R. Varala, V. Seema



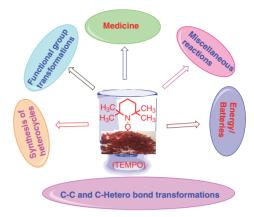
Spotlight

Recent Applications of TEMPO in Organic Synthesis and Catalysis

Ravi Varala*ª D Vittal Seema^b

^a Scrips Pharma, Mallapur, Hyderabad 500 076, Telangana, India ravivarala@gmail.com

^b Department of Chemistry, RGUKT Basar, Mudhole 504 107, Telangana, India



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Abstract In this spotlight article, authors highlighted the applications of TEMPO in organic synthesis and catalysis starting from 2015 to date.

Key words TEMPO, organic synthesis, catalysis, medicine, functional materials

Lebedev and Kazarnovskii published the first study on the stable, nonconjugated nitroxyl radical (2,2,6,6-tetramethylpiperidin-1-yl)oxyl or (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) (CAS: 2564-83-2) in 1960.1 It is made by oxidizing 2,2,6,6-tetramethylpiperidine. This solid, red-orange heterocyclic molecule is sublime. The four methyl groups provide adequate protection for the reactive radical, and the radical's stability is due to its delocalization into a two-center, three-electron N-O bond. It is used in both chemistry and biochemistry as a stable aminoxyl radical. TEMPO is employed as an electrode in all-organic radical batteries, as a reagent in organic synthesis, as a radical marker, as a structural probe for biological systems in conjunction with electron spin resonance spectroscopy, and as a mediator in controlled radical polymerization.² Furthermore, TEMPO is a common antioxidant in academic research.³ The price of TEMPO makes it suitable for laboratory use. TEMPO has certain limits in singlet oxygen detection, despite being a useful reagent in organic synthesis, particularly in medicinal chemistry and total synthesis. The TEMPOmediated oxidation process has excellent outcomes, but it has drawbacks for the environment due to the usage of halogenated chemicals, challenges with recycling (closed-loop operations), and high costs. The adaptability of TEMPO in organic synthesis and catalysis is highlighted in this Spotlight article.

Ethiraj and Pavithra sequentially cyclized cyclohexane-1.3-dicarbonyl compounds to produce a succession of xanthenediones from benzyl alcohols using TEMPO/CuCl₂-catalyzed one-pot aerobic oxidation (Table 1, A).⁴ Similar methods were used to produce the acridinediones from different benzyl alcohols. Iminyl radical cyclizations that were driven by microwaves were revealed by Castle and colleagues. Microwave-promoted iminyl radical cyclizations can be terminated by trapping with TEMPO, affording functionalized adducts (Table 1, B).⁵ The use of alkynes as radical acceptors furnishes 2-acylpyrroles by a process involving isomerization and fragmentation. To create 2,5-disubstituted 1,3,4oxadiazole derivatives, Ding and colleagues found a quick and effective cationic Fe(III)/TEMPO-catalyzed oxidative cyclization of aroyl hydrazones (Table 1, C).⁶ By using the reactions of ketones, aldehydes, or esters with amidines in the presence of an *in situ* produced recyclable iron(II) complex, Ji et al. came up with an effective method for the modular synthesis of several pyrimidine derivatives (Table 1, D).⁷ This research resulted in the synthesis of a novel metal-organocatalytic procedure that involves a series of TEMPO complexation, enamine addition, transient occupancy, TEMPO elimination, and cyclization to selectively β-functionalize unactivated ketones, aldehydes, and esters. Han and his team successfully developed an entirely novel, effective, and simple method for the synthesis of structurally significant pyrimidines by employing Cu-catalyzed and 4-HO-TEMPO-mediated [3+3] annulation of commercially available amidines with saturated ketones (Table 1, E).⁸ With the use of direct β -C(sp³)–H functionalization of saturated ketones and annulation with amidines, this procedure introduces a novel approach for the synthesis of pyrimidines.



