SHORT PAPER

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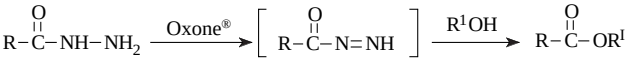
An efficient and selective conversion of hydrazides into esters and acids†

R. Srinivas, B.V. Subba Reddy, J.S. Yadav and T. Ramalingam*

Organic Chemistry Division-I, Indian Institute of Chemical Technology, Hyderabad-500 007, India

Hydrazides are selectively oxidised to esters/acids in high yields using Oxone® in the presence of an appropriate alcohol/water as a nucleophile at ambient temperature. A variety of functional groups including alkenes, alcohols, ethers, cyclopropyl groups and nitriles are unaffected.

Hydrazides are versatile intermediates for various transformations in organic synthesis.[1] Several hydrazides have been used for the synthesis of variety of heterocycles.[2] A variety of oxidising agents[3,4] have been used for the conversion of hydrazides into the corresponding acids, but with the formation of undesired side products along with the expected esters/acids. Sodium hexanitrocobaltate(III)[5] – catalysed oxidation of hydrazides leads to the formation of acyl azides rather than esters/acids. Recently thallium(III) nitrate trihydrate[6] (TTN), ceric(IV) ammonium nitrate[7] (CAN) and iodobenzene diacetate[8] have been reported for the oxidation of hydrazides to esters / acids. However, most of the methods for this transformation have several limitations, such as the reagents used are often toxic, expensive, hazardous and incompatible with other functional groups present in the substrate. In order to circumvent some of the problems associated with earlier methods, a mild and efficient method is still needed for this transformation.



R = aryl, aryloxyalkyl, benzyl, cyclopropyl and aliphatic, R^1 = H, alkyl.

Scheme 1

In recent years, Oxone® ($2KHSO_5.KHSO_4.K_2SO_4$) has been found to be an effective oxidant for various transformations[9] which include olefins to epoxides, sulfides to sulfoxides, Bayer-Villiger oxidation of ketones, aldehydes to acids and amines to nitro compounds. Although Oxone® is a well known oxidant for various transformations, it has not yet been explored for the oxidative conversion of hydrazides into esters/acids. Herein we report for the first time a new application of Oxone® for the oxidative conversion of hydrazides into corresponding esters/acids in high yield at room temperature. The reaction of hydrazides with an appropriate nucleophile, *viz*. alcohol or water, in presence of Oxone® resulted in the formation of the corresponding esters/acids. The reaction proceeds readily at room temperature by using a 1.5 mole ratio of Oxone® to hydrazide in the presence of alcohol/water.

A variety of hydrazides carrying aromatic, aliphatic and aryloxyalkyl moieties were treated with Oxone® in anhydrous methanol, ethanol, isopropanol and *t*-butanol, whereby the corresponding esters were isolated in high yields. Similarly, acids were isolated when water was used as a nucleophile. The results summarised in the Table indicate the generality of the reaction for various substituted aromatic, aliphatic and aryloxyalkyl hydrazides. Even though, the oxidation of sulfides, olefins and ketones with Oxone® has been reported, the hydrazides bearing these groups remained intact under the present reaction conditions.

In conclusion, we have described a mild and efficient method for the conversion of hydrazides into esters/acids using Oxone® in the presence of alcohols and water, respectively. The method adopted is economically viable, eco-friendly, high-yielding and involves a simple experimental procedure which may find application in organic synthesis.

Experimental

General Procedure for the preparation of esters: The hydrazide (5 mmol) and Oxone® (7.5 mmol) in dry methanol (15 ml) were stirred at room temperature for 3–8 h. After complete conversion as indicated by TLC, the reaction mixture was diluted with water and extracted with DCM. The organic layer was washed with aq. $NaHCO_3$ solution, dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to give crude product, which was purified by column chromatography on silica gel to afford pure ester.

General procedure for the preparation of acids: The hydrazide (5 mmol), water (15 ml), sodium bicarbonate (35 mmol) and acetone (5 ml) were stirred at room temperature for 10 min. To the reaction mixture, Oxone® (7.5 mmol) in aqueous EDTA (4×10^{-4} M, 50 ml) solution was added dropwise, keeping the temperature below 2°C. After complete conversion as indicated by TLC, the reaction mixture was quenched with sodium bisulfite, acidified with 3N HCl and extracted with ethyl acetate. The organic layer was washed with brine and dried over Na_2SO_4. Removal of the solvent *in vacuo* gave the acid product.

Spectroscopic data for t-butyl α-(4-chlorophenoxy)propionate (h): ^{1}H NMR ($CDCl_3$): δ 1.40 (s, 9H), 1.70 (d, 3H, *J*=7.0Hz), 4.90 (q, 1H, *J*=7.0Hz), 6.90 (d, 2H, *J*=8.0Hz), 7.30 (d, 2H, *J*=8.0Hz). Anal. Calcd. For $C_{13}H_{17}ClO_3$: C, 60.82; H, 6.68; Cl, 13.81. found: C, 60.90; H, 6.70; Cl, 13.76.

Methyl 2-decenoate (i): ^{1}H NMR ($CDCl_3$) : δ 0.8 (t, 3H, *J* = 7.8 Hz), 1.4 (m, 8H), 1.6 (m, 2H), 2.4 (m, 2H), 3.75 (s, 3H), 5.8 (d, 1H, *J* = 16.7 Hz), 6.95 (m, 1H). Anal. calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.93. found : C, 71.52; H, 10.90.

