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ENONE SYNTHESIS VIA α-PYRIDYLSELENO CARBONYL COMPOUNDS

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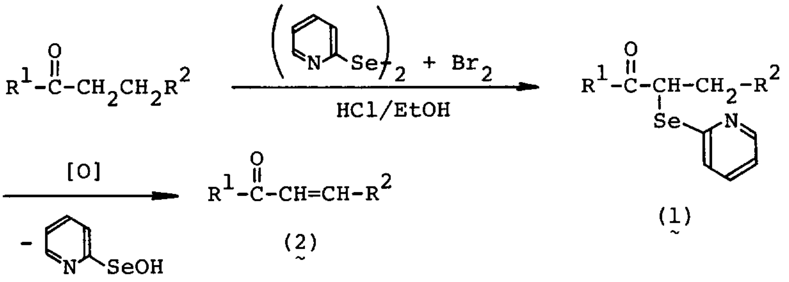
Summary: Oxidative elimination of α-pyridylseleno carbonyl compounds affords enones in excellent yields, providing an improved method for dehydrogenation of ketones and aldehydes. These results indicate that pyridylseleno group is a better leaving group than phenylseleno group in selenoxide elimination leading to enones.

Introduction of a phenylseleno group into α position of carbonyl functionality and the following selenoxide-elimination to afford enones constitute one of the most elegant procedures for dehydrogenation of carbonyl compounds.[1~3] Yet there have been pointed out some limitations: for instance, yields were not satisfactory in the selenoxide-elimination step for certain carbonyl compounds. We report here that the oxidative elimination of α-pyridylseleno carbonyl compounds affords enones in excellent yields,[4] even in the cases where satisfactory results were not obtained using phenylseleno compounds. We also found that α-pyridylseleno carbonyl compounds can be obtained in good yields by the reaction of 2-pyridylselenenyl bromide, prepared *in situ* from 2,2'-dipyridyl diselenide[4] and bromine, with ketones and aldehydes under acidic conditions. These two reactions may well provide an improved method for dehydrogenation of ketones and aldehydes.

In a typical reaction, a solution of bromine (1 mmol) in ethanol (2 ml) was added dropwise to a solution of 2,2'-dipyridyl diselenide (1 mmol) in ethanol (14 ml) and the resulting mixture was stirred at ambient temperature for 0.5 h. Then cycloheptanone (2 mmol) and hydrogen chloride (10 mmol; 36.5% aq. sol.) (in ethanol; 2 ml each) were added and the solution was stirred under reflux for 0.5 h. After the usual work-up, column chromatography [silica gel; hexane - ethyl acetate (2:1) as eluent] gave 2-(2'-pyridylseleno)-cycloheptanone [1; $R^1,R^2= -(CH_2)_4-$] (1.7 mmol; 84%) as a pale yellow oil. As shown in the Table, linear and cyclic ketones as well as aldehydes gave corresponding α-pyridylseleno compounds (1) in acceptable yields. The yield of (1) was not satisfactory when hydrogen chloride was not added. We succeeded in the isolation of 2-pyridylselenenyl chloride as a yellow powder from the reaction of 2,2'-dipyridyl diselenide and sulphuryl chloride. The yield of (1), however, was not improved when 2-pyridylselenenyl chloride was used as selenenylating reagent.[5]

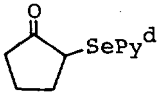
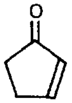
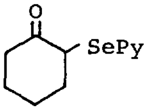
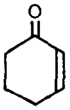
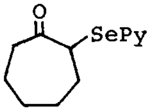
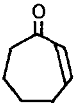
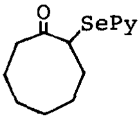
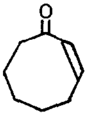
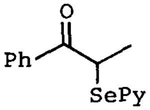
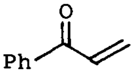
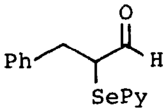
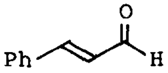
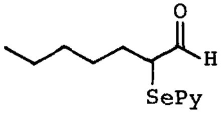
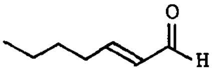


