXL-2014 software package [12]. The positions of hydrogen atoms were calculated geometrically and refined within the framework of the *rider* model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Molecular graphics were performed using the PLATON software [13]. The obtained crystallographic data were deposited with the Cambridge Crystallographic Data Center (CCDC 2090214).

(E)-5-[(1,2-Dichlorovinyl)thio]-1-phenyl-1H-tetrazole (2a). To a mixture of 3.8 g (21.3 mmol) of 1-phenyl-1H-tetrazole-5-thiol and 8.81 g (63.9 mmol) of K_2CO_3 in 6 mL of DMF was added 8.40 g (63.9 mmol) of trichlorethylene. The reaction mixture was stirred for 2.5 h at 80–90°C, then poured into 50 mL of cold water and extracted with chloroform (3×30 mL). The organic layer was washed with water (3×30 mL) and saturated NaCl solution, then dried with anhydrous Na_2SO_4 . The solvent was removed in vacuum. Yield 4.37 g (75%), yellow crystals, mp 87–89°C (EtOH). IR spectrum, ν , cm^{-1} (KBr): 3109 m (CH), 3031 m (C=C), 1594 m (C=N),

Table 1. Crystallographic data for compound **2c**

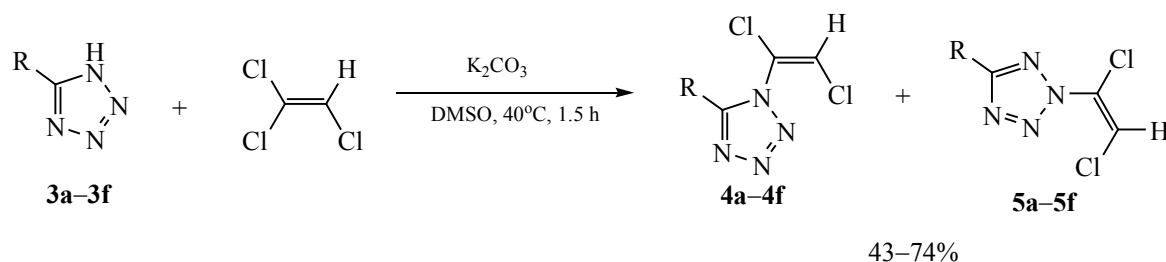
Parameter	2c
Formula	$\text{C}_{13}\text{H}_8\text{Cl}_2\text{N}_4\text{S}$
T , K	100
λ , Å	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
a , Å	19.1797(3)
b , Å	7.75882(2)
c , Å	18.4182(2)
β , deg	97.3825(9)
V , Å ³	2718.12(6)
Z	8
d_{calc} , g/cm^3	1.580
$\mu(\text{MoK}_\alpha)$, mm^{-1}	0.624
Crystal size, mm	0.42×0.41×0.16
Reflections collected:	
all	30050
independent	4162 (R_{int} 0.0175)
Refined parameters	181
GOOF	1.052
$I > 2\sigma(I)$	R_1 0.0275, R_2 0.0719
All data	R^1 0.0291, R_2 0.0730

1560 s (Ph), 1074 m (C–N), 736 m (C–Cl), 697 s (C–S). ¹H NMR spectrum, δ , ppm: 6.69 s (1H, CH), 7.56–7.60 m (5H, Ph). ¹³C NMR spectrum, δ_{C} , ppm: 122.8 (SC=), 124.6 (=CCl), 126.8 (Ph), 129.9 (Ph), 130.9 (Ph), 133.3 (Ph), 148.5 (C–N). Found, %: C 39.45; H 2.33; N 20.44. $\text{C}_9\text{H}_6\text{Cl}_2\text{N}_4\text{S}$. Calculated, %: C 39.58; H 2.21; N 20.51.

Compounds **2b–2g** were prepared similarly.

(E)-5-[(1,2-Dichlorovinyl)thio]-1-[2-(difluoromethoxy)phenyl]-1H-tetrazole (2b). Yield 49%, yellow

Scheme 2.



