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SYNTHESIS AND REACTIONS OF VINYLPHOSPHONATES BEARING ELECTRONEGATIVE SUBSTITUENTS

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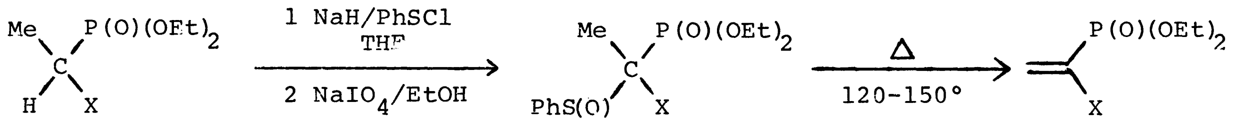
Ethyl α-(diethylphosphono)acrylate (1a) and α-(diethylphosphono)acrylonitrile (1b) prepared by thermolysis of ethyl 2-diethylphosphono-2-phenylsulfinylpropionate (2a) and 2-diethylphosphono-2-phenylsulfinylpropionitrile (2b) react with various nucleophiles to generate corresponding phosphonate anions, which subsequently react with carbonyl compounds to give annelated or acyclic olefinic compounds in good yields.

Whereas vinyltriphenylphosphonium bromide has been used as a versatile reagent for the synthesis of a variety of carbocyclic[1)] and heterocyclic compounds[2)], its analogues, vinylphosphonates have since found little synthetic use[3)] because of less stability of the phosphonate anions formed by the Michael addition of nucleophiles to the vinylphosphonates than the corresponding phosphonium ylides.

We wish to report here a new synthetic method of vinylphosphonates containing an electron withdrawing group such as a carboethoxy and a cyano group at the α-position for stabilization of phosphonate anions, and their applications to molecular designs.

Ethyl α-(diethylphosphono)acrylate (1a) and α-(diethylphosphono)acrylonitrile

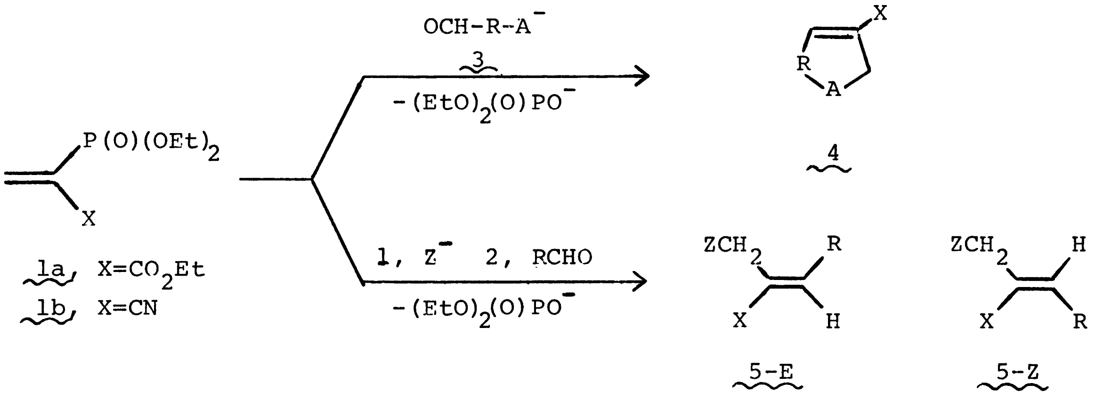


2a,b 1a,b

1a, X=CO_2Et
1b, X=CN

(1b) were synthesized in 82 and 77 % yields by thermolysis of the corresponding α-phenylsulfinylphosphonates 2a,b.

The phosphonate carbanions generated from the vinylphosphonate 1 and nucleophiles such as oxy, nitrogen, and carbon anions were observed to react subsequently with the intra or intermolecular carbonyl function to give annelated or acyclic olefinic products as shown in Tables I and II.



These results suggest that the vinylphosphonates 1 can serve as versatile reagents for molecular designs since 1 could be used as reagents suitable for coupling carbonyl compounds with nucleophilic compounds.

Vinylphosphonates 1a,b.

