ZNCL$_2$/ALCL$_3$/SILICA (ZAS) AS AN EFFECTIVE HETEROGENEOUS CATALYST FOR THE SYNTHESIS OF 5-ARYLOXY TETRAZOLES

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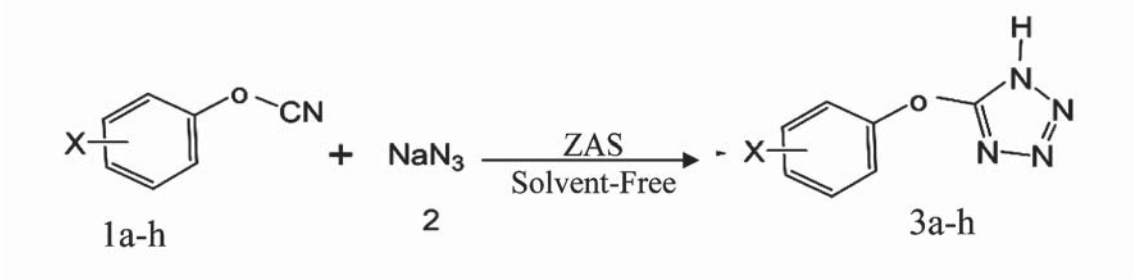
Abstract. A simple and efficient method for preparation of 5-aryloxy tetrazoles (**3a-h**) from arylcyanates (**1a-h**) with using $ZnCl_2/AlCl_3$/silica (ZAS) as an effective heterogeneous catalyst in solvent free is described with excellent yields and high purity. The rate of product formation was enhanced by introduction of electron donating substituents. The ^1H NMR and chemical shifts and multiplicities are also discussed.

Keywords: 5-Aryloxy tetrazoles, arylcyanates, guanyl azides, $ZnCl_2/AlCl_3$/silica (ZAS).

1. Introduction

The tetrazole ring system has attracted considerable attention in recent years [1-8], especially among medicinal chemists, as a potential surrogate for *cis*-peptide linkage [1,9-12], and carboxylic acids [1,13,14]. Indeed, the number of patent claims and publications related to medicinal uses of tetrazoles continue to grow rapidly and cover a wide range of applications: Tetrazoles have been found to exhibit antihypertensive, antiallergic and antibiotic activities [15-22], and they are currently used, for example, as activator [23-25], anticonvulsants [1,26], also in cancer [27-29], and AIDS treatment [1,30,31]. Furthermore aminotetrazoles derivatives have been patented for muscle relaxation, anti-inflammatory anti-arthritic, analgesic, ulcer therapeutic and coccidiostatic properties. Tetrazoles are also applied in agriculture, as plant growth regulators, herbicides and fungicides [32,33], stabilizers in photography and photoimaging [32,34], and explosives in rocket propellants [35-37]. Another important application of tetrazoles is the preparation of imidoylazides [38-43]. The addition of azide anion to nitriles, cyanates and cyanamides is the most common direction for preparing 5-substituted tetrazoles and 5-aryl/alkyl oxytetrazoles [1-7,38-45]. In most cases, reaction actually proceeds in solutions of hydrazoic acid in solvents such as benzene, toluene, xylene and chloroform. When hydrazoic acid is used, care must be taken by monitoring the concentration of hydrazoic acid in the reaction mixture to avoid an explosion [1-7,32,45,46,73]. A substitute for hydrazoic acid is a mixture of sodium azide and ammonium chloride with dimethylformamide as the solvent [1-7,17,32,45,47,72,73,74]. In dimethylformamide, the reaction mixture must be heated at ~150°C from several hours to several days. Additional disadvantage of dimethylformamide is the solubility in both organic solvents and water. Thus, removing the DMF from tetrazole is difficult. To resolve this problem, the reaction was carried out in several solvents, which allowed the temperature to be elevated to the necessary degree to enhance the reaction [32,45,47]. Another possible method of obtaining the 5-alkyltetrazoles was an adaption of the von Braun degradation of tertiary amines with cyanogens bromide. In this way it might be possible to eliminate an alkyl group from a 5-dialkyltetrazoles [48,52]. These methods suffer from one or more disadvantages such as low yield, long reaction times, harsh reaction conditions, lack of easy availability/preparation of the starting materials, difficulty of workup due to the application of homogeneous catalyst, use of expensive and toxic reagents and the in situ generated hydrazoic acid is highly toxic and explosive. Because of the safety considerations, we required a method that did not use hydrazoic acid or apply an azide source because of the in situ production of hydrazoic acid. Thus, a convenient and efficient method was required for preparation of the aryloxytetrazoles. From the standpoint of 'green chemistry', significant efforts have been made to find an alternative to organic solvents. A very attractive substitute for these solvents is a solvent–free reaction (industrially important due to reduced pollution, low cost, and simplicity in process and handling). In view of the importance of aryloxy tetrazoles and aryloxy imidoylazides [38-43], we want to report a facile, effective and less hazard method for synthesis the 5-aryloxy tetrazoles (**3a-h**) from arylcyanates (**1a-h**) in quantitative yields by using $ZnCl_2/AlCl_3$/Silica (ZAS) as an effective catalyst in solvent free (Scheme 1).