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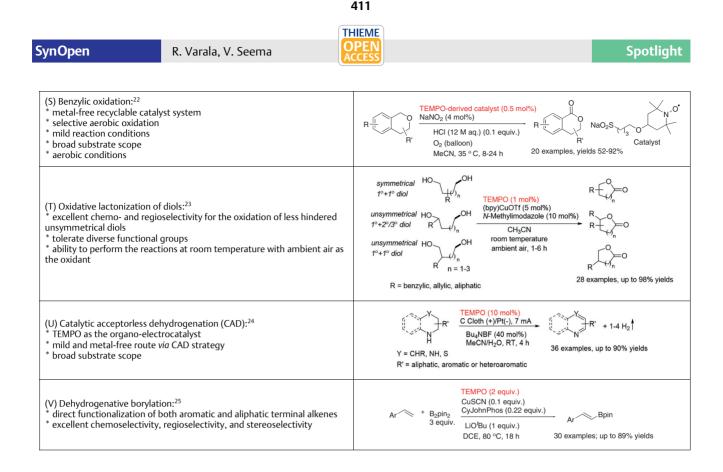
Table 1 Recent applications of TEMPO

 (A) Synthesis of xanthenediones and acridinediones:⁴ * simple experimental procedure * ease of access * short reaction period * without the use of any hazardous solvents and expensive chemicals * one-pot aerobic oxidation 	$R^{1} \xrightarrow{\text{TEMPO} (10 \text{ mol}\%)}_{CuCl_{2} (10 \text{ mol}\%)}$ $R^{1} \xrightarrow{\text{CH}_{2} OH} \xrightarrow{\text{KO'Bu} (1.2 \text{ equiv.})}_{CH_{2} CN, 90 \text{ °C}}$ $R = CH_{3} \text{ or } H \qquad 10 \text{ min}$ $R^{1} = CH_{3}, H, CI, F, OMe$ $Q_{1} \xrightarrow{\text{CH}_{3} CN, 90 \text{ °C}}_{NH_{4} OAc}$ $Q_{1} \xrightarrow{\text{CH}_{3} CN, 90 \text{ °C}}_{NH_{4} OAc}$ $R = CH_{3} \text{ or } H \qquad 10 \text{ min}$ $R^{1} = CH_{3}, H, CI, F, OMe$ $Q_{1} \xrightarrow{\text{CH}_{3} CN, 90 \text{ °C}}_{NH_{4} OAc}$ $R = CH_{3} \text{ or } H \qquad 10 \text{ min}$ $R^{1} = CH_{3}, H, CI, F, OMe$ $Q_{1} \xrightarrow{\text{CH}_{3} CN, 90 \text{ °C}}_{NH_{4} OAc}$ $R = CH_{3} \text{ or } H \qquad 10 \text{ min}$ $R^{1} = CH_{3}, H, CI, F, OMe$ $R = CH_{3} \text{ or } H \qquad 10 \text{ min}$ $R^{1} = CH_{3}, H, CI, F, OMe$ $R^{1} \xrightarrow{\text{CH}_{3} CN, 90 \text{ °C}}_{NH_{4} OAc}$
 (B) Synthesis of 2-acylpyrroles:⁵ * organotin-free * no initiator required * simple and mild conditions * without the use of any toxic or hazardous reagents such as azo compounds and peroxides * tolerates the presence of both acid- and base-sensitive functional groups 	PhO_N R" R' R"' TEMPO (3 equiv.) PhCF ₃ MW, 98 °C, 30 min R' R" 12 examples, yields 51-95%
(C) Synthesis of 2,5-disubstituted 1,3,4-oxadiazole: ⁶ *broad scope * good functional group tolerance * high yields under mild conditions in the presence of O ₂	$\begin{array}{c} \begin{array}{c} \text{TEMPO (0.1 equiv.)} \\ \text{Fe(NO_3)}_3 \bullet 9H_2O (0.1 equiv.) \\ \text{Fe(NO_3)}_3 \bullet 9H_2O (0.1 equiv.) \\ \text{MgSO4 (2 equiv.), O_2 (1 atm)} \\ \text{DCE (or CH_2Cl_2), 35 °C} \end{array} \\ R^1 = aryl, thienyl, 2-napthyl, phenethyl, t-Bu, i-Bu, n-phenyl \\ R^2 = H, Me,OMe, OH, CF_3, I, Br, Cl, NO_2 \end{array} \\ \begin{array}{c} \text{R}^2 & \text{Implies} \\ \text{up to 97\% yields} \end{array}$
	$Ar \longrightarrow 0^{+} H_2N \longrightarrow R^{+} VH_2CI$ $Ar \longrightarrow H_2N \longrightarrow Ar'$ $TEMPO (1.2 equiv.)$ $FeCI_3 \bullet 7 H_2O (0.1 equiv.)$ $1,10 \text{-phen} (0.1 equiv.)$ $DMF, 120 ^{\circ}C, 12.25 \text{ h}$ $Ar \longrightarrow N$ Ar'
 (F) Synthesis of pyridines:⁹ * cascade C(sp³)-H functionalization * broad substrate scope * simple reaction conditions * excellent regioselectivity * atom economy 	$Ar \leftarrow 0 + R + R + R + R + R + R + R + R + R +$
(G) Synthesis of benzothiazoles: ¹⁰ * transition-metal-free * photosensitizer-free * base-free * compatible with a wide range of functional groups	$R = \left(\begin{array}{c} S \\ R \\ H \end{array} \right) \left(\begin{array}{c} TEMPO \left(2 \text{ equiv.} \right) \\ additive \left(0.5 \text{ mol} \% \right) \\ hv \left(45 \text{ W CFL} \right) \\ CHCl_3, r.t, 12 \text{ h} \end{array} \right) \left(\begin{array}{c} R \\ R \\ H \end{array} \right) \left(\begin{array}{c} S \\ R \\ H \end{array} \right) \left(\begin{array}{c} S \\ R \\$
 (H) Synthesis of isoxazoles:^{11a} * water as solvent and air as oxidant * transition-metal-free and base-free * no toxic byproduct and no need of solvent extraction * diverse substrate scope * excellent chemo- and regioselectivity * heterogeneous version and catalyst recyclability 	$EWG NO_{2} + \iint_{H_2O, air} \xrightarrow{H_2O, air} NO_{0} + h$ $R = CH_2OAr, aikyl, Ph, TMS, CONHMe$ $EWG = CO_2Me, CO_2Et, COPh$ $EWG = CO_2Me, CO_2Et, COPh$



