An efficient procedure for the TEMPO-catalyzed oxidation of alcohols to aldehydes and ketones using ferric chloride hexahydrate as terminal oxidant

R. Senthil Kumar, K. Karthikeyan, and Paramasivan T. Perumal

Abstract: A simple, efficient procedure for the oxidation of alcohols by catalytic 2,2,6,6-tetramethyl-piperidyl-1-oxy (TEMPO) was developed using $FeCl_3 \cdot 6H_2O$ as the terminal oxidant. The reaction gives high yield of the corresponding aldehydes and ketones with no over oxidation to the acid.

Key words: oxidation, TEMPO, $FeCl_3 \cdot 6H_2O$.

Résumé : On a développé une méthode simple et efficace d'oxydation catalytique 2,2,6,6-tetramethyl-piperidyl-1-oxy (TEMPO) d'alcools faisant appel au $FeCl_3 \cdot 6H_2O$ comme oxydant terminal. La réaction donne des rendements élevés des aldéhydes et des cétones correspondants sans suroxydation vers l'acide.

Mots-clés : oxydation, TEMPO, $FeCl_3 \cdot 6H_2O$.

[Traduit par la Rédaction]

Introduction

Oxidation of alcohols to aldehydes and ketones is one of the important synthetic transformations that is widely employed in various simple and complex syntheses of organic compounds (1). Therefore, it is not suprising to note a number of new oxidants emerge in the literature claiming superiority over the others in terms of cost, ready availability, selectivity, and yield. These factors assume importance especially when the oxidations are performed on a larger scale. Traditional oxidants, mainly inorganic in nature, include CrO_3, $KMnO_4$, MnO_2, SeO_2, and so forth. Moreover, the derivatives of chromium based oxidants, like PCC (2) and PDC (3) that are still in use, are often required in excess stoichiometric amounts and hence result in considerable amount of chromium waste by-products. Also, since these reagents are used in two- or three-fold excess of the substrate, the cost factor also needs to be addressed.

The nitroxyl radical, 2,2,6,6-tetramethyl-piperidyl-1-oxy (TEMPO), is a stable free radical employed in various oxidations of primary and secondary alcohols (4). However, owing to the high cost of TEMPO, most protocols employ it in catalytic amount together with a stoichiometric re-oxidant. Examples include TEMPO with $NaIO_4$ (5), I_2 (6), NBS (7), polyoxometalate (8), hypochlorite (9), Oxone (10), oxygen, or air (11*a*–11*c*). Derivatives of TEMPO, such as 4-hydroxy TEMPO, 4-acetamido TEMPO, have also been reported (11*d*). Not only TEMPO oxidations were carried out in ionic liquids (12*a*) but also a task-specific TEMPO derived ionic liquid was developed (12*b*). To achieve facile separation of product from TEMPO, solid supported reagents like silica-supported TEMPO (13) and polyamine immobilized piperidinyl oxyl (PIPO) (14) were developed owing to their heterogeneous nature; they can be separated by simple filtration.

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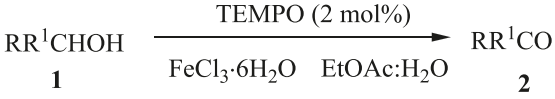
Scheme 1. Oxidation of primary and secondary alcohols with TEMPO/$FeCl_3 \cdot 6H_2O$.



R = alkyl, H
R^1 = alkyl, aryl

Results and discussion

The development of new terminal oxidants for TEMPO-mediated oxidations still continues to be an interesting area of research. The use of ferric chloride hexahydrate for its oxidising properties has been reported only in a few instances, including one by us (15). In continuing our interest in ferric chloride hexahydrate oxidation, we supposed that it could act as terminal oxidant in the TEMPO oxidation of alcohols (Scheme 1).

