Solvent-free MW-assisted direct conversion of 3-tri-organosilyl-(germyl)-prop-2-yn-1-ols to ynimines

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Dedicated to Academician Boris A. Trofimov on the occasion of his 65th birthday
(received 17 June 03; accepted 21 Aug 03; published on the web 10 Sept 03)

Abstract
The direct conversion of 3-tri-organosilyl- or 3-organogermyl-prop-2-yn-1-ols into the corresponding imines using a solvent-free MW-assisted approach is reported. This highly effective methodology demonstrates the exploitation of α-silicon- or germanium-containing propynals generated *in situ* in a one-pot synthesis of ynimines. The efficient solvent-free MW-mediated synthesis of the corresponding silyl- or germyl-prop-2-yn-1-als has been carried out by oxidation of the starting alcohols with manganese dioxide.

Keywords: Oxidation, α-silicon-(germanium)-containing propargylic alcohols, propynals, ynimines, one-pot, dry synthesis, MW-assistance

Introduction

Imines are widely applied as analitycal, medicinal, polymer and liquid crystalline materials,[1–3] and as synthons in organic synthesis.[4,5] Conjugation of the triple bond and imino group in 1,3-aza-enynes provides further synthetic possibilities.[6] Imines with α-silicon- or germanium-containing groups are of special interest in this series for the following reasons. The α-silicon- or germanium- containing groups stabilize imines and the products of their transformations, while subsequent heterolysis of the M–Csp bond will lead to analogs with a terminal triple bond. The successful use of α,β-acetylenic silicon- containing aldimines as key compounds in the synthesis of thienomycines stimulates the search for synthetic methods and new application of organometal aza-enynes in organic synthesis.[7]

α,β-Acetylenic aldimines are formed by the condensation of propynals with aliphatic and aromatic amines.[6,8] Problems can arise, however, in the isolation of propynals owing to their volatility, toxicity or high reactivity (e.g., to polymerisation). It is known that propynal is highly

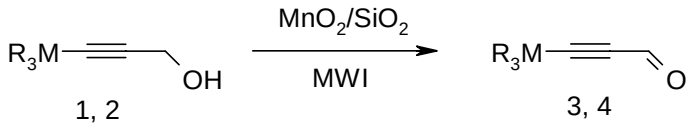
mutagenic.[9] Therefore the use in organic synthesis of propynals generated *in situ* is desirable. Our own preliminary studies involve the one-pot synthesis of acetylenic hydroxyimines from primary-tertiary acetylenic γ-diols and primary amines by oxidation with manganese dioxide.[10] This approach has been developed for some propargylic alcohols that were subjected to *in situ* oxidation and imine formation in high yield.[11]

The combination of supported reagents and microwave irradiation, as in the oxidation of benzylic alcohols using 35% MnO_2 'doped' silica [12] aroused our interest in applying this method in a solvent-free one-pot synthesis of acetylenic imines from the acetylenic alcohols **1** and **2** (both stable at room temperature) via oxidation/amination reactions. This technique can be used to carry out a wide range of reactions in short times, with high conversions and selectivity, without the need for solvents. It is also of special interest as an example of "green chemistry".[13]

To the best of our knowledge o*ne-pot* synthesis of imines from alcohols, as well as their acetylenic derivatives under MW conditions, has not been carried out. Our target aldehydes $R_3MC{\equiv}CCHO$ **3** and **4** (M = Si or Ge, respectively are representative of a class with high reactivity for application in the design of bioactive molecules, including natural analogs,[8,14a–d] and the method may have advantages over the oxidation of the corresponding alcohols with activated manganese dioxide or potassium chlorochromate.[15] The oxidation with MnO_2 is slow and requires a large excess of oxidant. The oxidation with pyridinium chlorochromate is more rapid, but 3-trimethylsilylprop-2-yn-1-al **1** prepared by this method is unstable and polymerizes on storage.

Results and Discussion

The 3-trimethylsilyl-(triethylgermyl)-prop-2-yn-1-ols, **1,2** were found to be readily oxidized to the corresponding propynals **3**,**4** by the MW-mediated solvent-free method with activated manganese dioxide doped on silica (Scheme 1).



