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A Facile Synthesis of 1-Substituted-1*H*-1,2,3,4-Tetrazoles Catalyzed by Ytterbium Triflate Hydrate

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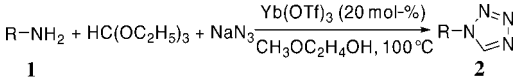
A series of 1-substituted 1*H*-1,2,3,4-tetrazole compounds have been synthesized in good yields from amines, triethyl orthoformate, and sodium azide through the catalyzed reaction with $Yb(OTf)_3$. Some of the 1-susbstituted 1*H*-1,2,3,4-tetrazole compounds showed strong phytocidal activity.

Introduction

Tetrazoles have been studied extensively since they were first described in 1885[1] and have been used in a variety of synthetic and medicinal chemistry applications.[2] Although many 5-substituted 1*H*-1,2,3,4-tetrazoles are known, only a few 1-substituted 1*H*-1,2,3,4-tetrazoles have been described. In 1947, Benson reported a review on tetrazole chemistry listing only seven examples of 1-substituted 1*H*-1,2,3,4-tetrazoles including the questionable 1-hydroxy-1*H*-1,2,3,4-tetrazole.[1b] After that time, several methods for the preparation of 1-substituted 1*H*-1,2,3,4-tetrazoles were reported,[3] because of their wide utility.[4] These include the cyclization reaction of amines, or its hydrochloride salt, with an orthocarboxylic acid ester and a hydrazoic acid metal salt in the presence of acetic acid or trifluoroacetic acid.[3e–3g] Unfortunately, all of these known methods suffered from some limitations, such as drastic reaction conditions, tedious workup procedures, the use of excessive amounts of glacial acetic acid or trifluoroacetic acid as the solvent, or even the need for excess amounts of dangerous and harmful hydrazoic acid. Therefore, it is desirable to develop a more efficient and convenient method for the synthesis of 1-substituted 1*H*-1,2,3,4-tetrazoles.

During the last decade, rare earth metal triflates have been found to be unique Lewis acids in that they are water tolerant, recyclable catalysts that can effectively promote several carbon–carbon and carbon–heteroatom bond formation reactions.[5] As part of our ongoing studies to test the effectiveness of lanthanide triflates as Lewis acid catalysts in heterocycloaddition reactions, we decided to investigate the $Yb(OTf)_3$ hydrate catalyzed cyclization of amines, triethyl orthoformate, and sodium azide for the synthesis of 1-substituted 1H-1,2,3,4-tetrazoles (Scheme 1).



1 2

Scheme 1.

Results and Discussion

A mixture of aniline (1 mmol), triethyl orthoformate (1.2 mmol), and sodium azide (1 mmol) in 2-methoxyethanol (3 mL) was stirred at room temperature for 10 h, but no reaction took place as indicated by TLC (Table 1, Entry 1). The mixture was then heated to 100 °C and stirred for 10 h. To our delight, the desired cyclization reaction eventually took place, but only produced 1-phenyl-1*H*-1,2,3,4-tetrazole in less than 5% yield (Table 1, Entry 2). This means that the cyclization process could take place spontaneously under high temperature, but the activity is too low to give the product in a reasonable yield. Bearing in mind that $Yb(OTf)_3$ as a novel Lewis acid was still active in the presence of many Lewis bases containing nitrogen, oxygen, phosphorus, and sulfur atoms,[6] we then added catalytic amounts of $Yb(OTf)_3$ hydrate to the reaction mixture. Fortunately, the expected product was obtained with a much improved yield (Table 1, Entry 3). Further studies showed that the yield could be increased to as high as 85% within 6 h when 0.2 mmol $Yb(OTf)_3$ hydrate was used (Table 1, Entry 4). However, excess $Yb(OTf)_3$ hydrate (beyond this amount) did not lead to a further increase in yield.