R = Ph (**a**), 4- ClC_6H_4 (**b**), 4- FC_6H_4 (**c**), 4- MeC_6H_4 (**d**), 4- $(\text{CH}_3)_2\text{NC}_6\text{H}_4$ (**e**), Bn (**f**).

oil. IR spectrum, ν , cm^{-1} (KBr): 3159 m (CH), 3029 m (C=C), 1598 m (C=N), 1510 s (Ph), 1246 m (CF_2), 1135 s (C=O), 1060 m (C=N), 760 m (C-Cl), 695 s (C-S). ^1H NMR spectrum, δ , ppm: 6.48 s (1H, CHF_2), 6.67 s (1H, CH), 7.40–7.51 m (3H, Ph), 7.62–7.66 m (1H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 115.20 t (CHF_2 , J_{HH} 264.5 Hz), 120.44 (OCPh), 122.98 (=CCl), 124.57 (SC=), 126.33 (Ph), 126.67 (Ph), 128.44 (Ph), 133.10 (Ph), 145.39 (Ph), 150.26 (C_{Tetr}). Found, %: C 35.60; H 1.59; N 16.41. $\text{C}_{10}\text{H}_6\text{Cl}_2\text{F}_2\text{N}_4\text{OS}$. Calculated, %: C 35.42; H 1.78; N 16.52.

(E)-5-[(1,2-Dichlorovinyl)thio]-1-(naphth-1-yl)-1H-tetrazole (2c). Yield 79%, colorless crystals, mp 106–108°C (EtOH– H_2O). IR spectrum, ν , cm^{-1} (KBr): 3104 m (CH), 3060 m (C=C), 1598 m (C=N), 1511 s (Ar), 1465 s (Ar), 1058 m (C=N), 727 m (C-Cl), 698 s (C-S). ^1H NMR spectrum, δ , ppm: 6.58 s (1H, CH), 7.27 d (1H, H_{Ar} , J_{HH} 4.0 Hz), 7.55–7.64 m (4H, H_{Ar}), 7.99 d (1H, H_{Ar} , J_{HH} 4.0 Hz), 8.11 d (1H, H_{Ar} , J_{HH} 4.0 Hz). ^{13}C NMR spectrum, δ_{C} , ppm: 121.77 (Ar), 122.6 (Ar), 125.01 (=CCl), 125.05 (SC=), 125.2 (Ar), 127.3 (Ar), 127.7 (Ar), 128.6 (Ar), 128.7 (Ar), 129.0 (Ar), 132.17 (Ar), 134.3 (Ar), 150.8 (C=N). Found, %: C 48.46; H 2.59; N 17.22. $\text{C}_{13}\text{H}_8\text{Cl}_2\text{N}_4\text{S}$. Calculated, %: C 48.31; H 2.50; N 17.34.

(E)-5-[(1,2-Dichlorovinyl)thio]-1-benzyl-1H-tetrazole (2d). Yield (80%), yellow crystals, mp 56–58°C (hexane– CCl_4). IR spectrum, ν , cm^{-1} (KBr): 3105 m (CH), 3039 m (C=C), 2923 m (CH_2), 1595 m (C=N), 1453 s (Ph), 1078 m (C=N), 748 m (C-Cl), 691 s (C-S). ^1H NMR spectrum, δ , ppm: 5.57 s (2H, CH_2), 6.66 s (1H, CH), 7.27–7.29 m (2H, Ph), 7.33–7.37 m (3H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 52.0 (CH_2), 123.4 (=CCl), 124.8 (SC=), 128.2 (Ph), 129.35 (Ph), 129.39 (Ph), 132.59 (Ph), 147.70 (C=N). Found, %: C 41.67; H 2.95; N 19.40. $\text{C}_{10}\text{H}_8\text{Cl}_2\text{N}_4\text{S}$. Calculated, %: C 41.83; H 2.81; N 19.51.

(E)-5-[(1,2-Dichlorovinyl)thio]-1-phenetyl-1H-tetrazole (2e). Yield 55%, yellow oil. IR spectrum, ν , cm^{-1} (KBr): 3109 m (CH), 3039 m (C=C), 2923 m (CH_2), 1559 m (C=N), 1492 s (Ph), 1078 m (C=N), 748 m (C-Cl), 670 s (C-S). ^1H NMR spectrum, δ , ppm: 3.23 t (2H, CH_2 , J_{HH} 8.0 Hz), 4.60 t (2H, CH_2 , J_{HH} 8.0 Hz), 6.66 s (1H, CH), 7.04 d (2H, Ph, J_{HH} 8.0 Hz), 7.24–7.29 m (3H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 35.97 (CH_2), 49.61 (CH_2), 124.65 (=CCl), 127.65 (SC=), 128.85 (Ph), 129.16 (Ph), 135.79 (Ph), 147.88 (C=N). Found, %: C 44.02; H 3.24; N 18.71. $\text{C}_{11}\text{H}_{10}\text{Cl}_2\text{N}_4\text{S}$. Calculated, %: C 43.87; H 3.35; N 18.60.

