Hypervalent Iodine Oxidation of *N*-Acylhydrazones and *N*-Phenylsemicarbazone: An Efficient Method for the Synthesis of Derivatives of 1,3,4-Oxadiazoles and Δ^3-1,3,4-Oxadiazolines

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The oxidation of ketone *N*-acylhydrazones 1 by phenyliodine(III) diacetate (PIDA) in alcohol gave 2-alkoxy-Δ^3-1,3,4-oxadiazolines 4 in excellent yields, while the oxidative cyclization of aldehyde *N*-acylhydrazone 2 by PIDA in methanolic sodium acetate gave 2,5-disubstituted 1,3,4-oxadiazoles in good yields. The oxidation of acetone 4-phenylsemicarbazone afforded 2-(*N*-phenylimino)-Δ^3-1,3,4-oxadiazoline in excellent yield.

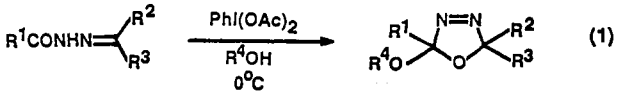
Introduction

Hypervalent iodine oxidation of organic compounds has been successfully used in organic synthesis in many aspects.[1] Carbon–carbon bond formation,[1g] the functionalization of organic compounds,[1h] and the conversion of ketones to hydroxyketals[1c] by hypervalent iodine oxidations are just a few examples. As an oxidant, phenyliodine(III) diacetate (PIDA) is the most frequently used and easily available reagent in the family of hypervalent iodine compounds. In a continuation of our study on the application of hypervalent iodine compounds in organic synthesis,[2] we report here the oxidative cyclization of aldehyde and ketone *N*-acylhydrazones as well as a ketone semicarbazone by PIDA, which affords derivatives of Δ^3-1,3,4-oxadiazolines and 1,3,4-oxadiazoles efficiently.

Results and Discussion

Synthesis of 2-Alkoxy-Δ^3-1,3,4-oxadiazolines. Although most Δ^3-1,3,4-oxadiazolines are unstable, they are very useful as intermediates in organic synthesis.[3] These compounds are known to decompose readily, affording the corresponding carbonyl ylides and N_2.[4] However, there are few methods for synthesis of Δ^3-1,3,4-oxadiazoline. Oxidation of ketone *N*-benzoylhydrazones with lead tetraacetate in methylene chloride at low temperature has been used to make a number of 2-acetoxy-Δ^3-1,3,4-oxadiazolines.[5] Under the same conditions, if an alcohol was used as the solvent instead of methylene chloride, 2-alkoxyoxadiazolines were obtained along with the corresponding 2-acetoxyoxadiazoline.[6] Moreover, cycloaddition of diaryl and arylmethyldiazomethane to penta- and hexafluoroacetone gave the corresponding difluoromethyl- and trifluoromethyl-substituted aryloxadiazolines.[7] Very recently, electrooxidative cyclization of ketone *N*-acylhydrazones in methanol was realized by Chiba[3b] to give 2-methoxyoxazolines in 30 to 77% yield. However, all these methods are inefficient, and some employ highly toxic materials. Thus, a new efficient method for the synthesis of 2-alkoxy-Δ^3-1,3,4-oxazolines remains to be discovered.

We found that the oxidative cyclization of ketone hydrazones could be effected by PIDA. To a methanol solution of ketone *N*-acylhydrazone 1 was added 1.0 equiv of PIDA at 0 °C. The reaction took place smoothly and was complete within 2 min to give 2-methoxy-Δ^3-1,3,4-oxadiazolines in excellent yields (over 90%) (eq 1). No



(1)

1 4

2-acetoxy-Δ^3-1,3,4-oxadiazolines could be detected. The substituents (R_1–R_3) of the ketone hydrazones have no significant influence on the yields of the products (Table I). When ethanol was used as solvent, the reaction was still complete within 2 min, and 2-ethoxy-Δ^3-1,3,4-oxadiazoline was obtained in 73% yield (entry 2 of Table I), somewhat lower than the yields in methanol. The reaction is noteworthy for its mildness, quickness, lack of toxic reagents, and high yield, and thus appears to be an efficient method for the synthesis of the 2-alkoxy-Δ^3-1,3,4-oxadiazolines.

