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AN IMPROVED METHOD FOR OLEFIN SYNTHESIS USING PYRIDYLSELENO GROUP AS A LEAVING GROUP

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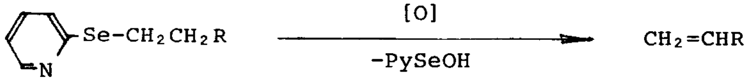
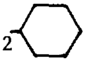
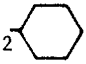
Summary: Alkyl pyridyl selenides are oxidized by 1.5 equiv. of 30% H_2O_2 in THF to give olefins in good to excellent yields. The yields are always higher than the case where alkyl phenyl selenides are used under the same conditions.

The utility of alkyl phenyl selenoxides for olefin synthesis under mild conditions has been well demonstrated.[1] However, some limitations have been pointed out; for instance, terminal olefins were formed in low yields by oxidation of primary alkyl phenyl selenides. In order to overcome this difficulty, there have been reported some improved methods[1] such as the introduction of electron withdrawing groups into the phenyl ring for rate enhancement,[2] the addition of secondary[3] or tertiary[4] amine in the elimination reaction, or the use of more powerful oxidizing reagents.[4] We expected a pyridylseleno group to be a good leaving group in the olefin-forming elimination reaction as pyridine itself is tertiary amine and also has an electron withdrawing effect. This was the case and we have now found that primary alkyl 2-pyridyl selenides produce terminal olefins in good to excellent yields under very mild oxidation conditions.

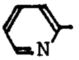


A pyridylseleno group is introduced to organic molecule in a quantitative yield by nucleophilic substitution reaction by sodium pyridyl selenate which is produced by $NaBH_4$ reduction of 2,2'-dipyridyl diselenide. The last compound is synthesized in one pot reaction from 2-bromopyridine and selenium powder in 75 - 80% yield.[5] In a typical example of oxidation reaction, 30% aq. H_2O_2 (3 mmol) was added dropwise to a pale yellow THF (10 ml) solution of n-hexadecyl 2-pyridyl selenide (2 mmol) at 32 °C and the resulted colorless solution was stirred for 0.5 h. After usual workup procedure GLC analysis showed that 1-hexadecene was produced in 87% yield (1.74 mmol). Under the same reaction condition n-hexadecyl phenyl selenide gave the same product only in a yield of 5%. Typical results are summarized in the Table. As the Table shows, the difference between the pyridylseleno and phenylseleno group is prominent when alkyl chain becomes longer or the reaction temperature is lowered. Here, it should be noted that we can avoid the use of a large excess of H_2O_2 (usually 5 - 10 equiv. of H_2O_2 has so far been used) without the expense of the product yields. These features, indicating a high ability of a pyridylseleno group as a leaving group in the oxidation-elimination reaction, should be advantageous for introduction of double bond into large molecules which have functional groups sensitive to oxidation.

TABLE Yields of Olefins by Oxidation-Elimination of Selenides[a)]

Selenide[b)]	Temp. (°C)	Time (h)	Olefin Yield(%)[c)]	Selenide	Temp. (°C)	Time (h)	Olefin Yield(%)[c)]
PySe-n-$C_{18}H_{37}$	32	0.6	82	PhSe-n-$C_{18}H_{37}$	32	0.6	22
PySe-n-$C_{16}H_{33}$	32	0.5	87	PhSe-n-$C_{16}H_{33}$	32	0.5	5
PySe-n-$C_{12}H_{25}$	25	0.5	65	PhSe-n-$C_{12}H_{25}$	25	1	14
PySe-n-$C_{10}H_{21}$	1	3	76	PhSe-n-$C_{10}H_{21}$	2	3	32
"	25	1	79	"	25	1	75
PySeCH$_2$-	32	2	71	PhSeCH$_2$-	32	2	61

a) Selenide (2 mmol), 30% aq. H_2O_2 (3 mmol), and THF (10 ml) were used.

b) PySe denotes  Se-. c) Determined by GLC.

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3. H. J. Reich and S. K. Shah, J. Amer. Chem. Soc., 97, 3250(1975); R. D. Clark and C. H. Heathcock, J. Org. Chem., 41, 1396(1976).
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5. We have modified the procedure given by H. Takaku, Y. Shimida, Y. Nakajima, and T. Hata, Nucleic Acid Res., 3, 1233(1976) as follows; 1) oxidation of 2-pyridyl selenol formed in situ from 2-bromopyridine and NaHSe was carried out in the same reaction vessel, 2) 2,2'-dipyridyl diselenide was isolated by column chromatography (silica gel; n-hexane - ethyl acetate 5∼1 : 1 as eluent).

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