* simple and mild conditions	
(J) Di- and trifluoromethoxylation: ¹³ * The first application of redoxneutral TEMPO [•] catalysis to achieve intermo- lecular di- and trifluoromethoxylation of (hetero)arenes * use of readily available and inexpensive TEMPO [•] catalyst * exhibits high functional group tolerance	$R - \underbrace{\begin{pmatrix} Arr \\ hete \end{pmatrix}}^{H} + \begin{pmatrix} R^{1} \\ N^{-} R^{2} \\ OR_{F} \end{pmatrix} \begin{pmatrix} \text{TEMPO (5-50 \text{ mol%}) \\ \text{Li}_{2}CO_{3} (1 \text{ equiv.}) \\ \text{MecN:DCE 1:1 (1 M), 60 °C} \end{pmatrix} R - \underbrace{\begin{pmatrix} Arr \\ Hete \end{pmatrix}}^{OR_{F}} OR_{F} \\ 35 \text{ examples, yields 28-84\%} \\ OR_{F} = OCF_{2}H \text{ or } OCF_{3} \end{pmatrix}$
 (K) Biomimetic aerobic oxidation of alcohols:¹⁴ * excellent yields * excellent functional group compatibility * mild reaction conditions 	$\begin{array}{ccc} & & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & &$
(L) α,β-Dehydrogenation: ¹⁵ * base-metal catalysis * broad scope: aldehyde, ketone, lactone, lactam, amine and alcohols * simple one-step reaction	$R \xrightarrow{\text{TEMPO (1 equiv.)}} R$ $R \xrightarrow{\text{FeCl}_3 (0.1 equiv.)} (1,10-\text{phen (0.1 equiv.)})$ $R \xrightarrow{\text{Cl}_3 (0.1 equiv.)} R$
(M) Oxidation from alcohols (also aldehydes) to carboxylic acids: ¹⁶ * O ₂ or air as terminal oxidant * scale-up * at ambient temperature	$R \xrightarrow{\text{TEMPO (0.1 equiv.)}}_{Fe(NO_3)_3.9H_2O (0.1 equiv.)} R \xrightarrow{\text{Fe(NO_3)_3.9H_2O (0.1 equiv.)}}_{NCI (0.1 equiv.)} R \xrightarrow{\text{OH}}_{\text{OH}} R = alkyl, CH_2OR'$
 (N) Oxidation of 1,2-diols to α-hydroxy acids:¹⁷ * chemoselective oxidation * formation of charge-transfer complex * synthesis of optically active α-hydroxy acids 	R = Ar, alkyl $R = Ar, alkyl$ $R = Ar, alky$
 (O) Aldehyde to nitrile:¹⁸ * wide substrate scope * oxidative conversion of primary alcohol to nitrile was achieved by a one-pot strategy * aerobic conditions 	R + NH ₄ OAc (2.4 equiv) AcOH, 50 °C, O ₂ NaNO ₂ (10 mol%) AcOH, 50 °C, O ₂ NaNO ₂ (10 mol%) AcOH, 50 °C, O ₂ NaNO ₂ (10 mol%) AcOH, 50 °C, O ₂
 (P) Synthesis of N-sulfinyl and N-sulfonylimines:¹⁹ * high functional group tolerance * first example of Fe-catalyzed aerobic oxidative one-pot synthesis of N-sulfinyl and N-sulfonylimines directly from alcohols 	Ar OH + H_2N R Y = SO, SO ₂ R = Ar, ¹ Bu $ \begin{array}{r} \text{4-OH-TEMPO (0.2 equiv.)} \\ \text{FeCl}_3 (0.1 equiv.) \\ \text{L-valine (0.1 equiv.)} \\ \text{O}_2 (1 \text{ atm}) \text{ toluene} \\ \text{MS 4 A}^\circ, 60 ^\circ\text{C}, 24 \text{h} \\ \text{30 examples, up to 93\% yields} \end{array} $
(Q) Dual C(sp ³)–H oxidation: ²⁰ * unprecedented tandem catalytic fashion * use of environmentally friendly reagents * selective and catalytic C(sp ³)–H oxidation	R, R' = alkyl, benzyl,allyl, Ph
 (R) Oxidative dearomatization:²¹ * metal-free oxidative dearomatization of indoles with aromatic ketones * broad substrate scope * excellent functional group tolerance 	$R + I_{H} + I_{Ar} $

