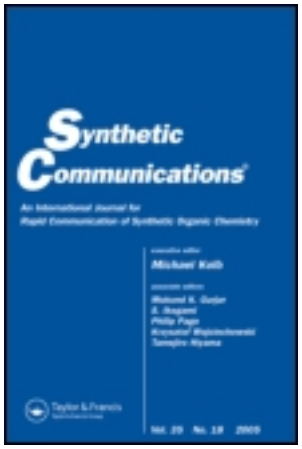

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KF/Al_2O_3: SOLID-SUPPORTED REAGENT USED IN 1,3-DIPOLAR CYCLOADDITION REACTION OF NITRILE OXIDE

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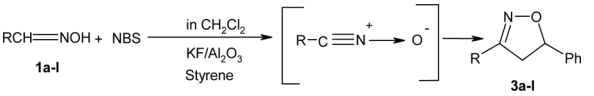
GRAPHICAL ABSTRACT



Abstract *The stereoselective synthesis of 2-isoxazolidine through 1,3-dipolar cycloaddition reaction of nitrile oxide, which is in situ generation from aldoxime in the presence of N-bromosuccinamide and solid-supported reagent KF/Al_2O_3 at room temperature, is reported. KF/Al_2O_3 is sufficiently basic such that it can replace organic bases such as Et_3N used in typical procedures and it catalyses the reaction to enhance the rate of the reaction.*

Keywords 1,3-Dipolar cycloaddition reaction; KF/Al_2O_3; NBS; nitrile oxide; solid-supported reagent

INTRODUCTION

1,3-Dipolar cycloaddition[1] reaction is an important synthetic methodology for the construction of five-membered heterocyclic rings. Nitrile oxide is known to be one of the most reactive 1,3-dipoles. The cycloaddition reactions of nitrile oxides to alkene dipolarophiles have been extensively used for the preparation of substituted 2-isoxazolines, which are versatile intermediates for the synthesis of a wide variety of natural products[1] and are important pharmacophores in medicinal chemistry.[2] 2-Isoxazolines are found in a number of pharmaceutically active compounds such as antifungal,[2a] antibacterial,[2b] anti-HIV,[2c] caspase inhibitory,[2d] antimuscarinic,[2e] anti-inflammatory,[2f] anticancer,[2g] and antidepressant[2h] compounds. In a typical method, nitrile oxide is generated by dehydrohalogenation of hydroximoyl chloride using Et_3N,[3] and it can be assumed that the tertiary amino group is compatible with the CNO group. It was reported that hydroximoyl chloride

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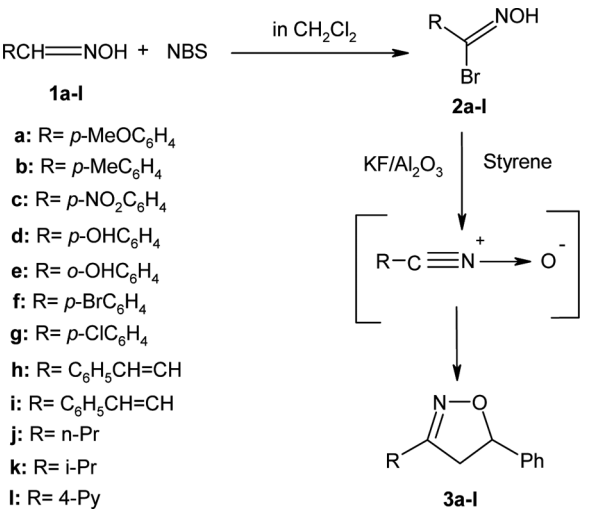
forms rather stable quaternary salts with tertiary amines, especially pyridine.[4] Moreover, triethylamine was added to the reaction mixture slowly to reduce the extent to which the nitrile oxide dimerizes to the corresponding furoxan,[5] and this time of addition was optimized to maximized the extent of conversion. In such a case, replacing the organic bases by solid-supported reagent KF/Al_2O_3 may overcome this difficulty and enhance the rate of the reaction. Moreover, it possesses a lot of advantages, such as solid-phase synthesis, and excess support-bound reagent can be used and removed by filtration, avoiding cumbersome aqueous workup and decreasing solvent waste.

