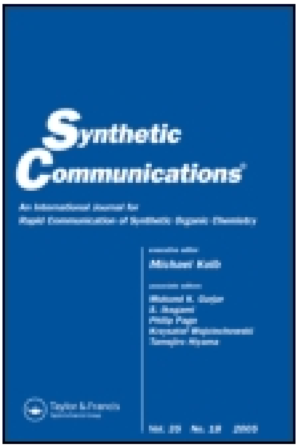

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Aluminum(III) Hydrogensulfate: An Efficient Solid Acid Catalyst for the Preparation of 5-Substituted 1H-Tetrazoles

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ALUMINUM(III) HYDROGENSULFATE: AN EFFICIENT SOLID ACID CATALYST FOR THE PREPARATION OF 5-SUBSTITUTED 1*H*-TETRAZOLES

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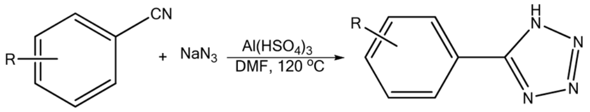
GRAPHICAL ABSTRACT



Abstract *An efficient method for preparation of 5-substituted 1*H*-tetrazoles via [2 + 3] cycloaddition of nitriles and sodium azide is reported using aluminum(III) hydrogensulfate as an effective solid acid. This method has the advantages of good yields, simple methodology, and easy workup.*

Keywords Aluminum(III); [2 + 3] cycloaddition; hydrogensulfate; nitrile; solid acid catalyst; 5-substituted 1*H*-tetrazole

INTRODUCTION

The growth of tetrazole chemistry over the past 25 years has been significant, mainly as a result of the roles played by tetrazoles in coordination chemistry as ligands, in medicinal chemistry as stable surrogates for carboxylic acids, and in material applications, including explosives, agriculture, and photography.[1–4]

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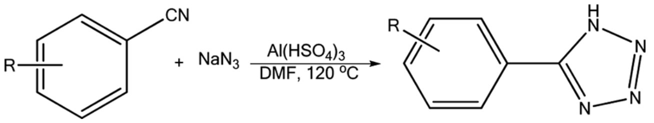


Scheme 1. Conversion of nitriles to the corresponding 5-substituted 1*H*-tetrazoles using $Al(HSO_4)_3$.

Another important application of tetrazoles is preparation of imidoylazides.[5] The conventional method of synthesizing tetrazoles is by addition of azide ions to organic nitriles or cyanamides.[6] Earlier reported methods for the synthesis of 5-substituted tetrazoles suffer from drawbacks such as the use of strong Lewis acids or expensive and toxic metals, and the in situ–generated hydrazoic acid, which is highly toxic and explosive.[7] Several syntheses of 5-substituted tetrazoles have been reported through the [2 + 3] cycloaddition of nitriles using NaN_3 or $TMSN_3$ in the presence of catalysts such as $FeCl_3$–SiO_2,[6f] $AlCl_3$,[8] $(C_2H_5)_2O \cdot BF_3$,[9] tetrabutyl ammonium fluoride (TBAF),[10] $Pd(PPh_3)_4$,[11] Zn/Al hydrotalcite,[12] and ZnO.[13]

The use of solid acid salt catalysts,[14] such as $Al(HSO_4)_3$, for synthesizing organic intermediates and fine chemicals is gaining increasing awareness and is a field of intense research activity.[15] This salt is a stable and nonhygroscopic solid material that is insoluble in most organic solvents.

We herein report a new protocol for preparation of 5-substituted 1*H*-tetrazoles derivatives from nitriles using aluminum(III) hydrogensulfate as a solid acid catalyst (Scheme 1).

EXPERIMENTAL

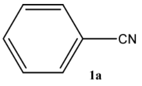
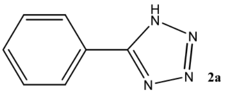
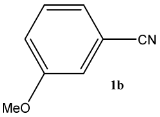
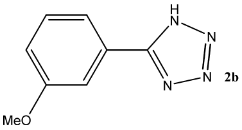
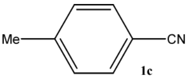
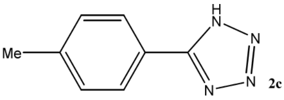
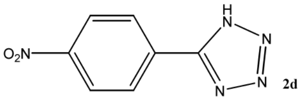
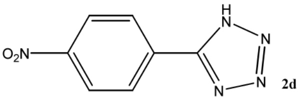
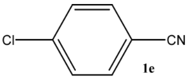
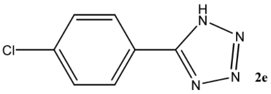
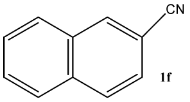
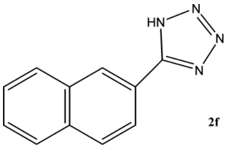
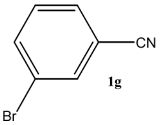
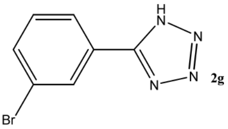
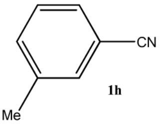
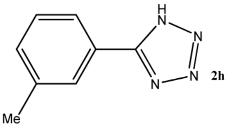
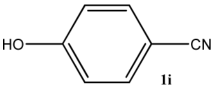
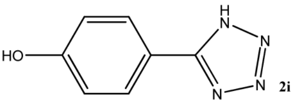
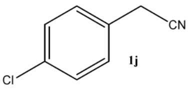
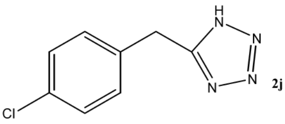
General