Scheme 1

2. Results and discussion

The cyanates **1a-h** were prepared according to literature [9,54,55]. In order to gain insight to the electronic effects. The nature of the substituent appears to play an important role for directing the course of the reaction. As shown in Table 1, among the various cyanates tested, electron-rich aromatic cyanates reach completion after 6-9 h, whereas electron-poor aromatic species require little higher times (compare entries 1-4 with 5-6 in Table 1). In addition, there is an excellent correlation between the effect of substitution on the benzene ring and the time of reaction. Scheme 1 and Table 1.

Table 1

The preparation of 5-aryloxy tetrazoles (3a-h) from arylcyanates by using ZAS at r.t.

Entry	Cyanate	Ar	Product (tetrazole)	Reaction time (h)	Yield (%)[a]	Mp °C	Mp(lit, ref) °C [8,16]
1	**1a**	4-$CH_3C_6H_4$	**3a**	8	89	139-140	140-142
2	**1b**	2,6-$(CH_3)_2C_6H_3$	**3b**	9	90	171-173	173-174
3	**1c**	4-$CH_3OC_6H_4$	**3c**	6	97	150-151	149-150
4	**1d**	C_6H_5	**3d**	9	87	136-138	137-138
5	**1e**	4-ClC_6H_4	**3e**	17	78	156-158	166-167
6	**1f**	4-$NO_2C_6H_4$	**3f**	20	53	161-163	162-163
7	**1g**	α-naphthyl	**3g**	11	80	174-176	-
8	**1h**	β-naphthyl	**3h**	10	81	152-154	-

[A] Yields refer to the pure isolated products.

The following important results is extracted from data in Table 1 and compared to those reported in literature [50-52]. In general, when the substitution is electron-donating group reaction is completed at shorter reaction time (starting cyanate **1a-c** consumes faster) than when the substitution is electron-withdrawing (compare entries 5 and 6 with 1, 2, 3 and 4 in Table 1). The entries 5 (17 h) and 6 (20 h) confirms this result. The rate of reaction was found to decrease with increasing the electronegativity of a substituent on the aryl group along. These results are the reverse of what was reported for the nitriles [45,65,66]. When the substitution on aryl ring is electron-donating in arylcyanates **1** the oxygen attached to aryl ring has more power basicity. On the other hand, the electron-donating group acts to increase the electron density on the oxygen attached to aryl group, and thus assists in the cyclisation of guanyl azides to give 5-aryloxy tetrazoles. Furthermore, it is worthy to mention that reaction of α– and β–naphthol (entries 7 and 8) did not proceed completely in the recently reported method [9]. Indeed, considerable amounts of starting material remained even after long times, and/or at high temperatures. However, the time to complete reaction in solvent free and room temperature (Table 1) is a good indication that, the first step, addition of hydrogen ion to arylcyanate **1a-h** the most important step or the rate determining step of reaction, because, when the substitution is electron-donating, reaction is completed at shorter reaction period the products were characterized by ^{1}H NMR,^{13}C NMR, IR, elemental analyses (CHN).