In recent years, development of ecofriendly processes using safer reagents has received renewed attention in the field of synthetic organic chemistry. The applications of solid-supported reagents such as KF/Al_2O_3 in organic synthesis are in demand.[6] Solid-supported reagents possess a number of the advantages of both solution and solid-phase chemistry, so that they are widely used in a variety of reactions. An important application of KF/Al_2O_3 in a number of organic reactions is as a replacement of organic bases because of its strongly basic nature.[7] Its use in 1,3-dipolar cycloaddition has been less explored.[8]

Our efforts to develop newer methods for the synthesis of heterocyclic compounds,[9] through 1,3-dipolar cycloaddition reactions encouraged us to develop an improved and efficient method for the synthesis of 2-isoxazolines under the solid-supported reagent KF/Al_2O_3. Here we use KF/Al_2O_3 as a replacement for organic base Et_3N for the in situ generation of nitrile oxide by dehalogenation of hydroximoyl bromide in the cycloaddition reaction. In this procedure, the solid-supported reagent KF/Al_2O_3 may be conveniently utilized because (i) the strong basisity of KF/Al_2O_3 derives from the generation of KOH in the initial preparation of the solid-supported material by reaction of KF with the alumina (Scheme 1).[10] So, the CNO group of the nitrile oxide is unaffected during the



Scheme 1. 1,3-Dipolar cycloaddition reaction of nitrile oxide in the presence of solid-supported reagent KF/Al_2O_3.

cycloaddition reaction. On the other hand, Et_3N is also attacked by N-bromosuccinimide (NBS); it is preferable to add the NBS to the oxime prior to the introduction of the amine. Moreover, olefins with electron-withdrawing groups undergo polymerization under highly basic conditions more readily than cycloaddition reaction. Therefore, all the reported methods used weak organic base for generation of nitrile oxide. (ii) It is believed that the solid support binds the substrate to its surface[11] and catalyzes the reaction to enhance the rate of the reaction by blocking the dimerization of dipoles and polymerization of dipolarophile. (iii) It is easy to weigh accurately, and excess amount does not affect the reaction. (iv) It avoids the cumbersome aqueous workup and decreases the solvent handling issue. To the best of our knowledge, this reagent has not utilized so far in the in situ generation of nitrile oxide.

Initially, we investigated this one-flask procedure[12] by using styrene as dipolarophile and KF/Al_2O_3 instead of an organic base to direct formation of 2-isoxazolines from hydroxymoyl bromide of corresponding aldoximes. *p*-Methoxybenzaldoxime (**1a**, 0.25 mmol) was first treated with an equimolar amount of NBS in dichloromethane at room temperature, and after 30 min aldoxime was completely brominated. Then solid-supported reagent KF/Al_2O_3 (2 g, 40% KF in alumina) and styrene (0.28 mmol) were added simultaneously and stirred at room temperature for a further 0.5–1 h. During the reaction, the produced side product (i.e., succinamide) was trapped by KF/Al_2O_3 and settled down in the reaction mixture. After completion of the reaction, the reaction mixture was diluted and the side product was removed by filtration through ciliate. Evaporation of the solution in vacuuo gave almost pure cycloaddition product 2-isoxazolidine (**3a**) with excellent yield (Scheme 1).

The reaction was investigated with different solvent conditions. Dichloromethane was established as good for all. We also used biphasic and homogeneous mixed solvent systems, but no significant result appeared during this investigation. Only the use of a catalytic amount of water enhanced the rate of the reaction.