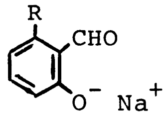
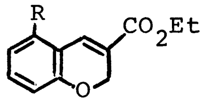
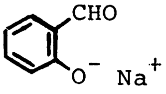
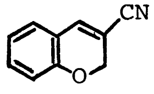
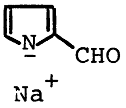
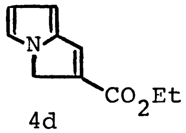
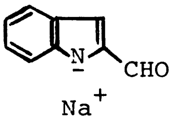
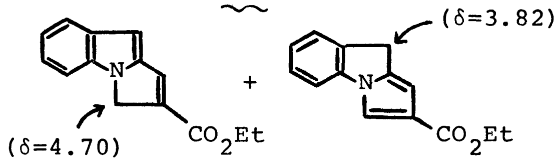
The reaction of the phosphonate carbanion generated from ethyl 2-diethylphosphonopropionate and sodium hydride with equiv. phenylsulfenylchloride in THF gave ethyl 2-diethylphosphono-2-phenylthiopropionate in quantitative yield, which was treated with sodium metaperiodate at room temperature in ethanol to give 2a. Distillation of 2a at 120-150°C produced 1a[4] having the following physical properties: bp 90-95°C/0.5 mmHg (Lit.[5] bp 101-102°C/1 mmHg), ir (neat) 1720 (C=O) and 1604 cm^{-1} (C=C), and nmr (CCl_4) δ 6.50 (1H, d-d, vinylic H) and 7.02 (1H, d-d, vinylic H).

The similarly prepared vinylphosphonate 1b had the following properties: bp 74-76°C/0.5 mmHg (Lit.[6] bp 82-83°C/1 mmHg), ir (neat) 2210 (CN) and 1620 cm^{-1} (C=C), and nmr (CCl_4) δ 6.44 (1H, d-d, vinylic H) and 6.83 (1H, d-d, vinylic H).

Heterocycles 4.

The vinylphosphonate 1 is added to a stirred solution of 3 in anhydrous THF or DMF at room temperature. The reaction mixture is subsequently heated at 60-80

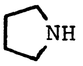
Table I. Heterocyclic compounds 4 from Vinylphosphonates 1 and 3[a)]

1	3	4	Bp [°C/mmHg], mp [°C]	Yield [%]
1a		 4a, R=H 4b, R=OMe	4a, 43.5-44.0 4b, 142-145/0.5	66 72
1b		 4c	48-49	79
1a		 4d	103-105/1	66
1a		 4e 4f	100-101	95 (4e+4f)[b)]

a) Correct elemental analyses and spectroscopic data were obtained in all compounds 4 listed in the Table.

b) The ratio of 4e and 4f was 3:2 by nmr.

Table II. Olefinic compounds 5 from 1a, Nucleophiles and Aldehydes[a)]

Nucleophiles Z^-(ZH/base)	R in aldehydes (RCHO)	Products 5 Bp [°C/mmHg]	Yield[%]	Ratio of E:Z[b)]
EtO_2CCH_3 / LDA	Ph	115-117/1	63	4 : 1
	MeCH=CH	87-90/1	51	3 : 1
	Me	65-67/1	59	2 : 1
 NH / NaH	Ph	136-137/1	87	3 : 1
	Et	56-58/1	67	3 : 2
$MeC(O)NH_2$/NaH	Ph	oil	75	mainly E
	Et	103-105/0.5	47	5 : 4

a) Correct elemental analyses and spectroscopic data were obtained in all compounds 5 listed in the Table.

b) Based on nmr.

°C for 2-3 hr, and then poured into water, followed by extraction with ether. After evaporation of solvent ether, the residue is distilled or recrystallized.

Olefinic products **5**.

The vinylphosphonate **1** is added to a stirred solution of ethyl α-lithioacetate prepared from ethyl acetate and equiv. lithium diisopropylamide (LDA) in anhydrous THF at -70°C. After stirring for 1 hr at that temperature, aldehyde is added to the reaction mixture. Then the reaction mixture is allowed to be elevated to refluxing temperature and kept at that temperature for 1-2 hr. After similar treatment, the residue is distilled to give a pure olefinic product **5**.

In the cases using other nucleophiles, similar reaction conditions were employed.

References and Notes

1) (a) E. E. Schweizer and G. J. O'Neill, *J. Org. Chem.*, **30**, 2082 (1965).
(b) I. Kawamoto, S. Muramatsu, and Y. Yura, *Tetrahedron Lett.*, **1974**, 4223 and references cited therein.
2) (a) E. E. Schweizer, J. Liehr, and D. J. Monaco, *J. Org. Chem.*, **33**, 2416 (1968) and references cited therein.
(b) For a recent review, see E. Zbiral, *Synthesis*, **1974**, 775.
3) S. D. Darling and N. Subramanian, *Tetrahedron Lett.*, **1975**, 3279.
4) We have been recently informed of an alternative synthesis of **1a** from ethyl 2-diethylphosphono-2-phenylseleninylpropionate by Professor C. H. Heathcock, private communication.
5) A. N. Pudovik, G. E. Yastrebova, and V. I. Nikitina, *Zh. Obshch. Khim.*, **37**, 2790 (1967). *Chem. Abstr.*, **69**, 43992s (1968).
6) A. N. Pudovik, G. E. Yastrebova, and V. I. Nikitina, *ibid.*, **36**, 1232 (1966). *Chem. Abstr.*, **65**, 15418g (1966).

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