Accordingly, reaction of benzyl alcohol with catalytic TEMPO and stoichiometric ferric chloride hexahydrate was conducted at room temperature in CH_2Cl_2/H_2O as solvent. The reaction proceeded smoothly giving 75% of benzal-

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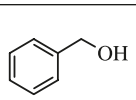
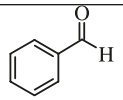
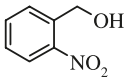
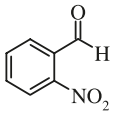
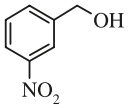
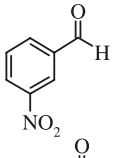
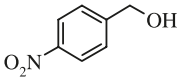
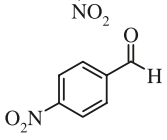
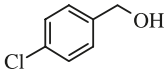
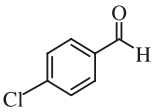
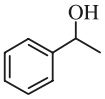
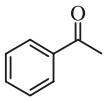
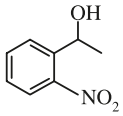
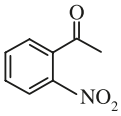
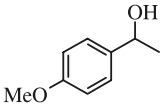
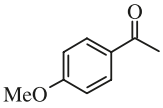
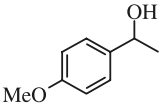
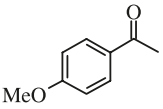
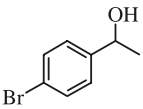
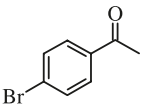
Table 1. Oxidation of alcohols by TEMPO/$FeCl_3 \cdot 6H_2O$

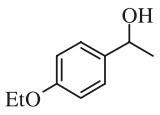
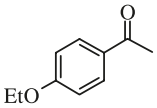
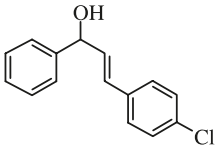
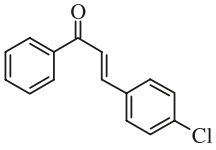
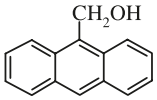
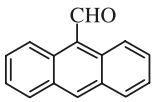
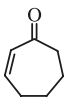
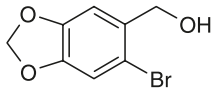
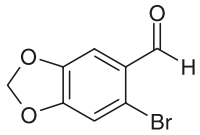
Entry	Alcohol	Aldehyde/Ketone	Time (hours)	Yield[a] (%)
1			6	90
2			8	85
3			8	68
4			6	88
5			3	80
6			10	95
7			10	96
8			5	96
9			5	98[b]
10			5	85

dehyde with no over oxidation to benzoic acid. Increasing the stoichiometry of $FeCl_3 \cdot 6H_2O$ to 1.30 equiv. increased the yield to 90%. Also, EtOAc/H_2O solvent system was found to give better result than CH_2Cl_2/H_2O. Various primary and secondary alcohols were oxidized to the corresponding aldehydes and ketones in good yield using this protocol (Table 1). 1-Phenyl ethanol gave 95% yield of acetophenone. Similarly, 4-methoxy-1-phenyl ethanol gave the corresponding acetophenone derivative in very good yield. Reaction of 9-anthryl alcohol at room temperature was incomplete; however, on refluxing conditions, it gave quantitative yield of 9-anthraldehyde. Additives like NaBr or NaOAc had no substantial effect (Table 1, entry 9). Similarly, 2-cyclopentenol, 2-cyclohexenol, and 2-cycloheptenol were oxidized to the corresponding ketones in good yield. In all cases, little or no oxidation was observed in the absence of TEMPO.

Oxidation of pyrazolyl alcohols

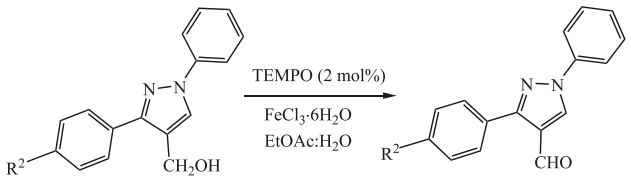
Pyraxzolyl aldehydes are important precursors for various pyrazole compounds, such as bispyrazolylmethane (16) and pyrazolyl quinolines (17) that display useful biological properties. Pyrazolyl alcohol and its substituted derivatives were oxidized to the corresponding pyrazolyl aldehyde using this protocol in good yield. (Scheme 2, Table 2).

