

Expedient Immobilization of TEMPO by Copper-Catalyzed Azide-Alkyne [3 + 2]-Cycloaddition onto Polystyrene Resin

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Abstract: TEMPO was readily grafted by copper(I)-catalyzed azide-alkyne cycloaddition onto polystyrene. Starting with commercially available Merrifield resin (4.3 mmol/g) almost quantitative loading of TEMPO onto the polymer was achieved (≥ 4 mmol/g). The so obtained PS-CLICK-TEMPO allowed the oxidation of alcohols to aldehydes with bleach or molecular oxygen as the terminal oxidant with high yields and selectivity in multiple cycles without loss of activity.

Keywords: catalyst immobilization; oxidation; oxygen; polymers; polystyrene resin; TEMPO

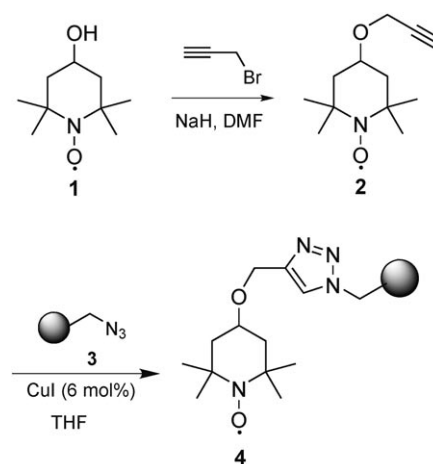
The copper-catalyzed^[1] azide-alkyne cycloaddition^[2] (CuAAC) reaction, coined as a click reaction,^[3] has proven to be most powerful for ligating functional molecules to supporting scaffolds or to each other.^[4] Following the seminal contributions of Gmeiner and co-workers,^[5] there is a growing awareness that this reaction can also be used for the synthesis of functional polymers and dendrimers.^[6] In addition, the CuAAC, offering wide tolerance for reactive or sensitive groups, should have great potential for the synthesis of heterogeneously immobilized catalysts and reagents.

Oxidation of alcohols using catalytic amounts of the stable nitroxyl radical 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) in combination with safe and easy to handle primary oxidants has received significant attention due to the low toxicity of the reagent and the good chemoselectivity achieved.^[7] The demands for inexpensive, environmentally friendly and renewable polymer-supported (PS) catalysts have led to the synthesis of several immobilized TEMPO moieties,^[8] including silica-supported TEMPO,^[8a,b] MCM-41-supported TEMPO,^[8c] sol-gel TEMPO,^[8d,e] PEG-TEMPO,^[8f-h] polynorbornene-derived TEMPO,^[8i] fluoros-tagged TEMPO,^[8j,k] acid functionalized Fibre-CatTM,^[8l] polyamine TEMPO (PIPO)^[8m] and polymer-

supported oxammonium salts.^[8n] These catalysts have shown good efficiency for the selective oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones. Alternatively, polymer bound co-oxidants have been proposed to overcome limitations associated with the necessity to employ stoichiometric amounts of the co-oxidant in solution, requiring additional purification steps.^[9]

We report here the simple and efficient preparation of a new polystyrene-supported TEMPO by using click chemistry as a practical tagging method and demonstrate its high activity for the oxidation of alcohols using bleach or molecular oxygen as a co-oxidant.

The catalyst could be prepared in an easy two-step sequence starting from commercially available 4-hydroxy-TEMPO **1** and polystyrene-supported azide **3** (Scheme 1).^[10] Propargylation of **1** was straightforward giving rise to **2**, which set the stage for the subsequent copper(I)-catalyzed cycloaddition: following a protocol developed by Gmeiner and co-workers^[5a] 6 mol% Cu(I) iodide were found to be optimal to achieve the smooth formation of **4** as judged by the complete disappearance of the typical IR absorption of the azide group (2095 cm^{-1}). No co-reductant had



Scheme 1. Synthesis of PS-CLICK-TEMPO **4**.

to be added, indicating that no oxidation of Cu(I) by TEMPO had occurred. The estimated catalyst loading based on elemental analysis and recovered **2** was 4 mmol g^{-1} of nitroxyl radical. This value is very close to that of the original Merrifield resin (*ca.* 4.3 mmol g^{-1}) showing the high efficiency of this tagging method. When 3 mol% Cu^I iodide were employed, only 50% conversion was achieved, resulting in a resin **4** with a catalyst loading of 2 mmol g^{-1} of nitroxyl radical.

