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Hypervalent Iodine in Synthesis XXXVIII: The Synthesis of Novel *Se*-Alkenyl *O,O*-Dialkyl Phosphoroselenoates by Reaction of Potassium *O,O*-Dialkyl Phosphoroselenoates with Alkenyl(phenyl)iodonium Salts

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Abstract: Novel *Se*-alkenyl *O,O*-dialkyl phosphoroselenoates have been prepared by the reaction of potassium *O,O*-dialkyl phosphoroselenoates with alkenyl(phenyl)iodonium tetrafluoroborates in good yields.

Esters of *O,O*-dialkyl phosphoroselenoic acids are of marked interest because they have played an important role in the synthesis of selenium dependent enzymes and seleno-t-RNAs[1] and are often used as synthetic reagents for the stereoselective preparation of olefins.[2] The preparation of alkyl esters of the acids is not difficult, they can be readily prepared by the alkylation of salts of the acids with alkyl halides,[3] and aryl esters can be prepared by the reaction of trialkyl phosphites with arylselenenyl bromides[4] or by the action of lithium selenophenolate on *O,O*-dialkyl phosphoryl chlorides.[5] However, these methods are not suitable for the preparation of *Se*-alkenyl *O,O*-dialkyl phosphoroselenoates and to the best of our knowledge *Se*-alkenyl *O,O*-dialkyl phosphoroselenoates were unknown.

Alkenyl(phenyl)iodonium salts have been recognized to be useful as alkenyl cation synthons and a variety of olefins have been synthesized using them.[6] On this basis, we have prepared *S*-alkenyl *O,O*-dialkyl phosphorodithioates and *S*-alkenyl *O,O*-dialkyl phosphorothioates.[7] The similarity between sulfur and selenium prompted us to investigate the possibility of synthesizing *Se*-alkenyl *O,O*-dialkyl phosphoroselenoates. In this paper, we report the first examples of *Se*-alkenyl *O,O*-dialkyl phosphoroselenoates.

Simple stirring of the mixture of potassium *O,O*-dialkyl phosphoroselenoates 1 with alkenyl-(phenyl)iodonium salts 2[8] in THF at room temperature for a short time gave the desired *Se*-alkenyl *O,O*-dialkyl phosphoroselenoates 3 in good yields after work up and isolation (Table 1). We found when (*E*)-(hex-1-enyl)phenyliodonium tetrafluoroborate was used, the products with complete inversion of configuration were obtained. However, when (*E*)-(2-phenylethenyl)phenyliodonium tetrafluorobroate was used, the product

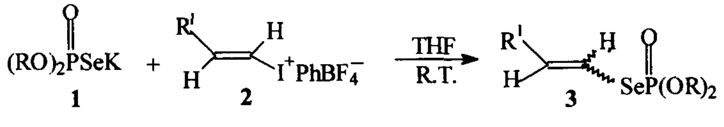

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Table 1. ***Se*****-Alkenyl** ***O,O*****-Dialkyl Phosphoroselenoates 3**

Product	R	R^1	E/Z	Reaction time(hr)	Yield(%)
3a	CH_3	Ph	60/40	0.5	66
3b	CH_3CH_2	Ph	70/30	0.5	67
3c	*i*-Pr	Ph	53/47	0.5	49
3d	*n*-Bu	Ph	55/45	0.5	52
3e	CH_3CH_2	*n*-Bu	0/100	0.1	61
3f	*i*-Pr	*n*-Bu	0/100	0.3	67

comprised two isomers, the main isomer was assigned the (*E*)-configuration and the minor one the (*Z*)-configuration by ^{1}H NMR. The products were characterized by IR, ^{1}H-NMR and MS.[9]

In summary, we have, for the first time, synthesized the novel *Se*-alkenyl *O,O*-dialkyl phosphoroselenoates **3** by a simple method and further investigation of this class of compound will be reported in due course.

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9. Spectroscopic data: **3a**. ^{1}H-NMR (500MHz, $CDCl_3$) δ 3.78-3.86 (m, 6H), 6.69 (dd, J=11.5, 10.0Hz, 0.4H), 6.90 (dd, J=15.8, 7.0Hz, 0.6H), 7.03 (dd, J=15.8, 2.0Hz, 0.6H), 7.12 (d, J=10.0Hz, 0.4H), 7.26-7.40 (m, 5H); IR (film) 1260, 1180, 1020, 730, 690cm^{-1}; MS m/z 291 (M^+). **3e**. ^{1}H-NMR (500MHz, $CDCl_3$) δ 0.91 (t, J=7.2Hz, 3H), 1.32-1.42 (m, 10H), 2.13-2.17 (m, 2H), 4.15-4.24 (m, 4H), 6.11(dtd, J=9.5,7.2,2.0Hz, 1H), 6.29 (dd, J=9.5, 9.5Hz, 1H) ; IR (film) 1260, 1160, 1010cm^{-1}; MS m/z 299 (M^+).