Further investigation of the feasibility of using solid-supported reagent KF/Al_2O_3 in this reaction under solvent-free condition continued. *p*-Methoxybenzaldoxime was treated with an equimolar amount of NBS in dichloromethane at room temperature. After stirring was continued for 1–2 h to confirm the completion of reaction, the reaction mixture was diluted with diethyl ether and washed with water and brine. The desire product hydroximoyl bromide was isolated from side product succinamide, followed by KF/Al_2O_3 and styrene. The reaction mixture was finely mixed and mechanically stirred with extra Al_2O_3 for 2–3 h. The cycloaddition product was extracted the reaction mixture by adding diethyl ether with 65% yield.

For comparison purpose, the in situ generation of nitrile oxide and the cycloaddition reaction were investigated by using KOH as a base instead of KF/Al_2O_3. In this investigation, the reaction did not provide the desired cycloaddition product. We thought that the presence of a strong inorganic base affected the hydroximoyl chloride and prevented the formation of nitrile oxide in the reaction mixture. On the other hand, the used of weak inorganic bases steered the reaction toward another type of addition reaction/polymerization rather than the 1,3-dipolar cycloaddition reaction. In contrast, KOH, generated initially from KF/Al_2O_3, reacts

in mild reaction conditions. Moreover, it is believed that the hydroximoyl bromide is bound with solid-supported reagent in reaction conditions and enhances the rate of reaction as compared to the other typical procedure.

To explore the scope of the reaction, we investigated the reaction with varieties of aliphatic, aromatic, and heteroaromatic aldoxime. Generally, aliphatic hydroximoyl chlorides/bromides are known to be less stable than aromatic derivatives. We thought that isolation and purification of aliphatic hydroximoyl bromide should be avoided because of undesired decomposition. Therefore, in this procedure, we directly applied KF/Al_2O_3 and styrene as dipolarophile for generation of nitrile oxide and then performed cycloaddition reaction in the same reaction mixture without any separation and purification of hydroximoyl bromide. The side product succinimide, which was produced along with the hydroximoyl bromide in the bromination step, was immediately trapped by the solid-supported reagent and settled, and then the hydroximoyl bromide was free in the reaction mixture. It was observed that the rapid cycloaddition gave very good yield as compared to the other typical procedure.

A variety of aromatic, aliphatic, and heteroaromatic aldoximes (**1a–l**) were successfully converted into the corresponding nitrile oxides, which were trapped with styrene as cycloadduct (**3a–l**, Table 1). Yields of cycloadducts were satisfactory for the three-step transformation including bromination of aldoxime by NBS, nitrile oxide generation, and cycloaddition to styrene. Regardless of the kinds of starting aldoximes, yields of styrene cycloaddition are comparable, indicating the wide synthetic versatility of this nitrile oxide preparation method from a verity of aldoximes. However, use of excess amount of KF/Al_2O_3 was not relatively effective in the reaction. On the other hand, excess amount of NBS did not lead to overbromination.

We also investigated the 1,3-dipolar cycloaddition reaction of the nitrile oxide generated from **1a** in the presence of solid-supported reagent KF/Al_2O_3, outlined in Table 2. Nitrile oxide cycloaddition to terminal alkenes proceeded regioselectively to

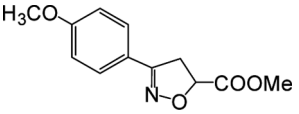
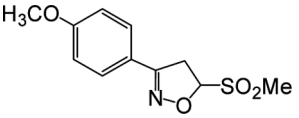
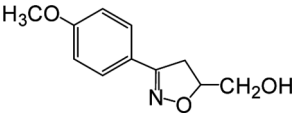
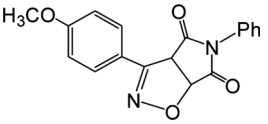
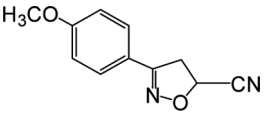
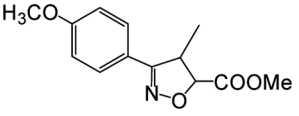
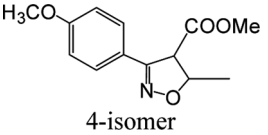
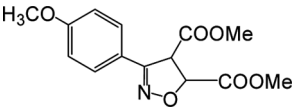
Table 1. 1,3-Dipolar cycloaddition reaction of nitrile oxide derived from aldoxime **1a–l** with styrene in the presence of KF/Al_2O_3