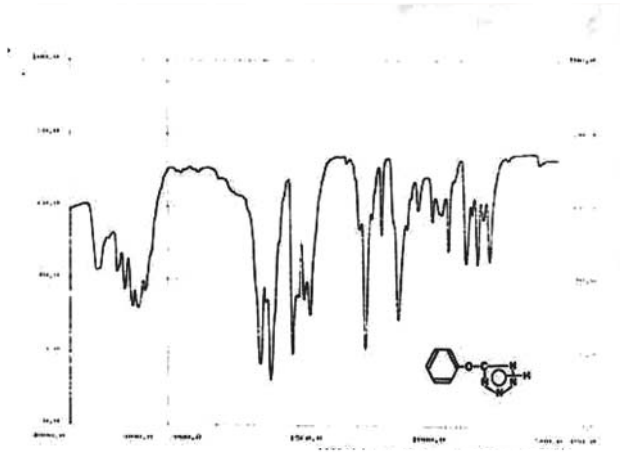


Fig. 1. IR spectrum (KBr) 5-phenoxy tetrazole (3d)

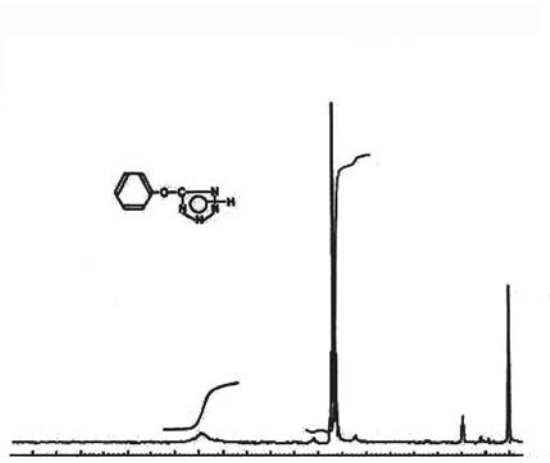


Fig. 2. ^{1}HNMR spectrum 5-phenoxy tetrazole (3d)

The disappearance of one strong and sharp absorption band (CN stretching band) and the appearance of a NH stretching band and CO stretching band in the IR spectra provided clear evidence for the formation of aryloxytetrazoles (Fig. 2). ^{13}C NMR spectra displayed signals at δ=154–157.5 ppm, indicative of C5 in the tetrazole ring. The free N–H bond of tetrazoles (NH) makes them acidic molecules, and not surprisingly it has been shown that both the aliphatic and aromatic heterocycles have pKa values that are similar to the corresponding carboxylic acids, due to the ability of the moiety to stabilize a negative charge by electron delocalization. In general, tetrazolic acids exhibit physical characteristics similar those of to carboxylic acids. Thus, the signal of the NH proton of the tetrazole ring (NH) shifted downfield (see Fig. 2 and ^{1}H NMR data of **3a–h**).

3. Conclusions

A facile, convenient and less hazard synthetic method for 5-aryloxy tetrazoles **3** from arylcyanates in solvent-free was achieved with quantitative yields high purity without involvement of expensive reagents or the formation of undesirable side products. To show the advantages of $ZnCl_2/AlCl_3$/Silica (ZAS) as a catalyst in comparison with other materials, we compared the reaction of $ZnCl_2/AlCl_3$/Silica (ZAS) with $ZnCl_2$, glacial acetic acid, PPh_3, HCl [9], $SnCl_4$ and LiCl in the synthesis of 5-(4-chlorophenoxy)-tetrazole (**3e**) (Table 1, Entry 5). As shown in Table 2, $ZnCl_2/AlCl_3$/ Silica (ZAS) is a better catalyst in the synthesis of 5-(4-Chloro phenoxy)- tetrazole (**3e**).

Table 2

Comparison effect of different catalysts in the synthesis of 5-(4-Chlorophenoxy)-tetrazole (3e)

Entry	Catalyst	Solvent	Time (min)	Temperature (ºC)	Yield%
1	PPh_3	DMF	120	120	57
2	HCl[b]	CH_3COCH_3	80	65	46
3	LiCl	DMF	110	120	55
4	CH_3COOH[a]	CH_3COOH	35h	25	59
5	$SnCl_4$	DMF	120	120	58
5	ZnCl2	DMF	100	120	71
6	ZAS	-	17h	25	76

[A] Glacial acetic acid as both solvent and proton donor source. [a]Added on work up. [9]

4. Experimental Section

CAUTION: Although aryloxytetrazoles are kinetically stable and in most cases are insensitive to electrostatic discharge, friction, and impact, they are nonetheless energetic materials and appropriate safety precautions should be taken, especially when these compounds are prepared on a larger scale. Hydrazoic acid is an unstable component which may decompose violently, forming nitrogen and hydrogen. Depending on the literature source, an explosive gas mixture can be formed with air or nitrogen above a concentration of more than 8-15% [56].

