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ADDITION OF ELEMENTAL SELENIUM TO PHOSPHONATE CARBANIONS- - A KEY STEP IN THE SYNTHESIS OF VINYLPHOSPHONATES. A NEW SYNTHETIC APPROACH TO 1,4-DICARBONYL SYSTEMS.

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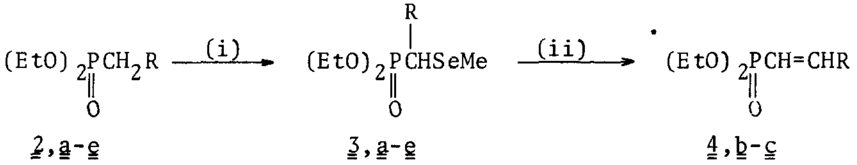
Summary: *A convenient synthesis of vinylphosphonates which involves addition of elemental selenium to phosphonate carbanions followed by alkylation and selenoxide elimination is described. A general approach to 1,4-dicarbonyl systems based on diethyl α-methylthiovinylphosphonate is also reported.*

Vinylphosphonates bearing electron withdrawing groups on the α-carbon atom have recently found an application as versatile reagents especially useful for the synthesis of heterocyclic or carbocyclic rings by the Michael addition and subsequent intramolecular Horner-Wittig reaction[1].

We wish to report here a convenient synthesis of vinylphosphonates which is based on the addition of elemental selenium to phosphonate carbanion followed by alkylation and oxidative elimination of the organoselenium moiety. In this report we also describe a new approach to the synthesis of 1,4-dicarbonyl compounds based on diethyl α-methylthiovinylphosphonate (**1**) as a key intermediate.

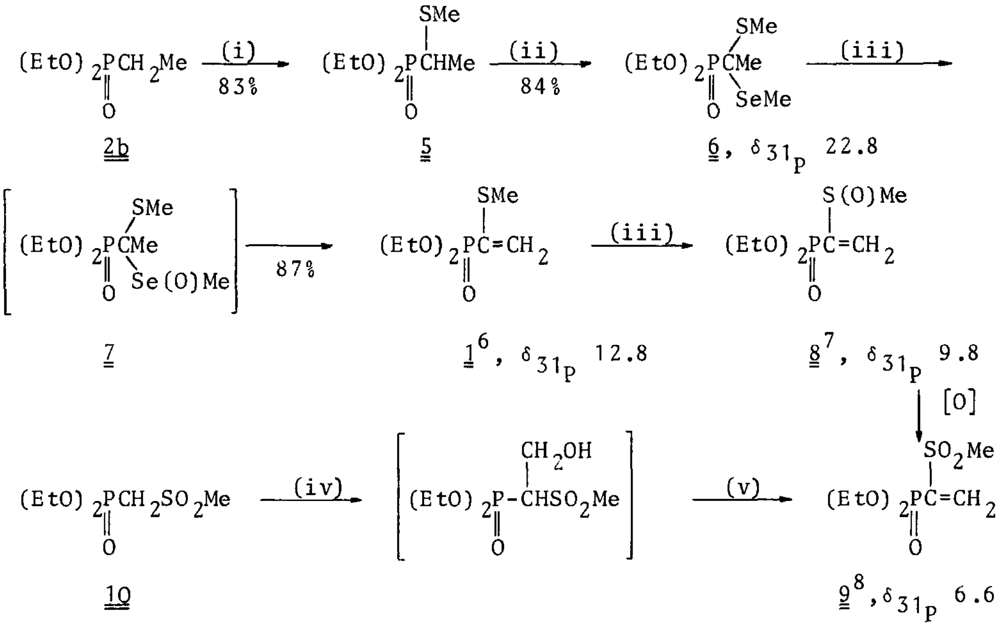
In an extension of our work on addition of sulfur to phosphonate carbanions[2], we found that elemental selenium reacts also readily with the lithium derivatives of phosphonates **2** [R=H(**a**), Me(**b**), *n*-Pen(**c**), Ph(**d**), MeS(**e**)] to give α-phosphoryl lithioselenols which, without isolation, are converted into the corresponding selenides **3** on treatment with methyl iodide. It is interesting to note that the yields of **3** usually exceed 80%. Furthermore, this modified preparation of α-phosphoryl selenides **3** has the advantage over other known routes[1a,3] to these compounds because the use of rather unpleasant selenophenol or phenylselenyl bromide is avoided.

The simple synthesis of α-alkyl substituted α-phosphoryl selenides **3** opened the way for the preparation of vinylphosphonates using a selenoxide elimination[4]. For instance, when selenides **3b** and **3c** were reacted with hydrogen peroxide in the presence of pyridine at room temperature, the corresponding vinylphosphonates **4b** and **4c** were obtained in 80 and 86% yield, respectively.



(i) *n*-BuLi, Se, MeI; (ii) H_2O_2, Pyr

The utility of our approach to the vinylphosphonate synthesis is further demonstrated by the synthesis of diethyl α-methylthiovinylphosphonate (**1**)[5] from **2b** as shown below.

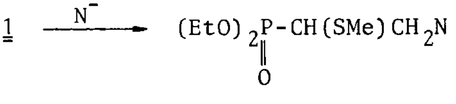


(i) *n*-BuLi, S_8, MeI; (ii) *n*-BuLi, Se, MeI; (iii) H_2O_2, Pyr; (iv) H_2CO, CH_3COOH, (v) piperidine

The overall yield of **1** obtained as above is 61%. With regard to the last step of the synthesis of **1** it is interesting that oxidation of the selenothioacetal **6** occurs selectively at selenium to give selenoxide **7** which undergoes spontaneous elimination to form the desired vinylphosphonate **1**. The use of oxidizing agent in an excess leads to the corresponding vinyl sulfoxide **8** or sulfone **9**.