The new heterogeneous “PS-CLICK-TEMPO” **4** proved to be very efficient for the selective oxidation of aliphatic and benzylic alcohols under Anelli's conditions^[7b], using sodium hypochlorite as terminal oxidant and KBr as co-catalyst (Table 1). In all cases 2.5 mol% of PS-CLICK-TEMPO **4** was used, allowing complete conversion of the substrates generally in 30 min. Primary benzylic alcohols (entries 1–5) gave the corresponding aldehydes with high yields and complete chemoselectivity, no overoxidation to the respective carboxylic acids was observed. Moreover, **4** was also effective for the oxidation of the more challenging aliphatic alcohols (entries 6–10). Formation of the aldehydes from primary alcohols (entries 6–8) was accompanied by minute amounts (<5%) of carboxylic acids, while oxidation of more demanding secondary alcohols (entries 9 and 10) required somewhat longer reaction times (1–5 h) to achieve complete conversion. In all cases, the purity of the isolated aldehydes was >95% without the need for purification by column chromatography.

We next examined the recyclability of our catalyst (Table 2). PS-CLICK-TEMPO **4** was easily recovered by filtration and reused for the next cycle without further activation in five subsequent runs employing 4-methylbenzyl alcohol as substrate. Virtually no loss of activity was observed, and also the chemoselectivity for the formation of the aldehyde remained very high in all cases. Only traces of carboxylic acid, being easily removed by washing the organic phase with sodium bicarbonate solution, were observed.

In 1984, Semmelhack reported that TEMPO/CuCl can oxidize allylic and benzylic alcohols to aldehydes using molecular oxygen.^[7a] This method was recently improved with the discovery of several variations of the original Cu/TEMPO catalytic systems.^[11,13b] Minisci et al. showed that the aerobic oxidation of both activated and unactivated alcohols can be performed under mild conditions using Mn(II)-Co(II) or Mn(II)-Cu(II) nitrates in acetic acid under ambient pressure and temperature.^[12] Although numerous immobilized TEMPO variants on both organic and inorganic supports were synthesized, only few examples are known where molecular oxygen is used as terminal oxidant.^[8c,h,i,13] We decided to investigate the catalytic properties of PS-CLICK-TEMPO **4** under the conditions developed by Minisci, being especially attractive

Table 1. PS-CLICK-TEMPO mediated oxidation of alcohols to carbonyl derivatives.^[a]

Entry	Alcohol	Conversion [%] ^[b]	Yield [%] ^[c]	Purity [%] ^[b]
1	benzyl alcohol	>98	99	>98
2	4-bromobenzyl alcohol	>98	93	>98
3	4-methylbenzyl alcohol	>98	98	>98
4	4-methoxybenzyl alcohol	>98	92	>98
5	2-phenylethanol	>98	95	>98
6	1-octanol	>98	95	95
7	1-decanol	>98	96	95
8	1-dodecanol	>98	99	96
9	3-nonanol ^[d]	>98	99	>98
10	cyclohexanol ^[e]	>98	98	>98

^[a] Alcohol (1 mmol) in CH₂Cl₂ (2 mL), KBr (0.3 mmol), PS-TEMPO (2.5 mol%), NaOCl (1.3 mmol), NaHCO₃ (0.2 mmol), 0°C. Reaction time = 30 min.

^[b] Determined by ¹H and ¹³C NMR; >98% indicates that no starting material or by-products could be detected.

^[c] Yields of isolated products.

^[d] Reaction time = 5 h.

^[e] Reaction time = 1 h.

Table 2. Recycling of PS-CLICK-TEMPO **4** in the oxidation of 4-methylbenzyl alcohol.^[a]

Run	Conversion [%] ^[b]	Yield [%] ^[c]	Purity [%] ^[b]
1	>98	95	>98
2	>98	94	>98
3	>98	93	>98
4	>98	95	>98
5	>98	92	>98

^[a] Alcohol (3 mmol) in CH₂Cl₂ (6 mL), KBr (1.0 mmol), PS-TEMPO (2.5 mol%), NaOCl (3.9 mmol), NaHCO₃ (0.6 mmol), 0°C. Reaction time = 30 min.

^[b] Determined by ¹H and ¹³C NMR; >98% indicates that no starting material or by-products could be detected.

^[c] Yields of isolated products.

for industrial processes since non-chlorinated solvents and oxygen as the terminal oxidant are used. PS-CLICK-TEMPO **4** showed outstanding activity in all experiments with generally employing only 5 mol% of catalyst loading (Table 3) at reaction times of 3–6 h. Only cinnamyl alcohol, which is known to be less reactive,^[8h] was cleanly oxidized within 24 h in the presence of 10 mol% catalyst.

Also under these conditions PS-CLICK-TEMPO **4** could be recycled efficiently. In five consecutive runs using 4-bromobenzyl alcohol as the substrate the catalyst was recovered by simple filtration and reused as such giving high yields of aldehyde in all cases (Table 4).