Entry	R of aldoxime	Time (h)	Product[a]	Yield (%)[b]
1	*p*-$MeOC_6H_4$	0.5	**3a**	96
2	*p*-MeC_6H_4	0.5	**3b**	98
3	*p*-$NO_2C_6H_4$	1.5	**3c**	88
4	*p*-OHC_6H_4	1	**3d**	85
5	*o*-OHC_6H_4	1	**3e**	81
6	*p*-BrC_6H_4	0.5	**3f**	91
7	*p*-ClC_6H_4	0.5	**3g**	88
8	$C_6H_5CH{=}CH$	1.5	**3h**	85
9	$C_6H_5CH_2$	3	**3i**	80
10	*n*-Pr	3.5	**3j**	75
11	*i*-Pr	3.5	**3k**	77
12	4-Py	2	**3l**	80

[a]Products have been identified from their respective spectral (IR, ^{1}H NMR, ^{13}C NMR, mass, GC), physical data and comparison with authentic samples.

[b]Yields mentioned are the isolated yield, determined by GC and based on reactant.

Table 2. 1,3-Dipolar cycloaddition reaction of nitrile oxide derived from aldoxime **1a** with different dipolarophiles in the presence of KF/Al_2O_3

Entry	Dipolarophile	2-Isoxazoline	Time (h)	Yield (%)
a	Methyl acrylate		2	90
b	Methyl vinyl sulfonate		1	65
c	Allyl alcohol		3.5	92
d	N-Phenyl maleimide		0.5	96
e	Acrylonitrile		3.5	55
f	Methyl crotonate	 5-isomer	3	45
		 4-isomer		40
g	Dimethyl maleate		2.5	80

give 5-subsituted 2-isoxazolines as single products (entries **a–e**, Table 2). On the other hand, the reaction with 1,2-disubsituted internal alkenes [e.g., methyl crotonate (entry f)] leads to a mixture of regioisomers 4 and 5 in an approximately 1:1 ratio.

It is believed that the substrate hydroxymoyl bromide and styrene were bound with the surface of the solid-supported reagent and then generated nitrile oxide and then cycloaddition immediately without formation of any dimers or polymers. Moreover, in this one-pot reaction, succinamide was produced as a major side product in the bromination step of aldoxime in the reaction mixture, but the further steps of the method, such a generation of nitrile oxide and then cycloaddition with

dipolarophile, were performed without removing the side product from the reaction mixture. This side product was bound with the solid-supported reagent and separated from the reaction mixture under reaction conditions. Skipping this separation step must be a greater advantage because the undesired side product did not isolate in between the reaction, and the resulting hydroximoyl bromide is not stable enough to be isolated.

In conclusion, we have provided an improved and efficient one-pot synthesis of 2-isoxazoline through 1,3-dipolar cycloaddition reaction of nitrile oxide in the presence of solid-supported reagent KF/Al_2O_3. In this process, a single cycloadduct is isolated from the reaction mixture by filtration, and avoiding the water workup enhanced the percentage of yield of the pure form as compared to reported methods.

EXPERIMENTAL

Melting points were determined on a Buchi melting-point B-540 apparatus and are uncorrected. Column chromatography was performed using silica gel (60–120 mesh). Thin-layer chromatography (TLC) was performed on EM reagents 0.25-mm silica 60-F plates. Infared (IR) spectra were obtained on a Perkin-Elmer system 2000 FT/IR spectrophotometer. Data for ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 300-MHz spectrometer. Chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane (TMS) with solvent resonance as the internal standard. Data for ^{1}H NMR are reported as chemical shifts (d ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), and integration. Data for ^{13}C NMR were reported as chemical shifts. Conversion and stereochemistry was determined by gas chromatography. Commercially available reagents were used directly.