Table 1 (*concluded*)**.**

Entry	Alcohol	Aldehyde/Ketone	Time (hours)	Yield[a] (%)
11			5	95
12			3	80
13			1	98[c]
14			1.5	90
15			2	80
16			2	78
17			3	75[c]

[a]Isolated yields.
[b]NaBr and NaOAc (0.5 equiv.) were added.
[c]Under reflux condition.

Scheme 2. Oxidation of pyrazolyl alcohols by TEMPO/$FeCl_3 \cdot 6H_2O$.



Conclusion

In sumary, a protocol for the efficient oxidation of various primary and secondary alcohols was developed using catalytic TEMPO and $FeCl_3 \cdot 6H_2O$ as co-oxidant. The procedure is operationally simple, as it requires no dry solvent or inert atmosphere and economical, as it employs the low cost $FeCl_3 \cdot 6H_2O$ in stoichiometric amount. Also, since the aldehydes and ketones are obtained in good to excellent yield, we hope this protocol will have good application in organic synthesis.

Table 2. Oxidation of pyrazolyl alcohols by TEMPO/$FeCl_3 \cdot 6H_2O$.

Entry	R^2	Product	Time (h)	Yield (%)
1	H	4a	4	85
2	Br	4b	4.5	50
3	Cl	4c	4	65
4	OEt	4d	5	60

Experimental

Materials and general

All chemicals were purchased from s.d. fine-chem ltd. and Spectrochem. All melting points are uncorrected. ^{1}H and

^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 using TMS as an internal standard on a JEOL spectrometer at 500 MHz and 125 MHz, respectively. Mass spectra were recorded on a Thermo Finnigan LCQ Advantage MAX 6000 ESI spectrometer. Column chromatography was performed on silica gel (100–200 mesh, SRL, India). Analytical TLC was performed on precoated aluminium sheets of silica gel G/UV-254 of 0.2 mm thickness (Merck, Germany).

Representative procedure for oxidation of primary and secondary alcohols to aldehydes and ketones

To 1.30 mmol of 3-(4-chlorophenyl)-1-phenylprop-2-en-1-ol in ethylacetate/water (7:3) (10 mL) was added TEMPO (0.02 equiv.), and the reaction mixture was stirred at room temperature. After 5 min, $FeCl_3 \cdot 6H_2O$ (1.69 mmol) was added, and stirring continued, following the progress of the reaction by TLC. After completion of the reaction, ethyl acetate layer was separated, and the aqueous layer was extracted with ethyl acetate (3 × 3 mL). Organic layers were combined and dried with sodium sulphate, filtered, and concentrated under reduced pressure.The residue thus obtained was purified by column chromatography to obtain the (2*E*)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one.

Benzaldehyde (100–52–7)

Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.49 (t, *J* = 7.7 Hz, 2H), 7.59 (t, *J* = 6.9 Hz, 1H), 7.84 (d, *J* = 7.7 Hz, 2H), 9.98 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 129.08, 129.81, 134.56, 136.45, 192.52. MS *m*/*z* = 106 M^+.

2-Nitrobenzaldehyde (552–89–6)

White solid (toluene/petroleum ether); mp 43 °C (lit. (18) 43–44 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.73–7.78(m, 2H), 7.91 (d, *J* = 9.5 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 10.38 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 124.58, 129.71, 131.40, 133.84, 134.21, 149.63, 188.29. MS *m*/*z* = 151 M^+.

3-Nitrobenzaldehyde (99–61–6)

Yellow solid (toluene/petroleum ether); mp 56 °C (lit. value (18) 58 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.76 (t, *J* = 8.4 Hz, 1H), 8.22 (d, *J* = 7.5 Hz, 1H), 8.47 (d, *J* = 7.0 Hz, 1H), 8.69 (d, *J* = 1.5 Hz, 1H), 10.11 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 124.53, 128.69, 130.51, 134.80, 137.45, 148.83, 189.90. MS *m*/*z* = 151 M^+.

