Metal Triflate Catalyzed Reactions of Alkenes, NBS, Nitriles, and TMSN3: Synthesis of 1,5-Disubstituted Tetrazoles

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Metal Triflate Catalyzed Reactions of Alkenes, NBS, Nitriles, and $TMSN_3$: Synthesis of 1,5-Disubstituted Tetrazoles

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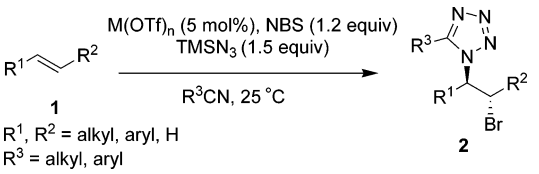

A versatile and highly efficient protocol for the synthesis of 1,5-disubstituted tetrazoles has been developed by metal triflate catalyzed one-pot reaction of alkenes, NBS, nitriles, and $TMSN_3$. Among the metal triflates, $Zn(OTf)_2$ was found to be the best catalyst. Use of different combinations of alkenes and nitriles generate a variety of 1,5-disubstituted tetrazoles containing an additional α-bromo functionality of the N1-alkyl substituent.

Tetrazoles are increasingly important heterocyclic compounds in medicinal chemistry.[1] 5-Substituted 1*H*- and 1,5-disubstituted tetrazoles are often used as metabolically stable surrogates for the carboxylic acid group and for the *cis*-amide bond, respectively.[2−4] An enormous number of tetrazole-containing biologically active compounds are known in the literature.[5,6] Recently, 1-benzyl-5-aryltetrazoles were found to be novel antagonists for the $P2X_7$ receptor.[7]

In the literature, 1*H*-tetrazoles[8] and polycyclic fused tetrazoles[6b,9] are mostly prepared by inter- and intramolecular [3 + 2]-cycloaddition, respectively, of azides and nitriles. 1,5-Disubstituted tetrazoles are usually obtained from secondary amides or thioamides on reaction with PCl_5/HN_3,[3] $TMSN_3/Ph_3P$/DEAD,[10] and $TMSN_3/Et_3N$/Hg(II),[11] mostly under noncatalytic conditions. Hassner reported $AgClO_4$-promoted reaction of alkenes, halogens (Br_2 or I_2), nitriles, and NaN_3, noting the ability to produce the 1,5-disubstituted tetrazoles.[12] Many methods for the synthesis of tetrazoles are known, but due to their importance, the development of new synthetic approaches using mild reaction conditions remains an active research area. In this paper, we describe a metal triflate catalyzed one-pot reaction of alkenes, *N*-bromosuccinimide (NBS), nitriles, and trimethylsilyl azide ($TMSN_3$) for the expedient synthesis of 1,5-disubstituted tetrazoles containing an additional α-bromo functionality of the N1-alkyl substituent that might provide a further avenue for structural elaboration.

We are involved in stereoselective 1,2-halo functionalization of alkenes and recently found that Lewis acids, in particular, metal triflates, activate NBS to facilitate the formation of halonium ions from alkenes.[13] Accordingly, we anticipated that a suitable metal triflate might catalyze the reaction of alkenes, NBS, nitriles, and $TMSN_3$ and that would produce the 1,5-

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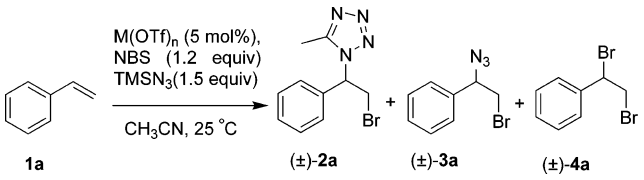
TABLE 1. Screening of Metal Triflates as Catalysts for the Reaction of 1a with NBS, Acetonitrile, and $TMSN_3$



entry	ML_n	*t* (h)	**2a**/**3a**[a]	yield of **2a**[b] (%)
1	none	12	50:50[c]	20
2	$La(OTf)_3$	10	78:22	70
3	$Yb(OTf)_3$	5	80:20	73
4	$Y(OTf)_3$	1	>95:05	82
5	$Sm(OTf)_3$	1	>95:05	84
6	$In(OTf)_3$	1	>95:05	70
7	$Zn(OTf)_2$	10 min	>95:05	87

[a] Determined from ^1H NMR analysis of the crude reaction mixture. [b] Isolated yield of pure **2a** after column chromatography. [c] Along with an equal amount of **4a**.