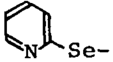
The best method for oxidative elimination of α-pyridylseleno ketones was found to be the ozonization of (1; R^1=alkyl or phenyl) at -78 °C in dichloromethane followed by the addition to refluxing carbon tetrachloride.[6] As shown in the Table, enones (2) were obtained in excellent yields. Especially, for the compounds in Expts. 3 and 4, yields of (2) were higher by *ca.* 20% than those obtained when a phenylseleno group was used as a leaving group under nearly the same reaction conditions.[7]

The oxidative elimination of α-pyridylseleno aldehydes, on the other hand, was carried out using sodium periodate in methanol-water (6:1) at 23 °C[8] to give (2) in excellent yields. It should be noted here that 2-hepten-1-al [2; R^1=H, $R^2=(CH_2)_3CH_3$] was obtained in 90% yield (Expt. 7), which had been obtained only in a low yield by the oxidation of 2-phenylseleno-1-heptanal.[2b]

These results clearly indicate that a pyridylseleno group is a better leaving group than a phenylseleno group in selenoxide elimination leading to enones.

TABLE. Yields of α-Pyridylseleno Carbonyl Compounds (1) and Enones (2).[a]

Expt.	Starting Material	Selenide (1)	Yield[b] (%)	Oxidation Method	Enone (2)	Yield[c] (%)
1	Cyclopentanone		52	O_3		85
2	Cyclohexanone		89	O_3		82
3	Cycloheptanone		84	O_3 O_3[e]		68 100
4	Cyclooctanone		59	O_3[e]		94
5	Propiophenone		73	O_3		97
6	3-Phenyl-1-propanal		64	$NaIO_4$		83
7	1-Heptanal		53	$NaIO_4$		90

a. Satisfactory i.r. and ^1H n.m.r. spectral data as well as combustion analytical data were obtained for all new compounds. Stereochemistry of 2 in Expts. 1~4 is Z and that in Expts. 6 and 7 is E (by ^1H n.m.r. and g.l.c. retention time). b. Isolated yield. c. Determined by g.l.c. using internal standard, on the basis of 1 used. d. PySe denotes . e. $HNEt_2$ (1.5 mmol) was added.

Acknowledgement. We thank the Ministry of Education for the Grant-in-Aid for Special Project Research.

References and Notes

1. For example, D. L. J. Clive, *Tetrahedron*, **34**, 1049(1978); H. J. Reich, "Oxidation in Organic Chemistry, Part C", W. Trahanovsky, Ed., Academic Press, New York, 1978, p.1; H. J. Reich, *Acc. Chem. Res.*, **12**, 22(1979); and references cited therein.
2. For aldehyde, see for example; (a) K. C. Nicolaou, R. L. Magolda, and W. J. Sipio, *Synthesis*, **1979**, 982; (b) D. R. Williams and K. Nishitani, *Tetrahedron Lett.*, **21**, 4417(1980); (c) M. Jefson and J. Meinwald, *ibid.*, **22**, 3561(1981).
3. For the use of benzeneseleninic anhydride, see for example; D. H. R. Barton, D. J. Lester, and S. V. Ley, *J. Chem. Soc. Perkin Trans. 1*, **1980**, 2209; T. G. Back, *J. Org. Chem.*, **46**, 1442(1981).
4. It has been reported that a pyridylseleno group is a better leaving group than a phenylseleno group in selenoxide-elimination to give linear terminal olefins; A. Toshimitsu, H. Owada, S. Uemura, and M. Okano, *Tetrahedron Lett.*, **21**, 5037(1980).
5. In the case of phenylselenenylation of carbonyl compounds, phenylselenenyl bromide was claimed to behave primarily as a brominating agent.[1]
6. The procedure is almost the same as that reported.[7] We used **1** (R^1=alkyl or phenyl) (1 mmol), CH_2Cl_2 (10 ml), CCl_4 (30 ml), and (in some cases) $HNEt_2$ (1.5 mmol).
7. H. J. Reich, J. M. Renga, and I. L. Reich, *J. Am. Chem. Soc.*, **97**, 5434 (1975).
8. To a MeOH (12 ml) solution of **1** (R^1=H) (1 mmol) was added $NaIO_4$ (2 mmol) in H_2O (2 ml), and the resulting white suspension was stirred at 23 °C for 1 h.

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