(E)-5-[(1,2-Dichlorovinyl)thio]-1-cyclohexyl-1H-tetrazole (2f). The product was purified by column chromatography in the ethyl acetate–hexane system. (2 : 8). Yield 42%, yellow crystals, mp 68–70°C (hexane). IR spectrum, ν , cm^{-1} (KBr): 3107 m (CH), 3021 m (C=C), 2944 m (CH_2), 1560 m (C=N), 1348 s [$(\text{CH}_2)_n$], 1075 m (C=N), 755 m (C-Cl), 610 s (C-S). ^1H NMR spectrum, δ , ppm: 1.23–1.48 m (4H, CH_2), 1.43 d (2H, CH_2 , J_{HH} 6.0 Hz), 1.94–2.02 m (4H, CH_2), 4.37–4.43 m (1H, CH), 6.75 s (1H, CH). ^{13}C NMR spectrum, δ_{C} , ppm: 24.8 (CH_2), 25.3 (CH_2), 32.7 (CH_2), 59.2 (CH), 124.0 (=CCl), 124.6 (SC=), 146.3 (C=N). Found, %: C 38.91; H 4.15; N 20.28; S 11.62. $\text{C}_9\text{H}_{12}\text{Cl}_2\text{N}_4\text{S}$. Calculated, %: C 38.72; H 4.33; N 20.07; S 11.48.

(E)-5-[(1,2-Dichlorovinyl)thio]-1-methyl-1H-tetrazole (2g). Yield 43%, yellow crystals, mp 48–50°C (EtOAc). IR spectrum, ν , cm^{-1} (KBr): 3121 m (CH), 3060 m (C=C), 2956 m (CH_3), 1565 m (C=N), 1089 m (C=N), 735 m (C-Cl), 670 s (C-S). ^1H NMR spectrum, δ , ppm: 4.08 s (3H, CH_3), 6.74 s (1H, CH). ^{13}C NMR spectrum, δ_{C} , ppm: 34.61 (CH_3), 123.36 (=CCl), 124.51 (SC=), 147.75 (C=N). Found, %: C 22.59; H 2.13; N 26.68. $\text{C}_4\text{H}_4\text{Cl}_2\text{N}_4\text{S}$. Calculated, %: C 22.76; H 1.91; N 26.55.

(E)-1-(1,2-Dichlorovinyl)-5-phenyl-1H-tetrazole (4a) and (E)-2-(1,2-dichlorovinyl)-5-phenyl-2H-tetrazole (5a). Trichlorethylene 1.35 g (10.27 mmol) was added to a solution of 1 g (6.85 mmol) 5-phenyl-1H-tetrazole and 1.15 g (20.55 mmol) of KOH in 20 mL of DMSO. The reaction mixture was stirred for 1.5 h at 40°C, then poured into 100 mL of chloroform and extracted with cold water (3×30 mL). The organic layer was washed with saturated NaCl solution, then dried with Na_2SO_4 . The solvent was removed in vacuum. The product was purified by column chromatography in the ethyl acetate–hexane system (1 : 9). Yield 1.22 g (74%) (**4a** : **5a** = 1 : 1.2, by NMR).

(E)-1-(1,2-Dichlorovinyl)-5-phenyl-1H-tetrazole (4a). Yellowish crystals, mp 63–65°C (hexane). IR spectrum, ν , cm^{-1} (KBr): 3093 m (CH), 3013 m (C=C), 1607 m (C=N), 1531 s (Ph), 1079 m (C=N), 733 m (C-Cl). ^1H NMR spectrum, δ , ppm (CDCl_3): 6.82 s (1H, CH), 7.63–7.53 m (3H, Ph), 7.87–7.85 m (2H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 122.3 (=CCl), 122.5 (N=C=), 123.0 (Ph), 128.3 (Ph), 129.5 (Ph), 132.4 (Ph), 154.3 (C=N). Found, %: C 44.75; H 2.58; N 23.18; $\text{C}_9\text{H}_6\text{Cl}_2\text{N}_4$. Calculated, %: C 44.84; H 2.51; N 23.24.