Synthesis of 1,3,4-Oxadiazoles. In contrast to the Δ^3-1,3,4-oxadiazoline, 1,3,4-oxadiazoles are stable compounds. They have been used as important substances in medicine or agrochemicals because of their special phys-

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Table I. Preparation of 2-Alkoxy-Δ^3-1,3,4-oxadiazolines from Ketone *N*-Acylhydrazones by PIDA

entry	hydrazone 1	R_1	R_2	R_3	R_4	oxadiazoline 4	yield[a] (%)
1	1a	Ph	Me	Me	Me	4a	93
2	1a	Ph	Me	Me	Et	4i	73
3	1b	Ph	$(CH_2)_5$		Me	4b	100
4	1c	Ph	*n*-Pr	*n*-Pr	Me	4c	99
5	1e	Bn	Me	Me	Me	4e	95
7	1f	Bn	*n*-Pr	*n*-Pr	Me	4f	100
8	1g	Bn	$(CH_2)_5$		Me	4g	97
9	1h	Bn	$(CH_2)_6$		Me	4h	92

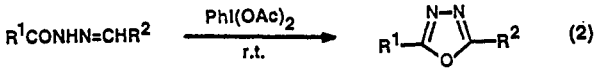
[a] Isolated yield.

Table II. Oxidative Cyclization of Aldehyde Hydrazones by PIDA[a]

entry	2	R_1	R_3	5	yield[b] (%)
1	2a	Ph	*n*-Pr	5a	48[c]
2	2a	Ph	*n*-Pr	5a	48[d]
3	2a	Ph	*n*-Pr	5a	57[e]
4	2a	Ph	*n*-Pr	5a	71
5	2b	Ph	*n*-Bu	5b	70
6	2c	Ph	*i*-Pr	5c	67
7	2d	Ph	Me	5d	63
8	2e	Ph	Ph	5e	41
9	2f	Bn	*n*-Pr	5f	58
10	2g	Bn	*i*-Pr	5g	57
11	2h	Bn	Me	5h	53
12	2i	Bn	*n*-Bu	5i	51

[a] All reactions were performed in methanol with 2 equiv of $NaOAc{\cdot}3H_2O$. [b] Isolated yield. [c] Reaction performed in methanol without any addition of salt. [d] Reaction conducted in CH_2Cl_2 without any addition of salt. [e] Reaction in methanol with 1 equiv of K_2CO_3.

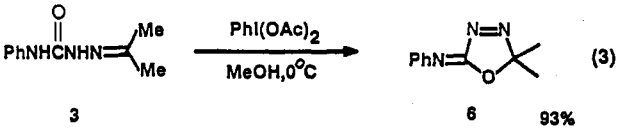
iological properties.[8] Generally, 1,3,4-oxadiazoles may be prepared by dehydration of 1,2-diacylhydrazines,[9] chemical oxidation of aldehyde *N*-acylhydrazones by the very toxic oxidant lead tetraacetate,[10] or by electrochemical oxidation of aldehyde *N*-acylhydrazones.[3b] By using PIDA as oxidant, the oxidative cyclization of aldehyde hydrazones, but not ketone hydrazones, also took place smoothly, and 1,3,4-oxadiazoles were obtained in good yields (eq 2).