As for the possible mechanism of this catalytic reaction, we believe that the Lewis acidity of the Yb^{III} ion in

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Table 1. The cyclization reaction of aniline, triethyl orthoformate, and sodium azide under different catalytic systems.[a]

Entry	Solvent	Catalyst	Amount of catalyst [mmol]	Reaction temp. [°C]	Reaction time [h]	Isolated yield [%]
1	2-Methoxyethanol	None	0	r.t.	10	0
2	2-Methoxyethanol	None	0	100	10	5
3	2-Methoxyethanol	$Yb(OTf)_3$ hydrate	0.05	100	6	62
4	2-Methoxyethanol	$Yb(OTf)_3$ hydrate	0.1	100	6	77
5	2-Methoxyethanol	$Yb(OTf)_3$ hydrate	0.2	100	6	85
6	2-Methoxyethanol	$Yb(OTf)_3$ hydrate	0.2	100	4	80
7	2-Methoxyethanol	$Yb(OTf)_3$	0.2	100	6	78
8	*i*PrOH	$Yb(OTf)_3$ hydrate	0.2	reflux	6	45
9	Ethanol	$Yb(OTf)_3$ hydrate	0.2	reflux	6	55
10	THF	$Yb(OTf)_3$ hydrate	0.2	reflux	6	34
11	1,4-Dioxane	$Yb(OTf)_3$ hydrate	0.2	reflux	6	51
12	AcOH	None	0	80	6	55

[a] Reaction conditions: 3 mL solvent, 1.0 mmol aniline, 1.2 mmol triethyl orthoformate, and 1.0 mmol sodium azide.

$Yb(OTf)_3$ hydrate plays an important role in the promotion of this cyclization process. It was proposed that the breakdown of triethyl orthoformate in the presence of acid[7] allows for the formation of 1-substituted 1*H*-1,2,3,4-tetrazole. In order to clarify the role of the Yb^{III} ion and the hydration water of $Yb(OTf)_3$ hydrate, anhydrous $Yb(OTf)_3$ was also tried as the catalyst for this reaction, and it gave similar results compared to those with $Yb(OTf)_3$ hydrate (Table 1, Entry 7). At this stage, it might be safe to say that it was only the Yb^{III} ion, rather than the Yb^{III} ion together with the hydration water of $Yb(OTf)_3$ hydrate, that acts as the real catalyst in this cyclization process. Of the two Yb^{III} salts used, although anhydrous $Yb(OTf)_3$ exhibited a similar catalytic activity for this reaction when compared to that of $Yb(OTf)_3$ hydrate, the latter was preferred because of its ease of recycling, convenient handling, and lower price.

In addition, several conventional organic solvents were also used, and the results compared with those of 2-methoxyethanol in the presence of $Yb(OTf)_3$ hydrate (Table 1, Entries 5, 8–11). It is shown that of the five solvents used, 2-methoxyethanol gave the highest yield for the desired product under the similar reaction conditions, because of its excellent solubility. Meanwhile, an established method was also tested under similar conditions (Table 1, Entry 12), but the yield (55%) was much lower than that of the present process (85%) (Table 1, Entry 5).

On the basis of the above results, this process was then extended to other substituted anilines, heterocyclic amines, and aliphatic amines to investigate its scope and generality. The results are listed in Table 2. It can be seen that under these similar conditions, a wide range of anilines containing chloro- or methyl groups easily undergo condensation with triethyl orthoformate and sodium azide to give 1-phenyl-1*H*-1,2,3,4-tetrazoles with short reaction times and in good to excellent yields (Table 2, Entries 1–9). It is worthwhile noting that both pyridylamines and aliphatic amines also give the corresponding tetrazole products in equally fair yields (Table 2, Entries 10–15). It is interesting to note that the specific rotation of (*S*)-1-phenylethylamine was negative $\{[a]_D^{18.7} = -24.39$ (c = 0.12, methanol)}, while its corresponding product (*S*)-1-phenylethyl-1*H*-1,2,3,4-tetrazole was positive $\{[a]_D^{17.4} = +23.04$ (c = 0.10, methanol)} (Table 2, Entry 14). When compared to the literature, the yields of selected compounds have improved from 67%[3e] to 79% (Table 2, Entry 12), and 66%[3e] to 75% (Table 2, Entry 13).

Table 2. $Yb(OTf)_3$ catalyzed the formation of 1-substituted-1*H*-1,2,3,4-tetrazoles.