R_3M = Me_3Si (1, 3); Et_3Ge (2, 4)

Scheme 1

The oxidation of the alcohols **1**, **2** was carried out with five equiv. of activated MnO_2 on silica, by irradiation in a domestic microwave oven (LG MS-1904H, 700W) in an ampoule or in a screw-capped pressure vial. This method has considerable advantages over the classical one, with shortening of the reaction time by a factor of five hundred or more, increase in propynal yields (Table 1), and simplicity of isolation. It should be noted that the synthesis of ynimines by

the method of ref. 11 requires 10 equiv. of MnO_2. Our method requires no more than 5 equiv. of oxidant.

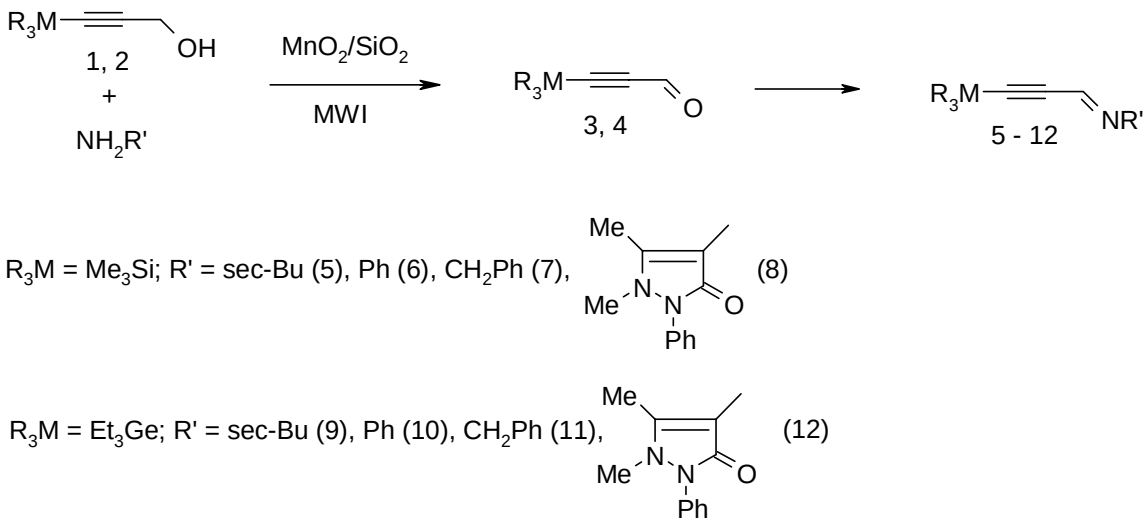
Comparison of the yields of propynals under microwave and conventional heating (oil bath) under otherwise the same conditions (vessel, reaction time, temperature) shows the specific microwave effect (non-pure thermal effect).[16a,b] For 3-triethylgermylprop-2-yn-1-al **4** this effect is greater than with the silicon analog **3**. The oxidation of 3-triethylgermylprop-2-yn-1-ol **2** into **4** proceeds more slowly than that of the silicon analog **1** (see entries 2, 5).

Table 1. Oxidation of alcohols $R_3MC{\equiv}CCH_2OH$ **1**, **2** to propynals $R_3MC{\equiv}CCHO$ **3**, **4** under various conditions

Entry	Alcohol	Method	Reaction time	Temperature, °C[a]	Yield of propynal, (%)[d]
1	$Me_3Si{\equiv}CH_2OH$	MnO_2/SiO_2 Classical	70 h	RT	95
2	$Me_3Si{\equiv}CH_2OH$	MnO_2/SiO_2 Δ	1 min	70-80	50
3	$Me_3Si{\equiv}CH_2OH$	MnO_2/SiO_2 MW	1 min	70-80	70[b]
4	$Et_3Ge{\equiv}CH_2OH$	MnO_2/SiO_2 Classical	16 h	RT	34
5	$Et_3Ge{\equiv}CH_2OH$	MnO_2/SiO_2 Δ	2 min	125-130	25
6	$Et_3Ge{\equiv}CH_2OH$	MnO_2/SiO_2 MW	2 min	125-130	95[c]

MW = activation by domestic microwave oven, LG MS-1904H, 700W.
Δ = heating in oil bath.
[a] Final temperature of alumina bath, according to glass thermometer immediately after stopping irradiation. [b] P = 420W. [c] P = 700W. [d] Yields determined by ^{1}H NMR.