4-Nitrobenzaldehyde (555–16–8)

Pale yellow solid (ethyl acetate/petroleum ether); mp 105 °C (lit. value (19) 104–106 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.06 (d, *J* = 8.4 Hz, 2H), 8.36 (d, *J* = 8.4 Hz, 2H), 10.14 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 124.38, 130.58, 140.13, 151.18, 190.49. MS *m*/*z* = 151 M^+.

4-Chlorobenzaldehyde (104–88–1)

White solid (petroleum ether); mp 45 °C (lit. (19) 45–46 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.49 (d, *J* = 8.6 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 9.95 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 129.53, 130.99, 134.77, 141.02, 190.97. MS *m*/*z* = 141 M^+.

Acetophenone (98–86–2)

Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.56 (s, 3H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.92 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 26.69, 128.38, 128.66, 133.21, 137.16, 198.30. MS *m*/*z* = 120 M^+.

2-Nitroacetophenone (577–59–3)

Yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.51 (s, 3H), 7.41 (dd, *J* = 1.5, 7.6 Hz, 1H), 7.55–7.58 (m, 1H), 7.69 (dt, *J* = 1.5, 7.6 Hz, 2H), 8.02 (d, *J* = 8.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 30.18, 124.40, 127.43, 130.81, 134.37, 137.88, 145.82, 200.00. MS *m*/*z* = 165 M^+.

4-Methoxyacetophenone (100–06–1)

Colourless solid (petroleum ether); mp 36 °C (lit. (18) 38–39 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.56 (s, 3H), 3.87 (s, 3H), 6.94 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 26.48, 56.62, 113.84, 127.42, 130.72, 163.60, 196.92. MS *m*/*z* = 150 M^+.

4-Bromoacetophenone (99–90–1)

White solid (petroleum ether); mp 51 °C (lit. (20) 51–52 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.58 (s, 3H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 26.64, 128.40, 129.93, 131.99, 135.91, 197.14. MS *m*/*z* = 198 M^+.

4-Ethoxyacetophenone (1676–63–7)

Colourless solid (petroleum ether); mp 39 °C (lit. (18) 36–37 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.42 (t, *J* = 6.9 Hz, 3H), 2.56 (s, 3H), 4.08 (q, *J* = 6.9 Hz, 2H), 6.90 (d, *J* = 9.1 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 14.75, 26.42, 63.83, 114.19, 130.22, 130.68, 163.00, 196.90. MS *m*/*z* = 164 M^+.

(2E)-3-(4-Chlorophenyl)-1-phenylprop-2-en-1-one

White solid (absolute ethanol); mp 110 °C (lit. (21) 111–113 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.48 (d, *J* = 6.9 Hz, 2H), 7.53 (t, *J* = 6.9 Hz, 2H), 7.63 (t, *J* = 6.9 Hz, 1H), 7.70 (d, *J* = 16.0 Hz, 1H), 7.88–7.94 (m, 3H), 8.12 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 123.27, 129.11, 129.33, 129.48, 131.13, 133.77, 134.15, 135.66, 137.96, 143.07, 189.60. MS *m*/*z* = 243 M^+. Anal. calcd. for $C_{15}H_{11}ClO$ (242.70): C, 74.23; H, 4.57; Cl, 14.61. Found: C, 74.28; H, 4.52; N, 14.69.

9-Anthraldehyde (642–31–9)

Yellow solid; (aq. acetic acid); mp 104 °C (lit. (18) 104–105 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.54 (t, *J* = 6.9 Hz, 2H), 7.67 (t, *J* = 7.6 Hz, 2H), 8.04 (d, *J* = 8.4 Hz, 2H), 8.66 (s, 1H), 8.97 (d, *J* = 9.2 Hz, 2H), 11.50 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 123.62, 124.77, 125.79, 129.23, 129.38, 131.15, 132.22, 135.35, 193.12. MS *m*/*z* = 206 M^+.

2-Cyclohexenone (930–68–7)

Brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.90–1.95 (m, 2H), 2.24–2.28 (m, 2H), 2.31–2.34 (m, 2H), 5.90–5.92 (m, 1H), 6.89–6.93 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 22.73, 25.69, 38.10, 129.85, 150.92, 199.86. MS *m*/*z* = 96 M^+.