(E)-2-(1,2-Dichlorovinyl)-5-phenyl-2H-tetrazole (5a). Yellow oil. IR spectrum, ν , cm^{-1} (KBr): 3080 m (CH), 3034 m (C=C), 1620 m (C=N), 1530 s (Ph), 1078 m (C-N), 731 m (C-Cl). ^1H NMR spectrum, δ , ppm: 6.82 s (1H, CH), 7.50–7.54 m (3H, Ph), 8.21–8.23 m (2H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 119.1 (=CCl), 124.7 (Ph), 126.3 (N-C=), 127.4 (Ph), 129.2 (Ph), 131.2 (Ph), 165.5 (C-N). Found, %: C 44.96; H 2.45; N 23.32; $\text{C}_9\text{H}_6\text{Cl}_2\text{N}_4$. Calculated, %: C 44.84; H 2.51; N 23.24.

Compounds **4b–4f** and **5b–5f** were prepared similarly.

(E)-5-(4-Chlorophenyl)-1-(1,2-dichlorovinyl)-1H-tetrazole (4b) and **(E)-5-(4-chlorophenyl)-2-(1,2-dichlorovinyl)-2H-tetrazole (5b).** Yield 43% (**4b** : **5b** = 1 : 1.7).

(E)-5-(4-Chlorophenyl)-1-(1,2-dichlorovinyl)-1H-tetrazole (4b). White crystals, mp 141–143°C (hexane). IR spectrum, ν , cm^{-1} (KBr): 3082 m (CH), 3012 m (C=C), 1600 m (C=N), 1520 s (Ph), 1089 m (C-N), 740 m (C-Cl). ^1H NMR spectrum, δ , ppm: 6.88 s (1H, CH), 7.55–7.59 m (2H, Ph), 7.83–7.86 m (2H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 120.9 (=CCl), 122.5 (N-C=), 122.8 (Ph), 129.5 (Ph), 129.9 (Ph), 138.9 (Ph), 153.3 (C-N). Found, %: C 39.15; H 1.73; N 20.46; $\text{C}_9\text{H}_5\text{Cl}_3\text{N}_4$. Calculated, %: C 39.23; H 1.83; N 20.34.

(E)-5-(4-Chlorophenyl)-2-(1,2-dichlorovinyl)-2H-tetrazole (5b). White crystals, mp 81–83°C (hexane). IR spectrum, ν , cm^{-1} (KBr): 3096 m (CH), 3025 m (C=C), 1628 m (C=N), 1545 s (Ph), 1068 m (C-N), 742 m (C-Cl). ^1H NMR spectrum, δ , ppm: 6.85 s (1H, CH), 7.50–7.54 m (3H, Ph), 8.16–8.19 m (2H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 119.1 (=CCl), 124.5 (Ph), 124.7 (N-C=), 128.6 (Ph), 129.4 (Ph), 137.3 (Ph), 164.6 (C-N). Found, %: C 39.06; H 2.11; N 20.32; $\text{C}_9\text{H}_5\text{Cl}_3\text{N}_4$. Calculated, %: C 39.23; H 1.83; N 20.34.

(E)-5-(4-Fluorophenyl)-1-(1,2-dichlorovinyl)-1H-tetrazole (4c) and **(E)-5-(4-fluorophenyl)-2-(1,2-dichlorovinyl)-2H-tetrazole (5c).** Yield 87% (**4c** : **5c** = 1 : 2).

(E)-5-(4-Fluorophenyl)-1-(1,2-dichlorovinyl)-1H-tetrazole (4c). Colorless crystals, mp 84–86°C (hexane). IR spectrum, ν , cm^{-1} : 3097 m (CH), 2992 m (C=C), 1608 s (C=N), 1540 m (Ph), 1091 s (C-N), 1022 m (C-F), 746 m (C-Cl). ^1H NMR spectrum, δ , ppm: 6.87 s (1H, CH), 7.27–7.31 m (2H, Ph), 7.90–7.94 m (2H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 116.8 (=C-Cl), 117.0 (N-C=), 118.7 (Ph), 122.4 (Ph), 122.9 (Ph), 130.6 (Ph), 153.3 (C-N).