2 5 (2)

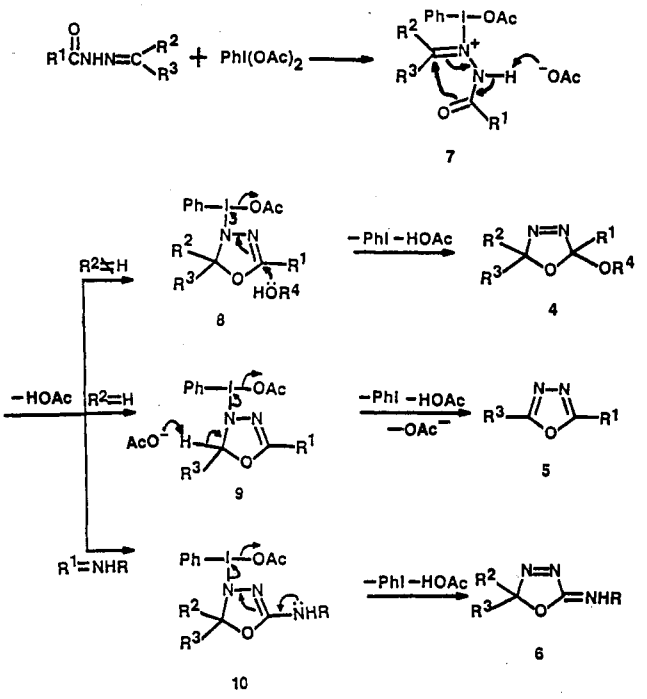
Reaction in methanol or methylene chloride gave product only in moderate yield. However, when 2 equiv of sodium acetate was added to the methanol the yield was increased to 71% (compared entry 4 to entries 1-3, Table II). The results of oxidative cyclization of other aldehyde *N*-acylhydrazones using these conditions are also listed in Table II. *N*-Benzoylhydrazones of aliphatic aldehyde generally gave slightly higher yields of oxadiazoles than those of aromatic aldehyde *N*-acylhydrazones. This reaction also took place rapidly and was complete within 2 min.

Synthesis of 2-Imino-Δ^3-1,3,4-oxadiazoline. Recently, it was found that 2-imino-Δ^3-1,3,4-oxadiazolines could be converted to the corresponding β-lactam 4-ylidenes which are very useful precursors to various β-lactam systems.[4e] We found that the oxidative cyclization of acetone *N*-phenylsemicarbazone by PIDA was completed within 10 min and 2-(*N*-phenylimino)-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline was obtained in 93% yield (eq 3). Previously, the preparation of this type of compounds also employed the highly toxic lead tetraacetate.[11]



3 6 93% (3)

Scheme I



The Reaction Path of These Oxidative Cyclizations. The present oxidative cyclizations of 1–3 might occur via the following pathway (Scheme I). First, the exchange of an acetoxy ligand of PIDA formed a hypervalent iodine intermediate 7. The cyclization of 7 was accomplished by an intramolecular carbonyl oxygen attack to form hypervalent iodine intermediates with mixed ligands 8–10. These intermediates are in agreement with the intermediate proposed in the oxidation of Schiff bases by PIDA.[12] When R_2 is a hydrogen, 9 undergoes an acetate-catalyzed intramolecular reductive elimination of PhI to give the stable 1,3,4-oxadiazole 5. When R_2 is not a hydrogen, an intramolecular reductive elimination of PhI could not occur; therefore, intermediate 8 could only be attacked by a nucleophilic solvent (alcohol) with the reductive elimination of PhI to form compound 4. When R_1 is *N*-phenylamino and R_2 is not a hydrogen, intermediate 10 may undergo an intramolecular reductive elimination of PhI to give 6.

In conclusion, PIDA was shown to be an efficient oxidant for the oxidative cyclizations of *N*-acylhydrazones and 4-phenylsemicarbazone. The method presented here provided a practical procedure for the preparation of 1,3,4-oxadiazoles and Δ^3-1,3,4-oxadiazolines. Regarding the preparation of Δ^3-1,3,4-oxadiazolines, like 4 and 6, this method appeared to be the most efficient and simple one.