disubstituted tetrazoles along the lines of the Hassner method.[12] In searching for an effective catalyst, we initiated the reaction of styrene with NBS, acetonitrile, and $TMSN_3$ in the presence of different Lewis acids, in particular, metal triflates (Table 1). Among the metal triflates studied, $Zn(OTf)_2$ was found to be the best catalyst. It should be noted that in the absence of Lewis acid, **1a** reacts very slowly with NBS, CH_3CN, and $TMSN_3$, and after 12 h, a mixture of 1,2-bromotetrazole **2a**, bromoazide **3a**, and dibromide **4a** (1:1:1) was obtained (Table 1, entry 1). When substrate **1a** was treated with 0.05 equiv of $Zn(OTf)_2$, 1.2 equiv of NBS, 1.5 equiv of $TMSN_3$, and 4 Å MS in CH_3CN at rt (25 °C), within 10 min, tetrazole **2a** was selectively obtained in 87% yield (entry 7). It is worth mentioning that presence of 4 Å MS in the reaction medium inhibits the formation of undesired halohydrin compounds.

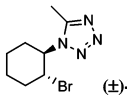
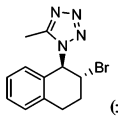
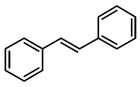
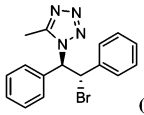
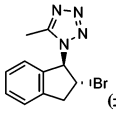
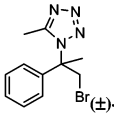
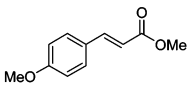
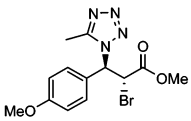
This method could produce an enormous number of 1,5-disubstituted tetrazoles, if different combinations of alkenes and nitriles are reacted. Initially, a variety of alkenes were subjected to the catalytic reaction in CH_3CN and selectively produced tetrazoles **2** ($R^3 = CH_3$; Table 2) with *anti*-stereochemistry as revealed by the ^1H NMR of the crude products. Reaction of α,β-unsaturated carbonyl compound methyl *p*-methoxycinnamate **1g** under the same reaction conditions also afforded tetrazole **2g** in 12% yield along with the bromoazide **3g** as a major product (entry 6).

Similarly, reactions of different alkenes independently with benzonitrile and benzylcyanide under the same reaction conditions (i.e., using nitrile as a solvent) gave tetrazoles in moderate to good yields (Table 3). Use of excess nitriles could be avoided when $TMSN_3$ in CH_2Cl_2 was slowly added over 1−2 h to the solution of $Zn(OTf)_2$ (0.05 equiv), alkene (1.0 equiv), NBS (1.2 equiv), nitrile (5 equiv), and 4 Å MS in CH_2Cl_2 and afforded the tetrazoles in comparable yields.

We also investigated the intramolecular reaction of substrate **5**. When **5** was subjected to the $Zn(OTf)_2$ catalyzed reaction with NBS, $TMSN_3$ and 4 Å MS in CH_2Cl_2, it produced exclusively bromoazide **8**, no cyclic fused tetrazole **6** or **7** was obtained (Scheme 1). The reaction of **5** was also carried out in CH_3CN instead of CH_2Cl_2 under the same reaction conditions and afforded the tetrazole **9**; here also, no cyclic fused tetrazole **6** or **7** was obtained (Scheme 1).

The synthesis of 1,5-disubstituted tetrazoles via halogen-promoted reaction of alkenes, nitriles, and azide is thought to

TABLE 2. Synthesis of 5-Methyltetrazoles via $Zn(OTf)_2$-Catalyzed Reaction of Alkenes, NBS, CH_3CN, and $TMSN_3$

entry	alkene	*t* (min)	product	yield[a] (%)
1	 **1b**	20	 **(±)-2b**	80
2	 **1c**	20	 **(±)-2c**	85
3	 **1d**	30	 **(±)-2d**	92
4	 **1e**	20	 **(±)-2e**	64
5	 **1f**	30	 **(±)-2f**	55
6	 **1g**	60	 **(±)-2g**	12[b]

[a] Isolated yields of tetrazoles **2** after column chromatography. [b] Obtained along with 60% of bromoazide **3g**.

proceed via nucleophilic[14] opening of halonium ion **10** with R^3-CN followed by reaction of the generated nitrilium ion **11** with azide to produce the tetrazole **2** (route a; Scheme 2).[12] Tetrazole **2** might have been produced via nucleophilic ring opening of the bromonium ion **10** by pregenerated tetrazole[15] (route b). However, no tetrazole was produced in the absence of either alkene or NBS or both under the same reaction conditions.