Entry	R	Time [h]	Products	Yield [%][a]
1	C_6H_5	6	**2a**	85
2	3-MeC_6H_4	7	**2b**	89
3	4-MeC_6H_4	6	**2c**	91
4	2-ClC_6H_4	7	**2d**	82
5	4-ClC_6H_4	6	**2e**	88
6	2-Me-3-ClC_6H_3	9	**2f**	75
7	2-Me-5-ClC_6H_3	9	**2g**	78
8	2,4-ClC_6H_3	8	**2h**	81
9	3,5-ClC_6H_3	7	**2i**	84
10	2-C_5H_4N	6	**2j**	89
11	2-(4-MeC_5H_3N)	6	**2k**	87
12	$C_6H_5CH_2$	7	**2l**	79
13	4-CH_3O–$C_6H_4CH_2$	8	**2m**	75
14	(*S*)-1-Phenylethylamine	7	**2n**	72
15	Furfurylamine	6	**2o**	71

[a] Isolated yields based on amines.

Our attention was then turned to the possibility of recycling the catalyst from the reaction media since the recovery and reuse of the catalyst are highly preferable for a greener process. At completion of the reaction, the solvent was removed under vacuum, then the residue was diluted with water and the organic impurities were extracted with ethyl acetate to obtain the desired product. Because of its much higher solubility in water, the catalyst was recovered almost quantitatively after removal of water under reduced pressure, and further evaporation was not necessary. The reus-

Table 3. Reusability of $Yb(OTf)_3$ hydrate catalyst.

Recycle no.	Catalyst recovered [%]	Isolated yield [%][a]
1	98	85
2	98	84
3	96	84
4	97	81
5	96	78

[a] Product: 1-phenyl-1*H*-1,2,3,4-tetrazole; reaction conditions: reaction time 6 h at 100 °C.

Table 4. The phytocidal activity of some products was tested by the plate method.[a]

Entry	Products	*Echinochloa crusgalli (L.) Beauv*	Broomcorn	*Digitaria sanguinalis (L.) Scop*	Edible amaranth	Cucumber	Cole
1	**2b**	0/20	0/0	0/50	98/98	The fibre tailed off.	0/0
2	**2c**	0/70	0/0	10/20	80/80	The fibre shortened	0/0
3	**2d**	0/40	40/65	50/75	10/75	10/60	70/60
						The border of leaves became yellow.	Rot.
4	**2e**	0/75	0/0	0/75	60/75	0/20	0/0
5	**2f**	0/0	0/0	30/0	70/75	The fibre shortened	0/0
6	**2g**	30/90	20/20	70/95	90/90	90/95	95/95
7	**2j**	0/0	0/0	0/0	0/0	The fibre shortened	0/0
8	**2l**	0/0	0/0	0/0	0/0	0/0	0/0
9	**2m**	0/0	0/0	0/0	0/0	0/0	0/0
10	**2n**	0/0	0/0	0/0	0/0	0/0	0/0
11	**2o**	0/0	0/0	0/0	0/0	0/0	0/0

[a] The phytocidal activity of each products was tested by the plate method three times at a concentration of 100 ppm. –/–: percent of above earth inhibition/percent of under earth inhibition.

ability of the catalyst was investigated by using aniline, triethyl orthoformate, and sodium azide as model substrates. After four recycles, the catalyst still had a high activity and gave the corresponding product in fairly good yield (Table 3, Recycle no. 5).

Furthermore, many strong weedicides that contain the tetrazole ring have been used widely in agriculture,[8] so it was of interest to find whether some of the 1-substituted 1*H*-1,2,3,4-tetrazoles exhibited similar biological activities. To our excitement, the preliminary bioassay showed that some of the 1-aromatic-substituted 1*H*-1,2,3,4-tetrazoles had strong phytocidal activity. Especially 1-(5-chloro-2-methylphenyl)-1*H*-1,2,3,4-tetrazole, which exhibited 90% activity under earth inhibition against *Echinochloa crusgalli (L.) Beauv* by the plate method at a concentration of 100 ppm. The preliminary bioassay results of some products are listed in Table 4.

Conclusions

In this paper we have demonstrated that $Yb(OTf)_3$ hydrate is an effective catalyst in promoting the reaction between amines, triethyl orthoformate, and sodium azide that affords the corresponding 1-substituted 1*H*-1,2,3,4-tetrazole products. The method offers several advantages over traditional methods: it leads to good yields and is environmentally friendly, a much safer procedure is used, and the product is easily isolated. All of these advantages make this process useful for the synthesis of 1-aromatic- and 1-aliphatic-ubstituted 1*H*-1,2,3,4-tetrazoles. Some of the 1-aromatic-substituted 1*H*-1,2,3,4-tetrazoles showed strong phytocidal activity in the preliminary bioassay. The investigation of the synthesis of some tetrazole-substituted pharmaceuticals and chiral products are in progress.

