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### 2-Selenophenemethanephosphonic Acid Derivatives-A New Class of Organophosphorus Compounds

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## SHORT COMMUNICATION

# 2-Selenophenemethanephosphonic Acid Derivatives— A New Class of Organophosphorus Compounds

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3-Methyl-2-selenophenemethanephosphonic acid dialkyl esters were obtained by reaction of dialkyl(3-methyl-1,2,4-pentatrienyl)phosphonates with methylselenenyl chlorides.

## INTRODUCTION

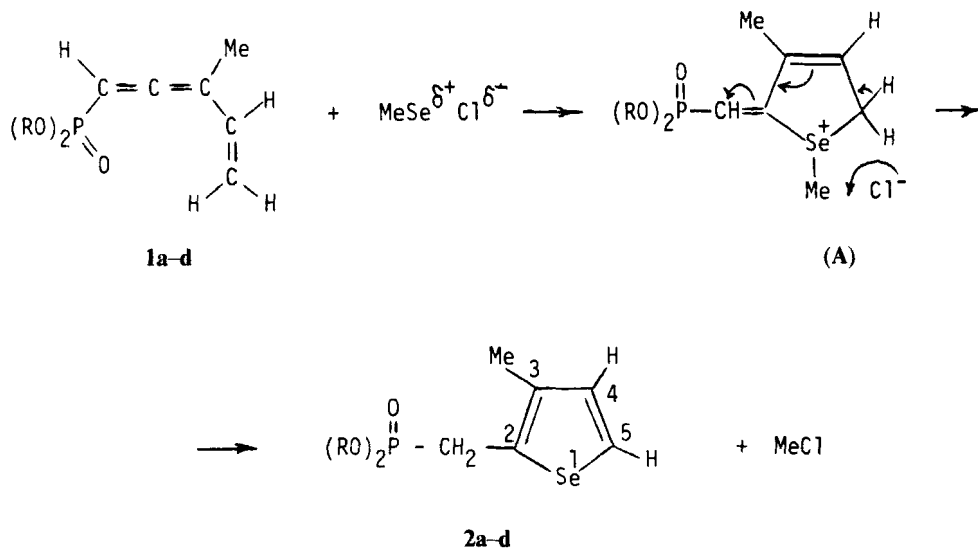
Except for our short communication,<sup>1</sup> there is no information in the literature concerning the reaction of alkyl(aryl)selenenyl chlorides with phosphorus-containing allenes. A simple method of preparation of dialkyl(3-methyl-1,2,4-pentatrienyl)phosphonates now available<sup>2</sup> allowed us to study their reactivity with electrophiles. Thus, our experimental data show that these compounds with halogens give 3-vinyl-1,2-oxaphosphol-3-ene derivatives<sup>3</sup> while with alkylsulfenyl chlorides the 2-thenylphosphonic esters are formed.<sup>4</sup>

## RESULTS AND DISCUSSION

Continuing our investigations on the interaction of allenylphosphonates with electrophilic reagents, we have now studied the reactivity of dialkyl(3-methyl-1,2,4-pentatrienyl)phosphonates, **1a-d**, towards methylselenenyl chloride. It was found that in this case the 1,3-dienyl system of  $\pi$ -bonds is involved in the reaction and selenophene ring cyclization occurs with formation of the previously unknown 2-selenophene methanephosphonates, **2a-d**.

The reactions were induced in a nonpolar solvent at temperatures of 15 to 20°C. The compounds **2a-d** are separated from reaction mixtures by vacuum distillation (yields 60–70%). Results of the elemental analyses of **2a-2d** were in agreement with theory.

The <sup>1</sup>H-nmr spectra of phosphonates **2a-d** (see Table I) display low field ( $\delta$  6.90–7.60) signals for protons H<sup>4</sup> and H<sup>5</sup>, characteristic of the selenophene ring. At higher field, two doublets for CH<sub>2</sub> and for Me at C<sup>3</sup> are observed. The <sup>31</sup>P chemical shifts (26.04–26.4 ppm, relative to 85% H<sub>3</sub>PO<sub>4</sub>) of **2a-d** are typical of compounds with tetra-coordinate phosphorus. The integrals of the signals in the spectra of all phosphonates correspond to the proposed structure. It is well known that the natural mixture of isotopes of selenium contains about 8% <sup>77</sup>Se which is magnetically active



( $I = \frac{1}{2}$ ) and interacts with other nuclei.<sup>5</sup> When the signal of  $\text{H}^5$  ( $\delta$  7.60) in **2a-d** was amplified two quartets, symmetrical with respect to this signal, having the same values of  $^3J_{\text{HH}}$  (5.2–5.8 Hz) and  $^5J_{\text{HP}}$  (2.8–3.2 Hz) were observed. These two quartets arise from spin–spin interaction of  $^{77}\text{Se}$  with  $\text{H}^5$  ( $^2J_{\text{HSe}}$  46.0 Hz). Coupling constants of similar magnitude were found in other selenophene compounds.<sup>6</sup>

TABLE I  
Parameters of the  $^1\text{H}$ -nmr spectra of dialkyl 3-methyl-2-selenophenemethanephosphonates

Comp.	R	Chemical shifts, $\delta$		R	Coupling constants, $J$ Hz			
		$\text{H}^4$ ( $\text{H}^5$ )	$\text{CH}_2$ (Me)		$\text{H}^4\text{—H}^5$	$\text{H}^5\text{—P}$	$\text{H}^5\text{—Se}$	$\text{CH}_2\text{—P}$ (Me—P)
<b>2a</b>	Me	6.92d (7.60dd)	3.28d (2.10d)	3.62d	5.8	2.8	46.0	21.6 (3.2)
<b>b</b>	Et	6.90d (7.60dd)	3.24d (2.06d)	Me 1.20t $\text{CH}_2$ 4.05dq	5.2	3.2	46.0	21.6 (3.2)
<b>c</b>	$\text{Pr}^i$	6.90d (7.60dd)	3.21d (2.08d)	Me 1.20d $\text{CH}$ 4.56dq	5.4	3.1	46.0	21.6 (3.2)
<b>d</b>	$\text{Bu}^s$	6.91d (7.60dd)	3.20d (2.06d)	$\text{CH}$ 4.30m $\text{CH}_2$ 1.47m Me 1.16d Me 0.80t	5.6	2.8	46.0	21.4 (3.2)

d- doublet, t- triplet, m- multiplet, dd- doublet-doublet, dq- doublet-quartet.

The cyclization thus observed is apparently due to the ability of selenium to participate in the 1,4-cycloaddition reaction, involving prototropic isomerization and formation of the selenophene ring.

The reaction described above is an original method of synthesis of a new class of organophosphorus compounds—esters of 2-selenophenemethanephosphonic acid.

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