Oxidation of Aldehyde Hydrazones, Hydrazo Compounds, and Hydroxylamines with Benzeneseleninic Anhydride

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Summary Aldehyde hydrazones, hydrazo compounds, and hydroxylamines can be readily oxidised by benzeneseleninic anhydride to afford high yields of azo- and nitroso-species.

We have recently reported the use of benzeneseleninic anhydride, $(PhSeO)_2O$, for the mild regeneration of ketones from their corresponding hydrazones, oximes, and semicarbazones.[1] Here we present our results with aldehyde derivatives and other nitrogen containing species.

A number of phenyl and *p*-nitrophenyl hydrazones of aldehydes on treatment with benzeneseleninic anhydride at 40—50 °C lead to the novel formation of acylazo-derivatives in good yield rather than regenerating the parent aldehydes

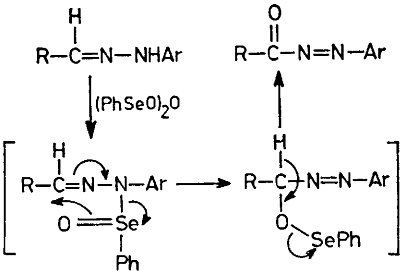
TABLE 1

Aldehyde	Derivative	Reaction conditions[a]	Product yield (%)[b]	Yield (%)[b] from hydrazide with $(PhSeO)_2O$[c]	Yield (%)[b] from hydrazide with *N*-bromo-succinimide
2-Furaldehyde	Phenylhydrazone	45 min	C_4H_3O-2-C(O)N : NPh[d] 87 (82)	92	65
”	*p*-Nitrophenylhydrazone	35 min	C_4H_3O-2-C(O)N : $NC_6H_4NO_2$-*p*[d] 70 (64)	95(86)	78(64)
”	Tosylhydrazone	2 h	2-Furaldehyde, 88	—	—
”	Oxime	6 h	” 36	—	—
Benzaldehyde	Phenylhydrazone	1 h	PhC(O)N : NPh, 73 (67)	85	80[e]
”	*p*-Nitrophenylhydrazone	1 h	PhC(O)N : $NC_6H_4NO_2$-*p* 76 (72)	99	79[e]
2-Naphthaldehyde	Phenylhydrazone	30 min	$C_{10}H_7$-2-C(O)N : NPh[f] 70 (49)	72	47
”	*p*-Nitrophenylhydrazone	20 min	$C_{10}H_7$-2-C(O)N : $NC_6H_4NO_2$-*p*[f] 90 (89)	89 (80)	70 (57
”	Tosylhydrazone	30 min	2-Naphthaldehyde 99 (87)	—	—
”	Oxime	20 min	” 94 (81)	—	—
Isobutyraldehyde	Tosylhydrazone	45 min	Isobutaraldehyde, 71[g]	—	—
Valeraldehyde	”	30 min	Valeraldehyde, 92	—	—
n-Heptaldehyde	”	30 min	*n*-Heptaldehyde, 89	—	—
Crotonaldehyde	”	45 min	Crotonaldehyde, 68	—	—
Cinnamaldehyde	”	40 min	Cinnamaldehyde, 91	—	—

[a] Tetrahydrofuran, 40—50 °C, 1 mol equiv. of $(PhSeO)_2O$. [b] Yield of crude product (yields after recrystallisation are in parentheses). [c] 1 mol equiv. of $(PhSeO)_2O$ was used. [d] C_4H_3O = Furyl. [e] H. Bock, *Chem. Ber.*, 1966, **99**, 3337. [f] $C_{10}H_7$ = Naphthyl. [g] Yield of distilled compound.

(Table 1). This new method for the preparation of acylazo compounds compares favourably with those reported[2] previously. Should one wish to regenerate the parent aldehyde then tosyl hydrazones or oximes are recommended as precursors (Table 1).

Mechanistically, the acylazo-derivatives are formed *via* loss of benzeneselenol from the intermediate selenenic ester (Scheme). In support of this idea, diphenyl diselenide can be isolated as the major by-product of the reaction.



SCHEME

The use of selenium dioxide as oxidant only produces low yields of azo-species. 2,4-Dinitrophenylhydrazones fail to react under the usual conditions and semicarbazones react poorly. For comparison, we have also studied the oxidation of other nitrogen containing compounds, including acylhydrazides, to azo-compounds using the anhydride (Tables 1 and 2). In order to show the variation of substrate, both aromatic and aliphatic analogues have been chosen and in all cases the reaction proceeds smoothly at room temperature in excellent yield. As a logical extension of this oxidation reaction, hydroxylamines can be converted into nitroso-compounds using benzeneseleninic anhydride (Table 2). Further oxidation to the nitro-group is not observed at room temperature.

TABLE 2

Starting material	Reaction conditions[a]	Product yield (%)[b]
PhNHNHPh	5—10 min	PhN=NPh, 99
$Me_2HCNHNHCHMe_2$	3 min[c]	$Me_2HCN{=}NCHMe_2$, 95
$Me_3CNH(OH)$	1 min	$Me_3CN{=}O$, 96[d]
PhNH(OH)	3 min	PhN=O, 89
4-Phenyl-1,2,4-triazolidine-3,5-dione	5—10 min	4-Phenyl-1,2,4-triazoline-3,5-dione,[e] 72

[a] Tetrahydrofuran, room temp., 1 mol equiv. of $(PhSeO)_2O$. [b] Yields of isolated products. [c] Reaction carried out on neat starting material. [d] Estimated by u.v. spectroscopy. [e] Trapped as the ergosterol acetate adduct.

Finally, oxidation of *p*-nitrophenylhydrazine with the anhydride gives, after 20 min at room temperature, a mixture of nitrobenzene (26%) and *p*-nitrophenyl phenyl selenide (63%). With an excess of reagent, the yield of nitrobenzene increases to 72% while the yield of phenylselenated product decreases (16%).

Clearly, the use of the anhydride as a mild oxidant for a variety of nitrogen containing compounds has been demonstrated.

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[1] D. H. R. Barton, D. J. Lester, and S. V. Ley, *J.C.S. Chem. Comm.*, 1977, 445.
[2] H. Bock, *Angew. Chem. Internat. Edn.*, 1965, **4**, 457.