Experimental Section

General Method: All reagents were commercially available and used without any purification. The melting points were recorded with a Digital Melting Point Apparatus WRS-1B and are uncorrected. ^{1}H- and ^{13}C NMR spectra were recorded with a Varian-400 MHz spectrometer. IR measurements were carried out with a Nicolet Aviatar-370 instrument. Mass spectra were measured with Thermo Finnigan LCQ-Advantage (EI). Specific rotations were measured with an AUTOPOL IV automatic polarimeter.

General Procedures: A mixture of amine (1 mmol), triethyl orthoformate (1.2 mmol), sodium azide (1 mmol) in 2-methoxyethanol (3 mL) was heated at 100 °C in the presence of a catalytic amount of $Yb(OTf)_3$ hydrate (0.20 mmol). The reaction was monitored by TLC. At completion of the reaction, the mixture was distilled under vacuum to remove the solvent and then diluted with cold water (10 mL). After extraction with ethyl acetate (20 mL × 3), the combined organic layers were washed with brine and dried with $MgSO_4$.The residue was concentrated and recrystallized from isopropyl alcohol to afford the pure products. The aqueous layer was distilled under reduced pressure to yield $Yb(OTf)_3$ hydrate. ^{1}H NMR, ^{13}C NMR, IR and MS data of products **2a**,[3f] **2b**,[3d] **2c**,[3f] **2d**,[3d] **2e**,[3f] **2j**,[9] **2l**,[3e] and **2m**[3e] are in full agreement with those reported previously (see Supporting Information).

1-Phenyl-1*H*-1,2,3,4-tetrazole (2a): Yield: 124 mg (85%).

1-(3-Methylphenyl)-1*H*-1,2,3,4-tetrazole (2b): Yield: 143 mg (89%).

1-(4-Methylphenyl)-1*H*-1,2,3,4-tetrazole (2c): Yield: 146 mg (91%).

1-(2-Chlorolphenyl)-1*H*-1,2,3,4-tetrazole (2d): Yield: 148 mg (82%).

1-(4-Chlorolphenyl)-1*H*-1,2,3,4-tetrazole (2e): Yield: 159 mg (88%).

1-(3-Chloro-2-methylphenyl)-1*H*-1,2,3,4-tetrazole (2f): Yield: 146 mg (75%) as colorless crystalline needles. M.p. 95–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.20 (s, 3 H), 7.27 (d, J = 8.0 Hz, 1 H), 7.37 (t, J = 8.0 Hz, 1 H), 7.63 (d, J = 8.0 Hz, 1 H), 8.84 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.18, 124.69, 127.47, 131.80, 132.87, 133.87, 136.40, 143.18 ppm. IR (KBr): $\tilde{\nu}$ = 1597, 1581, 1482, 1459, 1385, 1233, 1191, 1177, 1097, 1056, 993 cm^{-1}. MS (EI): *m*/*z* (%) = 194 (15), 165 (100). $C_8H_7ClN_4$ (195): calcd. C 49.37, H 3.63, N 28.79; found C 49.41, H 3.66, N 28.75.

1-(5-Chloro-2-methylphenyl)-1*H*-1,2,3,4-tetrazole (2g): Yield: 152 mg (78%) as colorless crystalline needle. M.p. 54–55 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.20 (s, 3 H), 7.40–7.38 (m, 2 H), 7.50–7.47 (m, 1 H), 8.87 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.65, 126.18, 131.23, 132.53, 132.92, 133.18, 133.81, 143.19 ppm. IR (KBr): $\tilde{\nu}$ = 1601, 1578, 1502, 1472, 1386, 1216, 1179, 1135, 1091, 1034, 1001, 962 cm^{-1}. MS (EI): *m*/*z* (%) = 165 (100). $C_8H_7ClN_4$ (195): calcd. C 49.37, H 3.63, N 28.79; found C 49.42, H 3.59, N 28.84.