We have developed a very efficient method for the dry synthesis of 1,3-aza-enynes **5–12** by tandem oxidation–amination of alcohols **1, 2** with manganese dioxide on silica under MW irradiation (Scheme 2). This method leads to the target 1,3-azaenynes **5–12** in very short reaction times (2–4 min) and in high yields, without isolation of the intermediate propynals **3, 4** (Table 2).



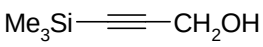
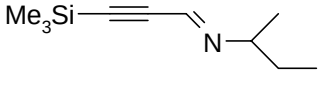
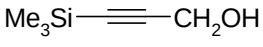
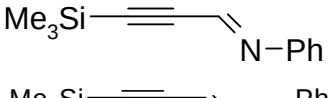
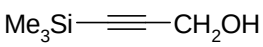
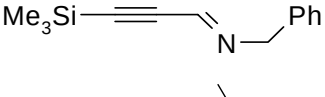
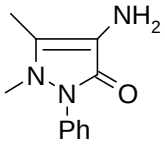
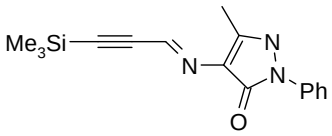
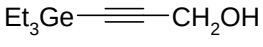
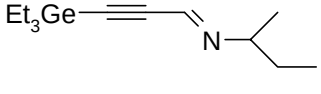
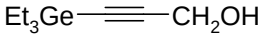
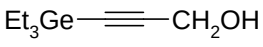
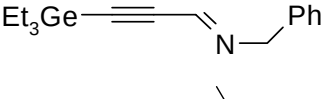
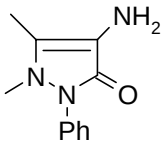
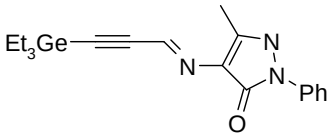
Scheme 2

The imines **8, 12** were isolated only as the *E*-isomers. In the imines **6,10** one isomer (*E*-configuration) dominates (ratio of *E*/*Z* isomers are 20/1 for **6** and 7/1 for **10**). The assignment of isomer structures used the data[17,18] which point out that the CH=N protons for *E*-isomers resonate at weaker field. The *E*-isomer dominates for the other imines; the *E*/*Z* ratios are 1.7/1 (**5,9**), 4.7/1 (**7**), 2.6/1 (**11**). Values of coupling constants $^{1}J_{CH=N}$ for *Z*-isomers of imines **6,7** are larger than for *E*-isomers: $^{1}J_{CH=N}$ 169.76 Hz (*E*-isomer), 191.34 Hz (*Z*-isomer) and 167.77 Hz (*E*-isomer), 189.74 Hz (*Z*-isomer) accordingly. In addition, it should be noted that for the imine **7** the isomer with larger coupling constant, $^{4}J_{CHCH2}$ (2 Hz), should be assigned to the *E*-configuration (with $^{4}J_{CHCH2}$ = 1 Hz for the *Z*-isomer).

In the reaction of aniline, a side reaction of oxidation into azobenzene **13** was observed (Scheme 3), in yields of compound **13** of 30% (entry 6) and 50% (entry 2), assessed by ^{1}H NMR. Compound **13** was isolated by column chromatography on Al_2O_3, and its structure confirmed by IR and NMR (^{1}H, ^{13}C) data, and its melting point matching literature data.[19]

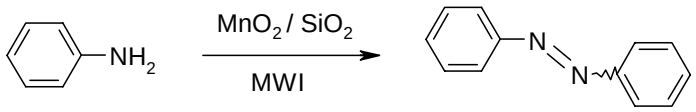
Recently, the oxidation of aniline and some substituted primary aromatic amines by potassium permanganate and copper sulfate pentahydrate under solvent-free conditions was described.[20] Azobenzene **13** was prepared in 75% yield using alumina as a solid support for 5 h at room temperature. The oxidation of aniline with MnO_2/SiO_2 under our conditions (420W, 4 min) leads to **13** in 84% yield (^{1}H NMR control, 55% isolated yield).

