Dehydrogenation of Hydrazines and of 4-Azacholestan-3-one with Benzeneseleninic Acid and Benzeneseleninic Anhydride

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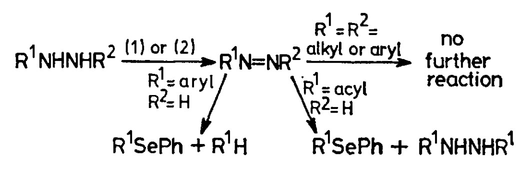
Summary A variety of hydrazines are readily oxidised with benzeneseleninic acid or benzeneseleninic anhydride to generate azo-compounds or unstable di-imide species while 4-azacholestan-3-one is dehydrogenated to the Δ^1-azasteroid in high yield.

BENZENESELENINIC ACID, $PhSeO_2H$, (**1**) and anhydride, $(PhSeO)_2O$, (**2**) are readily available, stable, mild oxidising agents. The anhydride has been employed in the oxidation of phenols[1] and primary amines,[2] and in the regeneration of ketones from their hydrazones, oximes, and semicarbazones.[3] The oxidising properties of the acid[4] have remained largely unexploited in synthesis. It has now been found that both (**1**) and (**2**) react vigorously with hydrazines at room temperature to form products determined by the location and nature of substituents in the substrate.

Thus, hydrazine hydrate reacted with (**1**) or (**2**) to generate di-imide. Slow addition of (**2**) (2·5 mol. equiv.) in dimethylformamide (DMF) to a DMF solution of azobenzene and hydrazine hydrate (1 and 10 mol equiv., respectively) at room temperature provided hydrazobenzene, isolated in quantitative yield. Somewhat poorer yields were obtained at lower temperatures or with smaller excesses of (**2**) and hydrazine hydrate. Similarly, the di-imide produced from (**1**) and hydrazine hydrate in pyridine reduced cinnamic acid to hydrocinnamic acid in 90% yield.

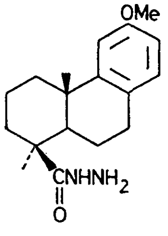
The oxidation of 1,2-diphenyl- and 1,2-di-isopropylhydrazine with (**1**) or (**2**) cleanly furnished the corresponding azo-compounds (Table). Azine formation, a side reaction observed in certain other syntheses of aliphatic azo-compounds,[5] does not occur even with an excess of oxidant and prolonged reaction times.

Treatment of monosubstituted arylhydrazines with (**1**) or (**2**) gave aryl phenyl selenides and arenes as the major and minor products respectively. Oxidation of acylhydrazines furnished phenyl selenol esters and 1,2-diacylhydrazines (Table). When the oxidation of aryl- or acyl-hydrazines was performed in the presence of added diphenyl diselenide, the yield of the selenide or selenol ester was significantly increased. The diselenide is normally obtained as a by-product and may function as a trapping agent of radicals produced from an unstable di-imide intermediate (Scheme 1).

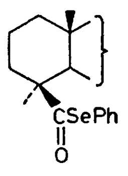


SCHEME 1

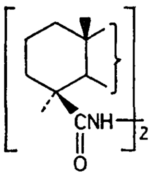
Finally, oxidation of the known[6] 4-azacholestan-3-one with (**2**) in diglyme (14 h, 120 °C) furnished the novel 4-azacholest-1-en-3-one, isolated in 88% yield, m.p. 226—227 °C (Scheme 2). Amides such as hydrocinnam-



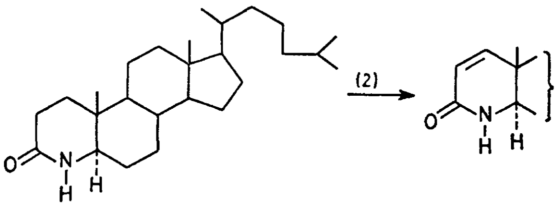
(**A**)



(**B**)



(**C**)



SCHEME 2

TABLE. Oxidation of mono- and di-substituted hydrazines.[a]

Hydrazine	Oxidant (mol equiv.)	Solvent	Product	Yield (%)[b]
PhNHNHPh	(**2**) (1·2)	CH_2Cl_2	PhN : NPh	97
$Me_2HCNHNHCHMe_2{\cdot}HCl$	(**1**) or (**2**) (1·1)[c]	CCl_4 or $CDCl_3$	$Me_2HCN : NCHMe_2$	100[d]
$H_2NNHC_6H_3NO_2$-*o*-NO_2-*p*	(**1**) or (**2**) (1·0—1·1)	CH_2Cl_2	$PhSeC_6H_3NO_2$-*o*-NO_2-*p*	56—58[e]
			$C_6H_4(NO_2)_2$-*m*	24—29
$H_2NNHC_6H_4NO_2$-*p*	(**2**) (1·1)	CH_2Cl_2	$PhSeC_6H_4NO_2$-*p*	60
			$PhNO_2$	20
$H_2NNHC(O)Ph$	(**1**) (1·1, 1·6) or (**2**) (0·55)	CH_2Cl_2 or $CHCl_3$	PhSeC(O)Ph	44—54
			$[PhC(O)NH]_2$	28—30
(**A**)	(**1**) (1·1)	CH_2Cl_2	(**B**)	61[f]
			(**C**)	19

[a] All reactions were very rapid at room temperature. [b] Isolated yield, unless otherwise noted. [c] K_2CO_3 added. [d] Yield determined by n.m.r. spectroscopy. [e] Yield increased to 77% with added PhSePh in reaction. [f] Yield increased to 71% with added PhSeSePh in reaction.

amide or its *N*-methyl or *NN*-dimethyl derivatives did not react in this manner.

All new compounds gave satisfactory spectra and microanalyses.

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