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Experimental Section

Melting points are uncorrected. ^1H NMR spectra were recorded in CCl_4 with TMS as external standard. *N*-Acylhydrazones **1** and **2** were prepared according to literature method[13] by refluxing *N*-acylhydrazines with aldehydes or ketones in methanol in the presence of two drops of acetic acid. Acetone 4-phenylsemicarbazone was prepared according to literature method.[11]

General Procedure for the Oxidative Cyclization of Ketone *N*-Acylhydrazones. To a stirred solution of **1** (1 mmol) in methanol (16 mL) at 0 °C was added 1 mmol of PIDA. The mixture was stirred for 2 min under 0 °C and then concentrated in vacuo. The residue was purified by column chromatography on silica gel using Et_2O–petroleum ether (1:6) as eluants.

2,2-Dimethyl-5-methoxy-5-phenyl-Δ³-1,3,4-oxadiazoline (4a):[3b] unstable oil: ^1H NMR δ 1.39 (s, 3H), 1.56 (s, 3H), 3.08 (s, 3H), 7.12–7.79 (m, 5H); IR (neat) 1280, 1235, 1105, 1060 cm^{-1}.

2,2-Pentamethylene-5-methoxy-5-phenyl-Δ³-1,3,4-oxadiazoline (4b): unstable oil: ^1H NMR δ 1.21–2.24 (m, 10H), 3.10 (s, 3H), 7.13–7.77 (m, 5H); IR (neat) 2930, 1440, 1265, 1090, 890 cm^{-1}.

2,2-Di-*n*-propyl-5-methoxy-5-phenyl-Δ³-1,3,4-oxadiazoline (4c):[3b] unstable oil: ^1H NMR δ 0.65–1.24 (m, 6H), 1.24–2.13 (m, 8H), 3.15 (s, 3H), 7.30–7.93 (m, 5H); IR (neat) 2940, 1450, 1090, 985, 900, 755 cm^{-1}.

2,2-Tetramethylene-5-methoxy-5-phenyl-Δ³-1,3,4-oxadiazoline (4d):[3b] unstable oil: ^1H NMR δ 1.55–2.44 (m, 8H), 3.04 (s, 3H), 7.10–7.74 (m, 5H); IR (neat) 2930, 1455, 1280, 1095, 760 cm^{-1}.

2,2-Dimethyl-5-methoxy-5-benzyl-Δ³-1,3,4-oxadiazoline (4e): clear oil: ^1H NMR δ 0.78 (s, 3H), 1.46 (s, 3H), 3.17 (s, 3H), 3.26 (s, 2H), 7.17 (s, 5H); IR (neat) 2950, 1455, 1220, 1200, 1100, 905, 710 cm^{-1}; MS *m/z* (relative intensity): 219 (M^+ − 1, 2.34), 193(25), 188(14), 177(28), 161(37), 135(100), 119(58), 91(97). Anal. Calcd. for $C_{12}H_{16}N_2O_2$: C, 65.45; H, 7.27; N, 12.73. Found: C, 65.68; H, 7.60; N, 12.41.

2,2-Di-*n*-propyl-5-methoxy-5-benzyl-Δ³-1,3,4-oxadiazoline (4f): clear oil: ^1H NMR δ 0.40–1.80 (m, 14H), 3.08 (s, 3H), 3.20 (s, 2H), 7.09 (s, 5H); IR (neat) 2950, 1470, 1170, 1110, 920, 700 cm^{-1}. Anal. Calcd for $C_{16}H_{24}N_2O_2$: C, 69.57; H, 8.70; N, 10.14. Found: C, 69.94; H, 9.07; N, 9.79.

2,2-Pentamethylene-5-methoxy-5-benzyl-Δ³-1,3,4-oxadiazoline (4g): clear oil: solidified on standing, mp 52–54 °C; ^1H NMR δ 1.25–1.91 (m, 10H), 3.00 (s, 3H), 3.20 (s, 2H), 7.08 (s, 5H); IR (KBr) 2930, 1445, 1235, 1180, 1080, 895, 725, 700 cm^{-1}; MS *m/z* (relative intensity) 261 (M^+ + 1, 0.75), 245(1), 232(4), 229(9), 201(16), 163(11), 151(10), 150(9), 135(62), 134(51), 119(6), 91(100). Anal. Calcd for $C_{15}H_{20}N_2O_2$: C, 69.23; H, 7.69; N, 10.77. Found: C, 69.42: H, 7.95; N, 10.52.

