SHORT PAPER

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A simple and efficient oxidation of hydrazides to N,N′-diacylhydrazines using Oxone® in an aqueous medium

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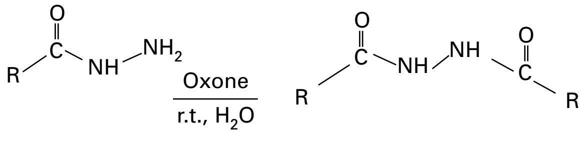
Substituted aromatic hydrazides have been oxidised to N,N′-diacylhydrazines in high yields using Oxone in an aqueous medium at room temperature.

N,N′-Diacylhydrazines are important starting materials in heterocyclic chemistry[1] especially for the preparation of 2,5-diaryl-1,3,4-oxadiazoles. They have been prepared earlier by oxidation of corresponding hydrazides with lead tetraacetate,[2a] halogens,[2b] diphenyl selenoxide,[2c] benzene seleninic acid,[2d] aryl sulfonyl peroxides,[2e] polymer supported periodate ion[2f], iodobenzene diacetate in organic solvents[2g,h] and in dry media[2i] and very recently using sodium perborate.[2j] All these methods require either expensive reagents, organic solvents or tedious workup procedures limiting their practical utility. In the light of ever increasing environmental concern about today's chemical research, attempts are on to perform the reactions in an aqueous medium.[3,4] We wish to report here the oxidation of hydrazides to N,N′-diacyl hydrazines using Oxone in an aqueous medium.

Oxone is a stable ternary composite of $KHSO_5$, $KHSO_4$ and K_2SO_4 in 2:1:1 molar ratio. Its oxidative property (E^O = 1.44 V) is closely related to conventional peracids and has found extensive applications in synthetic organic chemistry. Oxone has been used in reactions involving oxygen transfer such as epoxidation of alkenes[5a–c] and of allylic alcohols,[6] Baeyer Villiger type lactonization,[7] oxidation of sulfides to sulfoxides and sulfones,[8a,b] of selenides to selenones[9] and of s-alcohols.[10] In addition, the generation of carbonyl compounds from thioketals[11] as well as oximes,[12] preparation of nitroalkanes from oximes[13] and amines,[14] esters from acetals,[15] ketones from hydrocarbons,[16] aldehydes from nitriles,[17] α,ω-dicarboxylic acids from nitroalkanones[18] and oxidative Nef reaction[19] are a few of the striking applications of Oxone. The versatility of Oxone as a powerful oxidant prompted us to test it for the oxidation of hydrazides to N,N′-diacylhydrazines, essential in our ongoing programme towards the synthesis of oxadiazoles.



1 **2**

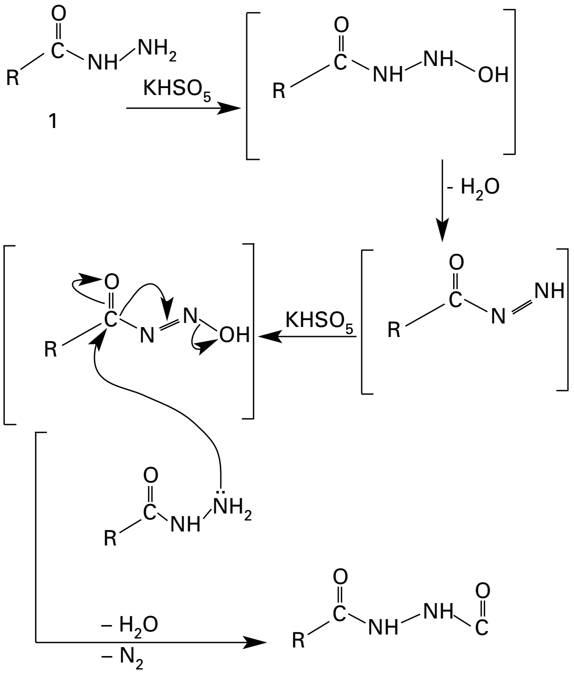
Scheme 1

Various substituted aromatic hydrazides **1** on stirring with 1 mole equivalent of Oxone in an aqueous medium furnished corresponding N,N′-diacylhydrazines **2** in high yields and excellent purity (Scheme 1).[20] All oxidation reactions were complete within 30 min. (Table 1) The resultant N,N′-diacylhydrazines, being insoluble in water, separate out as the reaction proceeds allowing the product to be separated merely by filtration. Although all hydrazides are practically insoluble in water, when added to the solution of Oxone in water (pH ≈ 1) they are completely dissolved allowing a single phase oxidation. Further, even if the hydrazide is added to the buffered solution of Oxone in water (pH ≈ 6.5–7), as the oxidation proceeds the pH of the solution gradually decreases

Table 1 The oxidation of hydrazides to N,N′ – diacylhydrazines

Compound	R =	Reaction time (min)	Yield[a,b] (%)	Melting point Obs. °C	°C
2a	C_6H_5	30	84	237	238–240 [21a]
2b	2 CH_3–C_6H_4	20	87	218	219–220[2b]
2c	2 Cl–C_6H_4	30	82	217	219–221[2b]
2d	4 MeO–C_6H_4	30	93	224	228[21b]
2e	4 Cl–C_6H_4	20	89	289	292[21b]
2f	4 O_2N–C_6H_4	20	89	291	291[21c], 298[21d]
2g	C_6H_5–CH_2	30	93	237	238[21e]
2h	4 HO–C_6H_4	30	49	264	260[2j]

[a]Isolated yields of pure products. [b]All products were characterized by IR and PMR spectra.



Scheme 2

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

causing the hydrazide to dissolve, again allowing a single phase oxidation. The method is well suited for oxidation of aromatic hydrazides but attempts to oxidise aliphatic hydrazides failed to yield the corresponding N,N′–diacylhydrazines. The plausible mechanism of oxidation of hydrazides is given in Scheme 2.

In conclusion, an inexpensive and convenient use of Oxone is an environmentally benign protocol for the oxidation of hydrazides to N,N′-diacylhydrazines in aqueous medium.

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20 **Typical procedure:** To a well stirred solution of Oxone (10 mmol) in water (20 mL) was added o-chlorobenzoic acid hydrazide (10 m/mol) in one lot and the reaction mixture was stirred at room temperature for 30 min. The resultant N.N’ – diacylhydrazine was filtered at the pump, washed with water, dried, and crystallised from ethyl acetate-pet. ether (1.32 g , 82%). ^{1}H NMR (DMSO-d$_6$) δ 7.5 to 7.7 (m, 8H), 10.50 (s, 2H) ; M/Z 309 (M$^+$, 7), 139 (100), 111(28), 75(9).

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