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In Situ Generation of the Ohira–Bestmann Reagent from Stable Sulfonyl Azide: Scalable Synthesis of Alkynes from Aldehydes

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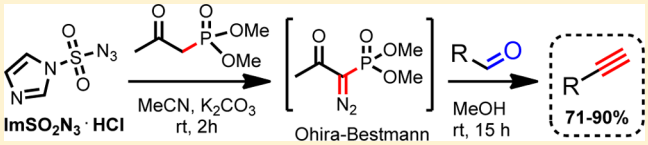
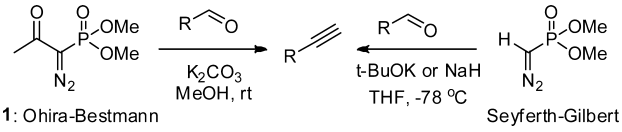
Supporting Information

ABSTRACT: We report an improved method for *in situ* generation of the Ohira–Bestmann reagent. Using the recently reported bench-stable imidazole-1-sulfonyl azide as diazotransfer reagent, this new method represents a scalable and convenient approach for the transformation of aldehydes into terminal alkynes. The method features an easier workup compared to the existing *in situ* protocol due to increased aqueous solubility of waste products.



The Corey–Fuchs reaction represents the first synthetically useful method for transforming aldehydes into alkynes by a two-step procedure using strong base.[1,2] A more convenient alternative, the Seyferth–Gilbert homologation[3,4] (Scheme 1), has proven to be a reliable and efficient method that has become very popular. The Ohira–Bestmann modification[5] uses even milder reaction conditions, employing a weak base in alcoholic solvent at ambient temperature in order to generate the same reactive species *in situ*. The Ohira–Bestmann modification has indeed evolved as an efficient procedure for preparation of alkynes from aldehydes, and modifications to the original procedure continue to be reported.[6−12]

Scheme 1. Homologation Reactions



Although the Ohira–Bestmann reagent (**1**) generally delivers high-yielding reactions with short reaction times, one of the drawbacks is the relatively high price of the commercially available material. In 2004 Bestmann and colleagues reported an *in situ* generation of the Ohira–Bestmann reagent.[13] The reagent was generated from dimethyl-2-oxopropylphosphonate and TsN_3 (Figure 1) in the presence of K_2CO_3 in MeCN followed by addition of the desired aldehyde in MeOH. Although it was a clear improvement with yields comparable to those of the original procedure, it still requires the use of an unstable and explosive diazotransfer reagent (TsN_3) that compromises the scalability of the reaction. Furthermore, the waste products of the reaction are, contrary to the *ex situ* procedure,[5] no longer removable by aqueous workup due to the formation of *p*-toluene-sulfonylamide, and thus further purification of the product is necessary.

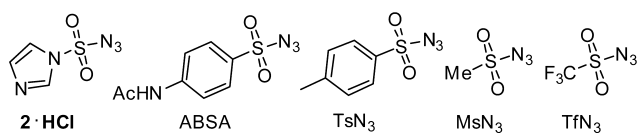


Figure 1. Commonly used diazotransfer reagents.

Here we report an improved method for the *in situ* generation of the Ohira–Bestmann reagent. In recent years several alternative diazotransfer reagents (Figure 1) with improved safety and handling properties have been developed.[17] Although frequently used, TfN_3, MsN_3, and TsN_3 are considered as highly unstable reagents, whereas alternatives, such as ABSA, are considerably safer to handle.[8] The crystalline, shelf-stable (when stored under anhydrous conditions!), and water-soluble imidazole-1-sulfonyl azide hydrochloride (**2**)[18−20] is one of the most convenient diazotransfer reagents available.[21] Thus, application of this reagent would provide a safer and more scalable procedure than the current *in situ* protocols. This imidazole-based diazotransfer reagent, contrary to most other alternatives, generates water-soluble waste products, which should predominantly be removable by aqueous workup, and thus allows easy purification, comparable to the *ex situ* Bestmann protocol.[5] We became interested in this transformation when we needed to prepare several grams of alkyne **4f**. With the aim of avoiding the scale-up using *p*-toluenesulfonylazide, we looked for alternatives. It was not obvious that **2** would be suitable for the task as imidazole-1-sulfonyl azide is known to possess poor reactivity toward activated methylene compounds,[22] and other water-soluble azides perform poorly in the preparation of **1**.[13] Various reaction conditions were screened in order to optimize the protocol (Table 1). Gratifyingly, the formation of the Ohira–Bestmann reagent proceeded smoothly with full conversion (judged by HPLC and TLC) of dimethyl-2-oxopropylphosphonate in all test reactions.