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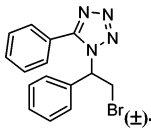
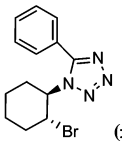
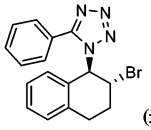
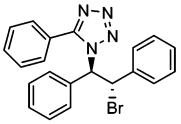
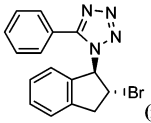
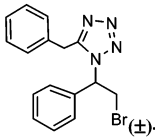
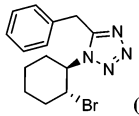
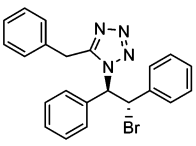
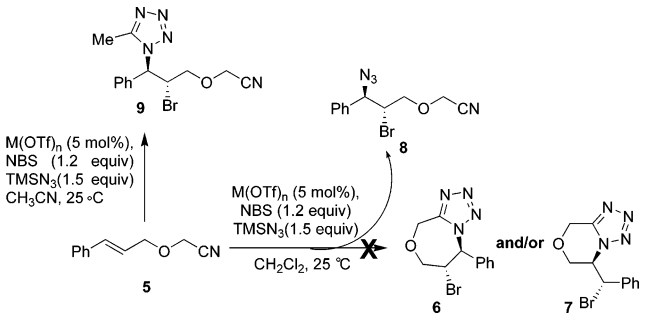
TABLE 3. Synthesis of 5-Phenyl- and 5-Benzyltetrazoles via $Zn(OTf)_2$-Catalyzed Reaction of Alkenes with NBS, R^3CN (R^3 = Ph, $PhCH_2$), and $TMSN_3$

entry	alkene	R^3CN	t (min)	product	yield[a] (%)
1	**1a**	PhCN	60	 (±)-**2h**	52
2	**1b**	PhCN	60	 (±)-**2i**	64
3	**1c**	PhCN	60	 (±)-**2j**	62
4	**1d**	PhCN	60	 (±)-**2k**	68
5	**1e**	PhCN	60	 (±)-**2l**	52
6	**1a**	$PhCH_2CN$	30	 (±)-**2m**	56
7	**1b**	$PhCH_2CN$	30	 (±)-**2n**	60
8	**1d**	$PhCH_2CN$	60	 (±)-**2o**	58

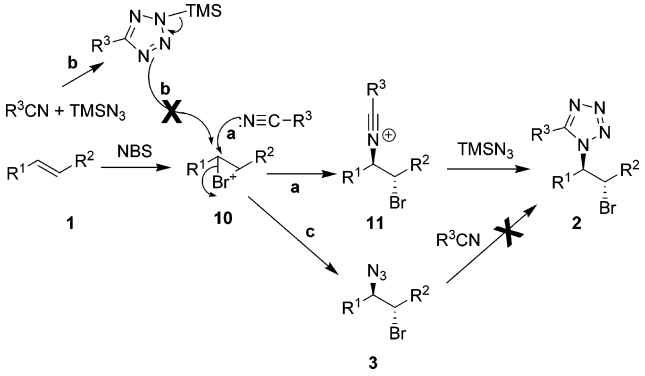
[a] Isolated yields of tetrazoles **2** after column chromatography. Obtained along with 10−20% of bromoazide **3**.

Alternatively, initial formation of intermediate compound bromoazide **3** followed by [3 + 2] cycloaddition reaction with nitriles might produce the tetrazole **2** (route c). When a solution of pure bromoazide **3a** in CH_3CN was stirred in the presence of $Zn(OTf)_2$ catalyst under the same reaction conditions, even after 10 h it did not yield any tetrazole **2a**. Thus, it can be concluded that the reaction might proceed via nitrilium ion **11** followed by reaction with azide as proposed by Hassner[12] (Scheme 2). The failure of the intramolecular reaction of **5** that may be due to excessive strain in the required six/seven-membered cyclic nitrilium ion intermediate also supports to the likelihood of a nitrilium ion intermediate **11**.

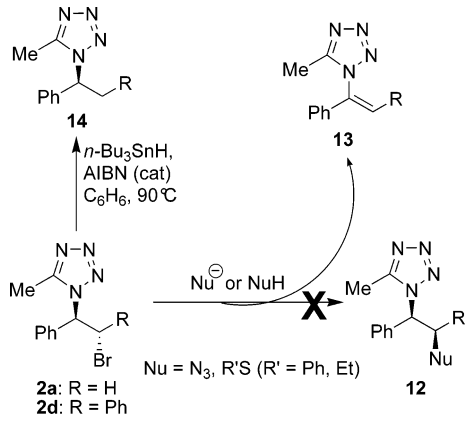
SCHEME 1



SCHEME 2



SCHEME 3



For further structural elaboration, tetrazoles **2a** and **2d** were separately treated with NaN_3 in DMF and R′SNa (R′ = Et, Ph) in MeOH (Scheme 3). However, it produced exclusively eliminated product **13** in high yield, no nucleophilic substituted product **12** was obtained. Eliminated product **13** was also obtained (92%) on reaction with NaOH in MeOH. *n*-Bu_3SnH mediated reduction of tetrazoles **2a** and **2d** smoothly provided compounds **14a** and **14b** in 89% and 75% yields, respectively (Scheme 3).