Table 3. Aerobic oxidation of alcohols to carbonyl compounds by PS-CLICK-TEMPO.^[a]

Entry	Substrate	Time [h]	Conversion [%] ^[b]	Yield [%] ^[c]	Purity [%] ^[b]
1	benzyl alcohol	3	> 98	98	> 98
2	4-bromobenzyl alcohol	3	> 98	95	> 98
3	4-methylbenzyl alcohol	3	> 98	98	> 98
4	1-octanol	6	> 98	97	95
5	1-decanol	6	> 98	96	95
6	cinnamyl alcohol ^d	24	> 98	96	> 98

^[a] Alcohol (1 mmol) in AcOH (1 mL), Mn(NO₃)₂·4 H₂O (0.2 mmol), Co(NO₃)₃·6 H₂O (0.2 mmol), PS-TEMPO **4** (2.0 mmol g⁻¹, 25 mg, 5 mol %), 40 °C.

^[b] Determined by ¹H and ¹³C NMR; > 98 % indicates that no starting material or by-products could be detected.

^[c] Yields of isolated products.

^[d] PS-TEMPO (10 mol %).

Table 4. Aerobic oxidation of 4-bromobenzyl alcohol by PS-CLICK-TEMPO. Recycling experiment.^[a]

Run	Conversion [%] ^[b]	Yield [%] ^[c]	Purity [%] ^[b]
1	> 98	94	> 98
2	> 98	95	> 98
3	> 98	93	> 98
4	> 98	91	> 98
5	> 96	93	96

^[a] Alcohol (3 mmol) in AcOH (3 mL), Mn(NO₃)₂·4 H₂O (0.6 mmol), Co(NO₃)₃·6 H₂O (0.6 mmol), PS-TEMPO **4** (4.0 mmol/loading, 38 mg, 5 mol %), 40 °C.

^[b] Determined by ¹H and ¹³C NMR.

^[c] Yields of isolated products.

In conclusion, we have developed an extremely simple and practical protocol for grafting TEMPO onto polystyrene resin from readily available and inexpensive starting materials using the copper(I)-catalyzed alkyne-azide cycloaddition as the ligation method. The resulting PS-CLICK-TEMPO **4** proved to be highly effective in the chemoselective oxidation of alcohols with both bleach and molecular oxygen under mild conditions. Moreover, it can be easily recovered and recycled without any loss of catalytic activity.

Experimental Section

General

DMF was distilled over P₂O₅ before use. Dichloromethane was distilled over calcium hydride. The Merrifield resin (*ca.* 4.3 mmol/g Cl loading, cross-linked with 2 % DVB, 200–400 mesh) was purchased from Fluka. All commercially available compounds were used as received.

Propargyl Ether TEMPO (2)

To a stirring suspension of NaH (60 % in mineral oil, 850 mg, 22.0 mmol) in dry DMF (100 mL) 4-hydroxy-TEMPO **1** (3.0 g, 17.44 mmol) was added portionwise at 0 °C and stirred at room temperature for 30 min. Propargyl bromide (2.0 mL, 22.0 mmol) was added dropwise at 0 °C. The resulting mixture was stirred for 3 h at room temperature. Water (100 mL) was added and the solution was extracted with EtOAc (5 × 50 mL). The combined organic phases were washed with water (10 × 50 mL) and dried over MgSO₄, filtered, evaporated under reduced pressure and purified by column chromatography (silica gel, 10 % EtOAc in hexanes) to give the title compound **2** as an orange solid; yield: 2.47 g (68 %); mp 58–59 °C; MS (PI-EI-MS 70 eV): *m/z* = 210.2 (M⁺); anal. calcd for C₁₂H₂₀NO₂: C 68.54, H 9.59, N 6.66; found: C 68.21, H 9.89, N 6.33.

Azidomethyl Polystyrene (3)

Merrifield resin (2.5 g, 4.3 mmol/g) in 25 mL DMSO was shaken at 50 °C with NaN₃ (2.45 g, 37.63 mmol) for 2 days. After being cooled to room temperature, the suspension was filtered and the resin was washed with MeOH (5 × 15 mL) and CH₂Cl₂ (5 × 15 mL) to give resin **3**; yield: 2.4 g; IR (KBr): ν = 2095 cm⁻¹.