2,2-Hexamethylene-5-methoxy-5-benzyl-Δ³-1,3,4-oxadiazoline (4h): clear oil, solidified on standing, mp 55–57 °C; ^1H NMR δ 1.16–2.18 (m, 12H), 3.07 (s, 3H), 3.22 (s, 2H), 7.10 (s, 5H); IR (KBr) 2920, 1440, 1240, 1205, 1175, 1090, 1060, 870, 715, 700 cm^{-1}. Anal. Calcd for $C_{16}H_{22}N_2O_2$: C, 70.07; H, 8.03; N, 10.22. Found: C, 70.29; H, 8.36; N, 9.94.

2,2-Dimethyl-5-Dimethyl-5-ethoxy-5-phenyl-Δ³-1,3,4-oxadiazoline (4i) was prepared by reacting **1a** with PIDA in ethanol: unstable oil; ^1H NMR δ 1.10 (t, *J* = 7 Hz, 3H), 1.37 (s, 3H), 1.53 (s, 3H), 3.29 (q, *J* = 7 Hz, 2H), 7.14–7.75 (m, 5H); IR (neat) 2950, 1450, 1280, 1105, 1105, 720 cm^{-1}.

General Procedure for the Preparation of 1,3,4-Oxadiazoles. To a stirred solution of **2** (1 mmol) and $NaOAc·3H_2O$ (2 mmol) in methanol (8 mL) at rt was added PIDA (1 mmol). The mixture was stirred for 2 min and then concentrated in vacuo. To the residue was added H_2O (8 mL) and the resulting mixture extracted with ether (10 mL × 3). The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel using Et_2O–petroleum ether (2:5) as eluants.

2-*n*-Propyl-5-phenyl-1,3,4-oxadiazole (5a):[3b] clear oil: ^1H NMR & 1.01 (t, *J* = 7 Hz, 3H), 1.48–2.19 (m, 2H), 2.83 (t, *J* = 7 Hz, 2H), 7.22–8.23 (m, 5H); IR (neat) 2950, 2860, 1580, 1555, 1450, 1185, 1140 cm^{-1}; MS *m/z* (relative intensity) 189 (M^+ + 1, 100), 160(22), 105(55), 90(18), 77(26), 43(24).

2-*n*-Butyl-5-phenyl-1,3,4-oxadiazole (5b): clear oil: ^1H NMR δ 0.97 (t, *J* = 7 Hz, 3H), 1.14–2.15 (m, 4H), 2.87 (t, *J* = 7 Hz, 2H), 7.14–8.22 (m, 5H); IR (neat) 2950, 2870, 1575, 1450, 1070, 1010, 780, 710, 690 cm^{-1}; MS *m/z* (relative intensity) 203 (M^+ + 1, 100), 173(29), 160(6), 105(21), 77(12), 57(4). Anal. Calcd for $C_{12}H_{14}N_2O$: C, 71.29; H, 6.93; N, 13.86. Found: C, 70.87; H, 6.72; N, 13.54.

2-Isopropyl-5-phenyl-1,3,4-oxadiazole (5c):[3b] clear oil: ^1H NMR δ 1.39 (d, *J* = 7 Hz, 6H), 3.22 (m, 1H), 7.33–8.22 (m, 5H); IR (neat) 2975, 2870, 1570, 1485, 1450, 1070, 710, 690 cm^{-1}; MS *m/z* (relative intensity) 189 (M^+ + 1, 69.68), 188(100), 173(17), 159(5), 145(8), 117(62), 105(96), 77(69), 43(64).