In summary, we have developed an efficient one-pot stereoselective method for the synthesis of 1,5-disubstituted tetrazoles by metal triflate catalyzed one-pot reaction of alkenes, NBS, nitriles, and $TMSN_3$. Among the metal triflates, $Zn(OTf)_2$ was

found to be the best catalyst. Use of different combinations of alkenes and nitriles produces a variety of 1,5-disubstituted tetrazoles containing an additional α-bromo functionality on the N1-substituent.

Experimental Section

General Procedure for the Synthesis of 1,5-Disubstituted Tetrazoles 2. To a well-stirred suspension of MS 4 Å (0.100 g) and $Zn(OTf)_2$ (0.009 g, 0.025 mmol) in dry R^3CN (1.0 mL) were successively added alkene **1** (0.50 mmol), $TMSN_3$ (0.1 mL, 0.75 mmol), and NBS (0.107 g, 0.60 mmol) under argon atmosphere at rt (25 °C). The reaction was monitored by TLC. On completion, it was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with water (25 mL) and brine (25 mL), dried over Na_2SO_4, and concentrated under vacuum. Flash column chromatography purification of the crude material using petroleum ether (60−80 °C)/ethyl acetate as an eluent afforded the pure tetrazole **2**. It is to be noted that quenching the reaction with aqueous solution is to be taken care as $TMSN_3$ is unstable near moisture with the generation of hydrazoic acid, an extremely dangerous product.

1-(2-Bromo-1,2-diphenylethyl)-5-methyl-1*H*-tetrazole ((±)-2d): white solid; mp 185−186 °C; FTIR (KBr) 3034, 2969, 2923, 2361, 2343, 1630, 1525, 1494, 1455, 1391, 1117, 1093, 773, 723, 705, 658, 569, 529 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.65−7.74 (m, 2H), 7.36−7.52 (m, 4H), 7.21−7.34 (m, 4H), 5.87 (d, J = 11.1 Hz, 1H), 5.66 (d, J = 11.1 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$/DMSO-d_6 = 10:1) δ 150.7, 137.3, 135.2, 129.5, 129.2, 128.9 (2C), 128.8 (2C), 128.2 (2C), 127.4 (2C), 67.9, 52.8, 8.5. Anal. Calcd for $C_{16}H_{15}BrN_4$: C, 55.99; H, 4.41; N, 16.32. Found: C, 55.78; H, 4.28; N, 16.35.

1-(2-Bromo-1,2-diphenylethyl)-5-phenyl-1*H*-tetrazole ((±)-2k): white solid; mp 160−162 °C; FTIR (KBr) 3062, 1611, 1493, 1468, 1454, 1391, 1119, 1101, 1075, 774, 742, 721, 698, 668, 579, 520 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.77−7.82 (m, 2H), 7.45−7.63 (m, 6H), 7.10−7.26 (m, 7H), 5.80 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 154.6, 137.0, 135.5, 131.4, 129.7, 129.1 (4C), 129.0 (3C), 128.8 (2C), 128.6 (2C), 127.6 (2C), 123.5, 68.1, 53.8. Anal. Calcd for $C_{21}H_{17}BrN_4$: C, 62.23; H, 4.23; N, 13.82. Found: C, 62.18; H, 4.21; N, 13.63.

5-Benzyl-1-(2-bromo-1,2-diphenylethyl)-1*H*-tetrazole ((±)-2o): white solid; mp 177−178 °C; FTIR (KBr), 3068, 3033, 2929, 1509, 1494, 1455, 1431, 1417, 1233, 1110, 1078, 773, 732, 723, 706, 697, 658, 636, 619, 584, 564, 528 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.26−7.37 (m, 8H), 7.15−7.25 (m, 5H), 6.96−7.05 (m, 2H), 5.80 (d, J = 11.1 Hz, 1H), 5.55 (d, J = 11.1 Hz, 1H), 4.04 (d, J = 16.2 Hz, 1H), 3.82 (d, J = 16.2 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 153.0, 137.4, 135.2, 133.5, 129.5, 129.4 (2C), 129.1, 128.9 (2C), 128.8 (2C), 128.7 (2C), 128.3 (2C), 127.8, 127.6 (2C), 68.0, 53.2, 29.3. Anal. Calcd for $C_{22}H_{19}BrN_4$: C, 63.02; H, 4.57; N, 13.36. Found: C, 63.29; H, 4.64; N, 13.29.

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Supporting Information Available: Spectral data and ^1H NMR, ^{13}C NMR, and DEPT spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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