Found, %: C 41.79; H 1.80; N 21.79. $\text{C}_9\text{H}_5\text{Cl}_2\text{FN}_4$. Calculated, %: C 41.73; H 1.95; Cl 27.37; F 7.33; N 21.63.

(E)-5-(4-Fluorophenyl)-2-(1,2-dichlorovinyl)-2H-tetrazole (5c). Yellowish crystals, mp 52–54°C (hexane). IR spectrum, ν , cm^{-1} : 3090 m (CH), 2997 m (C=C), 1604 s (C=N), 1541 m (Ph), 1093 s (C-N), 1023 m (C-F), 757 m (C-Cl). ^1H NMR spectrum, δ , ppm: 6.85 s (1H, CH), 7.22–7.27 m (2H, Ph), 8.23–8.27 m (2H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 116.4 (=CCl), 119.0 (N-C=), 122.5 (Ph), 124.6 (Ph), 129.4 (Ph), 129.5 (Ph), 163.3 (C-N). Found, %: C 41.61; H 1.89; N 21.45. $\text{C}_9\text{H}_5\text{Cl}_2\text{FN}_4$. Calculated, %: C 41.73; H 1.95; Cl 27.37; F 7.33; N 21.63.

(E)-5-(p-Tolyl)-1-(1,2-dichlorovinyl)-1H-tetrazole (4d) and **(E)-5-(p-tolyl)-2-(1,2-dichlorovinyl)-2H-tetrazole (5d).** Yield 65% (**4d** : **5d** = 1.3 : 1).

(E)-5-(p-Tolyl)-1-(1,2-dichlorovinyl)-1H-tetrazole (4d). Colorless crystals, mp 84–86°C (EtOH–H₂O). IR spectrum, ν , cm^{-1} (KBr): 3077 m (CH), 3036 m (C=C), 2859 s (CH₃), 1612 s (C=N), 1535 s (Ph), 1090 m (C-N), 736 m (C-Cl). ^1H NMR spectrum, δ , ppm: 2.42 s (3H, CH₃), 7.48–7.50 m (2H, Ph), 7.76–7.78 m (2H, Ph), 7.82 s (1H, CH). ^{13}C NMR spectrum, δ_{C} , ppm: 21.6 (CH₃), 119.2 (=CCl), 121.6 (N-C=), 124.8 (Ph), 128.3 (Ph), 130.8 (Ph), 143.6 (Ph), 154.2 (C-N). Found, %: C 47.15; H 3.04; N 21.85. $\text{C}_{10}\text{H}_8\text{Cl}_2\text{N}_4$. Calculated, %: C 47.08; H 3.16; N 21.96.

(E)-5-(p-Tolyl)-2-(1,2-dichlorovinyl)-2H-tetrazole (5d). Yellowish crystals, mp 88–91°C (EtOH–H₂O). IR spectrum, ν , cm^{-1} (KBr): 3088 m (CH), 3056 m (C=C), 2855 s (CH₃), 1611 s (C=N), 1565 m (Ph), 1071 m (C-N), 742 m (C-Cl). ^1H NMR spectrum, δ , ppm: 2.40 s (3H, CH₃), 7.41–7.44 m (2H, Ph), 7.85 s (1H, CH), 8.02–8.04 m (2H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 21.6 (CH₃), 122.0 (=CCl), 123.1 (N-C=), 123.3 (Ph), 127.3 (Ph), 130.5 (Ph), 142.1 (Ph), 165.4 (C-N). Found, %: C 46.94; H 3.25; N 22.02. $\text{C}_{10}\text{H}_8\text{Cl}_2\text{N}_4$. Calculated, %: C 47.08; H 3.16; N 21.96.

(E)-4-[1-(1,2-Dichlorovinyl)-1H-tetrazol-5-yl]-N,N-dimethylaniline (4e) and **(E)-4-[2-(1,2-dichlorovinyl)-2H-tetrazol-5-yl]-N,N-dimethylaniline (5e).** Yield 67% (**4d** : **5d** = 1 : 1.7).