Typical Experimental Procedure for Nitrile Cycloaddition in the Presence of KF/Al_2O_3

p-Methoxyphenyl aldoxime (**1a,** 0.25 mmol) was added to a stirred solution of NBS (0.28 mmol) in dichloromethane and vigorously stirred for 30 to 45 min. The reaction was monitored by thin-layer chromatography (TLC). After bromination of the aldoxime (**1a**) to hydroximoyl bromide (**2a**), KF/Al_2O_3 (2 g, 40% by weight) and styrene (0.28 mmol) were added and the reaction mixture was stirred for a further 2 h. The solid mass was filtered through cilite from the reaction mixture. CH_2Cl_2 was evaporated in vacuum, and residue was dissolved in EtOAc (20 mL). The organic layer was washed with water (10 mL × 3), dried over anhydrous sodium sulfate, concentrated under reduced pressure, and purified by silica-gel column chromatography to give 3-(*p*-methoxyphenyl)-5-phenyl-2-isoxazoline **(3a)** in 96% yield.

Analytical Data

3-(*p*-Methoxyphenyl)-5-phenyl-2-isoxazoline (3a). Colorless plates; mp 103–105 °C; ^{1}H NMR ($CDCl_3$) δ 3.35 (1H, dd, $J_{gem} = 16.7$ Hz and $J_{4-5} = 8.2$ Hz, one of H-4), 3.76 (1 H, dd, $J_{gem} = 16.7$ Hz and $J_{4-5} = 10.9$ Hz, the other of H-4), 3.84 (3H, s, MeO), 5.71 (1H, dd, $J_{5-4} = 10.9$ and 8.2 Hz, H-5), 6.93 (2H, dd,

$J = 8.9$ and 1.2 Hz, Ar), 7.29–7.41 (5H, m, Ph), and 7.63 (2H, dd, $J = 8.9$ and 1.2 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ 43.44 (C-4), 55.35 (MeO), 82.29 (C-5), 114.14, 122.04, 125.87, 128.14, 128.27, 128.72, 141.09 (Ph and Ar), 155.66 (C-3), and 161.09 (Ar); MS (m/z): 254 (M^{+1}, base peak), 253 (73, M^+), 221 (13), 207 (12), 154 (17), 147 (40), 136 (20), and 73 (24). Anal. found: C, 75.78; H, 6.03; N, 5.46. Calculated for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.96; N, 5.53.

3-Benzyl-5-phenyl-2-isoxazoline (3i). Colorless oil; IR (neat) 3040, 2920, 1610, 1500, 1460, 1430, 1080, 1040, 760, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.75 (1H, dd, $J_{gem} = 17.1$ Hz and $J_{4-5} = 8.4$ Hz, one of H-4), 3.18 (1H, dd, $J_{gem} = 17.1$ Hz and $J_{4-5} = 10.9$ Hz, the other of H-4), 3.64 (1H, d, $J_{gem} = 14.8$ Hz, one of $PhCH_2$), 3.71 (1H, d, $J_{gem} = 14.8$ Hz, the other of $PhCH_2$), 5.47 (1H, dd, $J_{5-4} = 8.4$ and 10.9 Hz, H-5), and 7.20–7.30 (10H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 33.91 ($PhCH_2$), 44.27 (C-4), 81.61 (C-5), 125.56, 126.92, 127.82, 128.44, 128.64, 135.47, 140.84 (each Ph), and 157.23 (C-3); MS m/z (rel. intensity, %) 238 (M^{+1}, base peak), 107 (6), 91 (16), and 77 (4). Anal. found: C, 80.67; H, 6.41; N, 5.85. Calcd. for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90.