2-Cycloheptenone (1121–66–0)

Pale brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.74–1.79 (m, 4H), 2.38–2.42 (m, 2H), 2.53–2.56 (m, 2H), 5.95 (d, J = 12.2 Hz, 1H), 6.50–6.55 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 21.78, 26.19, 30.31, 43.59, 132.55, 146.67, 204.53. MS m/z = 110 M^+.

2-Cyclopentenone (930–30–3)

Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.20–2.22 (m, 2H), 2.56–2.59 (m, 2H), 6.05–6.06 (m, 1H), 7.62–7.63 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 28.97, 33.99, 134.46, 165.11, 210.61. MS m/z = 82 M^+.

6-Bromopiperonal (15930–53–7)

White solid (absolute ethanol); mp 128 °C (lit. (22) 132–135 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 6.17 (s, 2H), 7.22 (d, J = 1.5 Hz, 1H), 7.35 (d, J = 1.5 Hz, 1H), 10.00 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 103.85, 107.92, 113.77, 121.25, 127.88, 148.62, 153.97, 190.51. MS m/z = 228 M^+.

Representative procedure for oxidation of pyrazolyl alcohol

To 1.30 mmol of pyrazolyl alcohol in ethylacetate:water (7:3) (10 mL) was added TEMPO (0.02 equiv.), and the reaction mixture was stirred at room temperature. After 5 min, $FeCl_3 \cdot 6H_2O$ (1.69 mmol) was added, and the stirring continued, following the progress of the reaction by TLC. After completion of the reaction, ethyl acetate layer was separated from water, and water layer was extracted with ethyl acetate (3 × 3 mL). Organic layers were combined and dried with sodium sulphate, filtered, and concentrated at reduced pressure. The residue thus obtained was purified by column chromatography to obtain the pyrazole aldehyde.

1,3-Diphenyl-1*H*-pyrazole-4-carbaldehyde (4a)

Yellow solid (absolute ethanol); mp 138 °C (lit. (23) 140 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.37 (t, J = 7.5 Hz, 1H), 7.47–7.49 (m, 5H), 7.78 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 6.8 Hz, 2H), 8.53 (s, 1H) 10.03(s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 119.82, 122.58, 128.06, 128.87, 129.07, 129.41, 129.77, 131.16, 131.42, 139.07, 154.85, 185.32. MS m/z = 248 M^+.

3-(4-Bromophenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (4b)

Pale green solid (absolute ethanol); mp 140 °C (lit. (24) 142–143 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.76 (t, J = 7.6 Hz, 4H), 8.52 (s, 1H) 10.02(s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 119.83, 122.57, 123.83, 128.23, 129.84, 130.37, 130.54, 131.99, 132.13, 138.96, 153.31, 184.5. MS m/z = 326 M^+.

3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (4c)

Yellow solid (absolute ethanol); mp 114 °C (lit. (25) 110–113 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.39 (t, J = 7.5 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.50 (t, J = 7.5 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 8.51 (s, 1H), 10.01 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 119.80, 122.56, 128.20, 129.01, 129.82, 129.93, 130.28, 132.18, 135.51, 138.95, 153.24, 184.57. MS m/z = 282 M^+.

3-(4-Ethoxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (4d)

Yellow solid (absolute ethanol); mp 142 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.44 (t, J = 6.8 Hz, 3H), 4.10 (q, J = 6.8 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 7.37 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.77 (t, J = 2.3 Hz, 4H), 8.51 (s, 1H), 10.03 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 14.89, 63.66, 114.81, 119.80, 122.42, 123.73, 127.95, 129.75, 130.33, 131.19, 139.14, 154.69, 160.02, 185.35. MS m/z = 292 M^+. Anal. calcd. for $C_{18}H_{16}N_2O_2$ (292.33): C, 73.95; H, 5.52; N, 9.58. Found: C, 73.86; H, 5.56; N, 9.69.

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