19 examples, yields 62-82%



Fan and coworkers reported a unique and effective method for synthesizing 3-acylpyridines and pyridine-3-carboxylates using oxidative one-pot sequential reactions of inactivated saturated ketones with electron-deficient enamines (Table 1, F).⁹

Lang and colleagues successfully accomplished intramolecular C(sp²)–H thiolation driven by visible light without the need of a photosensitizer, metal catalyst, or base. Thiobenzanilides undergo cyclization to become benzothiazoles as a result of this reaction. The substrate absorbs visible light, and when its excited state interacts with 2,2,6,6-tetramethylpiperidine N-oxyl, a reverse hydrogen-atom transfer (RHAT) occurs, resulting in the formation of a sulfur radical (Table 1, G).¹⁰ The aryl radical produced by the addition of the sulfur radical to the benzene ring rearomatizes into benzothiazole via RHAT. The research team of Praveen was able to successfully synthesize isoxazole/isoxazoline derivatives using the Machetti-De Sarlo reaction under environmentally friendly circumstances (Table 1, H).^{11a} In this process, primary nitroalkanes are cyclocondensed with alkynes or alkenes using the commonly available catalyst TEMPO to produce a library of isoxazole/isoxazoline derivatives.

By using homogeneous gold catalysis and 4-MeO-TEM-PO as an oxidant, Song et al. established a quick method for producing 5-oxazole ketones.^{11b} Under benign circumstances, the required 5-oxazole ketones were produced in respectable yields with excellent functional group compatibility. Han and colleagues developed a brand-new, metalfree, and regioselective method for the synthesis of isoxazoline/cyclic nitrone featured methylenes by using TEMPO to react with readily available β_{γ} and $\gamma_{\gamma}\delta$ -unsaturated ketoximes via tandem iminoxyl radical promoted cyclization and Cope-like elimination, respectively.^{11c} In this approach, the Cope-like elimination was carried out using the commercially available TEMPO as both the hydrogen acceptor and the iminoxyl radical initiator. By using readily available Narylmethyl-2-aminophenylketones as the starting point, Long and coworkers developed a novel, metal-free oxidative intramolecular Mannich reaction between secondary amines and unmodified ketones. This reaction uses TEMPO as the oxidant and KOt-Bu as the base to provide a straightforward and direct route to a variety of 2-arylquinolin-4(1H)-ones (Table 1, I).¹² The first TEMPO'-catalyzed, redoxneutral C-H di- and trifluoromethoxylation of (hetero)arenes is reported by Ngai and his research team (Table 1, J).¹³ The oxidation of alcohols to carbonyl compounds with dioxygen was discovered to be facilitated by a new mixture of FeCl₃, L-valine, and TEMPO. The production of aldehydes and ketones from a variety of primary/secondary benzyl, allylic, and heterocyclic alcohols was accomplished with good to exceptional isolated yields (Table 1, K).¹⁴

Kang et al. established an iron-catalyzed α , β -dehydrogenation of carbonyl compounds. In a straightforward onestep reaction with good yields, a wide range of carbonyls or analogues, including aldehyde, ketone, lactone, lactam, amine, and alcohol, could be transformed into their α , β -unsaturated equivalents (Table 1, L).¹⁵ By using a catalytic