Table 2. *One-pot* synthesis[a] of acetylenic imines **5-12** from alcohols **1**,**2** under microwave irradiation[b]

Entry	Alcohol	Amine	Time	Imine (yield, %[c])
1		*sec*-$BuNH_2$	1 min	 (78)
2		$PhNH_2$	3 min	 (43[d])
3		$PhCH_2NH_2$	3 min	 (89)
4			4 min	 (87)
5		*sec*-$BuNH_2$	2 min	 (70)
6		$PhNH_2$	3 min	 (70[d])
7		$PhCH_2NH_2$	3 min	 (75)
8			4 min	 (96)

[a] Oxidation on MnO_2/SiO_2. [b] Power = 700W unless otherwise stated.
[c] Determined by ^1H NMR. [d] Power = 420W. The azobenzene 13 was isolated as a side product.

Conditions: domestic MW oven (LG MS-1904H, 700W), in a screw-capped pressure vial.



13

Scheme 3

In conclusion, MW-assisted solvent-free oxidation of α-silicon- and germanium-containing propargyl alcohols with manganese dioxide on silica gave the corresponding propynals. A highly efficient, one-pot, solvent-free MW-mediated synthesis of ynimines from 3-tri-organosilyl-(germyl-)-prop-2-yn-1-ols has been developed.

Experimental Section

General Procedures. Melting points are uncorrected. IR spectra were recorded on a Specord 75, using KBr disks or liquid films: data are given as ν /cm^{-1}. ^{1}H- and ^{13}C- NMR spectra were obtained on a Bruker DPX–400 spectrometer in $CDCl_3$ solutions; internal standard $(Me_3Si)_2O$. 3-Trimethylsilylprop-2-yn-1-ol **1** was prepared by rearrangement of 1-trimethylsiloxy-2-propyne with Grignard reagent,[21] the 3-triethygermylprop-2-yn-1-ol **2** was obtained by the reaction of Iotsich reagent for 1-trimethylsiloxy-2-propyne with triethylbromogermane by our method.[22] A multimode domestic microwave oven (LG MS-1904H, 700W) was used for microwave irradiation. The oxidant was 35% MnO_2 doped on silica.

General procedure for the microwave-assisted oxidation of acetylenic alcohols (1, 2) Method A

Caution! The volume of the reaction mixture should not occupy more than 1/10–1/12 part of the ampoule volume.

A mixture of the acetylenic alcohol (1.5 mmol) and MnO_2/SiO_2 (2.5 g) was placed in an ampoule. The ampoule was sealed and dipped into the alumina bath placed into the 20 cm^3 screw capped vial and irradiated in the domestic microwave oven, with cooling after each impulse (1 min). The temperature was measured by placing the glass thermometer in the alumina bath immediately after stopping the irradiation. The reaction mixture was extracted with CH_2Cl_2 (3x20 ml) and the solvent removed by distillation. The residue was analyzed by ^{1}H NMR spectroscopy. The yields of the propynals **3**, **4** are presented in Table 1.

Method B

The mixture of the acetylenic alcohol (1.5 mmol) and MnO_2/SiO_2 (2.5 g) was placed in the ampoule. The ampoule was sealed and heated on an oil bath for some minutes at the temperature shown in Table 1. The reaction mixture was worked up as in method A and the solvent removed by distillation. The residue was analyzed by ^{1}H NMR spectroscopy. The yields of propynals **3**, **4** are presented in Table 1.

Method C

The mixture of the acetylenic alcohol (1.5 mmol) and MnO_2/SiO_2 (2.5 g) was placed in a closed vial, which was periodically shaken. After reaction, the mixture was extracted with CH_2Cl_2 (3x20 ml) and the solvent removed by distillation. The residue was analyzed by ^{1}H NMR spectroscopy. The yields of propynals **3**, **4** are presented in Table 1.