Isopropyl octadecanoate (j): ^{1}H NMR ($CDCl_3$): δ 0.85 (t, 3H, *J*=6.8Hz), 1.25 (d, 6H, *J*=6.8Hz), 1.40 (m, 28H), 1.60 (m, 2H), 2.30 (t, 2H, *J*=6.8Hz), 3.75 (m, 1H). Anal. calcd. for $C_{21}H_{42}O_2$: C, 77.24; H, 12.96. found : C, 77.35; H, 12.98.

Methyl 10-undecenoate (k): ^{1}H NMR ($CDCl_3$) : δ 1.35 (m, 10H), 1.65 (m, 2H), 2.05 (m, 2H), 2.30 (t, 2H, *J* = 7.8 Hz), 3.75 (s, 3H), 5.0 (m, 2H), 5.85 (m, 1H). Anal. calcd. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. found : C, 72.05; H, 11.12.

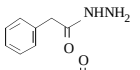
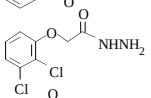
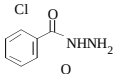
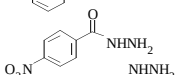
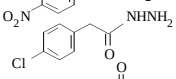
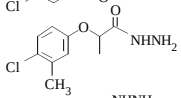
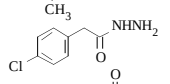
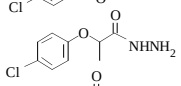
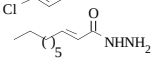
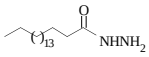
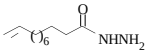
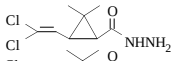
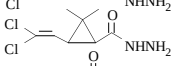
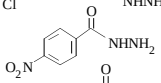
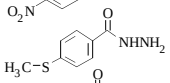
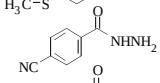
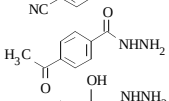
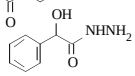
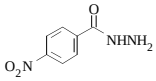
Methyl 2, 2-dimethyl-3-dichlorovinylcyclopropane-1-carboxylate (l): Cis isomer: ^{1}H NMR ($CDCl_3$) : δ 1.27 (s, 6H), 1.80 (d, 1H, *J* = 8.3 Hz), 2.0 (t, 1H, *J* = 8.3 Hz), 3.65 (s, 3H), 6.28 (d, 1H, *J* = 8.3 Hz). *Trans* isomer : ^{1}H NMR ($CDCl_3$) : δ 1.23 (s, 6H), 1.61 (d, 1H, *J* = 5.5 Hz), 2.22 (m, 1H), 3.67 (s, 3H), 5.6 (d, 1H, *J* = 8.3 Hz). Anal. calcd. for $C_9H_{12}Cl_2O_2$: C, 48.45; H, 5.42; Cl, 31.78. found : C, 48.23; H, 5.38; Cl, 31.70.

2,2-Dimethyl-3-dichlorovinylcyclopropane-1-carboxylic acid (m) : Cis isomer: ^{1}H NMR ($CDCl_3$) : δ 1.28 (s, 6H), 1.83 (d, 1H, *J* = 8.3 Hz), 2.04 (t, 1H, *J* = 8.3 Hz), 6.25 (d, 1H, *J* = 8.3 Hz), 11.62 (brs, COOH). *Trans* isomer : ^{1}H NMR ($CDCl_3$) : δ 1.25 (s, 6H), 1.65 (d, 1H, *J* = 5.5 Hz), 2.25 (m, 1H), 5.6 (d, 1H, *J* = 8.3 Hz), 11.65 (brs, COOH). Anal. calcd. for $C_8H_{10}Cl_2O_2$: C, 45.96; H, 4.82; Cl, 33.9. found : C, 45.91; H, 4.68; Cl, 33.72.

* To receive any correspondence.

† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Conversion of hydrazides into esters/acids

Entry	Substrate	Nucleophile	Reaction time (h)[a]	Yield (%)[b]	M.p or B.p. (torr) °C Obs./ Reported[10]
a		MeOH	5	90	214–216/215 (760)
b		EtOH	4	76	134–137/130–140 (0.2)
c		i-PrOH	6	72	217–219/218–219 (760)
d		H_2O	7	90	237–238/236–239
e		MeOH	6	88	114–116/114–115 (6)
f		H_2O	6	75	94–96/95-96
g		MeOH	5	87	112–114/114–118 (6)
h		t-BuOH	4	71	Semi solid
i		MeOH	3	78	92–98/93–100 (14)
j		i-PrOH	3	82	Semi solid
k		MeOH	4	81	245–247/248 (760)
l		MeOH	4	83	Liquid
m		H_2O	4	88	90–92/90–91
n		MeOH	6	84	94–95/96
o		MeOH	8	78	81–83/82
p		MeOH	7	81	61–63/62
q		MeOH	6	80	95–97/95.5
r		MeOH	5	75	57–59/59
s		i-PrOH	7	78	109–111/110

[a] Reaction time after the addition of the hydrazide to the reaction mixture.

[b] Yields of isolated products.

Methyl 4-(methylthio)benzoate (o) : ^{1}H NMR ($CDCl_3$) : δ 2.4 (s, 3H), 3.90 (s, 3H), 7.35 (d, 2H, *J* = 8 Hz), 8.0 (d, 2H, *J* = 8 Hz). Anal. calcd. for $C_9H_{10}O_2S$: C, 59.31; H, 5.53. found : C, 59.29; H, 5.51.

Methy 4-(acetyl) benzoate (q) : ^{1}H NMR ($CDCl_3$) : δ 2.35 (s, 3H), 3.85 (s, 3H), 7.25 (d, 2H, *J* = 8 Hz), 8.05 (d, 2H, *J* = 8 Hz). Anal. calcd. for $C_{10}H_{10}O_3$: C, 67.40; H, 5.65. found : C, 67.15; H, 5.59.

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