2-Methyl-5-phenyl-1,3,4-oxadiazole (5): mp 67–69 °C (lit.[3b] mp 67–69 °C); ^1H NMR δ 2.67 (s, 3H), 7.40–8.30 (m, 5H); IR (KBr) 1580, 1480, 1445, 1250, 780, 710, 690 cm^{-1}; MS *m/z* (relative intensity) 160 (M^+, 100), 77(72).

2,5-Diphenyl-1,3,4-oxadiazole (5e): mp 138–140 °C (lit.[14] mp 141 °C); ^1H NMR ($CDCl_3$) δ 7.44–8.48 (m, 10H); IR (KBr) 1550, 1485, 1445, 1070, 785, 710, 685 cm^{-1}; MS *m/z* (relative intensity) 222 (M^+, 96), 165(100), 105(67), 77(62).

2-Benzyl-5-*n*-propyl-1,3,4-oxadiazole (5f): amorphous: ^1H NMR δ 0.93 (t, *J* = 7 Hz, 3H), 1.50–2.00 (m, 2H), 2.68 (t, *J* = 7 Hz, 2H), 4.06 (s, 2H), 7.14 (s, 5H); IR (film) 1580, 1480, 1450, 1235, 1075, 1020, 970, 720, 695 cm^{-1}; MS *m/z* (relative intensity) 202 (M^+, 45), 187(11), 174(100), 111(47), 91(85), 77(7), 43(29). Anal. Calcd for $C_{12}H_{14}N_2O$: C, 71.29; H, 6.93; N, 13.86. Found: C, 70.96; H, 6.67; N, 13.59.

2-Benzyl-5-isopropyl-1,3,4-oxadiazole (5g): clear oil: ^1H NMR δ 1.22 (d, *J* = 7 Hz, 6H), 2.97 (m, 1H), 4.00 (s, 2H), 7.13 (s, 5H); IR (neat) 2970, 2860, 1565, 1545, 1480, 1435, 1250, 1005, 930, 730, 700, 640 cm^{-1}; MS *m/z* (relative intensity) 203 (M^+ + 1, 79), 202 (M^+, 100), 187(6), 159(5), 111(60), 91(94), 77(7), 43(28). Anal. Calcd for $C_{12}H_{14}N_2O$: C, 71.29; H, 6.93; N, 13.86. Found: C, 71.62; H, 6.45; N, 13.67.

2-Benzyl-5-methyl-1,3,4-oxadiazole (5h): clear oil; ^1H NMR δ 2.46 (s, 3H), 4.17 (s, 2H), 7.35 (s, 5H); IR (neat) 1590, 1480, 1435, 1370, 1250, 195, 1130, 1005, 930, 730, 700, 680, 640 cm^{-1}; MS *m/z* (relative intensity) 174 (M^+, 100), 91(96), 83(54), 77(14). Anal. Calcd for $C_{10}H_{10}N_2O$: C, 68.97; H, 5.75; N, 16.09. Found: C, 68.44; H, 5.42; N, 15.81.

2-Benzyl-5-*n*-butyl-1,3,4-oxadiazole (5i): amorphous: ^1H NMR δ 0.91 (t, *J* = 7 Hz, 3H), 1.12–2.02 (m, 4H), 2.72 (t, *J* = 7 Hz, 2H), 4.07 (s, 2H), 7.24 (s, 5H); IR (film) 1580, 1480, 1440, 1375, 1250, 1190, 1130, 1000, 930, 735, 680, 640 cm^{-1}; MS *m/z* (relative intensity) 217 (M^+ + 1, 100), 187(44), 174(17), 125(11), 91(61), 57(13), 43(11). Anal. Calcd for $C_{13}H_{16}N_2O$: C, 72.22; H, 7.41; N, 12.96. Found: C, 71.97; H, 7.37; N, 12.65.

2,2-Dimethyl-5-(*N*-phenylimino)-1,3,4-oxadiazoline (6): mp 70–71 °C (lit.[11] mp 72–73 °C); ^1H NMR δ 1.61 (s, 6H), 7.10–7.47 (m, 5H).

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