1-(2,4-Dichlorophenyl)-1*H*-1,2,3,4-tetrazole (2h): Yield: 174 mg (81%) as colorless crystalline needles. M.p. 146 °C. ^{1}H NMR

(400 MHz, $CDCl_3$): δ = 7.63 (dd, J = 2.8 Hz and 8.4 Hz, 1 H), 7.70 (d, J = 8.4 Hz, 1 H), 7.91 (d, J = 2.4 Hz, 1 H), 9.07 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.45, 123.34, 132.25, 133.00, 134.81, 134.89, 140.69 ppm. IR (KBr): $\tilde{\nu}$ = 1580, 1492, 1428, 1249, 1214, 1034, 875 cm^{-1}. MS (EI): *m*/*z* (%) = 219 (9), 217 (53), 215 (100). $C_7H_4Cl_2N_4$ (215): calcd. C 39.09, H 1.87, N 26.06; found C 39.14, H 1.83, N 26.11.

1-(3,5-Dichlorophenyl)-1*H*-1,2,3,4-tetrazole (2i): Yield: 181 mg (84%) as colorless crystalline needles. M.p. 128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (t, J = 1.6 Hz, 1 H), 7.70 (t, J = 1.6 Hz, 2 H), 9.07 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.66, 130.11, 135.01, 136.85, 140.35 ppm. IR (KBr): $\tilde{\nu}$ = 1588, 1477, 1428, 1068, 1007, 854, 665 cm^{-1}.MS (EI): *m*/*z* (%) = 219 (10), 217 (58), 215 (100). $C_7H_4Cl_2N_4$ (215): calcd. C 39.09, H 1.87, N 26.06; found C 39.14, H 1.84, N 26.13.

1-(2-Pyridine)-1*H*-1,2,3,4-tetrazole (2j): Yield: 131 mg (89%).

4-Methyl-2-(1*H*-1,2,3,4-tetrazol-1-yl)pyridine (2k): Yield: 140 mg (87%) as pink crystalline needles. M.p. 130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.50 (s, 3 H), 7.25–7.24 (m, 1 H), 7.89 (s, 1 H), 8.37 (d, J = 5.2 Hz, 1 H), 9.52 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.02, 115.17, 126.05, 140.44, 147.18, 148.86, 152.09 ppm. IR (KBr): $\tilde{\nu}$ = 1617, 1476, 1450, 1239, 1174, 1091, 995, 952, 838 cm^{-1}. MS (EI): *m*/*z* (%) = 162 (45), 134 (100). $C_7H_7N_5$ (161): calcd. C 52.16, H 4.38, N 43.46; found C 52.22, H 4.42, N 43.41.

1-Benzyl-1*H*-1,2,3,4-tetrazole (2l): Yield: 127 mg (79%).

1-(4-Methoxybenzyl)-1*H*-1,2,3,4-tetrazole (2m): Yield: 143 mg (75%).

(*S*)-1-(1-Phenylethyl)-1*H*-1,2,3,4-tetrazole (2n): Yield: 125 mg (72%) as colorless crystals. M.p. 72–73 °C. $[a]_D^{17.4}$ = +23.04 (c = 0.1, methanol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.04 (m, 3 H), 5.86 (m, 1 H), 7.42–7.29 (m, 5 H), 8.54 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.20, 59.18, 126.09, 126.51, 129.07, 129.22, 138.16, 141.61 ppm. IR (KBr): $\tilde{\nu}$ = 1495, 1467, 1456, 1425, 1383, 1258, 1208, 1163, 1112, 1097, 1069, 1051, 1027 cm^{-1}. MS (EI): *m*/*z* (%) = 117 (40), 105 (100). $C_9H_{10}N_4$ (174): calcd. C 62.04, H 5.79, N 32.17; found C 61.99, H 5.73, N 32.24.

1-(2-Furylmethyl)-1*H*-1,2,3,4-tetrazole (2o): Yield: 107 mg (71%) as colorless crystalline needles. M.p. 85 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.64 (s, 2 H), 6.42–6.41 (m, 1 H), 6.56–6.55 (m, 1 H), 7.46–7.45 (m, 1 H), 8.68 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.96, 111.24, 111.43, 142.69, 144.39, 145.79 ppm. IR (KBr): $\tilde{\nu}$ = 1506, 1476, 1430, 1354, 1260, 1165, 1154, 1104, 1016 cm^{-1}. MS (EI): *m*/*z* (%) = 151 (100). $C_6H_6N_4O$ (150): calcd. C 47.99, H 4.03, N 37.32; found C 48.07, H 3.99, N 37.38.

Supporting Information: (See footnote on the first page of this article.) ^{1}H NMR, ^{13}C NMR, IR, and MS data of the products are included.

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