NEW SYNTHETIC METHODS FOR THE PREPARATION OF 5-ARYLOXYTETRAZOLES WITH USING $\text{Mg}(\text{HSO}_4)_2$ AND $\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$ AS EFFICIENT AND GREEN HETEROGENEOUS CATALYSTS UNDER SOLVENT-FREE CONDITIONS

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ABSTRACT

An eco-friendly procedure for the preparation of 5-Aryloxytetrazoles under solvent-free conditions in the presents of magnesium hydrogen sulfate $\text{Mg}(\text{HSO}_4)_2$ and alumina sulfuric acid ($\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$) as heterogeneous catalysts was developed.

INTRODUCTION

The tetrazole ring system has attracted considerable attention in recent years, ¹⁻⁷ especially (specially) among medicinal chemists, as a potential surrogate for *cis*-peptide linkage and carboxylic acids.³ 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, ant (anti) allergic and antibiotic activities, and they are currently used, for example, as activator, anticonvulsants also in cancer and AIDS treatment.¹⁻⁵ Furthermore tetrazoles derivatives have been patented for muscle relaxation, anti-inflammatory, anti-arthritis, analgesic, ulcer therapeutic and coccidiostatic properties. Tetrazoles are also applied in agriculture, as plant growth regulators, herbicides and fungicides, photography and photo imaging stabilizers and rocket propellants explosives.¹⁻⁷ Another important application of tetrazoles is the preparation of imidoyl azides.^{8c} 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.¹⁰⁻¹¹ 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.^{1-7,10-11} A substitute for hydrazoic acid is a mixture of sodium azide and ammonium chloride with dimethylformamide as the solvent. In dimethyl formamide, the reaction mixture must be heated at ~150 °C from several hours to several days. Additional disadvantage of dimethyl formamide 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.⁶ The published method for the preparation of 5-aryloxy-tetrazoles derivatives was a reaction including the addition of NaN_3 to aryl cyanates in the presence of HCl and acetone under thermal conditions, lack of easy availability /preparation of the starting materials and difficult work-up. Using expensive and toxic reagents and the in situ generated hydrazoic acid is highly toxic and explosive.^{3,8b,8c,11,17} Because of the safety considerations, we required a novel method did not use the hydrazoic acid. Thus, a convenient and efficient method was required for preparation of the aryloxy tetrazoles. In recent years, organic reactions on heterogeneous catalysts have received considerable attention in organic synthesis because of their ease handling, enhanced reaction rates, greater selectivity, simple work-up, and recoverability of the catalysts.^{1a, 2a, 3a, 4a, 5a, 6a, 7a, 22} From the standpoint of 'green chemistry', significant efforts have been made to find an alternative organic solvents. A very attractive substitute for these solvents is a solvent-free reaction (industrially important due to their less pollution, low cost, and simplicity in process and handling. In view of the importance of aryloxy tetrazoles and aryloxy imidoyl azides,^{1-15,18-21} our aim was to find a facile and less hazardous methods for syntheses of the 5-aryloxy tetrazoles (**3a-h**) from aryl cyanates (**1a-h**) in quantitative yields by using $\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$ and $\text{Mg}(\text{HSO}_4)_2$ as two different effective heterogeneous catalysts in solvent-free conditions. However, many of these methods suffer from the draw backs inconsistent with green chemistry, such as the use of toxic chemicals and heavy metals.^{23,24} Therefore utilization of clean processes as well as eco-friendly and green catalysts has been a subject of intense research. The demand for synthesis of the 5-Aryloxytetrazoles with heterogeneous catalysts prompted us to develop a safe alternate methods for the synthesis

of 5-Aryloxytetrazoles as biologically important compounds in the presence $\text{Mg}(\text{HSO}_4)_2$ and alumina sulfuric acid ($\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$) as heterogeneous catalysts. In this research, $\text{Mg}(\text{HSO}_4)_2$ and alumina sulfuric acid ($\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$) deserve special mention as heterogeneous solid acid catalysts. These catalysts are safe, easy to handle, and present fewer disposal problems. $\text{Mg}(\text{HSO}_4)_2$ and alumina sulfuric acid (0.2 g of alumina sulfuric acid equal to 0.6 mmol H^+)^{23,24} were prepared according to the reported procedures. The amount of H^+ in the alumina sulfuric acid was determined by acid-base titration according to the following reaction (Equation 1).