All reagents were purchased from Merck and Aldrich and used without further purification. ^{13}C NMR and ^{1}H NMR spectra were recorded on Brucker 100- and 250-MHz instruments using tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported in parts per million (ppm), and coupling constants are reported in hertz (Hz). Infrared (IR) spectra were recorded on a Shimadzu 470 spectrophotometer. Thin-layer chromatography (TLC) was performed on Merck precoated silica-gel 60-F254 plates. $Al(HSO_4)_3$ was prepared from $AlCl_3$ and H_2SO_4, according to the literature.[14c,15] Massah and coworkers studied the characterization of the $Al(HSO_4)_3$ using DSC, TG-DTG, and FT–IR spectroscopy.[15b]

General Procedure for Preparation of 5-Substituted 1*H*-Tetrazoles

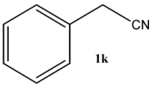
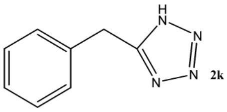
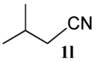
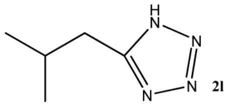
$Al(HSO_4)_3$(10 mol%) was added to a mixture of nitrile (2 mmol), NaN_3 (3 mmol), and distilled dimethylformamide (6 mL) and stirred at 120 °C for the appropriate time (Table 1). After completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature. The solid acid was filtered, and the filtrate was treated with ethyl acetate (35 mL) and 5 N HCl (20 mL) and stirred vigorously. The resultant organic layer was separated, and the aqueous layer was again extracted with ethyl acetate (25 mL). The combined organic layer was washed with water (8 mL)

Table 1. Synthesis of various 5-substituted 1*H*-tetrazoles in the presence of $Al(HSO_4)_3$ by reaction of sodium azide and nitriles at 120 °C

Entry	Substrate	Product	Time (h)	Yield (%)[a]	Ref.
1	 1a	 2a	18	91	6f
2	 1b	 2b	18	87	6f
3	 1c	 2c	18	85	6f
4	 2d	 2d	18	90	6f
5	 1e	 2e	18	89	6f
6	 1f	 2f	18	90	6f
7	 1g	 2g	18	84	6f
8	 1h	 2h	22	85	17
9	 1i	 2i	36	60	18
10	 1j	 2j	18	84	6f

(*Continued*)

Table 1. Continued

Entry	Substrate	Product	Time (h)	Yield (%)[a]	Ref.
11	 1k	 2k	18	85	6f
12	 1l	 2l	30	69	17

[a]Yields refer to the pure isolated products.

and concentrated to give a crude product. Column chromatography using silica gel gave pure product in excellent yield. The pure products were characterized by IR and NMR. All the products are known compounds, and the spectral data and melting points were identical to those reported in the literature.

RESULTS AND DISCUSSION

The general synthetic method is depicted in Scheme 1. 5-Substituted 1*H*-tetrazoles were obtained from the reaction of nitrile with sodium azide in the presence of $Al(HSO_4)_3$ as a solid acid catalyst at 120 °C for appropriate time in good yields, as summarized in Table 1.

First, we optimized the amount of $Al(HSO_4)_3$ catalyst required in the reaction between benzonitrile and sodium azide (Table 2). Water was not a suitable solvent for this reaction. Not many organic solvents are stable at the high temperatures necessary for cycloaddition reactions (sometimes as high as 130 °C), and for this reason dimethylformamide (DMF) is most commonly used for this purpose.[2a,9,12] The optimum amount of $Al(HSO_4)_3$ was found to be 10 mol% in the presence of nitrile (2 mmol) and sodium azide (3 mmol) in DMF (6 mL). We next examined a variety of structurally divergent benzonitriles possessing a wide range of functional groups to understand the scope and generality of the $Al(HSO_4)_3$-promoted [2 + 3] cycloaddition reaction to form 5-substituted 1*H*-tetrazoles, and the results are summarized in Table 1. The nature of the substituent on the benzonitrile did not affect the reaction time (Table 1, entries 1–7, 10, and 11). Reactions of the 3-methylbenzonitrile (Table 1, entry 8) and 4-hydroxybenzonitrile (Table 1, entry 9) were complete at 120 °C after 22 and 36 h, respectively, and gave the corresponding tetrazole in excellent yields.

The products were characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy and from melting points. The disappearance of one strong and sharp absorption band (CN stretching band) and the appearance of an NH stretching band in the IR spectra were evidence for the formation of 5-substituted 1*H*-tetrazoles. ^{13}C NMR spectra display signals for tetrazole ring carbons of arylaminotetrazoles in the range of 154–157 ppm (depending on the nature of the substituents in the amino functionality).[16]

Table 2. Preparation of 5-phenyltetrazole using varying amounts of $Al(HSO_4)_3$ under thermal conditions at 120 °C[a]

Entry	$Al(HSO_4)_3$ (mol%)	Solvent	Yield%[b]
1	5	DMF	54
2	7	DMF	76
3	10	DMF	93
4	10	DMSO	91
5	15	DMF	94
6	0	DMF	0[c]

[a] Reaction conditions: nitrile (2 mmol), NaN_3 (3 mmol), $Al(HSO_4)_3$ (10 mol%), and DMF, (6 mL), reaction time (18 h) at 120 °C.

[b] Isolated yield.

[c] In the absence of catalyst at 120 °C, no reaction occurred after 18 h.

CONCLUSION

In conclusion, we have developed a novel and highly efficient method for the synthesis of various 5-substituted 1*H*-tetrazoles by treatment of nitriles with sodium azide in the presence of $Al(HSO_4)_3$ as an effective catalyst. The significant advantages of this methodology are good yields, elimination of dangerous and harmful hydrazoic acid, simple workup procedure, and easy preparation and handling of the catalyst.

ACKNOWLEDGMENT

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