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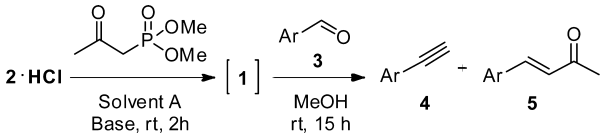
Table 1. Optimization of Reaction Conditions[a]



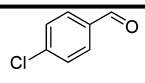
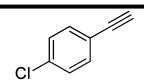
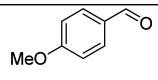
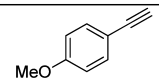
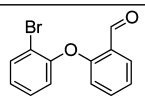
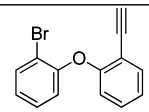
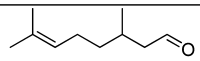
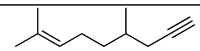
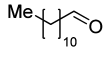
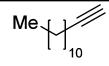
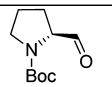
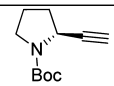
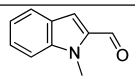
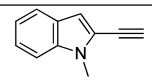
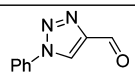
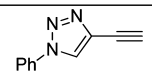
entry	solvent A	solvent ratio (A:MeOH)	LC–MS yield **3**:**4**:**5**
1[b]	DMF	no MeOH	100:0:0
2	DMF	2:1	44:39:17
3	MeCN/DMSO (5:1)	2:1	67:33:0
4	MeCN/H_2O (5:1)	2:1	51:49:0
5	H_2O	2:1	91:9:0
6	THF/H_2O (2:1)	2:1	79:21:0
7	MeCN	6:1	91:9:0
8	MeCN	2:1	10:90:0
9	**MeCN**	**1:1**	0:**100**:0
10[c]	MeCN	1:1	53:47:0
11[d]	MeCN	1:1	52:0:48
12[b,e]	MeOH		55:36:10
13[f]	MeCN/H_2O (5:1)	no MeOH	100:0:0
14[f]	MeOH		34:66:0

[a]General conditions: **2**·HCl (1.3 equiv), dimethyl-2-oxopropylphosphonate (1.2 equiv), K_2CO_3 (4.5 equiv), solvent A, 25 °C, 2 h; then *p*-chlorobenzaldehyde (**3**, 1.0 equiv), MeOH, 25 °C, 15 h. [b]Aldehyde was added without solvent. [c]Temperature was 50 °C. [d]DIPEA (4.5 equiv) was used instead of K_2CO_3. [e]Reaction time was 0.5 h before aldehyde addition. [f]All reagents were mixed in one pot.

However, the homologation step was rather sensitive to the specific reaction conditions, and the presence of MeOH and K_2CO_3 was crucial in order to generate the reactive anionic species. Moreover, the Horner–Wadsworth–Emmons product (**5**) was observed when DIPEA (entry 11) was used as a base and when DMF (entry 2) or MeOH (entry 12) was used as solvent A. MeCN was found to be superior for generating and stabilizing **1**, and interestingly we found that the ratio between solvent A and MeOH (added along with the aldehyde) was crucial to the conversion rate (entries 7–9). Attempts to utilize water as a solvent (entries 4–6) worked with minor success, although extended reaction time gave higher conversion than those listed in entries 4–6. Attempts to develop one-pot conditions (entries 13 and 14) proved inferior, and the optimized conditions ended up being entry 9 with full conversion into the desired alkyne **4** based on LC–MS. In this optimized protocol dimethyl-2-oxopropylphosphonate and imidazole-1-sulfonyl azide hydrochloride (**2**) were added to a suspension of K_2CO_3 in MeCN. After stirring for 2 h at 25 °C the desired aldehyde (dissolved in MeOH) was added, and stirring was continued at 25 °C for 15 h. The waste products formed were mostly removable by aqueous workup leaving a product pure enough for subsequent manipulation without the need for further purification.