Equation 1

The librated H_3O^+ was titrated by standard NaOH and the amount of H^+ in alumina sulfuric acid was calculated (0.2 g) of alumina sulfuric acid equal to 0.6 mmol)^{23, 24} also were provided BET measurements for $\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$ as following: Brunauer - Emmett-Teller surface area BET measurements and other methods were conducted using a micro metrics adsorption equipment (Quanta chrome instrument, model Nova 2000, USA) determining nitrogen (99.99% purity) as the analysis gas and the catalyst samples were slowly heated to 300 °C for 3 h under nitrogen atmospheric.²⁴ Characterization of the catalyst containing $\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$ was carried out using BET, DJH and BJH methods for determine specific surface area, total volume and pore diameter. The results are shown in Table 1. As it was shown, the specific surface area of this catalyst by BET method is 83.33 m^2/g and by other methods was shown in Table 1. It can be also observed that the catalyst which has a high specific total volume and a small pore diameter, this may be a reason for the good catalytic performance of this catalyst. For example BET area = 83 m^2/g ; total volume = 0.00982 cc/g; Pore diameter = 1.58 Ao. Table 1

Table 1. BET Measurements of $\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$.

Total volume(cc/g)	Pore diameter	Specific surface area (m^2/g)		
		BET	BJH	DH
0.00982	1.58 Ao	83.33	86.6	91.2

RESULTS AND DISCUSSION

A simple and efficient methods are described for the preparation of 5-aryloxytetrazoles (**3a-h**) in excellent yields and high purity from aryl cyanates (**1a-h**) with using $\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$ and $\text{Mg}(\text{HSO}_4)_2$ as effective catalysts in solvent-free (Scheme 1).

The cyanates **1a-h** were prepared according to literature.^{8a,8b,8c,11} 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 (15-20) h for $\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$ and after (19-24) h for $\text{Mg}(\text{HSO}_4)_2$, 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. The following important results are extracted from data in Table 1.

Scheme 1

Table 2. The preparation of 5-aryloxy tetrazoles (**3a-h**) from arylcyanates by using Al₂O₃-SO₃H and Mg(HSO₄)₂ at r.t.

Entry	Cyanate	Ar	tetrazole	Al ₂ O ₃ -SO ₃ H Time (h)/Yield (%) ^a	Mg(HSO ₄) ₂ Time (h)/ Yield (%) ^a	Mp °C	Mp(lit, ref) ^c [8,16]
1	1a	4-CH ₃ C ₆ H ₄	3a	19/94	22/90	139-140	140-142
2	1b	2,6-(CH ₃) ₂ C ₆ H ₃	3b	18/92	23/92	171-173	173-174
3	1c	4-CH ₃ OC ₆ H ₄	3c	15/95	19/96	150-151	149-150
4	1d	C ₆ H ₅	3d	20/84	24/84	136-138	137-138
5	1e	4-ClC ₆ H ₄	3e	24/77	27/76	156-158	166-167
6	1f	4-NO ₂ C ₆ H ₄	3f	29/51	35/48	161-163	162-163
7	1g	α-naphthyl	3g	21/79	20/87	174-176	-
8	1h	β-naphthyl	3h	20/83	17/83	152-154	-

^a Yields refer to the pure isolated products.

The following important results are extracted from data in Table 1. 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). For Al₂O₃-SO₃H the entries 5 (24 h) and 6 (29 h) confirms and for Mg(HSO₄)₂ the entries 5 (27 h) and 6 (35 h) confirms this result. The rate of reaction was found to decrease with increasing the electronegativity of a substituent on the aryl group. These results are the reverse of what was reported for the nitriles.³ when the substitution on aryl ring is electron-donating in arylcyanates (aryl cyanates) **1** the oxygen attached to aryl ring has more basic character. 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-aryloxytetrazoles. 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.^{8a,8b,8c,11} 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 aryl cyanate **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. Scheme 1. The plausible mechanism for the formation of 5-Aryloxytetrazoles is given below (Scheme 2).

In all cases, the products were characterized by ¹H NMR, ¹³C NMR, IR, elemental analyses (CHN), and melting points. The disappearance of one strong and sharp absorption band (CN stretching band) and the appearance of a NH stretching band in the IR spectra provided clear evidence for the formation of aryloxy tetrazoles (Fig. 1). ¹³C 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 pK_a 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 carboxylic acids. Thus, the signal of the NH proton of the tetrazole ring (NH) shifted downfield.

Fig. 1. ¹H NMR spectrum 5-phenoxy tetrazole (3d).

Fig. 2. IR spectrum (KBr) 5-phenoxy tetrazole (3d).