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amount of each of Fe(NO₃)₃·9H₂O/TEMPO/KCl, a series of carboxylic acids were produced from alcohols (also known as aldehydes) in high yields at room temperature (Table 1, M), demonstrating the effectiveness and applicability of the sustainable oxidation technology developed by Ma and colleagues.¹⁶ Shibuya and colleagues succeeded in achieving chemoselective catalytic oxidation of 1,2-diols to α -hydroxy acids in a cat. TEMPO/cat. NaOCl/NaClO₂ system. Hydrophobic toluene and water were used to create a two-phase situation, which reduced the accompanying oxidative cleavage (Table 1, N).¹⁷ For the manufacture of nitrile, the first aldehvde to nitroxyl radical/NOx system catalyzed aerobic oxidative conversion without the use of transition metals was presented. By using a one-pot sequential approach, it was also possible to convert a primary alcohol into an aldehyde via aerobic oxidation (Table 1, O).¹⁸ For the oxidation of alcohols followed by condensation with sulfinamide or sulfonamide in one pot for the production of N-sulfinvl and Nsulfonylimines compounds under benign circumstances, an effective Fe(III), L-valine, and 4-OH-TEMPO catalytic system was identified (Table 1, P).¹⁹

A new environmentally friendly protocol for the selective and catalytic TEMPO C(sp³)-H oxidation of piperazines and morpholines to 2,3-diketopiperazines (2,3-DKP) and 3morpholinones (3-MPs), respectively, was developed using inexpensive and safe reagents like NaClO₂, NaOCl, and catalytic amounts of TEMPO (Table 1, Q).²⁰ Further functionalization at the C-2 position of the morpholine skeleton is possible by preparing 2-alkoxyamino-3-morpholinone from morpholine derivatives by varying the quantities of TEMPO. Liu and colleagues (Table 1, R) described a metalfree oxidative dearomatization of indoles with aromatic ketones through the use of TEMPO oxoammonium salt.²¹ In the presence of H₂SO₄, the dearomatization went without a hitch and demonstrated a broad substrate range with respect to both indoles and aromatic ketones, producing the matching 2,2-disubstituted indolin-3-ones in good yields. A completely metal-free catalyst system was created for the selective aerobic oxidation of structurally varied benzylic C(sp³)–H bonds of ethers and alkylarenes. It consists of a novel, easily manufactured, recyclable sulfonic salt catalyst formed from TEMPO and mineral acids (NaNO₂ and HCl). From easily available alkyl aromatic precursors, the mild reaction conditions enable the production of physiologically and synthetically valuable isochromanones and xanthones in good yields (Table 1, S).²² Cu/nitroxyl catalysts that support mild reaction conditions and extremely efficient and selective aerobic oxidative lactonization of diols using ambient air as the oxidant have been found. By altering the nitroxyl cocatalyst's identity, the chemo- and regioselectivity of the reaction may be adjusted. While a Cu/TEMPO catalyst system exhibits excellent chemo- and regioselectivity for the oxidation of less hindered unsymmetrical diols, a Cu/ABNO catalyst system (ABNO = 9-azabicyclo[3.3.1]nonan-N-oxyl) exhibits excellent reactivity with symmetrical diols and hindered unsymmetrical diols (Table 1, T).²³ Using TEMPO as the organo-electrocatalyst, Lei et al. effectively created the first electrochemical acceptorless dehydrogenation (ECAD) of *N*-heterocycles. Under an undivided cell system, they were able to catalyze the dehydrogenation of *N*-heterocycles in the anode and release H₂ from the cathode. In this system, a variety of five- and six-membered nitrogen-heteroarenes may be synthesized with high yields (Table 1, U).²⁴ Shen and Lu described an effective method for producing alkenylboronates by copper catalysis. Starting with cheap and plentiful alkenes and pinacol diboron, the Cu/TEMPO catalytic system demonstrated high reactivity and selectivity for the production of alkenylboronates (Table 1, V).²⁵

Neutral polysaccharides have been subjected to TEMPO oxidation to produce polyuronides with enhanced functional characteristics.²⁶ The redox-active TEMPO fragment is a common element in organic systems due to its advantages, which include outstanding electrochemical performance and respectable physical characteristics, which allow it to be employed as an energy source in batteries or supercapacitors.²⁷ Lung cancer cells are killed off by the photochemical production of the TEMPO radical from caged nitroxides by near-infrared two-photon irradiation.²⁸ In the end, it has been revealed that TEMPO has numerous uses in organic synthesis, catalysis, material science, and biological applications. In accordance with the most recent TEMPO research, this reagent's full synthetic potential has not yet been realized.

Conflict of Interest

The authors declare no conflict of interest.

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