With this new protocol in hand we set out to compare the scope of the reaction with the previous syntheses. The experiments were performed on 1.0 mmol scale in order to compare directly with the previous procedures by Bestmann and colleagues.[5,13] Generally the isolated yields were comparable and in some cased even improved slightly, ranging from 71% to 90%, with LC/GC yields ranging from 85% to >95% (Table 2). In analogy to the procedures by Bestmann and colleagues the scope of this method is broad and effective with

Table 2. Comparison of This Method for the Synthesis of Alkynes 4a–4h with Existing Protocols[a]

Entry	Aldehyde (**3**)	Alkyne (**4**)	Isolated Yield (previous method[b])	Isolated Yield (this method)	LC/GC yield (this method)
a			83%[13]	86%	>95%
b			78% (NMR yield)[5]	74%	85%
c			91% (*ex situ*)[14]	88%	>95%
d			72%[13]	77%	>95%
e			89%[13]	90%	>95%
f			Up to 74%[6]	71%	90%
g			Up to 88%[15] (*ex-situ*)	87%	>95%
h			63%[16] (cycloaddition)[c]	81%	>95%

[a]General conditions: **2**·HCl (1.2 mmol), dimethyl-2-oxopropylphosphonate (1.2 mmol), K_2CO_3 (4.5 mmol), MeCN, 25 °C, 2 h; then aldehyde (**3**, 1.0 mmol), MeOH, 25 °C, 15 h. [b]Isolated yields based on Bestmann and colleagues previous protocols[5,13] if not noted otherwise. [c]According to the literature, **4h** has previously been prepared by 1,3-dipolar cycloaddition chemistry.[16] Our NMR data is inconsistent with those reported in the literature, and thus the literature yield should be viewed with caution.

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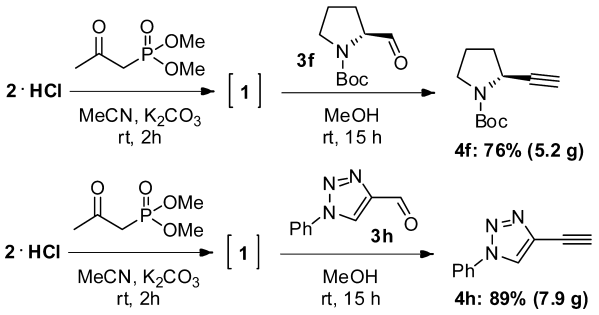
both aliphatic (**3d**–**3f**) and aryl aldehydes (**3a**–**3c**) as well as enolizable aldehydes (**3d**–**3f**). Even electron-rich aryl aldehydes (**3b**, **3c**) work successfully. Several functional groups have generally proven to be compatible with the methodology including bromoether (**3c**[23]), isolated olefin (**3d**), amino acid derivative (**3f**[24]), and indole and triazole derivatives (**3g**, **3h**). It should be noted that the highly volatile nature of a number of terminal alkynes (**4b**, **4d**, **4f**) influenced the isolated yields. LC/GC yields indicated full and clean conversion of starting material into the desired alkynes in most cases.

In order to demonstrate the scalability and robustness of this new procedure, two of the compounds were additionally prepared on multigram scale with even higher yields compared to the minor scale. Compound **4f** was prepared on 5.2 g scale (26.4 mmol) in 76% yield after chromatography compared to the 71% on 1.0 mmol scale. Compound **4h** was prepared on 7.9 g scale (46.5 mmol) in 89% yield after recrystallization compared to the 81% on 1.0 mmol scale (Scheme 2).

Scheme 2. Scale-Up Experiments



In summary, we have developed an improved procedure for the Bestmann modification of the Seyferth–Gilbert homologation. Our methodology takes advantage of a very convenient diazotransfer reagent, which is among the safest available, in the one-pot Ohira–Bestmann reagent preparation and subsequent homologation reaction in order to prepare alkynes from aldehydes. We have demonstrated comparable or improved yields in the synthesis of a various alkynes compared to the previous methods, and this protocol allows for more convenient product purification since most waste products are removable by aqueous workup, using a safer combination of reagents.