5-Phenyl-3-propyl-2-isoxazoline (3j). Light yellow oil; ^1H NMR ($CDCl_3$) δ 0.97 (3H, t, $J = 7.5$ Hz, CH_3 of *n*-Pr), 1.62 (2H, tt, $J = 7.5$ and 7.5 Hz, CH_2 of *n*-Pr), 2.36 (2H, t, $J = 7.5$ Hz, CH_2 of *n*-Pr), 2.89 (1H, dd, $J_{gem} = 16.9$ Hz and $J_{4-5} = 8.2$ Hz, one of H-4), 3.35 (1H, dd, $J_{gem} = 16.9$ Hz and $J_{4-5} = 10.9$ Hz, the other of H-4), 5.54 (1H, dd, $J_{5-4} = 10.9$ and 8.2 Hz, H-5), 7.29–7.38 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 13.71, 19.76, 29.57 (each *n*-Pr), 45.30 (C-4), 81.16 (C-5), 125.67, 127.94, 128.63, 141.37 (each Ph), and 158.34 (C-3); MS m/z (rel. intensity, %) 189 (M^{+1}, 55), 161 (21), 117 (18), 104 (base peak), 91 (17), and 77 (20). Anal. found: C, 75.89; H, 8.00; N, 7.39. Calcd. for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40.

5-Phenyl-3-isopropyl-2-isoxazoline (3k). Light yellow oil; ^1H NMR ($CDCl_3$) δ 1.18 (3H, d, $J = 7.0$ Hz, one of Me), 1.19 (3H, d, $J = 7.0$ Hz, the other of Me), 2.75 (1H, sep, $J = 7.0$ Hz, Me_2CH), 2.94 (1H, dd, $J_{gem} = 16.9$ Hz and $J_{4-5} =$ 8.2 Hz, one of H-4), 3.63 (1H, dd, $J_{gem} = 16.9$ Hz and $J_{4-5} = 10.9$ Hz, the other of H-4), 5.53 (1H, dd, $J_{5-4} = 10.9$ and 8.2 Hz, H-5), and 7.27–7.38 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 20.08, 20.09, 27.89 (each *i*-Pr), 43.24 (C-4), 81.24 (C-5), 125.67, 127.93, 128.62, 141.39 (each Ph), and 162.98 (C-3); MS m/z (rel. intensity, %) 189 (M^{+1}, 58), 117 (18), 104 (base peak), and 77 (21). Anal. found: C, 75.91; H, 7.98; N, 7.45. Calcd. for $C1_2H_{15}NO$: C, 76.16; H, 7.99; N. 7.40.

5-Phenyl-3-(4-pyridyl)-2-isoxazoline (3l). Colorless plates from CH_2Cl_2–hexane; mp 67–698° C; IR (KBr) 3000, 2200, 1590, 1400, 1350, 900, 810, 720, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.32 (1H, dd, $J_{gem} = 16.7$ Hz and $J_{4-5} = 8.5$ Hz, one of H-4), 3.76 (1H, dd, $J_{gem} = 16.7$ Hz and $J_{4-5} = 11.1$ Hz, the other of H-4), 5.81 (1H, dd, $J_{5-4} = 11.1$ and 8.5 Hz, H-5), 7.32–7.42 (5H, m, Ph), 7.54 (2H, dd, $J = 4.5$ and 1.7 Hz, Ar), and 8.68 (2H, dd, $J = 4.5$ and 1.7 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ 42.11 (C-4), 83.46 (C-5), 120.88, 125.81, 128.52, 128.88, 136.77, 140.19, 150.46 (Ph and Ar), and 154.59 (C-3); MS m/z (rel. intensity, %) 224 (M^{+1}, 58) and 104 (base peak). Anal. found: C, 74.98; H, 5.42; N, 12.44. Calcd. for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39; N, 12.49.

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