(E)-4-[1-(1,2-Dichlorovinyl)-1H-tetrazol-5-yl]-N,N-dimethylaniline (4e). Yellowish crystals, mp 76–78°C (EtOH). IR spectrum, ν , cm^{-1} (KBr): 3092 m (CH), 3035 m (C=C), 2823 s (CH₃), 1611 s (C=N), 1544 s (Ph), 1295 (R₂N), 1074 m (C-N), 744 m (C-Cl). ^1H NMR spectrum, δ , ppm: 3.10 s (6H, CH₃), 6.79–6.81 m (2H,

Ph), 6.84 s (1H, CH), 7.81–7.84 m (2H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 40.1 (CH₃), 108.8 (Ph), 111.9 (=CCl), 121.8 (N–C=), 123.8 (Ph), 129.4 (Ph), 152.5 (Ph), 154.2 (C–N). Found, %: C 46.55; H 3.85; N 24.73. C₁₁H₁₁Cl₂N₅. Calculated, %: C 46.50; H 3.90; N 24.65.

(E)-4-[2-(1,2-Dichlorovinyl)-2H-tetrazol-5-yl]-N,N-dimethylaniline (5e). Yellow crystals, mp 60–62°C (EtOH). IR spectrum, ν , cm⁻¹ (KBr): 3088 m (CH), 3062 m (C=C), 2820 s (CH₃), 1607 s (C=N), 1521 s (Ph), 1275 (R₂N), 1063 m (C–N), 750 m (C–Cl). ^1H NMR spectrum, δ , ppm: 3.09 s (6H, CH₃), 6.80 s (1H, CH), 6.87–6.89 m (2H, Ph), 8.10–8.12 m (2H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 40.1 (CH₃), 100.1 (Ph), 113.1 (=CCl), 118.4 (N–C=), 128.5 (Ph), 133.6 (Ph), 142.9 (Ph), 165.8 (C–N). Found, %: C 45.68; H 3.99; N 21.51. C₁₁H₁₁Cl₂N₅. Calculated, %: C 46.50; H 3.90; N 24.65.

(E)-1-(1,2-Dichlorovinyl)-5-benzyl-1H-tetrazole (4f) and (E)-2-(1,2-dichlorovinyl)-5-benzyl-1H-tetrazole (5f). Yield 47% (4f : 5f = 1 : 1.2).

(E)-1-(1,2-Dichlorovinyl)-5-benzyl-1H-tetrazole (4f). Colorless crystals, mp 56–58°C (hexane–EtOAc). IR spectrum, ν , cm⁻¹: 3093 s (CH), 3031 m (C=C), 2913 m (CH₂), 1622 m (C=N), 1502 s (Ph), 1094 m (C–N), 720 m (C–Cl). ^1H (CDCl₃) NMR spectrum, δ , ppm: 4.34 s (2H, CH₂), 6.71 s (1H, CH), 7.25–7.27 m (3H, Ph), 7.33–7.35 m (2H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 29.7 (CH₂), 121.9 (=CCl), 127.9 (N–C=), 128.9 (Ph), 129.0 (Ph), 132.6 (Ph), 142.8 (Ph), 154.6 (C–N). Found, %: C 47.23; H 3.30; N 21.79. C₁₀H₈Cl₂N₄. Calculated, %: C 47.08; H 3.16; N 21.96.

(E)-2-(1,2-Dichlorovinyl)-5-benzyl-1H-tetrazole (4f). Yellow oil. IR spectrum, ν , cm⁻¹: 3086 s (CH), 3028 m (C=C), 2957 m (CH₂), 1627 s (C=N), 1496 m (Ph), 1086 m (C–N), 737 m (C–Cl). ^1H NMR spectrum, δ , ppm: 4.36 s (2H, CH₂), 6.78 s (1H, CH), 7.30–7.32 m (3H, Ph), 7.35–7.37 m (2H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 31.8 (CH₂), 118.8 (=CCl), 124.5 (N–C=), 127.2 (Ph), 128.8 (Ph), 129.3 (Ph), 135.8 (Ph), 166.0 (C–N). Found, %: C 47.08; H 3.06; N 21.94. C₁₀H₈Cl₂N₄. Calculated, %: C 47.08; H 3.16; N 21.96.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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