CONCLUSIONS

A facile, convenient and less hazardous synthetic methods for 5-aryloxytetrazoles **3** from aryl cyanates in solvent-free were achieved giving quantitative yields and high purity without expensive reagents involvement or the formation of undesirable side products. To show the advantages of $\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$ and $\text{Mg}(\text{HSO}_4)_2$ as catalysts in comparison with other catalysts, we compared the reaction of $\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$ and $\text{Mg}(\text{HSO}_4)_2$ with glacial acetic acid, PPh_3 and HCl ^{8a,8b,8c,11} in the synthesis of 5-(4-chlorophenoxy)-tetrazole (**3e**) (Table 1, Entry 5). As shown in Table 3, $\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$ and $\text{Mg}(\text{HSO}_4)_2$ are a better catalysts in the synthesis of 5-(4-Chlorophenoxy)-tetrazole (**3e**).

Table 3 Comparison of $\text{Mg}(\text{HSO}_4)_2$ and $\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$ with Other Catalysts in the synthesis of 5-(4-Chlorophenoxy)-tetrazole (**3e**).

Entry	Catalyst	Solvent	Time (min)	Temperature (°C)	Yield%
1	PPh_3	DMF	120	120	57
2	HCl^b	CH_3COCH_3	80	65	46
4	CH_3COOH^a	CH_3COOH	35h	25	59
6	$\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$	-	24h	25	77
7	$\text{Mg}(\text{HSO}_4)_2$	-	27h	25	76

^a Glacial acetic acid as both solvent and proton donor source. ^b add in work up^{8b,8c,11}.

In order to be able to carry out cycle addition in a more efficient way and minimizing the reactions time and amount of the catalysts, the reaction of aryl cyanates **1a-h**, NaN_3 and different catalysts were selected as a model system to investigate the effects of the catalysts at reactions time and amounts of catalysts as shown in Table 4.

Table 4. Optimization Amount of $\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$ and $\text{Mg}(\text{HSO}_4)_2$ on the Reaction of tetrazole **3a** under Solvent-Free Conditions.

Entry	$\text{Al}_2\text{O}_3\text{-SO}_3\text{H}(\text{gr})$	$\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$: Time (h)/Yield (%) ^a	$\text{Mg}(\text{HSO}_4)_2(\text{gr})$	$\text{Mg}(\text{HSO}_4)_2$: Time (h)/Yield (%) ^a
1	0.5	15/62	0.40	19/51
2	0.65	15/72	0.50	19/67
3	0.8	15/80	0.60	19/81
4	0.95	15/87	0.70	19/96
5	1.05	15/95	0.65	19/96

Experimental Section

CAUTION: Although aryloxy tetrazoles 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 concentration of 8-15%.³ All products are known compounds and are identified by comparison of their spectral data (IR and ¹H-NMR) specify instruments work and physical properties with those of authentic samples.^{8a, 8b, 8c, 11} All starting materials and solvents were purified with the specific proper purification techniques before use, when necessary. $\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$ was prepared according to the literature.²⁴

Typical experimental procedure for the preparation of

5-Aryloxytetrazoles **3** with using $\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$ and $\text{Mg}(\text{HSO}_4)_2$

The cyanate (1 mmol), $\text{Al}_2\text{O}_3\text{-SO}_3\text{H}$ (1.05 g) or $\text{Mg}(\text{HSO}_4)_2$ (0.65 g) 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 via TLC. After completion of the reaction, H_2O was added and the mixture stirred for 5 min, then the mixture was filtered. The solid residue was isolated and for reuse of catalyst the solid residue was diluted with ethyl acetate (10 mL) and the catalyst was separated by simple filtration. Evaporation of the solvent under reduced pressure yielded crude product. Desired pure products were characterized by NMR and IR spectroscopy and melting points. The spectral data of 5-aryloxytetrazoles are given below.

Data for 5-aryloxy tetrazoles (3g-h):

5-(Naphthalen-1-yloxy)-tetrazole(3g): M.p. = 174-176 °C. IR (KBr, cm^{-1}

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. ¹H-NMR (500 MHz, (CD₃)₂CO), d 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 = 2.1 Hz, 1H), 7.92 (dd, J = 8.8 Hz, J = 2.1 Hz, 1H), 11.1 (s, 1H). ¹³C-NMR(500 MHz, (CD₃)₂CO), d 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 C₁₁H₈N₄O: 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. ¹H-NMR (500 MHz, (CD₃)₂CO), d 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 = 8.7 Hz, 2H), 11.3 (s, 1H). ¹³C-NMR(500 MHz, (CD₃)₂CO), d 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 C₁₁H₈N₄O: C, 62.26; H, 3.77; N, 26.42%. Found: C, 61.87; H, 3.61; N, 26.50%.

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