General procedure for MW-assisted solvent-free tandem oxidation–amination of alcohols 1 and 2 into the imines 5–12

A mixture of acetylenic alcohol (1.5 mmol), amine (1.5 mmol) and MnO_2/SiO_2 (2.5 g) was placed into a screw-capped pressure vial and irradiated in the domestic microwave oven. The reaction times and power are presented in Table 2. The reaction mixture was extracted with

$CHCl_3$:MeOH (10:1, 3x10 ml). The solvents were removed *in vacuo,* and the residue analyzed by ^{1}H NMR and IR spectroscopy. The compounds **6**,[23] **7**,[24] **10**,[25] and **11**[25]) are known.

***N*-[(*Z*,*E*)-3-(Trimethylsilyl)prop-2-ynylidene]-*sec*-butylamine (5).** Isolated as a dark red oil (78%); IR (neat), 1595 (C=N), 2170 (C≡C). ^{1}H NMR δ (*E*)-isomer 0.16 (9H, s); 0.76 (3H, t); 1.13 (3H, d); 1.50 (2H, m); 3.02 (1H, m); 7.43 (1H, s); (*Z*)-isomer 0.17 (9H, s); 0.79 (3H, t); 1.09 (3H, d); 1.49 (2H, m); 3.80 (1H, m); 7.38 (1H, d). ^{13}C NMR δ (*E*)-isomer -0.99, 10.36, 21.42, 29.79, 68.49, 96.37, 100.99, 142.28; (*Z*)-isomer 1.44, 10.36, 20.53, 30.06, 61.59, 96.15, 102.98, 140.49.

***N*-[(*E*)-3-(Trimethylsilyl)prop-2-ynylidene]-benzeneamine (6).** Dark red oil (30%) from column chromatography (neutral Al_2O_3, hexane–$CHCl_3$ 5:2). IR (neat), 1585, 1600 (C=N, Ph), 2170 (C≡C). ^{1}H NMR δ 0.17 (9H, s); 7.12-7.40 (5H, m); 7.68 (1H, s). ^{13}C NMR δ -0.13, 90.42, 102.12, 120.83, 127.39, 129.29, 143.55, 152.69. A side product, azobenzene **13**,was isolated in 38% yield, orange-red crystals, mp 67–68 °C (lit.[19] 68–69 °C). IR ($CDCl_3$) 1580, 1590sh (Ph, N=N), 3060 (C-H, Ph). ^{1}H NMR δ 7.39–7.52 (2H, m, *o*-Ph); 7.86–7.93 (3H, m, *m*-, *p*-Ph). ^{13}C NMR δ 122.84, 129.07, 130.95, 152.69. The ^{1}H- NMR spectrum is in accord with literature data.[26]

MW-assisted oxidation of aminobenzene. The mixture of aminobenzene (1.5 mmol, 0,1397 g) and MnO_2/SiO_2 (2.5 g) placed in a screw-capped pressure vial was irradiated in the domestic microwave oven (420W)for 4x1 min. After each impulse the vial was shaken and cooled to RT. The reaction mixture was then extracted with $CHCl_3$:MeOH (10:1) (5x10 ml) the solvents removed *in vacuo*. The residue, 0.0908 g (55%), was isolated and identified as the azobenzene **13** (mp 67–68 °C), with ^{1}H NMR spectrum identical that presented above.

***N*-[(*Z*,*E*)-3-(Trimethylsilyl)prop-2-ynylidene]-benzenemethanamine (7).** A dark red oil (89%); IR (neat) 1590, 1600 (C=N, Ph), 2165 (C≡C). ^{1}H NMR δ (*E*)-isomer 0.26 (9H, s); 4.71 (2H, d); 7.26–7.39 (5H, m); 7.59 (1H, t); (*Z*)-isomer 0.30 (9H, s); 4.89 (2H, d); 7.26–7.39 (5H, m); 7.63 (1H, t). ^{13}C NMR δ (*E*)-isomer -0.60, 65.53, 98.21, 101.40, 127.22, 128.19, 128.49, 138.90, 145.59; (*Z*)-isomer -0.57, 59.97, 96.48, 105.11, 126.93, 128.05, 128.40, 137.72, 143.48.