All reagents were purchased from the Merck and Aldrich chemical companies and used without further purification. Products were characterized by spectroscopic data [infrared (IR), fourier transform (FT)–IR,^{1}H NMR, and ^{13}CNMR spectra, elemental analyses (CHN), and melting points. The NMR spectra were recorded in chloroform and acetone.^{1}H NMR spectra were recorded on Bruker Avance DRX 500-MHz instruments. The chemical shifts (d) are reported in parts per million (ppm) relative to the tetrametleysilene (TMS) as internal standard. J values are hertz given in (Hz).^{13}C NMR spectra were recorded on Bruker Avance DRX 500-MHz instruments. IR (KBr) and FT-IR (KBr) spectra were recorded on Shimadzu 470 and Perkin-Elmer 781 spectrophotometers, respectively. Melting points were taken in open capillary tubes with a Buchi 510 melting-point apparatus and were uncorrected. The elemental analysis was performed using Heraeus CHN-O-Rapid analyzer.Thin-layer chromatography (TLC) was performed on silica gel polygram SIL G=UV 254 plates. All products are known compounds and are identified by comparison of some their spectral data (IR and ^{1}H-NMR) and physical properties with those of authentic samples [48,49,53,57]. All starting materials and solvents were purified with the proper purification techniques before use, when necessary [71]. The cyanates **1a-h** were prepared according to literature [9,54,55]. $ZnCl_2/AlCl_3$/Silica (ZAS) was prepared from silica gel and perchloric acid according to literature [75].

Typical Experimental Procedure for the Preparation of 5-Aryloxy tetrazoles 3 Using $ZnCl_2/AlCl_3$/Silica (ZAS)

The cyanate (1 mmol), (ZAS) (0.1 gr) and sodium azide (3 mmol) were added. the mixture was pulverized in a mortar (or the mixture was stirred by a magnet in a test tube) at room temperature for an appropriate time (Table 1). The reaction was monitored in TLC. After completion of the reaction, $CHCl_3$ was added and the mixture was filtered for separating the reagent. The solvent ($CHCl_3$) evaporated to give the product. Pure products were obtained at high yields, as summarized in Table 1. The desired pure products were then filtered and characterized by ^{1}H NMR, IR and melting points. This method did not require any further purification. No side product was observed under the reaction conditions. The spectral data of 5-aryloxy tetrazoles are given below.

Melting Point, IR and ^{1}H -NMR chemical shifts of 5-aryloxy tetrazoles (3a-h):

5-(4-Methylphenoxy)-tetrazole(3a): M.p. = 139-140°C. lit [9], 140-142°C. IR (KBr, cm^{-1}): 3005 (m), 2900 (m), 2705 (m), 2550 (m), 2455 (m), 2350 (m), 1620 (s), 1590 (s), 1500 (s), 1440 (m), 1190 (s), 1120 (m), 1050 (m), 820 (s). cm^{-1}. ^{1}H-NMR (500 MHz, $(CD_3)_2CO$), δ ppm; 2.20 (S, 6H), 7.12 (S, 3H), 10.3 (S, 1H).

5-(2,6-Dimethylphenoxy)-tetrazole(3b): M.p. = 171-173 °C. Lit [9], 173-174 °C. IR (KBr, cm^{-1}): 3010 (m), 2905 (s), 2855 (s), 2705 (s), 2605 (s), 2450 (s), 1605 (s), 1570 (s), 1470 (s), 1440 (s), 1410 (s), 1160 (s), 1045 (s), 785 (s), 775 (s). cm^{-1}. ^{1}H-NMR (500 MHz, $(CD_3)_2CO$), δ ppm; 2.38 (S, 3H), 7.30 (S, 4H), 9.8 (S, br, 1H).

5-(4-Methoxyphenoxy)-tetrazole(3c): M.p. = 150-151 °C. Lit [9], 149-150 °C. IR (KBr, cm^{-1}): 3060 (m), 2950 (m), 2900 (m), 2850 (m), 2750 (m), 2600 (m), 1620 (m), 1600 (m), 1590 (m), 1500 (s), 1470 (m), 1440 (s), 1190 (m), 1180 (m), 1040 (m), 1030 (m), 820 (s). cm^{-1}. ^{1}H-NMR (500 MHz, $(CD_3)_2CO$), δ ppm; 3.88 (S, 3H), 7.00 (d , J = 10.5 Hz, 2H), 7.4 (d, J = 10.5 Hz, 2H), 8.4 (S, 1H).