PS-CLICK-TEMPO (4)

Method A: To a suspension of Merrifield supported azide **3** (estimated loading 4.3 mmol/g of azide, 1.10 g, 4.76 mmol) in degassed DCM (100 mL), 4-propargyloxy-TEMPO **2** (1.87 g, 8.58 mmol) and CuI (27 mg, 3 mol %) were added. The resulting mixture was shaken at room temperature for 3 days. The resin was filtered and washed with CH₂Cl₂ (5 × 50 mL) and dried under vacuum to afford PS-TEMPO **4** with an estimated TEMPO loading of 2.0 mmol/g; yield: 1.40 g. The loading was determined by measurement the quantity of unreacted propargyl ether TEMPO **2**, elemental analysis and IR.

Method B. To a suspension of Merrifield supported azide **3** (estimated loading 4.3 mmol/g of azide, 570 mg, 2.43 mmol) in degassed THF (50 mL), 4-propargyloxy-TEMPO **2** (960 mg, 4.57 mmol) and CuI (27 mg, 6 mol%) were added. The resulting mixture was shaken at room temperature for 5 days. The resin was filtered and washed with CH₂Cl₂ (5 × 50 mL) and dried under vacuum to afford PS-TEMPO **4** with an estimated TEMPO loading of 4.0 mmol/g; yield: 1.05 g. The loading was determined by measurement the quantity of unreacted propargyl ether TEMPO **2**, elemental analysis and IR.

General Procedure for the Oxidation of Alcohols by PS-CLICK-TEMPO/Bleach

An alcohol (1.0 mmol) in 2 mL CH₂Cl₂, KBr (40 mg, 0.3 mmol) and PS-TEMPO **4** (2.0 mmol/g loading, 13 mg, 2.5 mol%) were added to a round-bottom flask. The reaction mixture was stirred at 0 °C before addition of 0.8 mL NaOCl (10%) and NaHCO₃ (40 mg, 50 mg mL⁻¹ bleach). The resulting suspension was stirred at 0 °C for 30 min. The reaction mixture was filtered, washed with CH₂Cl₂, dried over MgSO₄ and concentrated under vacuum to afford the corresponding aldehyde.

Oxidation of 4-Methylbenzyl Alcohol by PS-CLICK-TEMPO/Bleach; Recycling Experiments

4-Methylbenzyl alcohol (366 mg, 3 mmol) in 6 mL CH₂Cl₂, KBr (120 mg 1.0 mmol) and PS-TEMPO **4** (4.0 mmol/loading, 23 mg, 2.5 mol%) were added to a round-bottom flask. The reaction mixture was stirred at 0 °C before addition of 2.4 mL NaOCl (10%) and NaHCO₃ (120 mg, 50 mg mL⁻¹ bleach). The resulting suspension was shaken at 0 °C for 1 h. Then the reaction mixture was filtered, extracted with CH₂Cl₂ (2 × 10 mL), washed with a saturated NaHCO₃ solution (5 mL) and concentrated under vacuum to afford 4-methylbenzaldehyde. PS-TEMPO was washed with water and CH₂Cl₂ and reused without further purification.

General Procedure for the Aerobic Oxidation of Alcohols to Carbonyl Compounds by PS-CLICK-TEMPO

An alcohol (1.0 mmol), Mn(NO₃)₂·4H₂O (0.2 mmol), Co(NO₃)₃·6H₂O (0.2 mmol), PS-TEMPO **4** (2.0 mmol g⁻¹ loading, 25 mg, 5 mol%) and glacial acetic acid (1 mL) were added to a Schlenk flask and heated at 40 °C under an oxygen atmosphere until completion. Then, the reaction mixture was filtered, washed with water and CH₂Cl₂. The organic layer was washed with water (2 × 10 mL), dried over MgSO₄ and concentrated under vacuum to afford the corresponding aldehyde.

Aerobic Oxidation of 4-Bromobenzyl Alcohol by PS-CLICK-TEMPO; Recycling Experiments

4-Bromobenzyl alcohol (561 mg, 3 mmol), Mn(NO₃)₂·4H₂O (15 mg, 0.6 mmol), Co(NO₃)₃·6H₂O (18 mg, 0.6 mmol), PS-CLICK-TEMPO **4** (4.0 mmol g⁻¹ loading, 38 mg, 5 mol%) and glacial acetic acid (3 mL) were added to a Schlenk flask and heated at 40 °C under an oxygen atmosphere. After 4 h the reaction mixture was filtered, washed with water and CH₂Cl₂. The organic layer was washed with water (2 × 10 mL), dried over MgSO₄ and concentrated under vacuum to afford 4-bromobenzaldehyde. PS-TEMPO was washed with water and CH₂Cl₂ and reused without further purification. Fresh portions of Mn(NO₃)₂·4H₂O (15 mg, 0.6 mmol) and Co(NO₃)₃·6H₂O (18 mg, 0.6 mmol) were added to each run.

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