1,5-Dimethyl-2-phenyl-[(*E*)-2-(trimethylsilyl)prop-2-ynylideneamino]-1,2-dihydro-3*H*-pyrazol-3-one (8). Yellow crystals (87%), mp 186–187 °C (benzene); IR (KBr) 1510 (C=C), 1580, 1590 (C=N, Ph), 1650 (C=O), 2170 (C≡C). ^{1}H NMR δ 0.23 (9H, s); 2.42 (3H, s); 3.16 (3H, s); 7.10-7.58 (5H, m); 8.95 (1H, s). ^{13}C NMR δ -0.38, 10.10, 35.22, 100.60, 103.87, 118.14, 124.97, 127.39, 129.27, 134.25, 140.68, 151.66. Anal. Calcd for $C_{17}H_{21}N_3OSi$: C, 65.55; H, 6.79; N, 13.48; Si, 9.01. Found: C, 65.40; H, 6.76; N, 13.38; Si, 9.11.

***N*-[(*Z*,*E*)-3-(Triethylgermyl)prop-2-ynylidene]-*sec*-butylamine (9).** Isolated as a dark red oil (70%); IR (neat), 1585 (C=N), 2160 (C≡C). ^{1}H NMR δ (*E*)-isomer 0.76-1.15 (21H, m); 1.5 (2H, m); 3.86 (1H, m); 7.46 (1H, s); (*Z*)-isomer 0.76-1.15 (21H, m); 1.5 (2H, m); 3.01 (1H, m); 7.41 (1H, s). ^{13}C NMR δ (*E*)-isomer 5.69, 8.94, 10.91, 20.98, 30.60, 68.92, 98.11, 98.17, 142.89; (*Z*)-isomer 5.58, 8.89, 10.84, 20.95, 30.36, 61.92, 96.21, 102.65, 141.10.

***N*-[(*E*)-3-(Triethylgermyl)prop-2-ynylidene]-benzeneamine (10).** Isolated as a dark red oil (70%); IR (neat) 1590, 1605 (C=N, Ph), 2165 (C≡C). ^{1}H NMR δ 0.94 (2H, q); 1.12 (3H, t); 7.12-

7.30 (5H, m); 7.67 (1H, s). ^{13}C NMR δ 5.68, 9.00, 101.65, 103.45, 120.81, 127.08, 129.19, 143.81, 150.98. Azobenzene **13** was detected in yield 30%.

***N*-[(*Z*,*E*)-3-(Triethylgermyl)prop-2-ynylidene]-benzenemethanamine (11).** Isolated as a dark red oil (75%); IR (neat), 1590, 1600 (C=N, Ph), 2165 (C≡C). ^{1}H NMR δ (*E*)-isomer 0.80-0.95 (2H, m); 1.00–1.20 (3H, m); 4.84 (2H, d); 7.19–7.33 (5H, m); 7.57 (1H, t); (*Z*)-isomer 0.80-0.95 (2H, m); 1.00–1.20 (3H, m); 4.64 (2H, d); 7.19–7.33 (5H, m); 7.55 (1H, t). ^{13}C NMR δ (*E*)-isomer 5.58, 8.88, 65.39, 97.93, 104.59, 127.13, 128.19, 128.44, 139.07, 145.77; (Z)-isomer 5.48, 8.81, 59.84, 97.71, 102.57, 126.84, 128.04, 128.35, 137.91, 143.72.

1,5-Dimethyl-2-phenyl-[(*E*)-2-(triethylgermyl)prop-2-ynylideneamino]-1,2-dihydro-3*H*-pyrazol-3-one (12). Yellow crystals (96%), mp 103-104 °C (hexane+benzene); IR (KBr) 1520 (C=C), 1575, 1590 (C=N, Ph), 1650 (C=O), 2160 (C≡C). ^{1}H NMR δ 0.91 (2H, q); 1.10 (3H, t); 2.40 (3H, s); 3.13 (3H, s); 7.10–7.50 (5H, m); 8.97 (1H, s). ^{13}C NMR δ 5.76, 9.03, 11.27, 35.48, 100.42, 105.18, 118.42, 125.04, 127.44, 129.14, 134.53, 141.48, 151.78. Anal. Calcd for $C_{20}H_{27}N_3OGe$: C, 60.04; H, 7.30; N, 10.50; Ge, 18.15. Found: C, 60.05; H, 7.07; N, 10.58; Ge, 18.15.

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