5-(phenoxy)-tetrazole(3d): M.p. = 136-138°C. Lit [9], 137-138°C. IR (KBr, cm^{-1}): 2450-3000 (m), 1615 (s), 1575 (s), 1485 (s), 1440 (s), 1185 (s), 1050 (s),680- 820 (m). cm^{-1}. ^{1}H-NMR (500 MHz, $(CD_3)_2CO$), δ ppm; 7.20 (S, 5H), 13.00 (br, 1H).

5-(4-Chlorophenoxy)-tetrazole(3e): M.p. = 156-158°C. Lit [9], 166-167 °C. IR (KBr, cm^{-1}): 3010 (m), 3000 (m), 2850 (m), 2700 (s), 2600 (m), 2450 (s), 1610 (s), 1590 (s), 1480 (s), 1410 (m), 1190 (s), 1175 (m), 1080 (m), 1050 (s), 825 (s). cm^{-1}. ^{1}H-NMR (500 MHz, $(CD_3)_2CO$), δ ppm; 7.35 (S, 4H), 8.66 (br, 1H).

5-(4-Nitrophenoxy)-tetrazole(3f): M.p. = 161-163 °C. Lit [9], 162-163 °C. IR (KBr, cm^{-1}): 3120 (m), 3100 (s), 3000(m), 2750 (s), 2600 (s), 2450 (s), 1650 (vs), 1600 (s), 1570 (vs), 1540 (vs), 1480 (vs), 1450 (s), 1410 (s), 1350 (vs), 1310 (s), 1200 (vs), 1190 (s), 1120 (s), 1100 (s), 1060 (vs),860 (s), 850 (s). cm^{-1}. ^{1}H-NMR (500 MHz, $(CD_3)_2CO$), δ ppm; 7.55 (d, j=9Hz ,2H), 8.33 (d, j=9Hz, 2H), 14.1 (S, 1H).

5-(Naphthalen-1-yloxy)-tetrazole(3g): M.p. = 174-176°C. IR (KBr, cm^{-1}): 2750-3060 (m), 1630 (s), 1600 (s), 1500 (m), 1485 (m), 1390 (m), 1280 (m), 1170 (s), 1105 (m), 1050 (w), 680- 950 (m). cm^{-1}. ^{1}H-NMR (500 MHz, $(CD_3)_2CO$), δ ppm; 7.20 (d, J = 7.5 Hz, 1H), 7.35-7.45 (m, 3H), 7.63 (d, J = 8.2 Hz, 1H), 7.78 (dd, J = 9.3 Hz, J = 2.1Hz, 1H), 7.92 (dd, J = 8.8 Hz, J = 2.1 Hz, 1H), 11.1 (S , 1H). ^{13}CNMR(500 MHz, $(CD_3)_2CO$), δ ppm; 117.7, 120.8, 124.8,124.9, 125.6, 125.7, 126.9, 127.3, 134.0, 146.2, 156.7. Analysis Calcd. For $C_{11}H_8N_4O$: C, 62.26; H, 3.77; N, 26.42;% Found; C, 62.46; H, 3.66; N, 26.53%.

5-(Naphthalen-2-yloxy)-tetrazole(3h): M.p. = 152-154 °C. IR (KBr, cm^{-1}):): 2800-3070 (m), 1625(s), 1590(s), 1510 (m), 1475 (m), 1400 (m), 1275 (m), 1170(s), 1110 (m), 1070 (w), 660- 970 (m). cm^{-1}. ^{1}H-NMR (500 MHz, $(CD_3)_2CO$), δ ppm; 7.20 (dd, J = 8.7 Hz,J = 2.1 Hz, 1H), 7.34-7.41 (m, 2H), 7.49 (d, J = 2.1 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.7Hz, 2H)., 11.3 (S, 1H). ^{13}CNMR(500 MHz, $(CD_3)_2CO$), δ ppm; 117.9, 121.2, 124.8, 125.8, 126.9, 127.1, 128.5, 130.5, 133.1, 148.3, 156.5. Analysis Calcd. For $C_{11}H_8N_4O$: C, 62.26; H, 3.77; N, 26.42;% Found; C, 61.87; H, 3.61; N, 26.50%.

5. Acknowledgements

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6. References

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