EXPERIMENTAL SECTION

All reactions were carried out under a nitrogen atmosphere with HPLC grade solvents. Yields refer to chromatographically and spectroscopically (^{1}H and ^{13}C NMR) homogeneous materials. Reagents were purchased at the highest commercial quality and used without further purification. Reactions were monitored by LC–MS (ESI) or GC–MS (EI) and TLC carried out on 0.25 mm silica gel plates using UV light as visualizing agent and either ninhydrin or potassium permanganate stain as an indicator. Silica gel (60 Å, academic grade, particle size 15–40 μm) was used for short plugs and for dry column vacuum chromatography.[25] NMR spectra were recorded on 400 and 600 MHz instruments and calibrated using residual undeuterated solvent as an internal reference. Low-resolution mass spectra were obtained by either GC–MS (EI) or LC–MS (ESI). Abbreviations: THF, tetrahydrofuran; DMF, *N*,*N*-dimethylformamide; MeOH, methanol; MeCN, acetonitrile; EtOAc, ethyl acetate

General Procedure. 4a. Dimethyl-2-oxopropylphosphonate (199 mg, 166 μL, 1.2 mmol) was added to a suspension of K_2CO_3 (622 mg, 4.5 mmol) and 1*H*-imidazole-1-sulfonyl azide hydrochloride[20] (272 mg, 1.3 mmol) in MeCN (10 mL), and the colorless suspension was stirred at 25 °C for 2 h. Then a solution of aldehyde **3a** (141 mg, 1.0 mmol) in MeOH (10 mL) was added to the now pale yellow suspension and stirred at 25 °C for 15 h. The reaction mixture was filtered, the filter cake was washed with Et_2O (3 × 3 mL), and the clear solution was carefully evaporated onto Celite without evaporating the volatile alkyne products. The material was loaded onto a short plug (2 cm high), flushed with pentane (4 × 10 mL), and concentrated carefully *in vacuo* to afford alkyne **4a** (117 mg, 86%) with spectral data in accordance with previous characterizations.[13] R_f = 0.55 (silica gel, heptane/EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 3.11 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.9, 133.4, 128.7, 120.6, 82.5, 78.2; GC–MS 136 m/z (M^+)

4b. The general procedure was followed by using aldehyde **3b** (136 mg, 121 μL, 1.0 mmol), and the highly volatile alkyne **4b** (98 mg, 74%) was isolated with spectral data in accordance with previous characterizations.[26] R_f = 0.41 (silica gel, heptane/EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 3.81 (s, 3H), 3.00 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 133.6, 114.2, 113.9, 83.7, 75.8, 55.3; GC–MS 132 m/z (M^+)

4c. The general procedure was followed by using aldehyde **3c**[23] (277 mg, 1.0 mmol), and the desired alkyne **4c** (241 mg, 88%) was isolated with spectral data in accordance with previous characterizations.[14,27] R_f = 0.39 (silica gel, heptane/EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, J = 8.0, 1.6 Hz, 1H), 7.56 (dd, J = 7.7, 1.7 Hz, 1H), 7.27 (m, 2H), 7.12–7.00 (m, 2H), 6.94 (dd, J = 8.1, 1.5 Hz, 1H), 6.77 (dd, J = 8.3, 1.1 Hz, 1H), 3.25 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 153.4, 134.4, 133.8, 130.2, 128.6, 125.2, 123.4, 120.5, 117.7, 114.8, 114.0, 82.1, 79.0; GC–MS 274 m/z (M^+)

4d. The general procedure was followed by using aldehyde **3d** (154 mg, 180 μL, 1.0 mmol), and the highly volatile alkyne **4d** (115 mg, 77%) was isolated with spectral data in accordance with previous characterizations.[13] R_f = 0.48 (silica gel, heptane/EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.03 (m, 1H), 2.15–1.89 (m, 4H), 1.88 (t, J = 2.7 Hz, 1H), 1.65–1.56 (m, 4H), 1.54 (m, 3H), 1.44–1.33 (m, 1H), 1.25–1.14 (m, 1H), 0.93 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.5, 124.4, 83.4, 69.0, 36.0, 31.9, 25.7, 25.5, 22.3, 19.3, 17.6; GC–MS 150 m/z (M^+)