The latter was also prepared from sulfone 10 by treatment with formaldehyde in the presence of acetic acid followed by the water elimination.

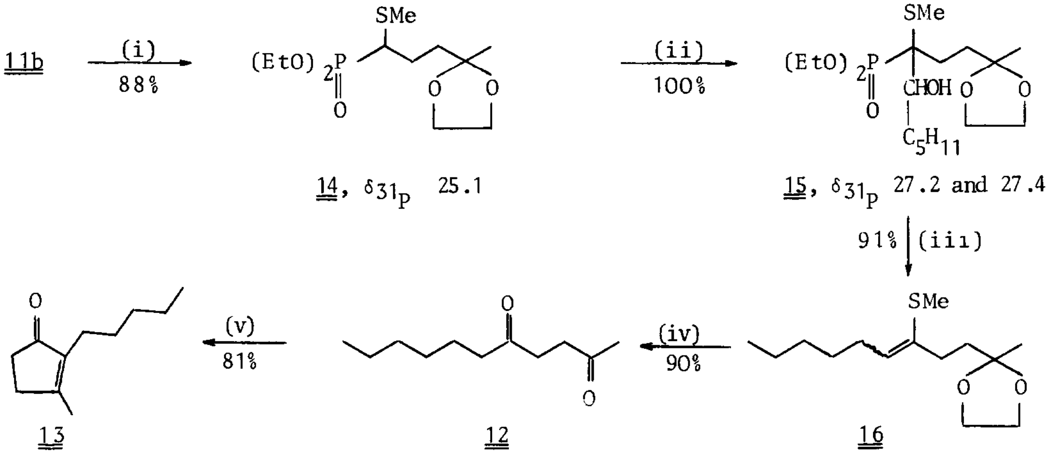
Vinylphosphonate 1 was found to react with a variety of anionic nucleophiles to produce the corresponding addition products 11 listed below.


$1 \xrightarrow{N^-} (EtO)_2P(O)\text{-}CH(SMe)CH_2N$

11

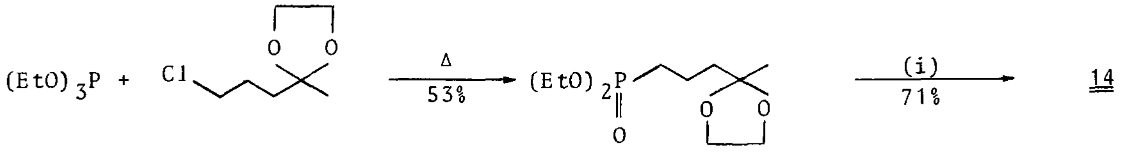
	N	yield(%)	$\delta^{31}P$ (ppm)
a	PhS^-	78	23.1
b	$CH_3C(O)CH_2^-$	51	25.2
c	$t\text{-}BuC(O)CH_2^-$	59	25.7
d	$(MeO_2C)_2CH^-$	81	23.5
e	$(EtO_2C)_2PhC^-$	70	23.8

Especially interesting are the products 11b and 11c because they are key intermediates for the synthesis of 1,4-dicarbonyl compounds via the Horner-Wittig reaction followed by hydrolysis of the vinyl sulfide formed. The synthesis of undecane-2,5-dione (12), which is a well-known precursor of dihydrojasmone (13)[9], best illustrates this novel strategy for the construction of the 1,4-dicarbonyl and cyclopentenone skeleton.[10]



(i) $(CH_2OH)_2$, H^+; (ii) n-BuLi, $C_5H_{11}CHO, H_2O$; (iii) NaH, 18-crown-6; (iv) TsOH
(v) NaOH, EtOH

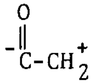
In this connection we would like to point out that the compound 14 may be prepared in a shorter way by the Arbusov reaction of triethyl phosphite with 5-chloro-2-pentanone ethylene ketal[11] followed by the sulfur addition and methylation.



(i) n-BuLi, S_8, MeI

$\delta\ ^{31}P$ 31.1

Finally, it should be noted that in terms of the Umpolung concept[12] the vinyl phosphonate 1 represents a new, masked reagent of the type shown below



$$^{-}\overset{O}{\overset{\|}{C}}-CH_2^{+}$$

and its synthetic utility is under current study in this laboratory.

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4. H.Reich, J.M.Renge, H.F.L.Reich, J.Am.Chem.Soc., 97, 5434 (1975).
5. An alternative synthesis of α-alkylthio substituted vinylphosphonates has recently been published by Durst at al. (see ref 1h).
6. 1: ^1H NMR(CCl_4): δ 2.30 (3H,s,CH_3S), 5.60 (1H,d,J_{PH}=43.3 Hz, trans C=CH), 6.12 (1H,d,J_{PH}=22.7 Hz, cis C=CH).
7. 8: ^1H NMR(CCl_4): 2.70 (3H,s,CH_3SO), 6.62 (1H,d,J_{PH}=19.3 Hz, cis C=CH), 6.72 (1H,d,J_{PH}=40.0 Hz, trans C=CH).
8. 9: ^1H NMR(CCl_4): 3.18 (3H,s,CH_3SO_2), 6.92 (1H,d,J_{PH}=17.3 Hz, cis C=CH), 7.08 (1H,d,J_{PH}=39.3 Hz, trans C=CH).
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10. In the same way 2-phenyl-3-methylcyclopent-2-en-1-one was obtained.
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