4e. The general procedure was followed by using aldehyde **3e** (184 mg, 222 μL, 1.0 mmol), and the desired alkyne **4e** (162 mg, 90%) was isolated with spectral data in accordance with previous characterizations.[13] R_f = 0.59 (silica gel, heptane/EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.17 (m, 2H), 1.92 (t, J = 2.7 Hz, 1H), 1.56–1.22 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.9, 66.2, 30.1, 27.8, 27.7, 27.5, 27.3, 26.9, 26.7, 20.8, 16.6, 12.3, 12.2; GC–MS 180 m/z (M^+)

4f. Dimethyl-2-oxopropylphosphonate (6.90 g, 5.74 mL, 41.6 mmol) was added to a suspension of K_2CO_3 (21.5 g, 156 mmol) and 1*H*-imidazole-1-sulfonyl azide hydrochloride (9.44 g, 45.0 mmol) in MeCN (300 mL), and the colorless suspension was stirred at 25 °C for 2 h. Then a solution of aldehyde **3f**[24] (6.90 g, 34.6 mmol) in MeOH (300 mL) was added to the pale yellow suspension and stirred at 25 °C for 15 h. The reaction mixture was filtered, the filter cake was washed with Et_2O (3 × 50 mL), and the clear solution was carefully evaporated onto Celite without evaporating the volatile alkyne. The Celite-absorbed material was purified by dry column vacuum chromatography (heptane → EtOAc, 5% gradient), and the highly volatile alkyne **4f** (5.16 g, 76%) was isolated with spectral data in accordance with previous characterizations.[6] R_f = 0.70 (silica gel, heptane/EtOAc, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.38 (m, 1H), 3.46–3.33 (m, 1H), 3.24 (m, 1H), 2.15 (s, 1H), 1.98 (m, 3H), 1.83 (m, 1H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 84.3, 79.7, 69.5, 47.9, 45.6, 33.6, 33.1, 29.0, 28.5, 28.5, 23.6, 22.7, 21.0; GC–MS 195 m/z (M^+)

4g. The general procedure was followed by using aldehyde **3g** (159 mg, 1.0 mmol). The Celite-absorbed material was purified by dry column vacuum chromatography (heptane → EtOAc, 2% gradient), and the desired alkyne **4g** (135 mg, 87%) was isolated with spectral data in accordance with previous characterizations.[15] R_f = 0.52 (silica

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gel, heptane/EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dt, J = 8.0, 1.0 Hz, 1H), 7.32−7.26 (m, 2H), 7.12 (ddd, J = 8.0, 4.8, 3.2 Hz, 1H), 6.83 (s, 1H), 3.82 (s, 3H), 3.47 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 126.9, 123.3, 121.1, 120.9, 120.2, 109.5, 108.3, 83.3, 75.6, 30.6; GC−MS 155 m/z (M^+)

4h. Dimethyl-2-oxopropylphosphonate (10.4 g, 8.62 mL, 62.4 mmol) was added to a suspension of K_2CO_3 (32.3 g, 234 mmol) and 1*H*-imidazole-1-sulfonyl azide hydrochloride (14.2 g, 67.6 mmol) in MeCN (450 mL), and the colorless suspension was stirred at 25 °C for 2 h. Then a solution of aldehyde **3h** (9.0 g, 52.0 mmol) in MeOH (450 mL) was added to the pale yellow suspension and stirred at 25 °C for 15 h. The reaction mixture was filtered, the filter cake was washed with Et_2O (3 × 50 mL), and the clear solution was carefully evaporated to dryness. Water was added (400 mL), the aqueous layer was extracted with Et_2O (4 × 100 mL), and the combined organic layers were washed with brine (2 × 50 mL), dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The crude material was recrystallized from EtOH/water to furnish alkyne **4h** with spectral data deviating from previous characterizations.[16] (7.86 g, 89%). R_f = 0.65 (silica gel, heptane/EtOAc, 1:1); ^{1}H NMR (400 MHz, CD_3OD) δ 8.74 (s, 1H), 7.90−7.78 (m, 2H), 7.65−7.46 (m, 3H), 3.87 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 131.9, 131.0, 130.4, 127.1, 121.7, 83.4, 73.4; LC−MS 170 m/z (M + 1)

■ ASSOCIATED CONTENT

Supporting Information

Spectral data for all compounds prepared. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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